



REȚINEREA IONILOR TOXICI DE Pb²⁺ DIN SOLUȚII APOASE PE GRANULE POROASE DE HIDROXIAPATITĂ[▲] REMOVAL OF Pb²⁺ TOXIC IONS FROM AQUEOUS SOLUTIONS ON POROUS HYDROXYAPATITE GRANULES

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Natural or synthetic hydroxyapatite [Ca₁₀(PO₄)₆(OH)₂] has a high exchange capacity for divalent heavy metal ions and is used to treat wastewater containing such ions. The reaction mechanism of hydroxyapatite with lead salts is carried out by dissolution followed by precipitation pyromorphite. As-synthesized HAp granules were analyzed by X-ray diffraction and FTIR spectroscopy. For the study of retention of lead ions were added Ca-hydroxyapatite granules in a solution of lead nitrate. By treatment with a solution of lead nitrate in all cases the chemical reaction leading to the formation pyromorphite, which is a positive result, as it is a compound of the less soluble lead.

Hidroxiapatita naturală sau sintetică [Ca₁₀(PO₄)₆(OH)₂] are o mare capacitate de schimb pentru ionii divalenți ai metalelor grele și se folosește pentru tratarea apelor uzate care conțin astfel de ioni. Mecanismul de reacție a hidroxiapatitei cu sărurile de plumb are loc prin dizolvarea acesteia urmată de precipitarea piromorfitei. Granulele HAp sintetizate au fost analizate prin difracție de raze X și spectroscopie IR. Pentru studiul reținerii ionilor de plumb s-au introdus granule de hidroxiapatită în soluție de azotat de plumb. Prin tratare cu soluție de azotat de plumb în toate cazurile reacția chimică duce la formarea piromorfitei, ceea ce este un rezultat favorabil, deoarece acesta reprezintă compusul cu plumb cel mai puțin solubil.

Keywords: hydroxyapatite, XRD, FTIR, pyromorphite

1. Introduction

Lead is sometimes found in surface water and underground water as a result of industrial activities such as galvanization, manufacture of electronic equipment, mining, and chemical processing for example. When dissolved and in liquid form, even very small quantities of lead salts are toxic to the human body. In addition, lead is known to accumulate in food and for this reason its presence in water has to be eliminated. Natural or synthetic hydroxyapatite [Ca₁₀(PO₄)₆(OH)₂] has a high exchange capacity for divalent heavy metal ions and it is used to treat wastewater containing them. Research literature shows that it can quickly and efficiently remove Pb²⁺.

It was found that hydroxyapatite reacts with lead soluble salts leading to the formation of hydroxypyromorphite ([Pb₁₀(PO₄)₆(OH)₂]. The reaction mechanism of the hydroxyapatite with lead salts takes place by its dissolution followed by pyromorphite precipitation [1-5] because hydroxyapatite is stable in a basic environment and pyromorphite in acid medium. The chemical reaction between the two components can result in

either pyromorphite or solid solutions in which calcium and lead ions respectively are in the same network [6]. Hydroxyapatite or carbonated hydroxyapatite are used to remove heavy metals from water and can be either natural or synthetic [3,7]. The chemistry of the lead retention was widely studied, particularly the lead adsorption although the phenomenon is more complex and is accompanied by double exchange chemical reaction.

2. Experimental

The synthesis procedure of hydroxyapatite used in this study is presented in the paper [8]. The used raw materials were Ca(NO₃)₂·6H₂O, Ca(OH)₂ and (NH₄)₂HPO₄ at pH=11. The reaction took place by microwave heating at 80 °C. The resulted product was thermally treated at 300 °C in order to eliminate the formed ammonium nitrate. The synthesized powder was characterized by X-ray diffraction (Schimadzu 6000), FTIR spectroscopy using Shimadzu 6100 apparatus and Scanning electron microscopy (Hitachi 2500N).

A mixture of hydroxyapatite and sodium

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alginate with 1:5 ratios was used to obtain the porous granules according to the procedure presented in paper [9]. These were obtained using ionotropic gelling technique in the presence of $CaCl_2$ as cross-linked agent. In order to obtain the granules, HAp powder was processed in several ways.

In the first method the hydroxyapatite was used and prepared from the chemical reaction (H_1). In the second case it was milled and then passed through a sieve of 200 μm (H_2).

