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***“Kinetic and equilibrium studies of some
retaining processes on apatite materials”***

PhD thesis abstract

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Keywords: hydroxyapatite, modified apatites, sodium silicate, metal ions, organic substances with application in medicine, sorption, kinetics, equilibrium, reaction mechanism.

Introduction

The central idea of the PhD thesis is the extrapolation of the application filed of apatite materials. The apatite materials are comprised in the calcium phosphates group in the main group of biomaterials. In this thesis, a new approach has been applied: structural modification of hydroxyapatite, by sodium silicate addition during the precipitation process and the application of these materials in sorption/adsorption processes.

Biomaterials are synthetic materials used in medicine, which interact with biological systems. These materials have the potential to be a long time in direct contact with body fluids and living cells, without causing adverse reactions. Although in recent decades a series of biomaterials have been developed as metals, ceramics, plastics and composites, they are still far from perfect, each showing some disadvantages.

Due to favorable reactions with bone tissue in contact with them, calcium phosphates are particularly suitable as bone substitution materials or materials deposited on the surface of the prosthesis. In the last 20-30 years the use of calcium phosphate biomaterials has increased, only certain compounds proved to be useful for implantation in the human body. The apatite compounds were the most investigated. Hydroxyapatite (HAP), $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ is the major mineralogical component in bones and teeth, which explains precisely why this material is of particular interest for bone substitutions [1].

High purity hydroxyapatite has been used in various forms and for various other applications. It was used as a dense and sintered ceramic (middle ear implant, cellular applications), porous or granular form for filling in bone or teeth and as a deposit on the surface of implant materials [2, 3].

Another application for apatites is its employment as filling material for chromatography columns for protein separation, albumins, as adsorbent material for low molecular weight organic acids, polysaccharides [4], medicinal organic substances [5, 6], hemoglobin.

Hydroxyapatite has the ability to exchange their calcium, phosphate and hydroxyl ions with other metal ions or anions without the loss of the crystalline structure. This is way it can be found some materials containing magnesium , cadmium, manganese, strontium, zinc, [7], borate, silicate, chloride and fluoride ions in their structure. Because their ion exchange capacity hydroxyapatite can be used for heavy metal retaining [8, 9].

The PhD thesis aims the application of hydrxyapatite and their silica and copper ion modified compounds in heavy metal ion retention processes and in adsorption processes of organic substances, in order to purificate waste water from heavy metal ions and various organic compounds. Also it is used as support material for medicinal substances and antioxidant compounds. By the kinetic study of the solid/liquid interface processes, the reaction mechanism has been undertaken in order to identify the rate determining step. The final goal has been the synthesis of material with better efficiency in retention/sorption processes.

Given the final goal of the PhD thesis and those described above the thesis is structured as follows: presentation, definition and classification of biomaterials, classification of the calcium phosphates, apatites and hydroxiapatites in the biomaterial classes, preparation, hydroxyapatites characterization, and presentation of the chemical and physical properties, as well as their application domains. Several methods for modeling the sorption and adsorption processes in solid-liquid systems have been presented. Also a survey of current literature on the retention of copper and cadmium ions on hydroxyapatite, and adsorption of organic substances and models for kinetic and equilibrium data processing have been enclosed. The experimental part describes the preparation and characterization methods of apatite materials, the obtained experimental data and their interpretation is presented concerning kinetics and equilibrium. Finally the main conclusions and novelty elements of this thesis are highlighted.

I. Theoretical part

I.1. Biomaterials

The application of materials to replace human body parts is not something new, substitution of bones in human skeleton was done before Christ. Then copper and bronze were used to bind bone fragments.

In 1880 Gluck [10] based on the analogy of the natural ivory made a bone implant prosthesis from ivory. In 1884 Pean [11] first synthesised a metal hip. 1902 is the year when Jones added a gold capsule in the articulation. In 1915 England made the first deposit of glass layers on metals, able of being implanted in living organisms. Petersen-Smith in 1923 [12] develops a program for providing a practical and stable orthoplastics. Discovers vitalium, a metal alloy that seemed the ideal material. The first prosthesis with vitalium was done in 1938, later to fix them methacrylate auto-polymerization was used. 1960, Muller [13] uses teflon capsule - intolerable by the tissue. In 1972 begins again the application of biologically inactive materials and is developed the Al_2O_3 , ZrO_2 based ceramics. In 1971 begins the production of bioactive glasses, this way in the '70 bioceramic increasingly integrate and develop as biomaterials.

A necessary property for any synthetic material to be implanted in the body is biocompatibility. This means that the material should not cause any inflammatory reaction with tissue.

According to a general and official accepted definition [14] a biomaterial is a material with optimal biocompatibility is that which is not imposing any tissue reaction.

Special requirements are imposed to biomaterials: they must simultaneously fulfill biological, chemical, mechanical and aesthetic criteria. Several types of ceramic biomaterials, namely: a) ceramic calcium phosphate (eg hydroxyapatite), b) of alumina ceramic c) ceramics with partially stabilized zirconium, d) phosphor-silicate glasses, e) ceramic, ceramic-metal, ceramic-plastic composites are studied, tested and currently used.

I.2. Apatitic materials. Hydroxyapatite (HAP), fluorhydroxyapatite (FHAP) and hydroxyapatite doped with silicate (HAP-Si)

The apatite materials have the general formula: $M_{10}(ZO_4)_6X_2$, where:

M cation with valance between 1-3 (eg. M= Ca, Pb, Cd, Sr, Ni, Al, Y, La, Ce, Na, K);

Z element with valance between 3-7 (Z=P, As, V, Si, C, Al, S, B, Re)

X anion with valance -3, -2, -1 or neutral molecule (eg. X= OH^- , F^- , Cl^- , Br^- , I^- , O^{2-} , N^{3-} , CO_3^{2-} , H_2O , □- vacancy).

