Synthesis and Characterization of Nano Hydroxyapatite Used for Immobilizing Heavy Metals

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The specific objectives of this study are to synthesize and characterize nano-scale hydroxyapatite particles in laboratory for use in immobilizing heavy metals. Nano hydroxyapatite (HAP) was synthesized by reacting $CaCl_2$ and Na_2HPO_4 as raw materials, a precipitation reaction occuring at the room temperature. Crystal phases were determined by X-ray diffraction (XRD). Scanning electron microscope (SEM) was applied to investigate the morphology. The microstructure of the HAP products was further observed by transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM) with energy-dispersive X-ray spectroscopy (EDX). The purity and chemical composition of the as-synthesized powder was analyzed by FTIR.

Keywords: hydroxyapatite, immobilizing heavy metals, SEM, TEM

Soil contamination by heavy elements represents therefore a worldwide environmental concern mainly because these elements can be transferred to the hydrosphere and biosphere, thereby posing a hazard to human health. Furthermore, apatite is an ideal material for long-term sequestration of metals due to its high affinity for actinides and heavy metals [1-3,12]. Hydroxyapatite powders can be synthesised via numerous preparation routes, using a range of different reactants [4-5]. Some processing techniques include: wet chemical methods (precipitation); hydrothermal techniques; hydrolysis of other calcium phosphates; sol-gel. Wet chemical methods suppose an acido/basic reaction; a *p*H higher than 9, assures the formation of apatitic structure. Hydroxyapatite powders exhibit a high degree of chemical variability.

Among the reported studies, however, little works has been done with the preparation of single crystal hydroxyapatite nanorods. The crystal lattice quite readily undergoes substitutions, with ions such as $(CO_3)_2^-$, $(HPO_4)_2^-$ and F^- often found in place of stoichiometric hydroxyapatite components. A number of materials have been used as adsorbents or reductants for removing hexavalent uranium from groundwater. Among available sorbent materials, apatites are one of the most promising candidates for adsorbing and immobilizing dissolved uranium from groundwater. This is because the apatite group of minerals has been found to be stable across a wide range of geological conditions for hundreds of years. The purpose of this study was to investigate the structural and morphological properties of nano hydroxyapatite powders prepared for immobilizing heavy metals.

Experimental part

In the present study, submicron hydroxyapatite powders synthesized in our laboratory were used**.** Hydroxyapatite (HAP) was obtained by wet chemical methods (precipitation), from $CaCl_2$(Sigma-Aldrich) and Na_2HPO_4 (Sigma-Aldrich) as raw materials. Precipitation reactions take place at the room temperature:

$$10CaCl_2 + 6\,Na_2HPO_4 + H_2O = Ca_{10}(PO4)_6(OH)_2 + 12NaCl + 8HCl$$

The resulted precipitates were maintained in the suspension at the ambient temperature, in the presence of crystallization admixtures, for 40 h then filtered, washed with de-ionized water, dried at 110^{0}C and thermally treated at 800, 900 and 1200^{0}C for 2 h. The HAP nanoparticles are synthesized by precipitation which were characterized: X-ray diffraction (XRD) patterns were obtained with a Bruker D8 Advance powder diffractometer working at 40 kV and 40 mA, using CuKα wavelength, with a germanium monochromator in the incident beam. The measurement was performed in the range angle 2θ=20-65^0 and in a step-scanning mode with a step $\Delta 2\theta$ = 0.01^0; IR spectroscopy using a Perkin-Elmer BX FTIR spectrophotometer from 500 to 4000 cm^{-1} using the KBr technique and operating in the transmittance mode; microstructural characterization by the transmission electron microscopy (TEM, HRTEM) and electron diffraction (SAED) on TECNAI F30 G2 and scanning electron microscope, energy-dispersive X-ray spectroscope (SEM/EDX, XL30).

Results and discussions

The synthesis precursors, *p*H value, reaction temperature and post-treatment process including ageing and heat treatment affect structural characteristics of hydroxy-apatite. The stability of hydroxapatite, i.e. dissolution in aqueous solution or physiological fluids, is governed by its crystallinity. The crystalline structure can be change by varying the conditions of synthesis, as well as the maturation conditions (time and temperature). When nucleation and growth of crystals process take place in calcium phosphate solutions at room temperature, homogenous and uniform micro crystals are obtained. Granulometric composition of the studied materials is in a wide range depending on technological parameters. Figures 1, 2, 3 show the results for IR, XRD, SEM and TEM analyses. The crystalline structure was investigated using X-ray diffraction (fig.1), the specific bands for HAP are found and the mineralogical composition of the synthesized powders was determined. After heating 2 or 3 h at 800, 900 and 1200^{0}C the main component of the heated powder is hydroxyapatite and a higher crystalline degree was found.