The third sample was obtained by milling in a planetary mill and then sieved on the 200 μm sieves (H_3). All the samples were thermally treated at 850 °C in order to eliminate the organic component and to promote pores formation.

The granules obtained in the experiment were analyzed by X-ray diffraction and FTIR Spectroscopy. For the lead ions retention study 0.8 g balls of hydroxyapatite were added in 100 ml solution of lead nitrate of 500 mg/l concentration using all types of granules.

Immobilization studies were realized in the discontinuous mode using a GFL3015 stirrer, with 150 rotations/min, at constant temperature ($25 \pm 1^\circ C$). The pH value of the initial solutions was modified to 2.5 by adding few drops of HNO_3 solution of 30% concentration.

3. Results and discussion

3.1. The mineralogical composition of the powders and granules of hydroxyapatite

X-ray diffraction, FTIR spectroscopy and Scanning electron microscopy techniques were used to characterize the synthesized hydroxyapatite. The X-ray diffraction pattern is presented in Figure 1.

The XRD pattern of the powder shows only the diffraction lines of hydroxyapatite.

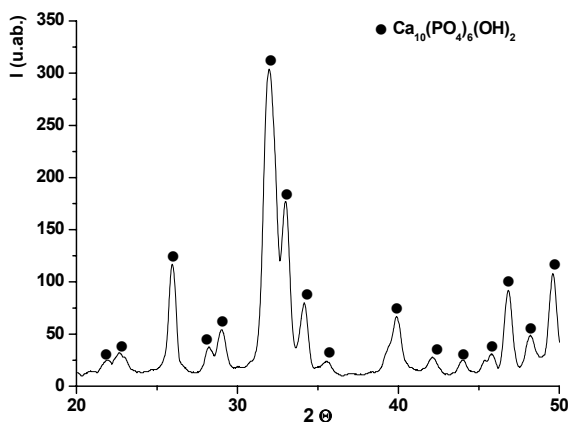


Fig. 1 - X-ray diffraction pattern of synthesised hydroxyapatite powder / Spectru de difracție de raze X pentru pulberea de hidroxiapatită sintetizată.

The crystallinity degree of the sample is suitable to be used as granules precursor and for the reaction with lead solution respectively.

Figure 2 shows the FTIR spectrum of the synthesized hydroxyapatite. The vibration bands of phosphate and hydroxyl groups are observed. The intense and sharp bands in the range 1036-1097 cm^{-1} are ascribed to the stretching vibration of phosphate ion in the structure of hydroxyapatite. The bands at 569 and 603 cm^{-1} correspond to bending vibrations of the same ion. The absorption bands at 630 and 3435 cm^{-1} are assigned to HO^- ions from hydroxyapatite network. The band at 1388 cm^{-1} is characteristic of CO_3^{2-} ions incorporated in the structure of the hydroxyapatite by substitution of PO_4^{3-} ion. The band at 1641 cm^{-1} is specific to the adsorbed water on the hydroxyapatite surface by hydrogen bonds.

The band at 3572 cm^{-1} shows the presence of molecular adsorbed water [10-12]. All bands corresponding to hydroxyapatite are well defined, indicating a high crystallinity degree.

Scanning electron microscopy shows that the powder consists of agglomerates of very fine particles (Figure 3), which favors reactions with large specific surface area.

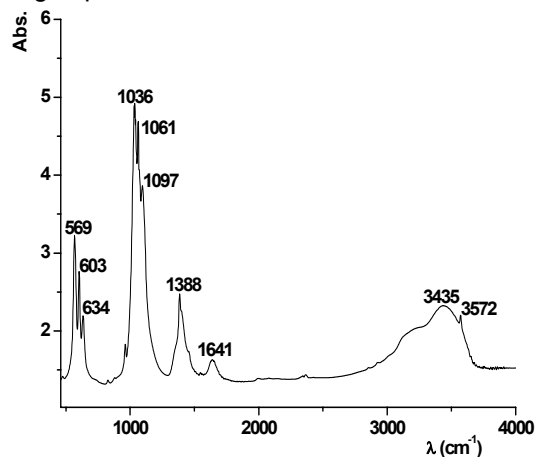


Fig. 2 - FTIR spectrum for synthesised Ca-HAp powder / Spectrul IR pentru pulberea Ca-HAp sintetizată.