The structural, chemical and physical properties for HAP, FAP și HAP-Si are compared in *Table I.1.*

Table I.1. The structural, chemical and physical properties for HAP, FAP și HAP-Si

	HAP	HAP-Si [15,16,17]	FAP
Mineral name	Hydroxyapatite	Silicate substituted hydroxyapatite	Fluorapatite
Formula	$Ca_{10}(PO_4)_6(OH)_2$	$Ca_{10}(PO_4)_{6-x}(SiO_4)_x(OH)_{2-x}$ (x=0-1)	$Ca_{10}(PO_4)_6F_2$
Structure	P6 ₃ /m a = 9.14-9.44 Å c=6.84-6.94 Å [18]	P6 ₃ /m a=b=9.42158, c=6.89155	hexag. P6 ₃ /m a = 9.36-9.37 Å c=6.87-6.89 Å
Density (g/cm ³)	3.14-3.17	3.02-2.94	3.18-3.20
Young Modulus	114		120
Solubility	1.2-3.2 ppm Ca		0.6 ppm Ca
pH 7	8-22 ppm Ca	0.8 % _{wt} h ⁻¹ 10 ⁻³	4 ppm Ca
pH 6	50-180 ppm Ca		18-24 ppm Ca
pH 5			
Solubility constant [19]	$Ca_5(PO_4)_3OH \rightarrow 5Ca^{2+} + 3PO_4^{3-} + OH^-$ $K_{s0}=10^{-58.3}$		$Ca_5(PO_4)_3OH \rightarrow 5Ca^{2+} + 3PO_4^{3-} + F^-$ $K_{s0}=10^{-60.6}$
Melting point	1450 °C (decomposition temperature)	>1500 °C	1615-1660°C
Relative permittivity		-	9.5-10.4
Heat conductance	0.013 W/cm•K	-	0.02 W/cm•K

	HAP	HAP-Si [15,16,17]	FAP
Fracture toughness K_{Ic} (MPa.m ^{1/2}) [15]	0.25 – 0.55	0.85 - 0.95 (phosphate-glass reinforced hydroxyapatite 5% PG-HA) 0.9 – 1.1 (calcium silicateglass reinforced hydroxyapatite 5% SG-HA)	
Bending strength (MPa) [15]	30 - 80	110- 125 (PG-HA) 150 – 160 (SG-HA)	
Particles size	200-26 nm	24 nm	20 µm
Specific surface	75 m ² /g	78 m ² /g (0.4% _{wt} Si), 78 m ² /g (0.8% Si) 87 m ² /g (1 şi 1,6% Si) [20] >100 m ² /g (Ca/Si= 0.1 – 0.8) [21]	
Refractive index	w = 1.649-1.652 c = 1.643-1.644	1.60 [22, 23]	1.633 1.629
pH interval for solubility in solutions [24]	9.5–12		7–12

Apatite occurs frequently in volcanic acidic and sedimentary rocks and is used in the manufacture of phosphate fertilizers, especially super-phosphates.

FAP containing elements such as Mn and Sn and contaminated with Nd³⁺ ions is used in fluorescent lamps and as crystals used in laser construction. Fluorhydroxiapatite (FHAP) is used as a biomaterial for bone replacement due to its ability to supply fluorine ions. In contrast to FAP, which is toxic due to the high fluorine content, FHAP can be used in medicine when the fluorine content in the range of 95÷195 µg/L⁻¹ [25].

Hydroxyapatite is used in water purification form heavy metal ions, as filling materials in chromatographic columns for separation of proteins, albumins and low molecular weight organic acids, the polysaccharides [4], medicinal organic substances [5, 6], hemoglobin, proteins [26].

HAP, FHAP and HAP-Si with maximum 5% silica content are used as layer materials on metal implants for clinical purposes [27], having the property to catalyze the bone tissue growth.

HAP powder can be prepared by different methods. Reactions to obtain hydroxiapatite may be classified as follows:

1. *Precipitation reactions*, eg. the reaction between calcium nitrate solution and ammonium phosphate, in the presence of ammonium hydroxide [28, 29, 30].
2. *Hydrolysis reaction*: dicalcium phosphate hydrolysis in alkaline solution [31].
3. *Solid state reaction* [32]:

$$3\text{Ca}(\text{PO}_4)_2 + 4\text{Ca}(\text{OH})_2 \rightarrow \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 + 6\text{H}_2\text{O} \quad (\text{I.1.})$$
4. *Hydrothermal reactions* [33, 34, 35]: from a mixture of calcium carbonate and dicalcium phosphate solutions at 2750°C, water vapor pressure 12000 psi.
5. *Sol-gel method*: using precursors as calcium acetate and triethyl-phosphate, with magnetic stirring for 24 hours. The gel is dried at 120°C, for 16 hour [36].

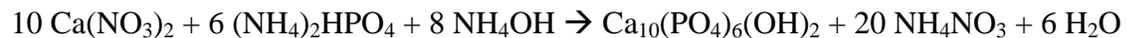
The preparation method and conditions applied to obtain synthetic HAP will influence both physical and chemical properties.

II. Experimental part.

II.1. Apatite materials preparation

a) Hydroxyapatite (HAP) preparation

A wet method involving precipitation of hydroxyapatite by mixing aqueous solutions containing Ca^{2+} and PO_4^{3-} ions, at $\text{pH} > 9$ has been chosen to prepare hydroxyapatite. Calcium nitrate as a source for calcium and diammonium hydrogen phosphate as phosphate source were used. pH was adjusted with NH_4OH . The reaction occurs as follows:



0,5 M calcium nitrate, 0,3 M diammonium hydrogen phosphate, and 25% ammonia solution were employed.

Calcium nitrate is dissolved in distilled water and ammonia is added to the reactor of 2.5 L total volume under mechanical agitation with of. Diammonium hydrogen phosphate and the rest remaining ammonia is added over the solution of calcium nitrate and ammonia, meanwhile the stirrer is set on 975 rpm and after complete addition is reduced to 450 rpm. pH was adjusted with ammonia solution, keeping it above the 9 and the temperature was maintained at 20 ° C. Reaction time was 20 hours.

At the end, the precipitate was washed several times to remove ammonia and filtered. The filtrate was dried in the oven (Memmert 200) for 24 hours at 105°C.

