



EVALUAREA PULBERILOR NANOMETRICE DE HIDROXIAPATITĂ PENTRU REȚINEREA IONILOR DE Pb^{2+} DIN SOLUȚIILE LOR APOASE

EVALUATION OF LAB SCALE NANO-HYDROXYAPATITES FOR REMOVAL OF LEAD IONS FROM AQUEOUS SOLUTIONS

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This study aimed to investigate the effect of preparation conditions on different hydroxyapatite nanopowders (n-HAP), obtained on the laboratory scale, by the solution-precipitation and sol-gel methods, and to correlate the main characteristics like crystallinity and specific surface area with the ion Pb^{2+} immobilization capacity. It is tested the increasing performance of nano-HAP so obtained, to remove heavy metals from aqueous solutions through dispersant addition (0.1...1.5%) and isomorphous substitution (Si_x -HAP, $x=0.5$; 1). Batch experiments were carried out using different synthetic nano-hydroxyapatites; powders were comparatively tested for lead removal process from aqueous solutions, under different conditions, i.e. initial metal ion concentration, and pH of the solutions. Results showed that all HAP powders obtained by precipitation contain hydroxyapatite as the only crystalline phase instead, the sol-gel HAP powders contains minor quantities of β -TCP. Experimental results shown that, the amount of metal ions (Pb^{2+}) removed correlates to the nature of the adsorbents (morphology and specific surface area), and to the concentration of the synthetic solution in metallic ions.

Scopul acestui studiu a constat în stabilirea influenței condițiilor de preparare asupra nanopulberilor de hidroxiapatită (n-HAP) elaborate în condiții de laborator prin reacții de precipitare și metode sol-gel și de asemenea, a corelațiilor principalelor caracteristici precum cristalinitatea și suprafața specifică cu capacitatea lor de a reține ioni de metale grele (Pb^{2+}). S-a testat îmbunătățirea capacității de reținere a Pb^{2+} din soluțiile sintetice apoase prin adaosul de dispersant (0.1...1.5%) și respectiv, prin substituții izomorfe (Si_x -HAP, $x=0.5$; 1). Experimentele au fost realizate în regim discontinuu utilizând diferite pulberi n-HAP, și au fost testate comparativ pentru îndepărtarea ionilor Pb^{2+} din soluțiile lor apoase, în condiții diferite precum concentrația inițială a ionilor metalici și pH-ul soluțiilor. Rezultatele au demonstrate că pulberile n-HAP obținute prin precipitare au ca unică fază compusul HAP în schimb, nanopulberile obținute prin procese sol-gel prezintă și cantități minore de β -TCP; testele au demonstrat că îndepărtarea ionilor metalici se corelează cu natura adsorbantului (morfologie și suprafața specifică) și concentrația inițială în ioni metalici din soluțiile lor apoase.

Keywords: nano crystalline hydroxyapatite, heavy metals, lead removal, adsorption

1. Introduction

Different water resources are increasingly contaminated by large volumes of wastewater from industrial processes. This need to protect water resources and, in the same time, there is an urgent need for a water treatment technique. Environments contaminated with metals have been extensively studied in recent years due to the negative effects of the heavy metals on living organisms (plants, animals, humans). The industrial wastewaters and urban wastes, by different sources, especially mining and industrial activities, and automobile exhausts (for lead) contain large number of toxic heavy metals [1, 3]. Most important technologies to remove heavy metals from wastewater include precipitation, ion exchange, electrodeposition, reverse osmosis, electrochemical treatment, adsorption, membrane processes, sequestration by cementation, and so on [4]. All these technologies have advantages and disadvantages. The most widely used

method is *adsorption* due to its efficiency, low cost and simple operation and maintenance conditions. The most commonly used adsorbents are activated carbon, zeolites, clays, biomass and polymeric materials [5, 6]. Different sources of phosphates, natural and/or synthetic hydroxyapatite has been used as a sorbent material to remove metal ions [7, 8]. Some of these adsorbents are characterized by low sorption capacity, with the inconvenience regarding their separation. Therefore, there is a need to develop new adsorbents with improved characteristics of surface area and performance in terms of selectivity and sorption capacity. It was demonstrated that hydroxyapatite (abbreviated as HAP below) is efficient in removal of many toxic metal ions [9, 10]. Hydroxyapatite also shows high capacity for ion exchange with heavy metal ions owing to its unique crystal structure and composition. As is known, the crystal structure (A_4)(A_6)(BO_4)₆(X_2) of HAP allows a high degree of disorder structural due to multiple chemicals substitutions.

