

Preparation and Characterization of Silicate Hydroxyapatites Used for Copper Sorption

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Abstract

Hydroxyapatite is a major bone component and for this reason it is mostly used as biomaterial. Due to its high absorption capacity new application fields can be approached for example in water purification as a metals retaining agent. The adsorption capacity is greatly influenced by the specific surface of the material. Several studies were made to increase the specific surface by introducing silicates in the crystal structure.

In our work a different quantity of soluble silica (sodium silicate) was added in preparation phase to hydroxyapatite. Some quantities of the prepared materials were heat treated (calcined) at 1000°C and both the calcined and non-calcined samples were characterized by: IR spectroscopy, SEM, RX measurements. Specific surface, porosity, particle size distribution was also determined. All these materials were engaged in copper retaining processes. Copper sorption was monitored with the copper selective electrode. The influence of silica content, granulometry, calcination, initial copper concentration and temperature was determined.

The sorption efficiency of the non-calcined and calcined materials differed greatly. The increase of the temperature and the decrease of the particles size decreased the reaction time. The increase of the initial copper concentration is in a direct ratio with the reaction time.

It was established that the best copper retaining ability (highest amount of retained copper, lowest reaction time) is silica-hydroxyapatite with 10% wt silica with low particle size.

Conclusively, the silica containing hydroxyapatite shows very good copper sorption capacity, which can lead to an enlargement of the application fields of apatites.

Introduction

Biomaterials have become an area of very active research worldwide due to its importance in medicine. Hydroxyapatite (HAP) is an important biomaterial. But hydroxyapatite does not possess all the needed properties to be the perfect biomaterial (mechanical strength, chemical reactivity, etc.). Because silica is also a component of the bone, several methods for the synthesis of silicon-substituted hydroxyapatites have been described. Ruys [1] suggested the use of a sol-gel procedure; however, these materials, besides the hydroxyapatite phase, include other crystalline phases depending on the substitution degree of silicon. Tanizawa and Suzuki [2] tried hydrothermal methods,

obtaining materials with a Ca/(P_Si) ratio higher than that of pure calcium hydroxyapatite. Boyer *et al.* [3] conducted studies on the synthesis of silicon-substituted hydroxyapatites by the solid-state reaction, but in these cases the incorporation of a secondary ion, like La³⁺ or SO₄²⁻, was needed. Gibson *et al.* [4] synthesized silicon-containing hydroxyapatite by using a wet method, and its *in vitro* bioactivity studies gave good results. These authors studied the effects of low substitution levels on the biocompatibility and *in vitro* bioactivity.

Silanol group (Si–OH) formation has been proposed as the catalyst of the apatite phase nucleation, and the silicon dissolution rate is considered to play a major role in the kinetics of this process. These events suggested the idea of incorporating Si or silicates into the HA structure. The amount of silicon, which can be incorporated, seems to be limited. The bibliography collects values ranging from 0.1 to 5% by weight in silicon. Small amounts of 0.5 and 1% are enough to yield important bioactive improvements [5].

The development of the silica substituted composites also depends on the delivery of Si. Silica is introduced as an organometallic carrier such as TEOS [6, 7, 8] or silicon acetate [4, 5, 9] rather than a nanophase SiO₂ [10]. Inorganic nanophase silica [12, 13], calcium silicate [14] or colloidal silica [5] is mostly used in the solid state preparation methods. Silicon substitution into the HAP lattice has been found to enhance the reactivity of pure hydroxyapatite and the composition of silica doped hydroxyapatite (HAP-Si) can be described as Ca₁₀(PO₄)_{6-x}(SiO₄)_x(OH)_{2-2x} [14].

According to the literature silica tends to inhibit grain growth to generate materials with fine microstructures [14]. Si at all levels tends to inhibit grain growth of HAP. In the mixed phase system Si leads to the preferential grain growth, yet the grain growth of both HA and TCP phases is limited at higher Si levels. Si has been detected at high levels at grain boundaries and at the surfaces of materials with higher Si levels, leading to a heterogeneous microstructure that may have specific effects relating to the biological activity of the material.