A part of the sample was heated for 1 hour at 1000°C (Barnstead 47900 oven) to study the influence of calcination on the sorption property and their behavior in heterogeneous systems reactions.

b) Silicate doped hydroxyapatite (HAP-Si)

The same preparation method was used for silicate doped hydroxyapatite unsubstituted hydroxyapatite, with the difference that sodium silicate in different amounts, depending on the desired percentage of silicon was added. Reaction time is 8 hours, instead of 20. Apatite materials with 5%, 10% and 15 mass percent silicate content were obtained.: Two varieties of silicate materials: HAP-Si 5 mass% were prepared, one of them, HAP-Si 5 mass%+ having 5 mass% silicate plus 10 mass% calcium. The substitution process of phosphate groups with silicate groups is as follows:



The washing, drying and thermal treatment were as presented above

Copper doped apatite preparation

To synthesize copper doped apatite non-calcined hydroxyapatite (ncHAP) and HAP doped with in different percentages with silicate (ncHAP-Si 5 mass% + silicate, ncHAP-Si 10 mass % silicate) were used. Three procedures were applied:

- ***exchange reaction*** with copper ions

Non-calcined hydroxyapatite, silicate substituted hydroxyapatite with 5% + and 10% silicate were used and cupric solution was added over the material,.Cu²⁺ initial concentration was 10⁻³ M. To prepare 1 g of material, 200 ml cupric solution was used. The reaction was carried out under continuous magnetic stirring until the equilibrium was reached. A certain amount was calcined at 1000°C for one hour.

- ***solid state reaction*** (HAP+Cu(NO₃)₂)

To prepare copper doped apatites, non-calcined hydroxyapatite with different granularity ($\Phi > 180 \mu\text{m}$ și $\Phi < 45 \mu\text{m}$) and copper nitrate were mortared in an agate mortar for several minutes. The apatite / Cu(NO₃)₂ ratio was: 1 g HAP/0.048 g copper nitrate (equivalent for 10⁻³ mol L⁻¹ copper ion concentration in the final material). The obtained materials were heat treated for one hour at 1000°C.

- ***co-precipitation***

This method is similar to that used in the preparation of apatite materials, with the exception that copper nitrate solution ($m = 0.48 \text{ g Cu(NO}_3)_2$) was added in the reaction vessel. pH was adjusted with ammonia solution, keeping it around 11, and the temperature was maintained at 20°C , the reaction time is 20 hours. After the end of the reaction, the precipitate was washed, filtered and the filtrate was dried for 24 hours at 105°C . Heat treatment was performed at 1000°C .

After drying all materials were crushed by ball mill (FRITSCH, Planeten-Monmuhle model "Pulverisette 6" ceramic balls) for 40 minutes (hydroxyapatite) or one hour (silicate doped apatite).

II.2. Material characterization

Solid phase particle size separation

After ball milling all the materials were separated with vibration sieves (Retsch AS200) with four bolter having the mesh diameter: $180 \mu\text{m}$, $90 \mu\text{m}$, $63 \mu\text{m}$, $45 \mu\text{m}$. The average size of the materials are situated between 90 and $45 \mu\text{m}$. The amount of material having particle size over $180 \mu\text{m}$ size is low.

Particle size determination with Counter Coulter

The diameters of the particles in suspension for five samples was determined by means of a Shimadzu SALD-7101 Counter Coulter analyzer. Values obtained fall in the domain of $700\text{-}800 \text{ nm}$ for materials doped with 5% 5% + and 15% silicate and is 15 nm for ncHAP and ncHAP-Si 10% . Comparing the two methods is apparent that particle size determined in suspension by ultrasound disintegration is much smaller, suggesting that during drying agglomerates are formed.

IR spectroscopy

The specific vibrations of hydroxyapatite groups were determined by using IR spectroscopy

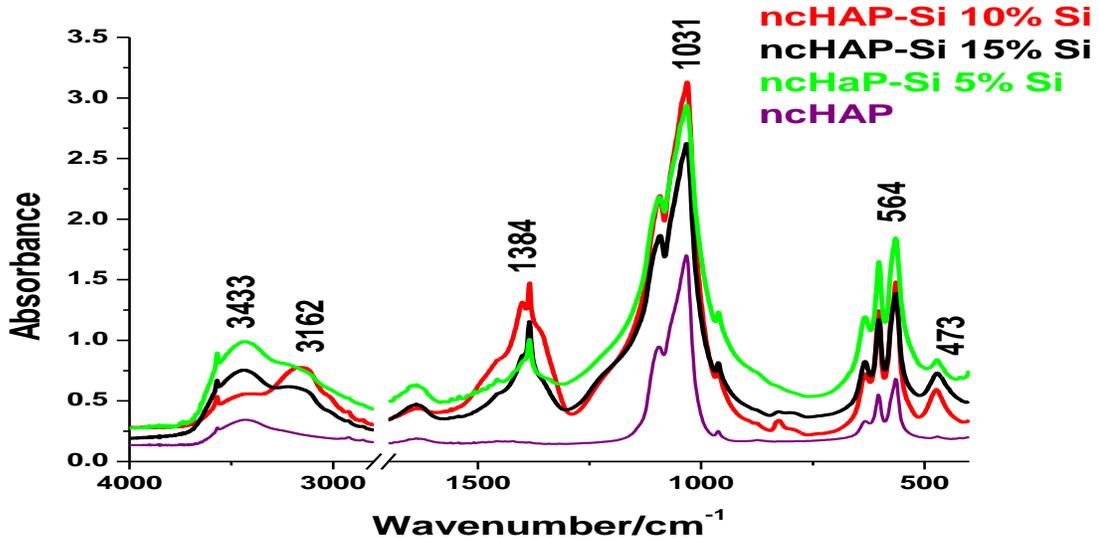


Figure II.1. IR spectra for ncHAP, ncHAP-Si 5%, ncHAP-Si 10% and ncHAP-Si 15%

The main bonds and their corresponding frequencies for hydroxyapatite and silicate doped apatite are presented in **Table II.1**:

Table II.1. The main bonds and their frequencies for hydroxyapatite and HAP-Si [37, 38, 39, 40]

Material	Wavenumber (cm ⁻¹)	Bonds
non-calcined HAP	963	P-O symmetrical stretching
	1047	P-O degenerate vibration
	1090	
	565	P-O deformation vibration
	572	
	602	
	633	O-H rotation vibration
	3573	O-H---O deformation vibration

Material	Wavenumber (cm ⁻¹)	Bonds
	1384	N-O symmetrical stretching
non-calcined HAP-Si	950 – 1200	Si – O – Si stretching vibrations Si-O stretching vibrations
	1100, 802, 467	Si-O-Si, silica source condensation
	3750	Si – OH, isolated groups
	3400-3200	Si-OH, hydrogen bounded –OH groups

