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Chemical Papers 63 (5) 568–573 (2009)
DOI: 10.2478/s11696-009-0059-x

ORIGINAL PAPER

# Hydroxyapatite modified with silica used for sorption of copper(II)‡

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Received 14 October 2008; Revised 1 March 2009; Accepted 3 March 2009

This paper aims to increase the sorption capacity of hydroxyapatite and to find the best apatite-based material for metal ions sorption. The sorption process of copper ions from water solutions by HAP and structurally modified HAP was carried out in this work. Structural modifications of HAP were realized in the preparation phase by an addition of sodium silica into the reaction medium. The prepared materials were characterized by physical-chemical methods: IR, electron-microscopy and X-ray diffraction. The composites characterized were tested in kinetic studies regarding ion exchange and adsorption of $Cu^{2+}$. It was revealed that the silica content, particle size and initial copper ion concentration influence the process rate.


**Keywords:** hydroxyapatite, silica addition, sorption capacity, sorption efficiency



## Introduction

Hydroxyapatite (HAP) is a mineral, from the group of apatites, having the chemical formula: $Ca_{10}(PO_4)_6(OH)_2$. Basic method for the preparation of commercial HAP was described by Tiselius et al. (1956) and it involves boiling brushite in the presence of an excess of NaOH. The method describes preparation of hydroxyapatite as a filling material for complex substances chromatography. Since then, many preparation methods were analyzed and, depending on the material application and its specific properties, the preparation procedure can be monitored. The synthesis conditions significantly influence both the chemical and the physical properties of HAP which are in strong interdependence with their chemical reactivity (Vallet-Regí, 2001).

Hydroxyapatite has been used for over 20 years in medicine and dentistry, mainly as a biomaterial (dense bioceramics, porous bioceramics, coatings for implants or powder for gap filling). It also can be used in chromatography as a filling material for columns because of its excellent ion exchange properties for different heavy metals and because of its adsorption ability of complex organic materials as proteins and albumins (Czerniczyniec et al., 2007; Corami et al., 2008; Barábas et al., 2007)

As trace elements, some heavy metals (e.g. copper, selenium, zinc) are essential to maintain the metabolism of the human body. However, at higher concentrations, they can lead to poisoning. Heavy metals are dangerous because they tend to bioaccumulate. Copper is an essential substance to human life but in high doses it can cause anemia, liver and kidney damage, and stomach and intestinal irritation. Copper normally occurs in drinking water from copper pipes, as well as from additives designed to control algal growth.

Phosphate minerals have been shown to possess the potential to adsorb heavy metal ions from aqueous solutions (Monteil-Rivera & Fedoroff, 2002). Apatites of different origins (mineral, synthetic, and derived from animal and fish bones) have been used as sorbents of heavy metals such as Pb, Zn, Cu, Cd, Co (Deydier

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‡Presented at the 8th Conference on Solid State Chemistry, Bratislava, Slovakia, 6–11 July 2008.

et al., 2003; Chen et al., 1997a; Young et al., 2005; Sheha, 2007; Chaturvedi et al., 2006; Xu et al., 2008; Cao et al., 2004).

In the present paper, preparation of structurally modified hydroxyapatite and sorption process of copper ions from water solutions by HAP and structurally modified HAP were carried out. Structural modifications of HAP were realized during the preparation phase by an addition of sodium silica to the reaction medium. Silica copolymerizes and forms a water enriched gel that is gradually lost by drying and calcinations. By water evaporation, micro- and macropores are formed in the apatite substituted with silicate. Pore sizes and total porosity can be controlled by the drying rate and also modification of the preparation mixture pH.

A substitution mechanism describing the substitution of a phosphate group by a silicate group, with an appropriate mechanism of the charge balance, is shown in Eq. (1) (Gibson et al., 1999)

$$\mathrm{Ca_2(PO_4)_6(OH)_2} + x\mathrm{SiO_4^{4-}} \rightarrow \quad (1)$$
$$\rightarrow \mathrm{Ca_2(PO_4)_{6-x}(SiO_4)_x(OH)_{2-x}} + x\mathrm{PO_4^{3-}} + x\mathrm{OH^-}$$