Silica doped hydroxyapatite was mainly used for biomedical purposes. Besides the biocompatibility, hydroxyapatite shows a very high reactivity with metal ions, which can lead to use this material in new application fields, like water purification agents for heavy metal immobilization.. Based on their ion exchange, the properties between calcium and other metal ions, HAP is widely used as a metal retainer material [14, 15, 16]. Due to the introduction of silica the specific surface, porosity and in this way the chemical reactivity of the apatite material is enlarged

doping the hydroxyapatite with silica can be a better material for metal removal [17].

The aim of this paper was to study new application possibilities of HAP-Si. The goal was the comparative study of the copper retaining properties of pure hydroxyapatite and silica doped HAP.

Experimental

Preparation

Hydroxyapatite was prepared by the precipitation method described in the previous work [18], 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°C by means of the FALC FA-90 thermostat. The reaction mixture was stirred by the FALC mechanical stirrer for 20 hours. For the structurally modified hydroxyapatite, sodium silicate together with the diammonium phosphate and ammonia solution was added to the preparation mixture.

The reaction pH was also adjusted to a value between 9 and 9.5, the temperature was 20 °C 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 as compared to other materials. After the reaction was accomplished, the precipitate was washed and filtered. The filtered material was dried for 24 hours at 105°C. Thermal treatment of the samples was carried out at 1000°C for one hour, in the Barnstead 47900 furnace.

Characterisation methods

Infrared spectroscopy

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

Particle size distribution determination

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

RX measurements

The samples morphology and crystallinity 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.

Specific surface and porosity determination

The surface area of powders was determined by the BET analyzer N2 adsorption-desorption isotherms

model *QSURF M3*, work domain: 0,015-2000 m²/g. The specific surface and porosity were determined for ncHAP with granulometry higher than 90 µm and lower than 45 µm, heat treated hydroxyapatite (cHAP) with particle size higher than 90 µm, ncHAP-Si 5%_{wt} silica >45 µm, ncHAP-Si 10%_{wt} silica >63 µm and <45 µm, nc Hap-Si 15%_{wt} silica >45 µm. The measurements were carried out three times for each material.

Chemical analysis

The calcium, phosphor and silica content was determined by inductively coupled plasma emission spectrometer; the measurements were carried out with the Bergh-F Spectro Ciros CCD apparatus. The measurements were carried out on three samples for each material.

Copper retaining, sorption measurements

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 5·10⁻³ mol L⁻¹. A copper selective electrode (Tacussel PCU 2M), previously calibrated, and a reference saturated calomel electrode were used to monitor copper (II) concentration. The digitronic DXP-2040 potentiometer was employed. The experiments were carried out in a double walled reactor, connected to the FALC FA-90 thermostat under continuous magnetic stirring provided by the 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 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 Cu²⁺ 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 Cu²⁺ was 5 µmol L⁻¹.

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

Results and Discussions

RX measurements

Fig. 1 presents diffraction patterns of hydroxyapatite HAP, calcined and uncalcined and silicon and copper substituted hydroxyapatite. The silicon substitution does not appear to affect the diffraction patterns of hydroxyapatite. X-ray diffraction patterns of calcined silicon substituted hydroxyapatite shows good crystallinity. The materials were all hydroxyapatite,

having the space group $P6_3/m$ [19]. Non-calcined samples prepared appeared to be poorly crystalline. The samples have lower crystallinity and there is no significant difference between the copper and silica containing hydroxyapatite X-ray diffraction diffractograms. No secondary phases, such as CaO, were observed for HAP-Si samples.

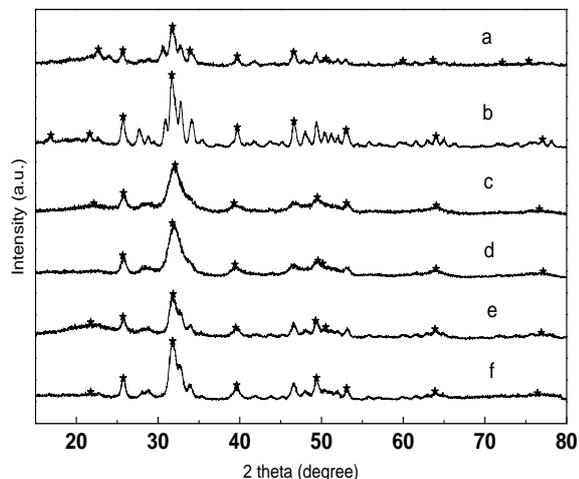


Fig. 1 X-ray diffractograms for cHAP-Si 10 mass % Si (a), cHAP (b), ncHAP-Si 10 mass % with Cu (c), ncHAP-Si 10 mass % (d), ncHAP with 4 mmol g^{-1} of Cu (e), ncHAP (f).