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No.	Interplanar Distance d[Å]	Relative Intensity I / I_0	Diffraction Angle (radiation Co) $2\theta_t$
1.	2.81	100	37.12
2.	2.78	60	37.55
3.	2.70	60	38.40
4.	2.63	25	39.76
5.	2.26	20	46.62
6.	1.94	30	54.94
7.	1.84	40	58.20

Table 1
RDX- HYDROXYAPATITE $Ca_5(PO_4)_3 \cdot (OH)$ – PDF 9-432 - AT 1200^{0}C

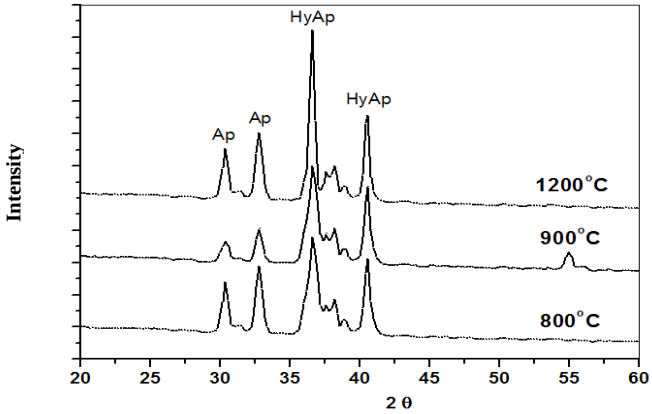

Fig. 1. XRD patterns for HAP at 800, 900 and 1200^{0}C

The XRD patterns of our HAP samples show that there is an increase in crystalline phase with increasing temperature and evidence the trace of tricalcium phosphate, octacalcium phosphate and carbonate-apatite. The HAP lines corresponding to the Powder Diffraction File PDF 9- 432- $Ca_5(PO_4)_3(OH)$ is shown in table 1.

Our experiments provide little information on the mechanism of this effect or on the kinetics of the crystallization process, partly because the calcium and phosphate concentrations decreased during precipitation. Diffraction circles marked by diameters correspond to the interplanar distances that are specific to the families of crystalline planes of $Ca_5(PO_4)_3OH$ with hexagonal network that evidenced nanostructured nanoparticles and bigger particles of 0.1-0.3 μm hydroxyapatite.

FTIR analysis (fig. 2) revealed the presence of carbon on the surface of the HAP and shown the transmittance of infrared spectrum. Weak and sharp band at 3572 cm^{-1} attributed to free OH valence vibration, and broadband more intense at 3432 cm^{-1} is attributed to OH's connected via hydrogen bonds. The two characteristic bands at 1090 and 1050 cm^{-1} corresponding to asymmetric vibration of P-O bond and the sharper band at 964cm^{-1} corresponds to the symmetrical valence vibration of the P-O. The position of these carbonate bands indicated that carbonate groups replace phosphate and hydroxyl groups in the hydroxyapatite lattice. Phosphate ν_1 band is present near 962 cm^{-1}. The two sharp P-O bands at 561.2 cm^{-1} and 601.7 cm^{-1}(P-O deformation in PO_4), indicated a crystallized octacalcium phosphate structure. The band in the region of 1640-1600 cm^{-1} is due to H-O-H deformation. Atmospheric CO_2 is detected by the band at 2349 cm^{-1} (800^{0}C).

The high-resolution picture transmission (HRTEM) (fig. 3) the two – zone correspond to nanocrystalline area of hydroxyapatite. The EDX spectrum of the nanorod shows that these are only elemental O, Ca and P(fig. 2).

The results presented here demonstrate the value of texture analysis for quantifying the appearance of mineral deposits in scanning electron micrographs. The morphology of the obtained powders was studied by SEM electron microscopy (fig. 3). The sample powders present different shapes: the powder HAP at 1200^{0}C is spherical with an average grain size under 50 nm; the powder HAP revealed grain with different shapes with an average size under 0.5 μm, which is substantially higher than the grain size of sample HAP. In general, apatites are known as having the capacity to adapt easily to a wide range of changes that may occur inside the network apatite by substitutions, ionic valences and solid solutions.