In practice, this reaction would probably not occur as there is no driving force for stable HAP to undergo such a substitution; such an "ion-exchange" reaction was carried out for a carbonate substitution, the reaction time was approximately 30 days. In order to prepare a silicon-substituted hydroxyapatite, a reaction mechanism replacing some of the phosphate ions, required for stoichiometric HAP preparation, with silicate ions is needed, as proposed in Eq. (2). To compensate for the extra negative charge of silicate groups, some OH groups will be lost thus retaining charge balance. This mechanism was used to prepare the silicon-substituted hydroxyapatite described in this study

$$10\mathrm{Ca^{2+}} + (6-x)\mathrm{PO_4^{3-}} + x\mathrm{SiO_4^{4-}} + (2-x)\mathrm{OH^-} \rightarrow$$
$$\rightarrow \mathrm{Ca_{10}(PO_4)_{6-x}(SiO_4)_x(OH)_{2-x}} \quad (2)$$

Chen et al. (1997b) discussed metal sorption on calcium phosphates and reported that for the best results, apatite should: (1) have as much carbonate ion substituted as possible, (2) have no fluorine substitution, (3) have no trace metals in the initial structure, (4) be poorly crystalline or even amorphous, and (5) have high internal porosity.

Corami et al. (2007) published that the possible reaction mechanisms for metal immobilization include: (a) ion exchange processes, (b) surface complexation, (c) dissolution of HAP and precipitation of new metal phosphates, and (d) substitution of Ca in HAP by other metals during recrystallization (coprecipitation). However, because of the limited knowledge on the relative contribution of each metals removing process, it seems that all four above mentioned processes can be involved.

The sorption capacity of hydroxyapatite was 0.016–0.764 mmol $g^{-1}$ for the materials used by Corami et al. (2007).

## Experimental

Hydroxyapatite was prepared by the precipitation method described in a previous work (Fábián et al., 1999), under continuous mechanical stirring. The used materials were: 0.5 mol $L^{-1}$ solution of calcium nitrate, 0.3 mol $L^{-1}$ solution of diammonium phosphate, and 25 % ammonia solution (Merck, Germany). The diammonium phosphate and the ammonium solution were slowly added to the calcium nitrate solution. The reaction mixture pH was adjusted with ammonia solution to maintain in the range of 9 and 9.5, and the reaction temperature was kept at 20 ℃ by means of a FALC FA-90 thermostat. The reaction mixture was stirred by FALC mechanical stirrer for 20 h. For the structurally modified hydroxyapatite, sodium silicate together with the diammonium phosphate and ammonia solution were added to the preparation mixture. The reaction pH was also adjusted to a value between 9 and 9.5, the temperature was 20 ℃ and the reaction time was 8 h. Four types of silica-hydroxyapatite (HAP-Si) were prepared: with 5 %, 5 %+, 10 %, and 15 mass % of silica. The HAP-Si with 5 %+ of silica content contained by 10 mass % more calcium compared to the other materials. After the reaction was accomplished, the precipitate was washed and filtered. The filtered material was then dried for 24 h at 105 ℃. Thermal treatment of the samples was carried out at 1000 ℃ for one hour, in a Barnstead 47900 furnace.

The prepared materials were characterized by infrared spectroscopy (in KBr pellets) with a Jasco FT/IR-615 spectrophotometer. The studied materials were: non-calcined hydroxyapatite (ncHAP), calcined hydroxyapatite (cHAP), HAP with 5 mass % of silica (HAP-Si 5 mass % Si), and HAP with 15 mass % of silica (HAP-Si 15 mass % Si).

Particle size was determined by two different methods: (1) separation by particle size with an EasySieve vibrational automatic sieve, Retsch AS200 and (2) suspension method using a Coulter Counter micro- and nano particle analyzer, Shimadzu SALD-7101.

General structure of the materials was determined by means of a scanning electron microscope, Philips XL30 ESEM-FEG, by coating them with a thin layer of gold. The samples morphology and crystallinty were studied by RX measurements on a Shimadzu XRD-6000 apparatus. Scans were conducted from 10° to 80° modifying the angle by 2° each step.

Sorption is the loss of a chemical species from an aqueous solution to a contiguous solid phase. The mechanism of sorption includes two dimensional accumulation of ions at the mineral-solution interface, precipitation (or complexation) and three-dimensional growth of solid phase (Lower et al., 1998).

The prepared and characterized materials were employed in kinetic studies of Cu(II) ion retention. For the experiments, copper nitrate solution was used, in the concentration range between $10^{-4}$ mol $L^{-1}$ and 5 $\times$ $10^{-3}$ mol $L^{-1}$. A DigitronicDXP-2040 potentiometer equipped with a calibrated copper selective electrode (Tacussel PCU 2M) and a reference saturated calomel electrode was used to monitor Cu(II) concentration. The experiments were carried out in a double walled reactor, connected to a FALC FA-90 thermostat under continuous magnetic stirring provided by a FALC FA-20 magnetic stirrer. Replicate runs were made and each time values corresponding to the given potential were mediated.