Cristallinity determination by X-ray diffraction method

RX measurements were performed to study the crystalline state of the materials and to determine the presence of any secondary phases. Hydroxyapatite diffractograms was compared with those doped with silicate and copper, to observe any changes in structure, caused by the presence of silicate and copper ions. Silicate substitution does not seem to affect hydroxyapatite diffractograms. The calcined samples show a higher crystalline state. Materials were all identified as hydroxyapatite, with P6₃/m space group [41]. On the X-ray diffractograms, the presence of other secondary phases, such as CaO and tricalcium phosphate, were not observed.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM)

The differences in surface and agglomeration for calcined and non-calcined materials, doped with copper and silicon at different resolutions can be observed in **Figure II.2**. At hydroxiapatite un-doped and doped with copper can be seen that the agglomerates have a more spherical structure compared to silicate doped HAP. HAP-Si 10% is more compact, with cornered larger agglomerations. At cHAP and cHAP+Cu prepared with solid phase reaction at higher resolution can be observed that the individual particles are slightly elongated, which is a typical sintering characteristic (**Figura II.2. c, l**). At calcined materials doped with copper by ion exchange it can be seen at higher resolution, a finer particle distribution, which can be caused by the precipitation of copper ions on the material surface, after their reaction with hydroxyl groups [42].

At non-calcined materials doped with copper by ion exchange SEM images show at higher resolution, a finer particle distribution, which can be caused by precipitation of copper ions on the surface in reaction with hydroxyl groups.

TEM measurements are consistent with results of SEM analysis, where can be observed the necks formed after calcination are caused by the melting of the material surface between the individual particles. With this method is also seen the morphology difference between the materials, but even this method does not demonstrate the existence of any secondary phase. This can be explained by the formation of a silicate layer around the phosphate particles.

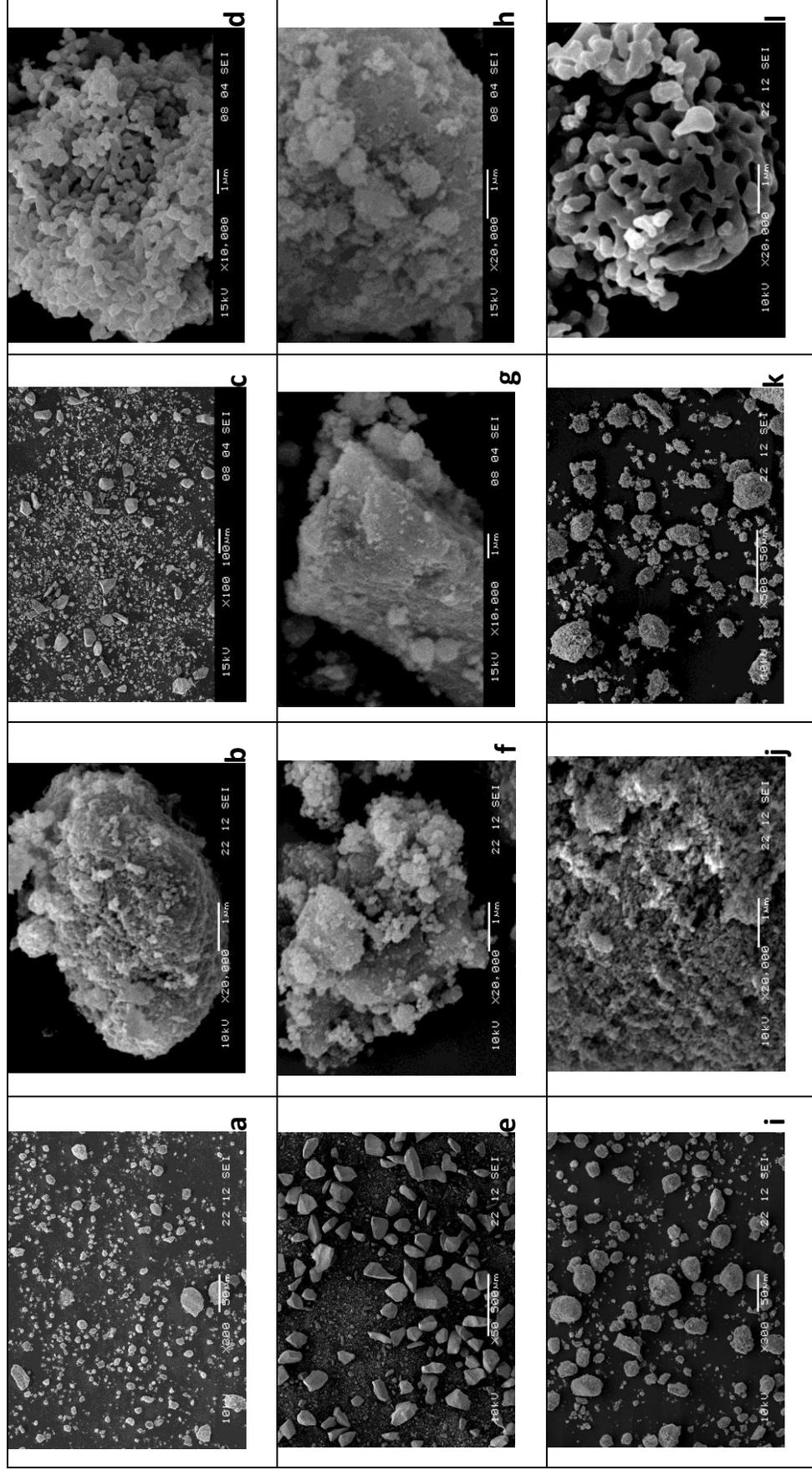
Specific surface determination by BET method

According to BET measurements the material with the best characteristics, meaning highest specific surface ($124.4 \text{ m}^2/\text{g}$) and high pore volume (0.46 mL/g), is non-calcined hydroxyapatite, doped silicate 10 mass % [43]. Heat-treated materials have lower specific surface and pore volume.

Chemical analysis with Inductive Coupled Plasma Electrode - ICP

By this method it was examined calcium, sodium and silicon content, at nHAP-Si doped with 5% and 15% silicate and at different granulosity for nHAP-Si 10%. The results show that Ca content values differ from the theoretical ones, that could indicate the formation of one more secondary phases. Materials with $>90 \text{ }\mu\text{m}$ particle size have higher silicate content than those with $<45 \text{ }\mu\text{m}$ granulosity. This can be explained by the formation of a silicate polymer layer around the grains [44].