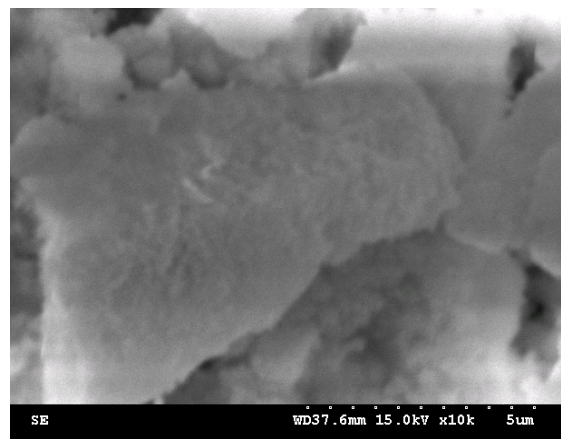


Fig. 3 - SEM image of synthesised Ca-HAp powder / Imaginea SEM a pulberii Ca-HAp sintetizate.

The mineralogical composition of obtained granules was evaluated by X-ray diffraction and the results obtained for the H_1 – H_3 samples are presented in the Figure 4. It can be seen that when hydroxyapatite is in granular state it is conserved, while the powder is mechanical processed the crystallinity of the Ca-HAp decreases. Thus, the highest crystallinity degree is observed for the H_1 sample without mechanical processing. The granules prepared from the hydroxyapatite processed by three methods, were used for the reactions study between Ca-HAp and Pb(II) solution of 500 mg/L concentration. They treated with the lead nitrate solution for 24 hours. The resulted granules after Pb(II) adsorption were dried and investigated by X-ray diffraction and FTIR Spectroscopy.

3.2. Change of the mineralogical composition of Ca-HAp granules as a consequence of Pb(II) ions adsorption

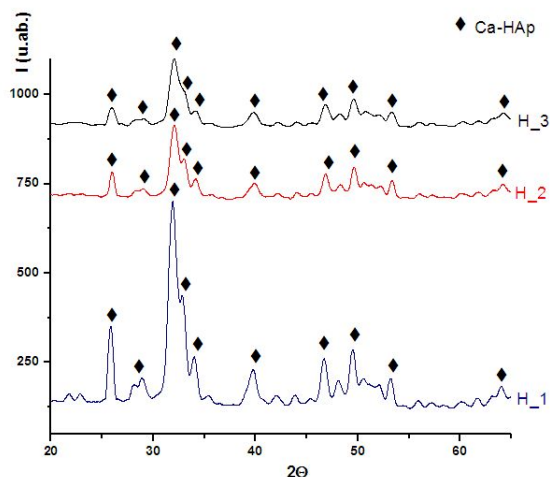


Fig.4 - X-ray spectra of the prepared granules prior to immersion in the solution of lead nitrate / Spectrele de raze X pentru granulele preparate înainte de imersare în soluția de azotat de plumb.

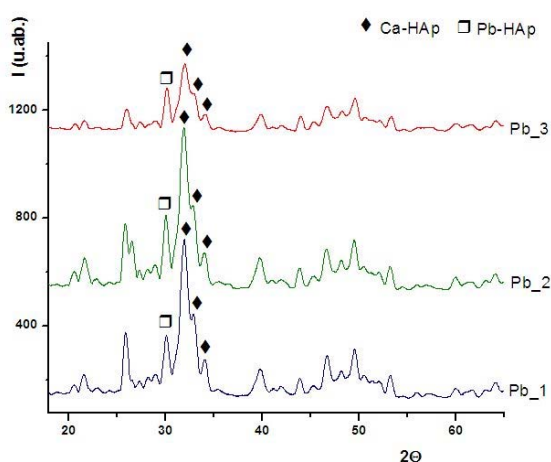


Fig.5. - X-ray diffraction spectra of the granules immersed in the solution of lead nitrate for 24 h. Spectrele de difracție de raze X pentru granulele imersate în soluția de azotat de plumb timp de 24 de ore.