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This inherent defects contributing to increased network adsorption capacity and so, easily retaining impurities on ceramic compound. Hydroxyapatite powder can be synthesized using various techniques such as hydrothermal technique, solid-state reaction, precipitation, sol-gel, mechanochemical, mechanochemical-hydrothermal, microemulsion and others [11-13]. Differences in preparative routes lead to deviations in morphology, stoichiometry and level of crystallinity with significant differences in physical and chemical characteristics like, phase stability and dissolution behaviour [14]. Nanomaterials typically show increased reactivity and thus, the ability to uptake heavy metals compared to the same materials with micron and submicron size. The effect of some surfactants on the crystallization and morphology of HAP nanoparticles was also investigated. The presence of surfactants (anions or cationic) in a precipitation process influences the dispersion and morphology of obtained products [15, 16]. The pH of the solution is also an important controlling parameter for the adsorption of heavy metals on the sorbents, it governs a series of phenomena like site dissociation, solubility, mobility, and chemistry of the metals ions. According to the literature data are proposed and agreed two main mechanisms in the overall uptake capacity of heavy metal ions, ion exchange between Pb^{2+} and Ca^{2+} at the apatite lattice, and apatite dissolution followed by lead-phosphate precipitation. Beside these two main mechanisms, metal complexation on the HAP surface also occurs as a secondary mechanism [17, 18].

This study aimed to investigate the effect of preparation conditions of different HAP nanopowders, and the correlation the main characteristics like crystallinity and specific surface area of hydroxyapatites nano-adsorbents with the ion immobilization capacity and finally, the Pb^{2+} ion adsorption behaviour by the adsorbents. Two HAP sorbents types were prepared for this study, and kinetic reaction of lead removal was examined by a batch experiments.

2. Materials and methods

2.1. Preparation of nano-hydroxyapatite sorbents

Two methods for obtaining nano-hydroxyapatite (HAP) are described, and consist in obtaining on the laboratory scale, by the solution-precipitation and sol-gel methods. HAP nanoparticles were synthesized by a *wet chemical precipitation method*, under atmospheric pressure, using nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$) as calcium source and diammonium hydrogen phosphate ($(NH_4)_2HPO_4$) as phosphorous source. All the chemicals used were of analytical grade

reagent. The starting materials were dissolved initially in distilled water, together with desired amounts of concentrated NH_4OH , and temperature was fixed at $80^\circ C$. After two hours of homogenization at this temperature the precipitate obtained was kept for 24h at room temperature. The pH of the slurry was measured digitally during the precipitation reaction, and was maintained at a constant value (about 9) by addition of NH_4OH . The precipitate is filtered and thoroughly washed with distilled water three times to remove the ammonia solution. After filtration, the cake was dried at $90^\circ C$ for 12 h and finally calcined at $600-900^\circ C$ for 2 h. By the second method, a nano-sized HAP ceramic crystals were prepared by simple *sol-gel technique*, using calcium nitrate tetra hydrate [$Ca(NO_3)_2 \cdot 4H_2O$] and phosphorus pentoxide [P_2O_5] as precursors, and ethanol (p.a), as dispersion medium. The phosphate solution has been introduced into calcium solution, drop wised, from a burette for 20 min; The solutions were mixed for 10 minutes by magnetic stirrer, at medium speed and the pH measured was 0.5-1. The obtained clear, transparent sol was placed in a water bath at $60^\circ C$ for 60 min while continuously stirring with a magnetic stirrer, then the yellowish obtained gel was kept for ageing 72 hours at ambient temperature. Production of HAP nanoparticles were made by varying the agitation rate between 100-500rpm and the sintering temperature $600^\circ C-800^\circ C$.

2.2. Optimization of nano-hydroxyapatite sorbents

Motivation

As stated above, the performance to retain heavy metals from aqueous solutions is influenced by characteristics of synthetic adsorbent among which particle size and degree of crystallinity as follows: the size and particle size distribution of HAPs surface correlates with specific surface, relevant factor in removal efficiency of heavy metals by adsorbents; the amorphous ceramic compounds would be less stable than those with a high degree of crystallinity and thus in the aqueous medium will dissolved more quickly. HAP ceramic powder becomes more reactive and thus increasing sorption capacity.

Modalities:

a. Addition of dispersant

Due to the nanometric size of HAP ceramic powder, there is a strong tendency to agglomeration; to reduce this tendency was used dispersant (Na-PAA) at a rate of $0.1 \div 1.5 wt\%$. It was intended to reduce the average crystallite size and thus, increasing specific surface.

b. Isomorphic substitutions

By its nature, HAP is a stable compound, poorly soluble in aqueous medium (Log Kps = -110). Increased solubility was achieved by ionic substitutions like (SiO_4) in the position of (PO_4);

neutrality of the compound is accomplished through (OH) vacancies, according to the formula: Ca₁₀(PO₄)_{6-x}(SiO₄)_x(OH)_{2-x□(OH)} [19].