Figure II.2. SEM images for ncHAP (a, b), cHAP (c, d), ncHAP-Si 10% Si $\Phi < 45 \mu\text{m}$ (e, f), cHAP-Si 10% Si $\Phi > 90 \mu\text{m}$ (g), cHAP-Si 10% Si $\Phi < 45 \mu\text{m}$ (h), ncHAP+Cu $[\text{Cu}^{2+}] = 10^{-3} \text{ M}$ $\Phi < 45 \mu\text{m}$, prepared by ion exchange (i, j), cHAP+Cu prepared with solid state reaction $\Phi < 45 \mu\text{m}$ (k, l)



III. Applications. Sorption and adsorption processes

III.1. Metal ions retention on apatite materials

Retention experiments were performed in batch conditions in a double walled vessel under continuous magnetic stirring (FALC FA-20), at several initial metal ion concentrations ($c_1=5 \cdot 10^{-3}$ M, $c_2= 10^{-3}$ M, $c_3= 5 \cdot 10^{-4}$ M, $c_4=10^{-4}$ M) and constant temperatures (4°C, 20°C, 30°C, 40°C, 50°C) ensured by a FALC FA-90 thermostat. The material/solution volume rapport was maintained constant 0.25 g/50 mL of metal nitrate solution. In addition to temperature and initial concentration the effect of granulosity, and kind of material (HAP or silicate doped HAP), the percentage of silicate and heat treatment were also studied.

The copper sorption experiments were made on the following materials: HAP, HAP-Si 5%, HAP-Si 5% +, HAP-Si 10%, HAP-Si 15% silicate with particle size <45 μ m and >90 μ m calcined and non-calcined, at initial metal concentrations $5 \cdot 10^{-3}$ M, 10^{-3} M, $5 \cdot 10^{-4}$ M, 10^{-4} M. At non-calcined hydroxyapatite and HAP-Si 10% the effect of temperature increase was studied in order to determine activation energy.

In the cadmium ion experiments the same procedure was applied, except that the influence of heat treatment has not been studied and the effect of initial concentration was monitored in $10^{-3} \div 10^{-4}$ M concentration range.

The obtained potential - time data served to calculate the sorption capacity and efficiency. The maximum sorption capacity and the highest sorption rate were determined.

$$q_t = \frac{m_{sorb}}{m_{HAP}} \quad \left(\frac{g}{g} \right) \quad \text{or} \quad q_t = \frac{n_{sorb}}{m_{HAP}} \quad \left(\frac{mmol}{g} \right) \quad (III.1.)$$

where: $m_{sorb}=c_{sorb} \cdot V \cdot M$, and $n_{sorb}=c_{sorb} V$

$$\eta = \frac{c_0 - c_i}{c_0} 100 \quad (\%) \quad (III.2.)$$

where: c_0 – initial concentration (M)

c_i - concentration at t time (M)

V - metal solution volume (mL)

c_{sorb} - metal ion concentration variation at t time (M)

M - molar weight (g/mol)

m_{sorb} - metal quantity retained on the material (mg)

m_{HAP} - amount of used apatite (g)

η – sorption efficiency (%)

All the results obtained from each sample were represented to highlight the differences in order to establish the most adequate material and most advantageous conditions for the retention of metal ions.

In order to elucidate the relationship between the retention of copper/cadmium ions and calcium and hydrogen ion release, calcium concentration change and pH were monitored for ncHAP and ncHAP-Si 10% at 10^{-3} M copper/cadmium initial concentration, at $T=293K$. The copper/cadmium retained ion concentration was graphically represented in function on the calcium ions concentration during the sorption process, until the concentration remained constant.

To determine the sorption kinetics data were processed according to several kinetic models: pseudo-first order, shrinking core model, intraparticle diffusion, pseudo-second order model.

In order to apply the pseudo-first order kinetics it was assumed, as submitted by Corami et. al. [45], a mechanism of two consecutive processes: in the first step of the sorption process a fast complexation of metal ions on specific sites of the HA surface occurs, and the second step can be attributed either to the formation of a heavy metal-containing hydroxyapatite or to the metal diffusion into the HA structure. This way it was represented $-\ln(1-\eta)=f(t)$, based on first order rate equation for irreversible reactions:

$$r = k_1 c_A \quad (III.3.)$$

Slope of the linear portion represents the rate constant. By Arrhenius type representation ($\ln(k)= f(1/T)$) in the range of $T = 297-323$ K based on III.4.equation the activation energy was calculated, representative of the two processes for hydroxyapatite and ncHAP-Si at two initial concentrations: 10^{-3} M și $5 \cdot 10^{-4}$ M.

$$k = A \cdot \exp\left(\frac{E_a}{RT}\right) \quad (III.4.)$$

where: k - rate constant; A - pre-exponential factor, characteristic for each reaction, ($A=r \times Z$; Z is the number of collisions in which molecules are undertaking in one second / unit area and r is the fraction of effective collisions).

The possibility that intraparticle diffusion affects the sorption process was investigated using diffusion model described by equation III.5. [46]:

$$q_t = K_{id} \cdot t^{1/2} + I \quad (\text{III.5.})$$

q_t was plotted against $t^{1/2}$, where the k_{id} is intraparticle rate diffusion constant and I is a constant that provides information about the boundary layer thickness limit. As this value is greater as the boundary layer effect is stronger.

Pseudo-second order kinetic model, which describes the adsorption kinetics by the equation III.6. The plot of $\frac{t}{q_t}$ in function of t and processing the k_2 values (pseudo-second order rate constant) at different temperatures the activation energy was calculated.

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \quad (\text{III.6.})$$

With the **shrinking core model**, it was considered that the **diffusion through the ash is the rate determining step**. The equation III.7 was plotted $1 - 3(1 - \eta)^{2/3} + 2(1 - \eta) = f(t)$. When **chemical reaction is considered the rate determining step**, equation III.8. was used [47, 48].

$$\frac{t}{t_\infty} = 1 - 3(1 - \eta)^{2/3} + 2(1 - \eta) \quad (\text{III.7.})$$

$$\frac{t}{t_\infty} = 1 - (1 - \eta)^{1/3} \quad (\text{III.8.})$$

where η is the process efficiency.