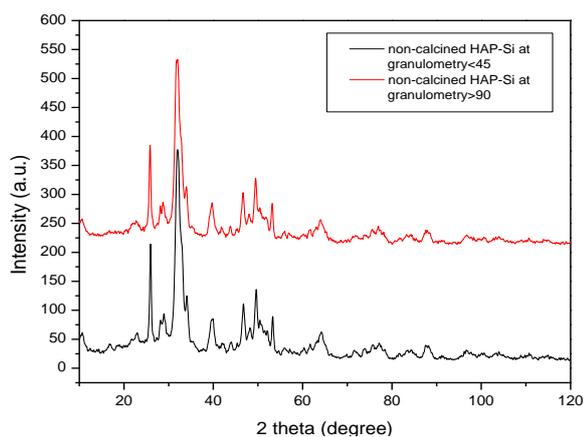


Fig. 2 XRD patterns of non-calcined silicate hydroxyapatite (10% Si) at two different granulometries (<45 black line and >90 red line).

According to Fig. 2 there are no major differences between the spectra of HAP-Si (10% Si) <45 μm and HAP-Si (10% Si) >90 μm , despite of the observed differences between the chemical composition (see Table 1).

Chemical composition analysis

The results of the chemical composition analysis show that the measured Ca, P and Si content is a different form of theoretical values which could indicate the formation of one or more secondary phases. However, XRD results relieved the absence of any secondary phase. This deviation explains the difference between the measured and the theoretical value of Ca/P+Si ratio presented in Table 1.

According to the literature [5], maximum 5% Si can be incorporated into the HAP structure. It is possible that the excess of Si above this value will be retrieved in a polymer form. This fact could explain the observed differences of Si content for the same sample, but with different granulometries. The particles with granulometry >90 μm have higher Si content than those with granulometry <45 μm , because of the Si polymer coating. To prove the polymer existence further investigations are needed.

Infrared spectroscopy

The IR spectrum of ncHAP was compared with that of the non-calcined silica-hydroxyapatite (ncHAP-Si) samples (see Fig. 3.). Gibson *et al.* [4] 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 [20]. Isolated Si–OH groups on silica show a sharp band at 3750 cm^{-1} [21]. The peak at 1384 cm^{-1} appeared due to a small amount of inorganic nitrate present in the sample.

Table 1 Theoretical and measured Ca, P and Si content of HAP-Si at different Si content and granulometries.

Material	Ca % wt	P % wt	Si % wt	$\frac{Ca}{P+Si}$	Ca % wt	P % wt	Si % wt	$\frac{Ca}{P+Si}$
	theoretical				measured			
HAP-Si 10% >90 μm	38.4	17.7	10	1.38	29.08	19.21	8.92	0.77
HAP-Si 10% <45 μm	38.4	17.7	10	1.38	27.68	19.83	3.14	0.92
HAP-Si 5% <45 μm	38.4	17.7	5	1.69	35.98	26.48	3.26	0.93
HAP-Si 15% <45 μm	38.4	17.7	15	1.17	31.54	23.68	7.01	0.78

Table 2 Specific surface and pore volume of Hap and HAP-Si samples.

Material	Specific surface med m ² /g	Pore volume med mL/g
ncHAP >90 μm	54.3769	0.1483
ncHAP >45 μm	73.6811	0.24025
ncHAP-Si 5% _{wt} silica >45 μm	120.9163	0.4132
ncHAP-Si 10% _{wt} silica >63 μm	89.7856	0.2765
ncHAP-Si 10% _{wt} silica <45 μm	124.3709	0.4562
ncHAP-Si 15% _{wt} silica >45 μm	87.7182	0.2512
cHAP >90 μm	2.7815	-

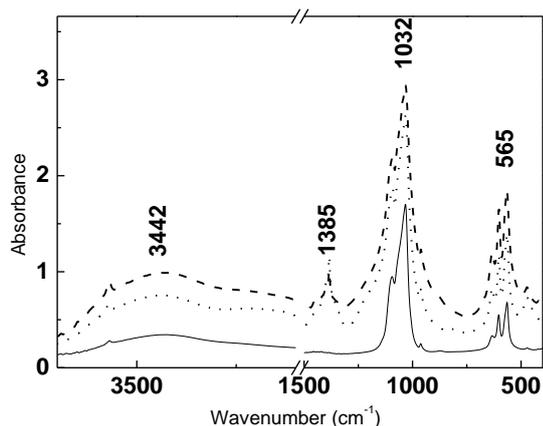


Fig. 3 IR spectra of ncHAP-Si 15 mass % Si (dotted line), ncHAP-Si 5 mass % Si (dashed line) and ncHAP (solid line).