2.3. Batch adsorption experiment

The amount of lead retained in the solid sample was determined by batch experiments. Stock solutions of 100/1000 mg/L of Pb(II) were prepared by dissolving the corresponding salt (Pb(NO₃)₂) (Merck) in distilled water. Aqueous solutions of Pb(II) used were prepared by diluting the stock solutions. The effect of pH on the uptake of Pb(II) ions from aqueous solution was also studied. To determine the optimum pH corresponding to a maximum uptake capacity, experiments were performed in the range of pH values 2.5-8. The sorption capacity (mg/g) was calculated using eq. (1).

$$Q = \frac{(C_i - C_f) \cdot V}{m} \quad (1)$$

where Q – sorption capacity (mg/g), C_i - the concentration of lead ions in the initial solution (mg/L), C_f - the concentration of lead ions remaining in solution (mg/L), V - volume of the solution (L) and m - mass of chitosan/hydroxyapatite composite used (g). Metallic ion concentration in initial solutions, and in solution after the adsorption on the adsorbents was determined by atomic adsorption spectrometry using a type AAS 1N Carl Zeiss Jena Atomic Adsorption Spectrophotometer. The solids collected at the end of the experiments were characterized by X-ray diffraction and infrared spectroscopic measurements.

2.4. Powder characterization

X-ray diffraction (XRD) with the help of X-ray diffractometer D8 ADVANCE-GERMANY type, with CuKα radiation (k = 1.5404 Å) and XPERT software, was used to observe the crystal phases and compared with JCPDS (JCPDS, 09-0432, for hydroxyapatite). Spectroscopic investigation was performed by the use of FT-IR 620 (Jasco, Japan) Spectrometer (400-4000 cm⁻¹ range with KBr

pellets). The FT-IR spectra were recorded to identify the functional groups characteristics to hydroxyapatite. Micromeritics ASAP 2020 automated gas adsorption system was used. The Brunauer-Emmett-Teller (BET) equation was involved in calculation of specific surface areas (S_{BET}). The average crystallite size D_(hkl) in nm was calculated according to the fraction of crystalline phase from X-ray diffraction data, following Scherrer equation (2):

$$D_{hkl} = \frac{k\lambda}{FWHM \cos \theta} \quad (2)$$

where, K is the shape factor equal to 0.9, λ the X-ray wavelength (equal to 1.541 Å for Cu K radiation), θ the Bragg's diffraction angle (in degrees), β/2 the full-width at half-maximum (FWHM). The average particle size can be determined directly from the BET results using following equation, D_{BET} = 6000/ d · S_{BET}, where D_{BET} denotes an average particle size (nm), S_{BET} is the specific surface area (m²/g) and d density of investigated material (g/cm³). In the case of calcium hydroxyapatite theoretical density of 3.16 g/cm³ was taken.

3. Results and discussion

3.1. Preparation and characterization of HAP nano-adsorbents

Precipitation and sol-gel processes represent most practical and economical unconventional methods of nanopowders synthesis, that can be easily adapted to the needs of the lab-scale conditions. In Figure 1a, b is shown diffractograms of the reaction products prepared by precipitation method (further denoted HAP-T) respectively, by sol-gel method (further denoted HAG), and clearly shows the HAP phase as the major product phase with the intensity of HAP peaks considerably increased at 900°C (fig. 1a and fig.1b-calcined at 600°C); at 900°C sol-gel HAP decomposes with the formation of β-TCP, as minor phase (fig. 1b). X-ray diffraction on the dried material (80°C for 24 h) shows the HAP as a unique mineralogical compound with a high degree of amorphization (fig. 1a).