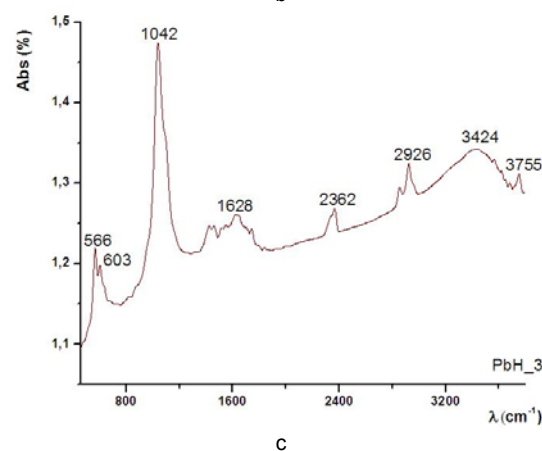
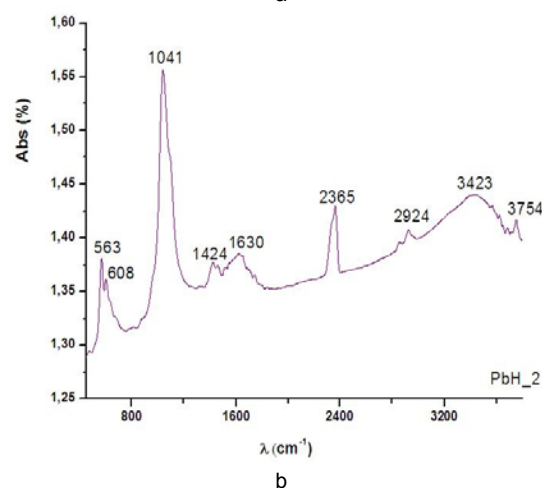
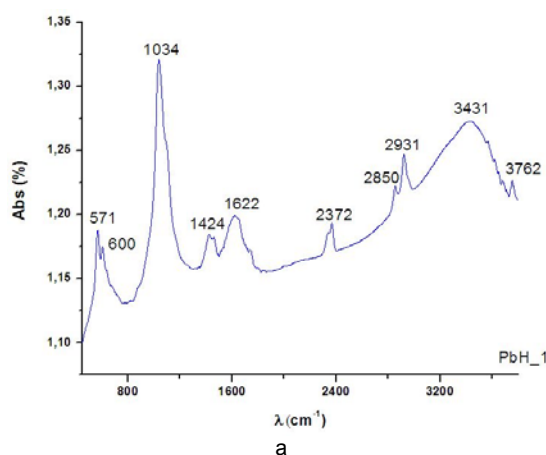


Fig. 6 (a-c) - FTIR spectra for the samples immersed in the specific solution of lead nitrate / Spectrele FTIR specifice probelor imersate în soluția de azotat de plumb.

The XRD patterns presented in Figure 5 were obtained after treating the porous granules with Pb(II) solution and drying. It is observed that both components react to form pyromorphite $Pb_{10}(PO_4)_6(OH)_2$. Beside pyromorphite the diffraction lines corresponding to hydroxyapatite are observed. The pyromorphite formation occurs as a result of the reaction between hydroxyapatite and lead solution through a dissolution mechanism of Ca-HAp unstable in acid environment followed by Pb-HAp precipitation that is stable in this medium.

The FTIR spectra were recorded for the samples immersed in lead solution and the results are depicted in the Figure 6 (a-c). Significant changes of the IR spectra, which represent a mixture of the two phase favors and pyromorphite respectively, are observed. It can be noted the lower crystallinity degree for both components that can be explained by reaction mechanism which implies Ca₁₀(PO₄)₆(OH)₂ dissolution in acid environment and Pb₁₀(PO₄)₆(OH)₂ crystallisation.

The FTIR spectra show only the characteristic bands of (PO₄)³⁻ under 1050 cm⁻¹ without the evidence of the band corresponding to Ca₁₀(PO₄)₆(OH)₂ at 630 cm⁻¹. The presence of Ca-HAp is however confirmed by the presence of the band at 3431 cm⁻¹ ascribed to HO⁻ ions from its structure. The three characteristic bands of the (PO₄)³⁻ ion from Ca₁₀(PO₄)₆(OH)₂ are not presented in the samples treated with lead solution. Practically only one band that is specific of (PO₄)³⁻ groups in the pyromorphite structure was observed. The bands at 1424 cm⁻¹ and 1622 cm⁻¹ are assigned to CO₃²⁻ and adsorbed water by hydrogen bonds slightly shifted due to the higher ionic radius of lead in comparison to calcium [13,14]. The bands at 2368, 2850 and 2931cm⁻¹ are characteristic of CO₂ entered in the network of the two components during processing resulted from the calcination of alginate.