The reagents were of analytical grade and twice-distilled water was used to prepare all solutions and suspensions. All experiments were run at least in duplicate. In order to reproduce conditions existing during the purification of waste water, no pH adjustment was made during the experiments. However, pH was monitored with a pH selective electrode during the experiments.

0.25 g of sample and 50 mL of copper nitrate solution of different concentrations were used for each experiment. The decrease of electrode potential with time was measured and the data were recorded by a computer. From the remaining $Cu^{2+}$ amount, the retained copper quantity, sorption efficiency, and capacity of the material were calculated using the Microsoft Excel and Origin 6.0 software. Analytical detection limit for $Cu^{2+}$ was 5 μmol $L^{-1}$.

Influence of the used material type, particle size as well as initial copper ion concentration was studied. The best material for copper sorption was identified.

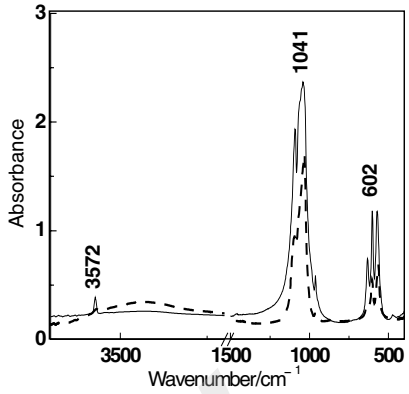


**Fig. 1.** IR spectra of ncHAP (dashed line) and cHAP (solid line).

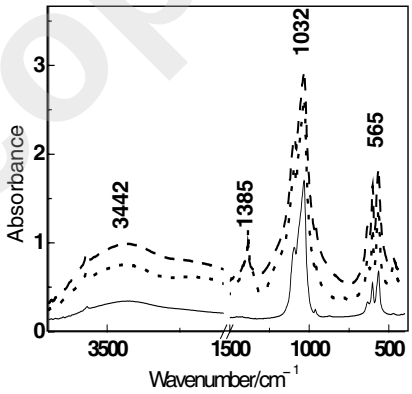


**Fig. 2.** IR spectra of ncHAP-Si 15 mass % Si (dotted line), ncHAP-Si 5 mass % Si (dashed line), and ncHAP (solid line).

## Results and discussion

### *Material characterization*

The IR spectrum is specific for hydroxyapatite. As seen in Fig. 1, the phosphate ion, $PO_4^{3-}$, is the main specie giving rise to HAP absorbance in the range of 900–1200 $cm^{-1}$ which contains symmetric and antisymmetric stretching vibration $\nu_1$ and $\nu_3$. The $\nu_1$ absorbance occurs at 962 $cm^{-1}$, while two components of $\nu_3$, at 1041 $cm^{-1}$ and 1091 $cm^{-1}$ were identified using the calcined material. The peaks for the calcined samples are more defined. The broad peak at around 3250 $cm^{-1}$ to 3500 $cm^{-1}$ corresponds to adsorbed water; for the calcined species, the corresponding peak cannot be found.

The IR spectrum of ncHAP was compared with that of the non-calcined silica–hydroxyapatite (ncHAP-Si) samples (see Fig. 2). Gibson et al. (1999) stated that the incorporation of silicon in the HAP lattice, even in small amounts, resulted in an increase of the $PO_4^{3-}$ tetrahedral distortion, silicon substitution seemed to affect the FTIR spectra of HAP, in particular the P—O vibrational bands. The distortion is caused by the stretching vibrations assigned to the Si—O—Si bonds that should appear in the range of 950–1200 $cm^{-1}$, but, due to the presence of the phosphate groups, these peaks cannot be observed. (Karakassides et al., 1999). Isolated Si—OH groups on silica show a sharp band at 3750 $cm^{-1}$ (Launer, 1987). The peak at 1384 $cm^{-1}$ appeared due to a small amount of inorganic nitrate present in the sample.

Particle size was determined in the solid phase. The average particle size lies between 63–45 μm for all compounds. To eliminate the error caused by agglomeration of particles in the solid phase, particle size was also determined in suspension. The results are significantly different from those obtained in the solid phase: particle size is: 15 nm for ncHAP and ncHAP-Si 10 mass % Si; 800 nm for ncHAP-Si 5 mass % Si; 782 nm for ncHAP-Si 5 mass %+ Si, and 790 nm for ncHAP-Si 15 mass % Si.