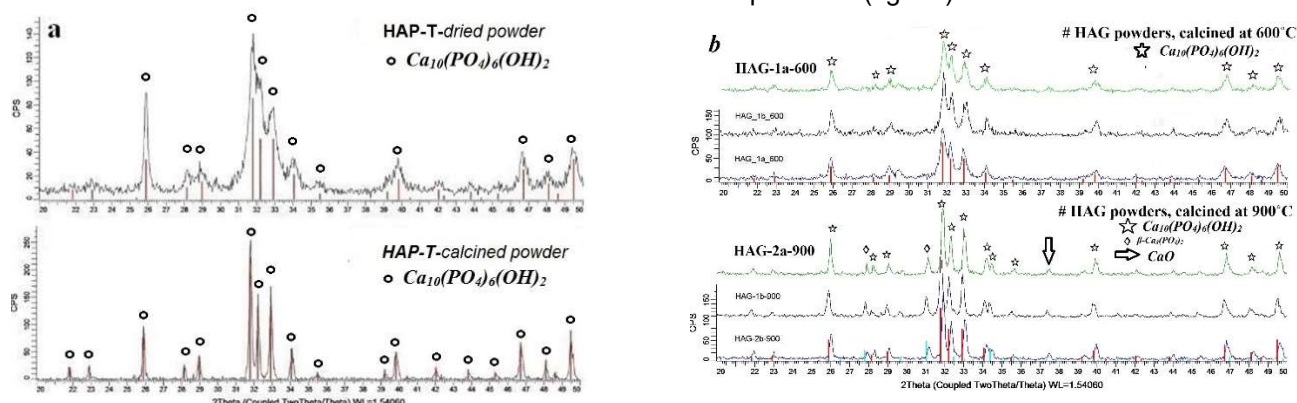


Fig. 1 -XRD pattern for nano-HAP samples obtained by precipitation (fig. 1a), and sol-gel processes calcined at 600°C and 900°C (fig. 1b)/ Spectre de difracție Rx pentru probele de nano-HAP elaborate prin precipitare (fig. 1a) și procese sol-gel, calcinate la 600°C și 900°C (fig. 1b) .

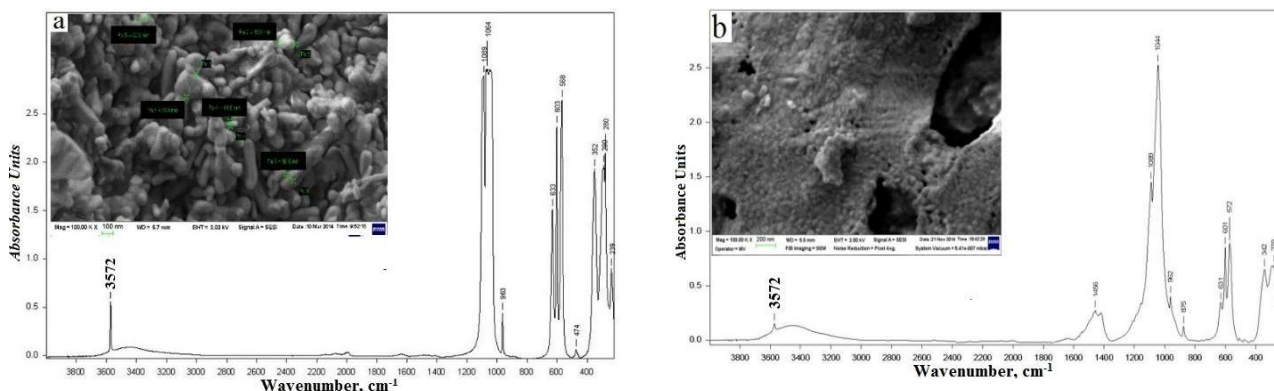


Fig. 2 - FTIR spectra and the microstructure images (SEM) of the two HAP nano-adsorbents, obtained by precipitation (fig. 2a) and sol-gel process (fig. 2b) / Spectrele FT-IR și imagini de microscopie electronică pentru nanoadsorbantii HAP elaborați prin precipitare (fig. 2a) și proces sol-gel (fig. 2b)

Fourier transform infrared spectroscopy (FT-IR) was used to confirm the chemical groups in the synthesized apatite samples. Characteristic for all compounds are the representative peaks of HAP, where all the bands attributed to the PO_4^{3-} ions are present (1089, 1064, 963, 603, 568 cm^{-1}), as well as the bands characteristics of hydroxide ions at 3572 and 633 cm^{-1} for precipitated HAP and, 3572 and 631 cm^{-1} for sol-gel HAP.

From SEM pictures (fig 2a) it show elongated crystals, very thin (~ 250 nm long and the thickness of ~20-30nm), comprised in agglomerates of 10-15 μm , microporosity and macroporosity (pores 350-500nm) evenly distributed, useful in adsorption capacity of heavy metals from solutions. Sol-gel nano-adsorbents presents nanoscale size crystallite of 30-45nm, well-densified, with a non-interconnected macroporosity (250-400nm) (Fig. 2b). The products are highly agglomerates, as a consequence of higher reactivity.

3.2. Optimization of nano-hydroxyapatite sorbents

3.2.1. Optimization through dispersing agent addition

The effect of the dispersant addition (in proportion of 0.1, 0.35, 0.5, 1 and 1.5%) is evidenced by average crystallite size reduction and consequently by increasing the specific surface area.

Corresponding samples are denoted further as, HAP-T-0.1D; HAP-T-0.35D; HAP-T-0.5D; HAP-T-1D; HAP-T-1.5D and respectively, HAP-T-0.1DA for sample finely washed with alcohol. The results are shown in Table 1.