Due to the decrease in pH, it was assumed that ion exchange occurs between metal ions and protons. For modeling this process in the case of copper sorption the **quasi-homogeneous resin phase kinetic model** was applied. The calculations for **FSV model** were made using the analytical solution for Fick's second law, equation III.9, for finite solution volume (FSV) [49, 50, 51].

$$F = 1 - \frac{2}{3\omega} \sum_{n=1}^{\infty} \frac{\exp(-S_n \tau)}{1 + \frac{S_n^2}{9\omega(\omega+1)}} \quad (\text{III.9.})$$

The input data in the program are: t , F , average particle radius of adsorbent, in meters, ω . The output files are: t , F , τ , D (diffusion coefficient).

F was calculated with the formula:

$$F = \frac{C_{initial} - C_{la\ momental\ t}}{C_{initial} - C_{final}}, \text{ and } \omega \text{ with the formula: } \omega = \frac{C_{initial} - C_{final}}{C_{final}}.$$

Simulations were made for two materials: ncHAP and ncHAP-Si 10%Si at two granulosesities: $\Phi > 90 \mu\text{m}$ and $< 45 \mu\text{m}$, at 10^{-3} M initial copper concentration. The calculations were made taking into account the grain size determined by sieving calculating an average value, $15 \mu\text{m}$ for $< 45 \mu\text{m}$ and $65 \mu\text{m}$ for $\Phi > 90 \mu\text{m}$ particle sized materials.

Results . Sorption of copper and cadmium ions

Apatite materials have good metal ion retention properties. Both the copper and cadmium sorption depends from the material nature and particle size. Heat-treated materials have a much lower retention property, which may be due to low value of the specific surface. The reaction rate is positively influenced by the decrease of initial metal ion concentration and granulosity, and by the increase of temperature. Material doped with silicate in the amount of 10% shows the best retention properties: high sorption capacity at high initial concentrations ($5 \cdot 10^{-3}$ M) and for calcined materials too, increased reaction rate at low concentrations ($10^{-3} \div 10^{-4}$ M), both for copper and cadmium ions.

To determine the reaction mechanism, the kinetic curves were processed with the above mentioned kinetic models. Based on the results of these models it can be concluded that diffusion has a substantial role in the mechanism and the model with highest correlation coefficient is the pseudo-second order model.

For copper retention the activation energy was determined, based on the values of rate constants calculated with the pseudo-second order model, which ranges between

20÷35 kJ/mol. According to the literature the activation energy in the range 8–16 kJ/mol is representative of ion exchange mechanism [52]. The value calculated in our case gives indications that the main mechanism is based on a process that implies chemical forces, and the copper/cadmium ion exchange, internal diffusion are not rate determining steps. In conclusion the investigated system, copper and cadmium ions sorption on apatite materials, follows a pseudo-second order model [53], involving both chemical reactions (copper/cadmium ions complexation on the surface of the material, interaction with surface hydroxyl groups) and intraparticle diffusion.

III.2. Organic substances sorption on apatite materials

Anthocyanins sorption on apatite materials

The anthocyanine is an antioxidant substance [54, 55, 56], used both for food and health protection. Given this striking property it is a potential compound to combat cancer by destroying free radicals. Thus it is important to study the antioxidant activity. Unfortunately this substance, as other substances with antioxidant effects, is quite unstable and decomposes if stored under normal conditions. To stabilize the compound, or at least prolong their life time, sorption experiments were made on apatite materials, which in those described in previous chapters, are biocompatible and as support materials exhibit good properties as adsorbent for organic substances.

With this purpose anthocyanine was extracted from red beet, and the antioxidant effect was determined by means of Briggs-Raucher method (BR), which is based on the inhibition of oscillations by capturing free radicals in the system [57,58, 59, 60, 61, 62].

Anthocyanine sorption extracted from beetroot from solutions of different concentrations, with fixed volume of 25 mL was performed on different apatite materials: calcined and non-calcined hydroxyapatite and HAP-Si 5%, 5%+, 10% și 15% silicat, calcined hydroxyapatite doped with copper (0.048 g $\text{Cu}(\text{NO}_3)_2$ /1 g apatite) prepared with solid phase synthesis, co-precipitation and ion exchange: ncHAP, ncHAP-Si 5% și 10% silicate. The materials employed had > 63 și < 90 μm granulosity. Adsorption was studied in batch conditions in a double walled vessel under continuous magnetic stirring (FALC FA-20). The reaction was stopped at 5, 10, 20, 30, 60 minutes.

The suspension was filtered and the remaining solution was analyzed spectrophotometrically for the determination of the remaining anthocyanine concentration. Experiments were done at different initial anthocyanine concentrations : $3,5 \cdot 10^{-3}\%$, $4,5 \cdot 10^{-3}\%$ și $5,5 \cdot 10^{-3}\%$ (0.4-0.25 mg/mL) and at different temperatures: 15°C, 20°C, 30°C, 40°C and 50°C.

Thus the effect of time, material, the presence of copper ions and initial concentration of anthocyanine and temperature was studied. The sorption capacity (mg/g) and efficiency was presented graphically for each material.

To determine the mechanism and sorption kinetics, data were processed according to several kinetic models: pseudo-first order, intraparticle diffusion, pseudo-second order model.

Results - Anthocyanine sorption on apatite materials

To determine the antioxidant effect different concentrations of anthocyanine solutions were introduced in the BR system, which caused the interruption of the oscillation. At concentrations above $9,857 \cdot 10^{-3}\%$ (98,863 mg/L) (BR active system) the added amount caused total stoppage of the oscillations. The inhibition time was established within the $9,857 \cdot 10^{-3} \% \div 2,862 \cdot 10^{-3} \%$ anthocyanine concentration interval, concentration calculated for the total volume of the oscillatory system. Linear regression shows that this method is suitable for determining the antioxidant effect of anthocyanine extract [63].

The apatite sorption capacity of materials can be increased by the addition of small quantities of silicate and copper. This may be due to the formation of copper containing active centers on the surface of a material, this way enhancing anthocyanine sorption reaction. Adsorption is influenced by material type silicate content, heat treatment, initial concentration of adsorbent and temperature. Calcined materials have low sorption efficiency. Both silicate and copper substitution has a positive effect on the sorption efficiency. With increasing temperature the sorption capacity of materials decreases. The material with the highest sorption capacity and sorption rate is ncHap-Si 10%-Cu [Cu^{2+}] = 10^{-3} M.