On the scanning electron microscope (SEM) images (Figs. 3a–3e), the difference between the materials agglomeration and surface can be seen. ncHAP shows almost spherical granulation compared to those

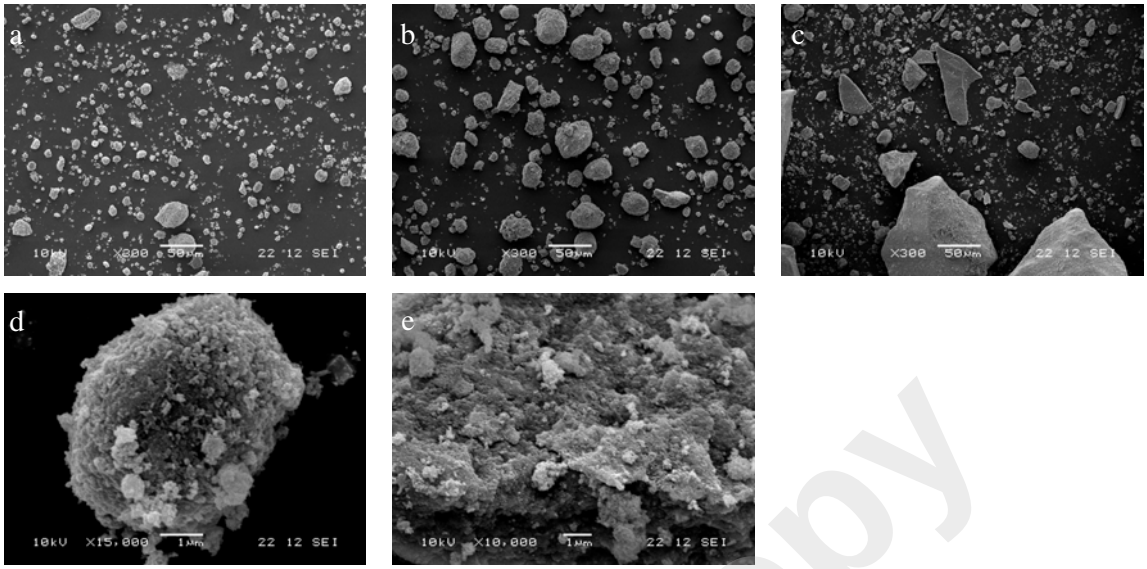


**Fig. 3.** Scanning electron microscope images for ncHAP (a), ncHAP + 20 mmol $g^{-1}$ of Cu (b), HAP-Si 10 mass % Si (c), HAP (d), and HAP doped with 21 mmol $g^{-1}$ of Cu (e).

containing silica. It can be observed that HAP-Si is much more compact and the structure is different. For samples doped with copper at lower resolution, agglomeration of the particles can be seen, at higher resolutions, a much finer distribution of the copper hydroxyapatite particles on the surface of the material can be observed (Fig. 3d and 3e). It is due to the copper ions on the granules' surfaces bonding to the hydroxyl function of hydroxyapatite. All characterized materials were non-calcined.

### *X-ray diffraction measurements*

Non-calcined samples appeared to be poorly crystaline as can be seen from the X-ray images (Fig. 4). The materials were all hydroxyapatite, having the space group $P6_3/m$ (Sudarsanan & Young, 1978). The samples have lower crystallinity and there is no significant difference between the copper and silica containing hydroxyapatite X-ray diffraction diagrams. Calcined materials are highly crystalline, characterized by the $P6_3/m$ space group. A slight shift of the peaks was caused by the modification of the unit cell parameters, which indicates the incorporation of silica and copper into the crystal structure.

### *Copper sorption measurements*

As mentioned above, copper sorption measurements were carried out with five types of material of two different particle sizes ($> 90$ μm and $< 45$ μm) and with calcined and non-calcined samples for each material at four different copper concentrations ($10^{-4}$ mol $L^{-1}$, $5 \times 10^{-4}$ mol $L^{-1}$, $10^{-3}$ mol $L^{-1}$, $5 \times 10^{-3}$ mol $L^{-1}$). pH of the solutions increased from 4.5 to 6.7.