Table 1

Effect of dispersant addition on the physical properties of HAP nano-adsorbents obtained by precipitation/ Efectul adaosului de dispersant asupra caracteristicilor fizice pentru nano-adsorbantii de HAP elaborați prin precipitare

Sample	Dispersant (Na-PAA), [%]	Average crystallite size, [nm]	Specific surface area [m ² /g]	Observation
HAP-T	-	52.46	36.19	dried precipitate
HAP-T-0.1D	0.1	50.67	37.47	dried precipitate
HAP-T-0.35D	0.35	40.10	47.35	dried precipitate
HAP-T-0.5D	0.50	39.91	47.58	dried precipitate
HAP-T-1D	1	36.88	51.48	dried precipitate
HAP-T-1.5D	1.5	36.38	52.19	dried precipitate
HAP-T-0.1DA	0.1	42.42	44.76	wash with alcohol

Finally washing the precipitate with alcohol, even in small amounts of dispersant, cause a reduction in the average crystallite size from 50,67nm to 42,76nm and also, stopped the tendency to agglomeration.

3.2.2. Optimization through ionic substitutions, (SiO₄)

They were tested HAP nano-adsorbents synthesized by precipitation with fractions of

Table 2

Effect of ionic substitutions (SiO₄) on the physical properties (average crystallite size, specific surface area) of HAP nano-adsorbents obtained by precipitation and sol-gel process/ Efectul substituțiilor ionice (SiO₄) asupra proprietăților fizice (dimensiune medie de cristalit, suprafața specific) ale nano-adsorbantilor HAP obținuți prin precipitare și proces sol-gel

Sample	Molar fraction x (SiO ₄)	Average crystallite size, [nm]	Specific surface area [m ² /g]	Observation
HAP-T	-	52,46	36,19	nano-HAP-precipitated
Si-HAP-T0.5	0,5	48,36	39,26	dried precipitate
Si-HAP-T1.0	1	38,39	49,46	dried precipitate
4HAG				aging time- 3h
Si-4HAG0.5	0,5	39,60	47,95	calcinated at 600°C
Si-4HAG1.0	1	33,76	56,24	calcinated at 600°C
5HAG				aging time- 5h
Si-5HAG0.25	0,25	35,63	53,29	calcinated at 600°C
Si-5HAG0.5	0,5	32,23	58,91	calcinated at 600°C
Si-5HAG1.0	1	30,02	63,25	calcinated at 600°C
Si-5HAG1.5	1,5	-	-	long gelation time

substitution of 0.5 and 1 (denoted further Si-HAP-T0.5/ Si-HAP-T1.0) and respectively, prepared by sol-gel with fractions of substitution 0.25, 0.5, 1 and 1.5, with aging time of 3 or 5 hours (corresponding denoted as 4HAG/5HAG). Substitutions with (SiO₄) were carried out by the addition of a solution of Tetraetilortosilicat (TEOS). Results are presented in Table 2.

For the compounds synthesized by the precipitation process (HAP-T) addition of x = 0.5/1 (SiO₄) has an obvious effect in reducing the average crystallite size from 52,46nm for compound without substitution to 38.39nm for compound with x=1; X-ray diffraction patterns shows for both compounds only peaks corresponding to HAP compound. For HAP compounds synthesized by the sol-gel technique (HAG), SiO₄ substitution reduce the average crystallite size for both samples with aging time of 3h/5h from 39.60nm to 33.76nm and respectively, from 35.63nm the 30.02nm; additional amount of silicate (molar fraction > 1.5) cause a major delay (> 10 days) of the gelling process. Basically, these substitutions distort the network lattice, the inherent defects contributing to increasing adsorption capacity.

3.3. Sorption experiments

3.3.1. Qualitatively aspects

Solid HAP sorbents in contact with Pb²⁺ ions led to the formation of solid-solutions Pb_{10-x}Ca_x(PO₄)₆(OH)₂, which is rapidly followed by formation of the very stable pyromorphite phase Pb₁₀(PO₄)₆(OH)₂. It is structurally different, with 100% Pb substitution for Ca on the HAP lattice, identified by X-ray diffraction and denoted as Pb-HAP. For experiments were used microcrystalline ceramic powders (only for comparison) (micrometre size of crystallite, specific surface area ~ 2m²/g, and a higher degree of crystallinity, sintered at 1100°C, denoted HAP-mc), and two nanometre powders synthesized by precipitation, denoted HAP-T (crystallite size of ~ 40nm, specific surface area ~ 11m²/g, sintered at 900°C), and by sol-gel (30-40nm crystallite size, surface area ~16m²/g, sintered at 800°C). The concentration of Pb²⁺ ions

in the first experiment was 100mg/L, and for the second experiment concentration was increased to 1000mg/L. For both experiments the initial pH of the solution was ~ 3.5.