The kinetic data correlate best with the pseudo-second order model, and the principal mechanism is the formation of chemical bonds between the active centers on surface material and anthocyanine.

Nicotinic acid sorption on apatite materials

Nicotinic acid pertains to B vitamins group, being hydro-soluble. It also has some beneficial effects on organisms by its vaso-dilator effect by stimulating prostaglandin release [64], helps in the decrease cholesterol concentration and low density lipoprotein level - responsible for fatty acids - and triglycerides deposition on arteries, and helps in the increase of high density lipoprotein quantity, which destroys fat deposits in blood vessels [65].

For sorption measurements different concentration nicotinic acid (Reactivul) solution were used. Calibration curve was performed by measuring the absorbance of the solutions at 261 nm.

For sorption experiments in the first step 50 ml of 10^{-2} M nicotinic acid solution was used and 1 g of material (non-calcined hydroxyapatite). At different times (0.5, 1, 2, 4, 6, 8, 10, 15, 20, 30, 40, 60, 90, 120, 140, 160, 180, 200, 220, 240, 260 and 280 min) the reaction was stopped and samples were taken for spectrophotometric analysis. The temperature was maintained at 20°C. At this concentration the maximum sorption capacity was established for hydroxyapatite.

In the second stage the sorption was performed using 0.2 g of hydroxyapatite over which was added 10 ml solution of nicotinic acid of $2 \cdot 10^{-4}$ or 10^{-4} M. The solution was agitated for 5, 15, 30 or 60 minutes in a thermostatic bath. Then, the solution was filtered and the filtrate was analyzed by means of an UV-Vis spectrophotometer.

Knowing the absorbance, based on the calibration curve the remaining nicotinic acid solution concentration was calculated, and then adsorbed nicotinic acid concentration and sorption efficiency was determined. ncHAP, ncHAP-Si cu 5% și 10% silicat și ncHAP-Si 10% Si + Cu (10^{-3} M) materials were used. The effect of substitution (copper ions and silicate groups), concentration and temperature was studied.

To determine the mechanism and sorption kinetics data were processed according to several kinetic models: pseudo-first order, intraparticle diffusion, pseudo-second order model.

For equilibrium studies the experiments were carried out at different nicotinic acid concentration ($4 \cdot 10^{-5} \div 8 \cdot 10^{-4}$). 10 mL of solution was mixed with 0.2 g apatite material under continuous stirring at room temperature. After achieving the equilibrium (1 hour) the suspension was filtered and the absorbance was measured. The data were processed according to Langmuir and Freundlich models of isotherms.

Results - Nicotinic acid sorption on apatite materials

In order to achieve sorption of nicotinic acid on apatites, it appeared that silicate substituted hydroxyapatite gives higher sorption efficiency than for unsubstituted hydroxiapatite because these materials have a higher specific surface. The percentage of silicate substitution is also an important factor leading to sorption efficiency increase. The best material proved to be silicon and copper substituted hydroxyapatite. The introduction of copper ions increases the sorption efficiency of the material and decreases the sorption heat (ΔH). It was assumed that copper ions on surface create additional active centers [66, 67] or by forms chemical bonds between organic substances and copper ions.

By carrying out experiments at different temperatures - 15, 20 and 30°C – it can be observed that the sorption efficiency increases with decreasing temperature, which can be explained if the sorption process is exothermic (negative values of ΔH). Van't Hoff-Arrhenius equation was applied to represent the sorption capacity dependence on temperature at equilibrium [68]:

$$\left(\frac{\partial \ln q_e}{\partial \frac{1}{T}}\right) = -\frac{\Delta H}{R}$$

(III.10.)

Equilibrium capacity, calculated from pseudo-second order model, values were represented graphically in function of temperature (15, 20, 30°C) $\ln q_e = 1/T$, and the heat

sorption of the process was calculated (ΔH). Calculated values are negative, corresponding to exothermic processes. Sorption heat value varies, depending on the material and it is lower for materials with higher sorption capacity.

Another parameter was modified, namely the initial nicotinic acid concentration. Experiments were performed using nicotinic acid solution of 10^{-4} M and $2 \cdot 10^{-4}$ M concentration. It was noted that with higher concentrations increased efficiency was achieved.

Adsorption follows a pseudo-second order kinetic model. This model corresponds to the best fit of data and yields the best correlation coefficients.

Equilibrium data can be processed with Freundlich model, a model applicable to low surface occupancy.

Final conclusion

The PhD thesis aims the application of hydroxyapatite and their silicate and copper ion modified compounds in heavy metal ion retention and adsorption processes of organic substances. The study reveals the possibilities of wastewater purification from heavy metal ions and organic substances, and as support material for medicinal substances and antioxidant compounds. By the kinetic study of the solid/liquid interface processes, the reaction mechanism and the rate determining step had been described, having the final goal the synthesis of a material with the highest efficiency in retention/sorption processes.

Given the proposed objectives more sorts of apatite materials were prepared by several methods. Hydroxyapatite was synthesized by precipitation method and silicate doped materials were synthesized, using Na_2SiO_3 as silica source. The method and reagents used in our case represents a novelty in the preparation of silicate doped hydroxyapatite. Materials with different content of silicate were prepared: 5, 10, 15 mass%. On the other hand the calcium content influence on metal sorption was monitored and for this two materials were prepared with 5% silicate (HAP-Si 5% and HAP-Si 5%+), the last having 10% more calcium.

In addition to silicate doped hydroxyapatite copper substituted materials were also prepared (48 mg $\text{Cu}(\text{NO}_3)_2$ / 1 g apatite) by different methods (ion exchange, co-precipitation and by solid phase reaction) with the purpose to create more active centers on the apatite materials to enhance surface sorption processes of organic substances.

These materials were analyzed by different methods: particle size analysis, IR spectroscopy, X-ray diffraction, scanning and transmission electron microscopy (SEM and TEM), specific surface determination by BET method, chemical analysis by emission spectrometry with inductively coupled plasma electrode- ICP.

The average particle size determined by vibration sieves is situated between 90 and 45 μm . The Coulter Counter analysis shows that hydroxyapatite and HAP-Si 10% Si have the smallest particle size, with a difference of one order magnitude comparing with other materials.