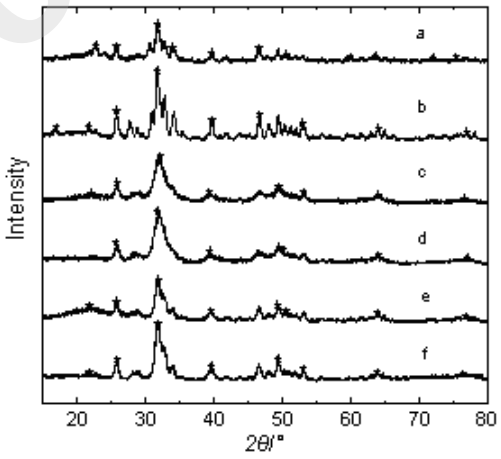


**Fig. 4.** X-ray diffractograms for cHAP-Si 10 mass % Si (a), cHAP (b), ncHAP-Si 10 mass % with Cu (c), ncHAP-Si 10 mass % (d), ncHAP with 21 mmol $g^{-1}$ of Cu (e), ncHAP (f).

For all non-calcined materials at the $10^{-3}$ mol $L^{-1}$ copper concentration, the sorption capacity was almost identical, meaning that the $\eta$ (efficiency) was around 99.7 %, the difference consists in the saturation time. For the calcined samples, the efficiency was about 60–70 %.

The sorption efficiency is defined as:

$\eta = \dfrac{c_0 - c_i}{c_o}\%$, $c_0$ being the initial copper concentration, $c_i$ the copper concentration at a specific time, and the sorption capacity given as:

$Q = \dfrac{c_{ads}}{m}$, $c_{ads}$ being the adsorbed amount of copper at a specific time in moles, and $m$ the quantity of the material on which it was adsorbed in grams.

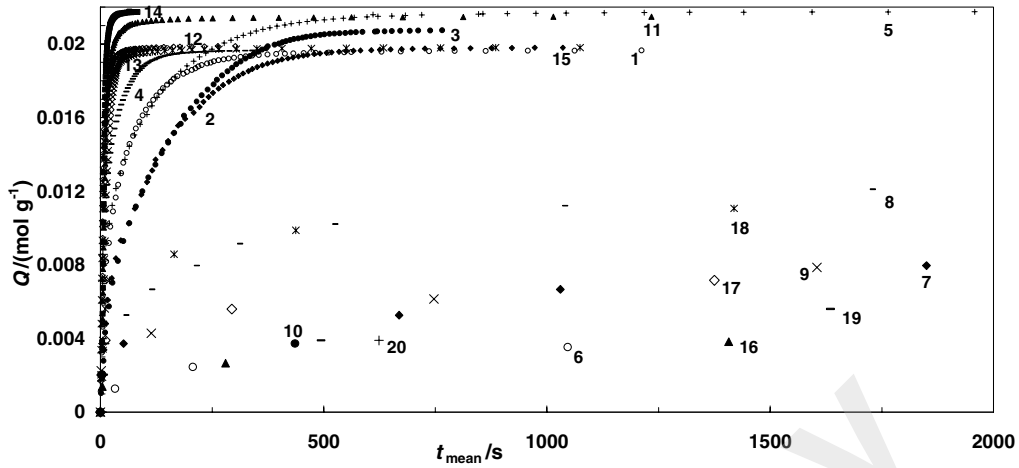


**Fig. 5.** Sorption capacity modification with time for hydroxyapatite and silica modified hydroxyapatite ($t_{\mathrm{mean}}$ is the value of time obtained from 2–3 individual measurements): ncHAP > 90 μm (1), ncHAP-Si 5 mass % Si > 90 μm (2), ncHAP-Si 5 %+ mass % Si > 90 μm (3), ncHAP-Si 10 mass % Si > 90 μm (4), ncHAP-Si 15 mass % Si > 90 μm (5), cHAP > 90μm (6), cHAP-Si 5 mass % Si > 90 μm (7), cHAP-Si 5 %+ mass % Si > 90 μm (8), ncHAP-Si 10 mass % Si > 90 μm (9), cHAP-Si 15 mass % Si (10), ncHAP < 45μm (11), ncHAP-Si 5 mass % Si < 45 μm (12), ncHAP-Si 5 %+ mass % Si < 45 μm (13), ncHAP-Si 10 mass % Si < 45 μm (14), ncHAP-Si 15 mass % Si < 45 μm (15), cHAP < 45μm (16), cHAP-Si 5 mass % Si < 45 μm (17), ncHAP-Si 5 %+ mass % Si < 45 μm (18), ncHAP-Si 10 mass % Si < 45 μm (19), ncHAP-Si 15 mass % Si < 45 μm (20).