Preliminary experiments for testing the uptake ability of the sorbents for Pb²⁺ ions primarily showed the uptake capacity dependence with physico-chemical and morphological characteristics of the sorbents. Powder X-ray diffraction results (Fig. 3-experiment 1, at initial concentration of 100mg/L) show mixed phases of HAP and Pb-HAP, with a major proportion for nanoadsorbent HAP-T, compared to microcrystalline adsorbent with low solubility. The results of XRD analysis strongly argue the ion-exchange mechanism for microcrystalline adsorbent and dissolution/precipitation as the main mechanism for Pb (II) removal for nanoadsorbent. At higher concentration (1000mg/L- Fig. 3, experiment 2) the two adsorbents show a relatively similar adsorption capacity, sensible for HAP-T. It can be observed that, with lead concentration value increasing, the diffraction peaks of Pb-HAP increase in intensity to the detriment of HAP. Although in major proportion, Pb-HAP compound shows diffraction lines larger, easily displaced to large angles, suggesting a predominant dissolution-precipitation mechanism with the formation of solid solutions. So, the amount of metal ions (Pb²⁺) adsorbed is directly related to the nature of the adsorbents (morphology and specific surface area), and to the concentration of the synthetic solution in metallic ions.

3.3.2. Quantitatively measurements

For experiments were used more reactive HAP nano-ceramic powders obtained by precipitation and sol-gel methods, also with optimized characteristics (high surface area and morphology) through dispersant addition and by SiO₄ substitution. Batch experiments were carried out for initial metal concentration of Pb(II) ions (107mg/L and, 1000mg/L respectively, in agreement with data from the literature). Was assessed sorption capacity and correlated with the nature of the sorbents and the concentration of the

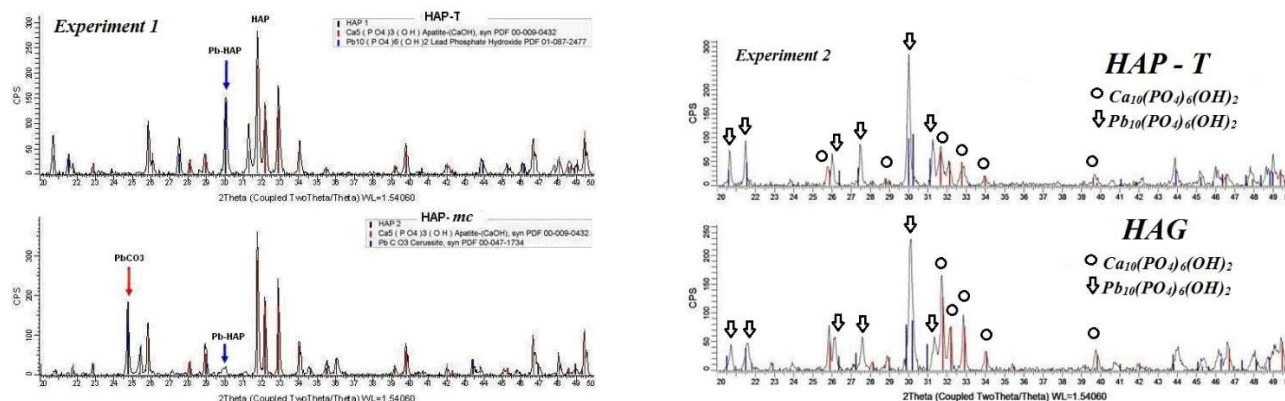


Fig. 3 - XRD patterns of HAP nano-adsorbents after 24h of Pb²⁺ sorption, at initial concentration of 100 and 1000mg/L /Difractogramele nano-adsorbantilor HAP după 24h sorbție de ioni Pb²⁺ pentru concentrația inițială de 100 si 1000mg/L.

Tables 3, 4.

Lead quantity uptake by nano-adsorbents in function of time/initial solution concentration, 1000 mg/L, and 107 mg/L
 Cantitatea de Pb reținută de nanoadsorbanti în funcție de timp și concentrația inițială a soluției 1000 mg/L, and 107 mg/L

	HAP-T0.1D.A	HAG	HAP-T	Si-5HAG0.5
Time (minutes)	Cantitate Pb(II)/g HAP	Cantitate Pb(II)/g HAP	Cantitate Pb(II)/g HAP	Cantitate Pb(II)/g HAP
0	0	0	0	0
5	160.4	281.7	231.8	187.85
10	297.8	470.3	299.01	298.71
15	309.75	495.8	326.78	307.43
30	380.28	625.5	338.04	331.58
60	420.45	718.9	356.21	347.82
120	511.34	783.21	369.99	359.38
180	601.24	855.6	377.15	365.29
240	765.25	882.4	423.56	418.22
300	801.22	894.23	504.5	506.14
360	836.99	911.58	678.89	653.49
420	857.66	937.77	735.25	704.58
480	900.75	950.67	814.44	803.12
540	940.74	984.33	947.88	935.21
600	993.81	997.96	998.55	991.68