Specific surface analysis (BET)

The specific surface and also the porosity of the materials are increasing with the decreasing of the particle size. The silica content of the materials (up to a specific value 10%) increases the specific surface and porosity, due to the formation of a water enriched polymer silica gel, which during the drying process partially loses the OH content forming a porous material with a high specific surface. ncHAP-Si 10%wt silica has the highest specific surface and porosity. The heat treated materials have a very low specific surface compared to the non-calcined materials.

Copper retaining, sorption measurements

In order to interpret the result it is necessary to definite the meaning of sorption. According to Lower *et al* [22], sorption is the loss of a chemical species from an aqueous solution to a contiguous solid phase. The mechanism of sorption includes two dimensional accumulations of ions at the mineral-solution interface, precipitation (or complexation) and three-dimensional growth of the solid phase.

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, 5·10⁻⁴ mol L⁻¹, 10⁻³ mol L⁻¹, 5·10⁻³ mol L⁻¹). pH of the solutions increased from 4.5 to 6.7.

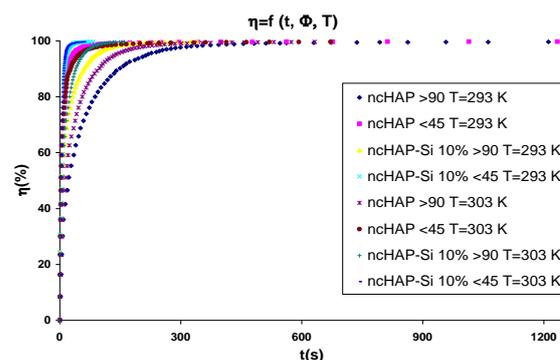
The sorption efficiency is defined as:

$$\eta = \frac{c_0 - c_i}{c_0} \%$$

where c_0 being the initial copper concentration, c_i the copper concentration at the specific time.

At the concentration of 5 mmol L⁻¹, the copper sorption efficiency for ncHAP was about 60 %, comparable to HAP-Si with 10 %wt silica that reaches the efficiency of above 99.6 %. For all non-calcined materials at the 10⁻³ mol L⁻¹ copper concentration, the sorption capacity was almost identical, meaning that the η (efficiency) was around 99.7 %, the difference consists in the saturation time. For the calcined samples, the efficiency was about 60-70 % [18]. The best material, meaning the lowest saturation time for copper sorption was the ncHAP-Si 10%wt silica >45 μm.

The increase of the temperature catalyzed the copper sorption for all materials. At higher temperature the end time of the sorption for cHAP-Si 10%wt silica >45 μm at 10⁻³ mol L⁻¹ copper concentration is below one minute.


 Fig. 4 The variation of the saturation time depending of the material type, granulometry and temperature at 10⁻³ mol L⁻¹ copper concentration.

Conclusions

HAP-Si preparation using sodium silicate proved to be a viable method. XRD and IR measurements show that the samples contain a single crystalline phase: HAP. The chemical data indicate that the obtained samples are none stoichiometric, the Ca/(P+Si) ratio is smaller than the theoretical, which can be caused by SiO₂ polymerization. Within the same samples, at different granulometric fractions, major differences

were observed. The samples with different granulometric fractions are heterogeneous, regarding to the chemical composition.

HAP doped with inorganic silica has an increased specific surface, porosity and chemical reactivity. The heat treated materials have a very low specific surface, which explains the weak metal sorption properties of these materials. The silica containing materials have better sorption efficiency than unmodified hydroxyapatite and the 10 %wt silica containing hydroxyapatite with the low particle size has the highest copper sorption efficiency. The increase of the initial copper concentration decreases the saturation time and the increase of the temperature increases the copper sorption.

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