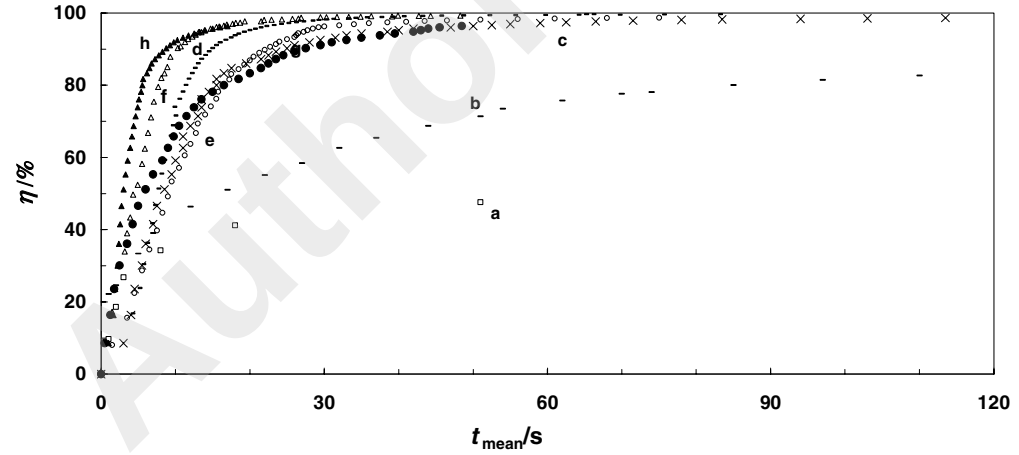


**Fig. 6.** Sorption efficiency for different concentrations ($c_1$ = 5 mmol $L^{-1}$, $c_2$ = 1 mmol $L^{-1}$, $c_3$ = 0.5 mmol $L^{-1}$ and $c_4$ = 0.1 mmol $L^{-1}$) of: ncHAP < 45 μm, $c_1$ (a); ncHAP-Si 10 mass % Si < 45 μm, $c_1$ (b); ncHAP < 45 μm, $c_2$ (c); ncHAP-Si 10 mass % Si < 45 μm, $c_2$ (d); ncHAP < 45 μm, $c_3$ (e); ncHAP-Si 10 mass % Si < 45 μm, $c_3$ (f); ncHAP < 45 μm, $c_4$ (g); ncHAP-Si 10 mass %.

The effect of the initial concentration of copper ions was also studied. Its efficiency was calculated for each material at four copper nitrate concentrations: $c_1$ = 5 mmol $L^{-1}$, $c_2$ = 1 mmol $L^{-1}$, $c_3$ = 0.5 mmol $L^{-1}$ and $c_4$ = 0.1 mmol $L^{-1}$. The sorption efficiency was plotted as a function of time for each material and concentration.

At the concentration of 5 mmol $L^{-1}$, the copper sorption efficiency for ncHAP was about 60 %, comparable to HAP-Si with 10 mass % silica, reaching the efficiency of the above 99.6 %, and has the sorption capacity of 82 mmol $g^{-1}$. cHAP does not sorb copper at such high concentrations, and HAP-Si 10 mass % Si retains the amount of 50 %. At concentrations lower than 5 mmol $L^{-1}$, sorption takes place at the 99.8 % efficiency for non-calcined materials, and also for calcined materials at concentrations equal or lower than 0.1 mmol $L^{-1}$.

These results show that, for a rapid and complete copper sorption, the most suitable material is silica hydroxyapatite with 10 mass % of silica.

Further investigations are needed to elucidate the mechanism of copper sorption on silica doped hydroxyapatites.

## Conclusions

Hydroxyapatite modified with silica can be synthesized by an addition of sodium silicate to the reaction mixture. Particles sizes of ncHAP and HAP-Si 10 mass % Si are much smaller than those of the other materials prepared. The introduction of sodium silicate causes a distortion of phosphate vibrations, which demonstrates the incorporation of silica into the hydroxyapatite structure. The X-ray images of silica and copper doped samples do not exhibit significant differences as compared to hydroxyapatite. Calcined materials show weak metal sorption properties which can be explained by the elimination of hydroxyl groups from the surface of the material. The silica containing materials have better sorption efficiency than unmodified hydroxyapatite and the 10 mass % silica containing hydroxyapatite has the highest copper sorption efficiency.

*Acknowledgements. The authors thank for the financial support from programs financed by The National University Research Council (No. 1483/2006-2008 and No. 5946/18.09.2006).*

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