	HAP-T0.1D.A	HAG	HAP-T	Si-5HAG0.5
Time (minutes)	Initial Pb(II) concentration/g HAP			
0	0	0	0	0
5	94.75	105.59	99.78	98.43
10	104.1	105.68	99.95	98.27
15	105.58	105.71	101.25	99.87
30	105.78	105.76	101.82	100.31
60	105.92	105.88	102.36	101.52
120	106.01	105.94	103.67	102.35
180	106.34	106.17	104.56	103.14
240	106.45	106.33	105.21	104.52
300	106.67	106.52	105.89	104.78
360	106.77	106.76	106.24	105.09
420	106.96	106.96	106.98	105.87

synthetic solution in metallic ions, details have been given in our previous work [20]. The first solid sorbent tested was a precipitated hydroxyapatite (HAP-T, with and without dispersant addition), with specific surface area ($S_{BET}=16.02\text{m}^2/\text{g}$ and $32.46\text{m}^2/\text{g}$), and the second compound obtained by sol-gel process, denoted hereafter as HAG, with and without SiO_4 substitution, had a specific surface area ($S_{BET}=36\text{m}^2/\text{g}$ and $47.69\text{m}^2/\text{g}$, respectively). Results are presented in Table 3, 4.

At lower concentration ($C=107\text{mg/L}$), in Table 4, it can be seen that adsorption maximum is reached after 30 minutes for lead ions because the lead quantity retained by this time not vary greatly. Data presented lead to the conclusion that a further kinetic study in the time between 0 and 30 minutes is necessary. Our findings on rapid lead kinetic adsorption process on nano-HAP adsorbents agreed with those described by elsewhere [10, 20]. At high concentration ($C=1000\text{mg/L}$), in table 3 are shown results of adsorption capacity for the nanoadsorbents in a long kinetic of more than 10 hours. At high concentrations, a major removal of metal ions (85%) occurs after about 3 hours. Retaining yields of over 99% are recorded for 10 hours for all adsorbents. Its stands out the positive influence of the optimization process in the removal process of metal Pb(II) ions. *In conclusion*, we can say that the removing mechanism of Pb ions is more complex, and can be described by the cation exchange, formation of Pb-precipitates (solid-solutions) after HAP dissolution, and finally surface complexation. Additional studies should be done in order to characterize these mechanisms, and combination of the XRD, chemical analysis, and pH studies must be performed.

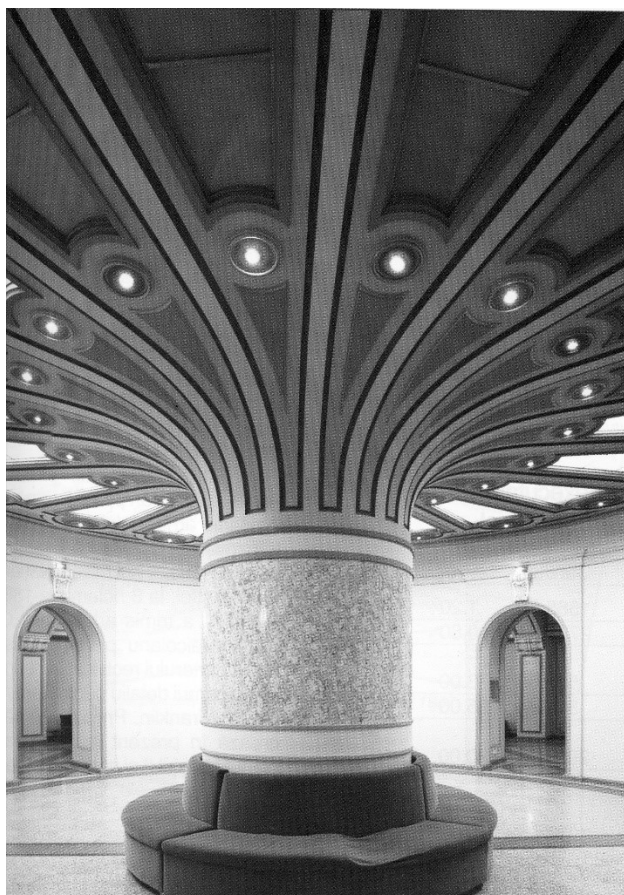
4. Conclusion

Two methods for obtaining nano-hydroxyapatite are described, and consist in obtaining HAP nanopowders under laboratory conditions, by the solution-precipitation and sol-gel methods. To increase sorption capacity its synthesized nano HAP powders in the presence of surfactants, and through anionic substitution (SiO_4 for PO_4), ways that dictated the final properties of the HAP adsorbents. This study evaluated crystalline and poorly-crystalline hydroxyapatite sorbents on removal of aqueous Pb(II) in correlation to solution pH, and Pb(II) concentration. Batch experiments were conducted using two poorly-crystalline hydroxyapatites, synthesized from solution-precipitation and sol-gel methods. Our results shown that ion adsorption capacity increased with decreasing crystallinity and increasing specific surface area. The mechanism of sorption involved was dissolution/precipitation, surface complexation and ion exchange process. These results showed that both nano-adsorbents evaluated exhibited high adsorption capacity, and can be successfully used to remove lead from wastewater.

