

Iron-Substitution in Hydroxyapatite Using a Simple Ion Exchange Soaking Procedure

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Statement of Purpose: Hydroxyapatite (HA) is the main mineral component of natural bone and teeth. As such, it has excellent biocompatibility and bioactivity and is a commonly used biomaterial. Additionally, the structure of HA allows for the substitution of a wide range of elements directly into the apatite lattice. Many efforts have been made in the synthesis of iron-substituted HA, but most of them involve harsh preparation conditions such as high temperature and pH [1-4]. In this study, a new simplified processing technique was developed to synthesize iron-substituted HA particles at room temperature, and the resulting particles were characterized using a series of evaluation techniques.

Methods: HA nanoparticles were prepared using a wet synthesis procedure at 70°C. The resulting apatite powder was soaked in iron containing solutions at room temperature under moderate stirring to achieve ion substitution. Soaking times were varied from 1 to 24 h. The Fe²⁺ solution contained iron (II) chloride tetrahydrate (Acros) in DIW, and the Fe³⁺ solution contained diluted ferric chloride solution (Fisher). The resulting powders were collected by filtration, dried, and ground prior to characterization.

Structural and chemical characterizations were conducted using powder x-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), and Energy Dispersive X-Ray Spectroscopy (EDX). Magnetic properties were measured using a Vibrating Sample Magnetometer (VSM).

Results: EDX was used to check for the presence of iron in the apatite powders. In samples soaked in ferric chloride, iron was present in greater quantities than calcium. In addition, Ca:P ratio was greatly decreased as compared to pure HA control samples, which suggests that calcium was partially replaced by iron. In samples soaked in ferrous chloride, Ca:P ratio remains comparable to that of the HA control which suggests that iron did not substitute for calcium, but some iron ions may have adsorbed onto the HA surface.

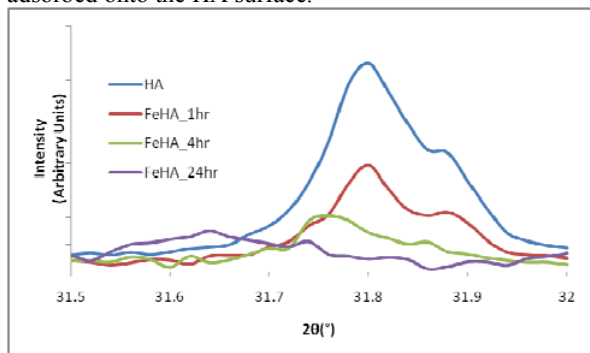


Figure 1. XRD results showing increasing peak shift with increased soaking time in ferric chloride solution.

XRD results show that after soaking in ferric chloride the sample maintains a pure apatite crystal structure. This verifies that the iron previously detected with EDX is present only in calcium sites in the apatite lattice and not as a new phase. Increasing peak shift with decreasing peak intensity and peak broadening as soaking time increases indicates an increase in iron content in the apatite lattice (Figure 1).

FT-IR further verifies that the ferric chloride soaked powder maintains an apatite structure. No new functional groups are present.

VSM was used to measure the magnetic properties of pure HA and soaked samples to determine the effect of iron (Figure 2) on the magnetic properties. Both pure HA and HA soaked in ferrous chloride were shown to have diamagnetic properties by the negative slope of the magnetization-magnetic field curve. In the case of HA soaked in ferric chloride, the positive slope indicated paramagnetic properties. Paramagnetism results from the presence of iron in the apatite lattice.

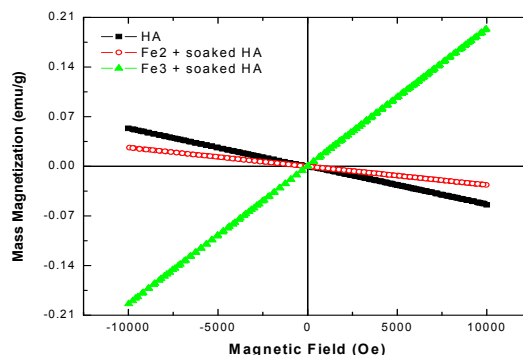


Figure 2. Magnetic properties of pure HA and HA samples soaked in iron containing solutions for 1 hour at room temperature.

Conclusions: Using a simple soaking procedure, iron can be exchanged with calcium ions in the apatite lattice via a ferric chloride solution. This procedure does not work for ferrous chloride solution. Iron substitution results in FeHA powders with magnetic properties. As indicated by XRD, an increase in soaking time results in higher iron content in the apatite lattice. Further work will focus on in depth study of the magnetic properties. These magnetic HA nanoparticles have great potential for biomedical applications, such as drug delivery, therapeutic hyperthermia, medical imaging, and regenerative medicine.

References:

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