4. Conclusions

These studies have shown that by using porous microspheres Pb(II) ions can be removed from solutions by chemical reaction with hydroxyapatite. The microspheres were prepared by using hydroxyapatite with or without mechanical processing, sodium alginate as pore-forming and thermal treatment at 850°C. The crystallinity degree decreases when mechanical processing is applied. When the treatment with lead nitrate solution is used, in all cases, the chemical reaction leads to pyromorphite formation, which is a favorable result as it is the compound in which lead is less soluble.

REFERENCES

1.M.Y.Ma, J.Samuel J.Terry, and R.James., Effects of Aqueous Al, Cd, Cu, Fe(II), Ni, and Zn on Pb Immobilization by Hydroxyapatite, Environ. Sci. Technol., 1994, **28**, 1219.

- 2.L.Seungbae, A.Jinsung, K.Young-Jin, and N.Kyoungphile, Binding strength-associated toxicity reduction by birnessite and hydroxyapatite in Pb and Cd contaminated sediments, Journal of Hazardous Materials, 2011, **186**, 2117
- 3.T.Kaluđerović, and S. Raičević, In situ lead stabilization using natural and synthetic apatite, Chemical Industry & Chemical Engineering Quarterly, 2008, **14** (4), 269
- 4.R.Bazargan-Lari, M.Ebrahim, and B.A. Nemati, Dependence of Equilibrium, Kinetics and Thermodynamics of Zn (II) Ions Sorption from Water on Particle Size of Natural Hydroxyapatite Extracted from Bone Ash, World Academy of Science, Engineering and Technology 2012, **61**, 1117
- 5.I.Mobasherpour, E.Salahi and M. Pazouki, Potential of nano crystalline hydroxyapatite for lead (II) removal from aqueous solutions: Thermodynamic and Adsorption isotherm study, African Journal of Pure and Applied Chemistry, 2011, **5** (11), 383.
- 6.V.Shevade, L.Erickson, G.Pierzynski, and S.Jiang, Formation and stability of substituted pyromorphite: a molecular modeling study, Journal of Hazardous Substance Research Volume Three, 2007, 1.
- 7.D.Liao, W.Zheng, X.Li., X.Yue, L.Guo, and G.Zeng, Removal of lead(II) from aqueous solutions using carbonate hydroxyapatite extracted from eggshell waste, Journal of Hazardous Materials, 2010, **177**, 126
8. I.Teoreanu, M. Preda, and A. Melinescu, Synthesis and characterization of hydroxyapatite by microwave heating using CaSO₄·2H₂O and Ca(OH)₂ as calcium source, Journal of Materials Science: Materials in Medicine, (2008),**19**(2), 517.
9. Ch.Țârdei, M.Spătaru, F.Albu, Șt.Stoleriu, and A.Ioncea, Preparation and characterization of porous ceramic microspheres on the basis of tricalcium phosphate, Romanian Journal of Materials (2013), 43 (1), 41
- 10.D.K.Pattanayak, S.Upadhyay, R.C.Prasad, B.T.Rao and T.R.Rama Mohan, Synthesis and Evaluation of Hydroxyapatite Ceramics, Trends Biomater. Artif. Organs, 2005, **18** (2).
- 11.G.Gergely, F.Weber, I.Lukacs, AL.Toth, Z.E.Horvath, J.Mihaly, and C.Balazsi, Preparation and characterization of hydroxyapatite from eggshell, Ceramics International 36 2010, **36**, 803.
- 12.M.Markovic, B.O.Fowler and M.S.Tung. Preparation and Comprehensive Characterization of a Calcium Hydroxyapatite Reference Material, [J. Res. Natl. Inst. Stand. Technol. , 2004, **109**, 553.
- 13.D.E.Ellis, J.Terra, O.Warschkow, M.Jiang, G.B.Gonzalez, J.S.Okasinski, M.J.Bedzyk, and A.M.Rossi, A theoretical and experimental study of lead substitution in calcium hydroxyapatite, Phys. Chem. Chem. Phys., 2006, **8**, 967.
- 14.H.Adler, Infrared spectra of phosphate minerals: symmetry and substitutional effects in the pyromorphite series, The American Mineralogist, 1964, **49**, 1002.