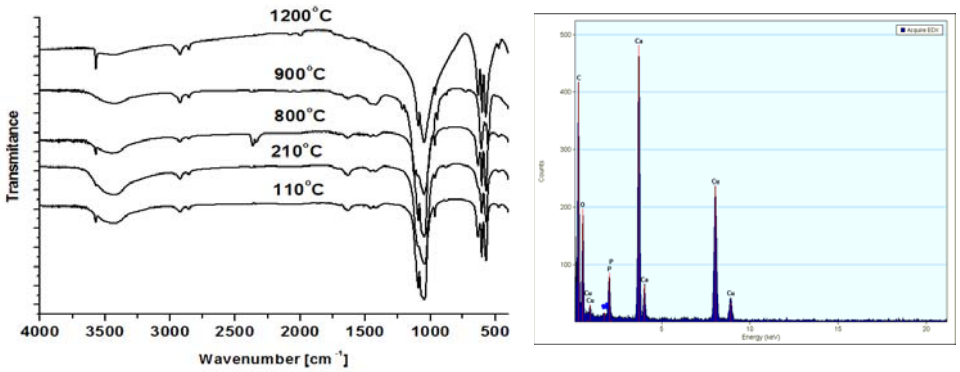

Fig. 2. FTIR spectra and EDX for HAP

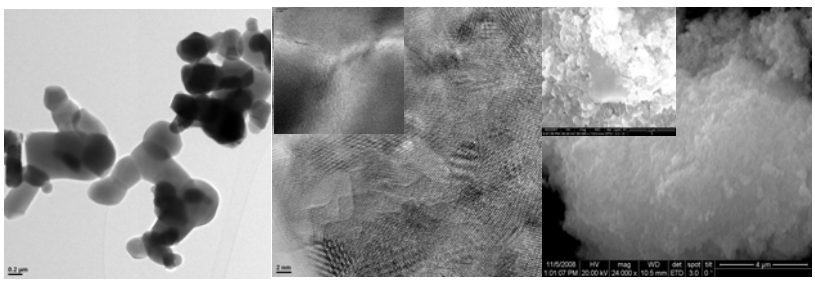
Fig.3. TEMBF, HRTEM and SEM images of HAP

In hydroxyapatites case, the most common structural form is the hexagonal one. The 10 calcium ions are occuping two different positions of symmetry. Four calcium ions Ca^{2+} are located in columns in three different lengths, Ca1 positions (or the Ca column). The six ions left of calcium Ca^{2+}, form two sets of triangular Ca2 positions. Adjacent Ca1 and Ca2 polyhedron are linked by oxygen atoms of PO_4^{3-}-tetrahedrons. Location of hydroxylyc OH^- groups allows replacement with F^- or Cl^-, or with a ionic pause. Thus, hexagonal hydroxyapatite is never strictly stoichiometric[6].

Apatite structure and chemistry is permissive for numerous substitutions and may include a variety of metallic cations (i.e., K, Na, Mn, Ni, Cu, Co, Zn, Sr, Ba, Pb, Cd, Sb, Y, U) that replace Ca in structure, and complex anions (i.e., AsO_4^{3-}, CO_3^{2-}, SO_4^{2-}, SiO_4^{4-}, etc.) that replace PO_4^{3-}ions [7,8]. Really apatite incorporates half of atomic system in its arrangement. Generally, substitutions are in higher concentrations, but for specific placeholders, it is possible to embed the high concentrations or even to complete solid solution formation. This complex and variable chemistry has large implications, with a high potential for use in decontamination of soils by heavy metals ions [7,8]. Use of apatite for this type of decontamination is based on their capacity to integrate into their crystalline structure of other metals without producing significant changes at the level the crystal lattice.

Apatite is the most ample natural form of phosphate from the earth, the major source of phosphor. Apatite may be considered as a solid solution of calcium phosphate and calcium fluorine, but it is in fact a crystallized compound, consisting of Ca^{2+}, PO_4^{3-}, and F^- ions, - corresponding to $Ca_5[(PO_4)_3F]$ formula [11]. Based on the slow action of atmospheric agents, (CO_2 and H_2O) converts to hydroxyapatite (HA), $Ca_5[(PO_4)_3(OH)]$, and carbonate apatite $[(PO_4)_6CO_3]\,H_2O$. Natural hydroxyapatite can be regarded as a double salt of calcium orthophosphate $Ca_3(PO_4)_2$ and calcium hidroxide $Ca(OH)_2$ [14-16]. Being hardly soluble, it can be turned easily soluble to monocalciumphosphate by treating it with concentrated sulfuric acid. In terms of chemical composition and structure, hydroxyapatite it is a part of a group of inorganic compounds of the apatitic type, having the general formula $A_5[(XO_4)_3Z]$; these types of compounds have in common a structure of crystal clear prismatic hexagonal, having either the form of well developed needle beans crystals or compact granular masses form, finely crystallized (9).

Conclusions

The results of this study demonstrate that nano-scale hydroxyapatite materials could be used for developing treatment approaches for removing and/or immobilizing heavy metals. The conducted experiments show that precipitated rapid HAP is non-stoichiometric. Ageing HAP non-stoichioetric in an aqueous medium leads via surface phenomena, which will increase the stoichiometric and will decrease the soluble phase. Given all these considerations it is obvious that the process of synthesis of HAP has a major role in the implementation of immobilizing heavy metals. Future objective of the research is to use these HAP materials in order to manufacture SLS/SLM air filters, to decrease the environmental pollution.

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