IR spectrum for hydroxyapatite is similar to that described in the literature. In the case of silicate doped hydroxyapatite, one can be observed the deformation in the P –

O.... vibration bands, caused by the distortion of the tetrahedral PO_4^{3-} groups. The distortion is caused by the stretching vibration assigned to Si – O – Si bonds, that should appear in the range $950\text{-}1200\text{ cm}^{-1}$, but due to the presence of phosphate groups these peaks can not be observed. Nevertheless, characteristic peaks appear at 467 cm^{-1} and 798 cm^{-1} corresponding to Si-O-Si bands, which involves condensation of silicate anions with siloxane bond formation. At ncHAP-Si 10% appears a new peak at 3162 cm^{-1} , and the peak from 3442 cm^{-1} is diminished.

By performing X-ray measurements, the spectra indicate that silicate substitution does not seem to affect hydroxyapatite diffractograms. The calcined samples show a higher crystalline state. Materials were all identified as hydroxyapatite, with $P6_3/m$ space group. Non-calcined materials seem less crystalline. Wider peaks suggest a lower crystallinity and there is no significant difference between apatites doped silicate and/or copper. The X-ray diffractograms reveals no presence of other secondary phases such as CaO and tricalcium phosphate. Applying the Debye-Scherrer formula to calculate the crystal size it can be observed that addition of copper and silicon during synthesis inhibits crystal growth.

With SEM and TEM methods morphological differences between calcined and non-calcined materials were observed. Silicate doped materials are more compact and cornered, and the calcination effects differs from that of hydroxyapatite. TEM images show the size difference between cHAP și cHAP-Si 10% agglomeration.

According to BET measurements the material with the best characteristics, meaning higher specific surface and pore volume, has the sort of non-calcined 10 mass% silicate doped hydroxyapatite. Heat-treated materials have lower specific surface and pore volume.

The ICP results show that Si content values vary with the granulometry. Materials with $>90\text{ }\mu\text{m}$ particle size have higher silicate content than those with $<45\text{ }\mu\text{m}$ granulosity, that could indicate the formation of one more secondary phase. The materials do not contain any residual sodium ions.

After materials preparation and characterization copper and cadmium ions sorption was studied. Apatite materials have good metal ions retention properties. The sorption of copper and cadmium depends on the material nature and particle size. Heat-

treated materials have a much lower retention capacity, which may be due to low specific surface value. Sorption rate is positively influenced by the decrease of initial metal ion concentration and granularity, and temperature increase. Silicate doped materials with 10 mass% silicate shows the best retention properties: high sorption capacity at high metal ion initial concentrations ($5 \cdot 10^{-3}$ M) and calcined materials, high reaction rate at lower concentrations ($10^{-3} \div 10^{-4}$ M), both for copper and cadmium ions sorption.

To determine the sorption mechanism different kinetic models were applied: 1) where the rate determining step is a chemical reaction – pseudo-first and pseudo-second order kinetic model, 2) when the rate determining step is intraparticle diffusion or diffusion in the reacted layer (shrinking core model).

From data processing according to these models, it may be concluded that diffusion has a substantial role in the mechanism and the model with highest correlation coefficient is the pseudo-second order kinetic model.

For copper retention the activation energy was determined, which ranges between 20÷35 kJ/mol. This value indicates that the main mechanism is not copper/cadmium ion exchange with calcium ions. Intraparticle diffusion has a substantial role, but simultaneously appears processes that implies chemical forces. This explains the high activation energy value.

The antioxidant effect of anthocyanine extract was determined with Briggs-Raucher method. Sorption experiments were carried out on calcined and non-calcined hydroxyapatite, on materials doped with silicate and copper. It was found that anthocyanine retained its antioxidant effect after sorption and that sorption is influenced by material type, silicate content, heat treatment, initial concentration and temperature.

Copper substitution in the materials greatly influence the sorption capacity. Calcination of the materials increases the metal intercalation in the crystalline structure, reduces the specific surface. The sorption efficiency of calcined copper doped materials is lower. The copper substituted non-calcined materials synthesized by coprecipitation sorption efficiency is lower as compared those prepared by ion exchange. It is assumed that in the case of ion exchange the copper ions are concentrated on the material surface, being this way more accessible to form chemical coordinative bond formation with organic substances.

The material with the highest sorption capacity and sorption rate is ncHap-Si 10%-Cu [Cu²⁺] = 10⁻³ M. The kinetic data are best correlated with the pseudo-second order model. The rate determining step is a chemical reaction.

In the case of nicotinic acid sorption higher efficiency was achieved with the decrease of temperature, and for higher initial concentrations increased efficiency was achieved. Adsorption follows a pseudo-second order kinetic, with the best correlation coefficients. Equilibrium data were processed with Freundlich isotherm, a model applicable to low surface occupancy.

Given the above mentions, we can conclude that hydroxyapatite substitution with silicate has beneficial effects on metal ions retention and organic substances adsorption. Hydroxyapatite with 10% silicate has superior properties (low particle size, high specific surface and pore volume, as modified hydroxyl group structure) and high sorption capacity and reaction rate in case of metal ions retaining. In the case organic substances sorption the substitution of silicate containing materials with small amounts of copper (mg) increases the efficiency compared to ncHAP-Si 10%.

Prospects

According to the results, structural modified hydroxyapatite with sodium silicate containing 10% silicate has superior properties. The appearance of a peak at 3162 cm^{-1} , the high specific surface and porosity, the results of ICP, SEM images, all suggest the presence of secondary phases. For the determination of this phase, another method of characterization is required, for future experiments.

Non-calcined material, although it has a superior sorption capacity compared to those with thermal treatment, has the disadvantage of dissolving in acidic pH. Stability at low pH can be enhanced by heat treatment at temperatures lower than $1000\text{ }^{\circ}\text{C}$.

Based on the experiments performed under batch conditions as well as the results presented in the literature, it is certain that apatite can be used in wastewater treatment. Testing the material in industrial water purification either under static or dynamic conditions, in the presence of metal ions and organic substances (surface active substances, phenols, etc.) represents another future approach.

The materials containing adsorbed organic medical compounds need to be tested in conditions simulating biological systems. They can be applied locally, with retarded desorption. This can be realized by placing them on apatite materials used for metal implants wrapping. To prepare these apatite depositions will be applied a new method, replacing "plasma spraying" with "flame spraying" method [69].

In conclusion this new material can be applied for waste water treatment or as a substrate for active drugs.

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