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REFERENCES

1. H.B. Li, S. Yu, G.L. Li, H. Deng, X.S. Luo, Environ. Pollut., 2011, **159**, 3536.
2. J.R. Miller, L.F. Villarroel, Encyclopedia of Environmental Health, 2011, 421.
3. M.A. Hashim, S. Mukhopadhyay, J.N. Sahu, B. Sengupta, Remediation technologies for heavy metal contaminated groundwater, J. Environ. Manage., 2011, **92**, 2355.
4. M. A. Barakat, "New trends in removing heavy metals from industrial wastewater," Arabian J. Chem., 2011, **4**(4), 361.
5. S. Babel, T.A. Kurniawan, Cr(VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan, Chemosphere, 2004, **54**(7), 951.
6. El.I. Basaldella, P.G. Vázquez, F. Lucolano, D. Caputo, Chromium removal from water using LTA zeolites: effect of pH, J. Colloid Interface Sci., 2007, **313**, 574.
7. J. Oliva, J. De Pablo, J.L. Cortina, J. Cama, C. Ayora: Removal of cadmium, copper, nickel, cobalt and mercury from water by Apatite II™: Column experiments, J. Hazard. Mater., 2011, **194**, 312.
8. D. Liao, W. Li. Zheng, X. Yang, Q. Yue, X. Guo, G.L. Zeng: Removal of lead(II) from aqueous solutions using carbonate hydroxyapatite extracted from eggshell waste, J. Hazard. Mater., 2010, **177**, 126.
9. Y. Takeuchi, H. Arai, Removal of coexisting Pb²⁺, Cu²⁺ and Cd²⁺ ions from water by addition of hydroxyapatite powder, J Chem Eng Jpn., 1990, **23**(75), 80.
10. I. Mobasherpour, E. Salahi, M. Pazouki: Comparative of the removal of Pb²⁺, Cd²⁺ and Ni²⁺ by nano crystallite hydroxyapatite from aqueous solutions: Adsorption isotherm study, Arabian J. Chem., 2012, **5**, 439.
11. M. Sadat-Shojai, M.T. Khorasani, E. Dinpanah-Khoshdargi, A. Jamshidi, Synthesis methods for nanosized hydroxyapatite with diverse structures. Acta Biomaterialia, 2013 **9**(8), 7591.
12. N.Y. Mostafa, Characterisation, Thermal Stability and Sintering of Hydroxyapatite Powders Prepared by Different Routes", Materials Chemistry and Physics, 2005, **94**(2–3), 333.
13. E. Dinu, C.D. Ghițulică, G. Voicu, E. Andronescu, Pulberi de fosfat de calciu obținute prin metoda Pyrosol, Romanian Journal of Materials, 2011, **41**(3), 248.
14. I. Smiciklas, A. Onjia, S. Raicevic, D. Janackovic, M. Mitric, Factors influencing the removal of divalent cations by hydroxyapatite, J. Hazard. Mater., 2008, **152**, 876.
15. J.M. Coelho, J.A. Moreira, A. Almeida, F.J. Monteiro, Synthesis and characterization of HAp nanorods from a cationic surfactant template method, Journal of Materials Science: Materials in Medicine, 2010, **21**, 2543.
16. T. Ma, Z. Xia, L. Liao, Effect of reaction system and surfactant additives on the morphology evolution of hydroxyapatite nanorods obtained via a hydrothermal route, Applied Surface Science, 2011, **257**, 4384.
17. Y. Hashimoto, T. Sato, Removal of aqueous lead by poorly-crystalline hydroxyapatites, Chemosphere, 2007, **69**, 1775.
18. A. Melinescu, C. Rizea-Orbeci, M. Preda, Immobilization of lead ions in solutions by precipitation with calcium hydroxyapatite, Romanian Journal of Materials, 2010, **40**(3), 237.
19. S. Hayakawa, T. Kanaya, K. Tsuru, et.al., Heterogeneous structure and in vitro degradation behavior of wet-chemically derived nanocrystalline silicon-containing hydroxyapatite particles", Acta Biomaterialia, 2013, **9**(1), 4856.
20. C. M. Simionescu, A. Tatarus, C. Tardei, D. Patroi, M. Dragne, D.C. Culita, Rev. Chim., 2015, **66** (5), 732.



Coloana principală din subsol, pe care se sprijină planșeul (pg. 57 - Nicolae St.Noica - ATENEUL ROMÂN ȘI CONSTRUCTORII SĂI)