U.P.B. Sci. Bull., Series B, Vol. 76, Iss. 4, 2014 ISSN 1454 – 2331

SYNTHESIS AND CHARACTERISATION OF DEXTRAN COATED HYDROXYAPATITE FOR ENVIRONMENTAL APPLICATIONS

Adrian COSTESCU[1], Ecaterina ANDRONESCU[2], Bogdan Ştefan VASILE[3], Roxana TRUŞCĂ[4], Philippe LE COUSTUMER[5], Emil Ştefan BARNA[6], Simona Liliana ICONARU[7], Mikael MOTELICA-HEINO[8], Carmen Steluța CIOBANU[9]*

The aim of this study is to prepare a novel compound based on dextran coated hydroxyapatite (DHAp) nanoparticles as adsorption material for lead removal in aqueous solutions. Removal experiments of Pb^{2+} ions were carried out in aqueous solutions with controlled Pb^{2+} content at pH ~ 6. The structure and the composition of the dextran coated hydroxyapatite composite were determined by X-ray diffraction measurements, transmission electron microscopy (TEM), scanning electron microscopy (SEM) and Fourier transform infrared (FT-IR) spectroscopy. The diffraction patterns show that HAp nanoparticles were successfully coated with dextran without any structural changes. HAp coated with dextran composite is transformed into DHAp_Pb via the adsorption of Pb^{2+} ions followed by the cation exchange reaction.

Keywords: dextran, hydroxyapatite, nanoparticles, co-precipitation

1. Introduction

Heavy metal pollutants such as lead, cadmium, mercury, copper or zinc have attracted much attention due to their harmful effects on the environment. For instance, lead is widely used in many industrial applications such as ammunition

---

[1] PhD student, Eng., University of Bordeaux, France, University of Bucharest, Faculty of Physics, Magurele, Romania, e-mail: adrian.costescu@gmail.com

[2] Prof., Faculty of Applied Chemistry and Materials Science, University POLITEHNICA of Bucharest, Romania, e-mail: ecaterina.andronescu@upb.ro

[3] PhD Eng, Faculty of Applied Chemistry and Materials Science, University POLITEHNICA of Bucharest, Romania, e- mail: vasile_bogdan_stefan@yahoo.com

[4] PhD Eng, S.C. METAV R&D S.A., Bucharest, Romania, e-mail: truscaroxana@yahoo.com

[5] Prof., University of Bordeaux, France, e-mail: plc@lnet.fr

[6] Prof., Faculty of Applied Chemistry and Materials Science, University POLITEHNICA of Bucharest, Romania, e-mail: barna_emil@yahoo.com

[7] Assistant Researcher, Faculty of Physics, University of Bucharest, National Institute of Materials Physics, Bucuresti-Magurele, Romania, Institute for Earth Sciences, CNRS-University of Orléans, France, e-mail: simonaiconaru@gmail.com

[8] Prof., Institute for Earth Sciences, CNRS-University of Orléans, France, e-mail: mikael.motelica@univ-orleans.fr

[9] Assistant Researcher, National Institute of Materials Physics, Bucuresti-Magurele, Romania, e-mail: ciobanucs@gmail.com

and automotive industry, building materials and paints. Its toxicity could damage human reproductive and nervous systems [1].

Many decontamination methods of heavy metals from wastewaters have been investigated in the past few years. Nanomaterials showed a great interest in a wide range of fields due to their high surface area, sorption and ability to disperse in aqueous solutions. Among other adsorbents such as silica, zeolite, chitosan, activated alumina, activated carbon, many apatite based materials (biological or synthetic) such as hydroxyapatite (HAp), were used as potential sorbents for neutralizing numerous heavy metals in soil and water [1-4]. It has been shown that calcium hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), which is the main inorganic component of vertebrates bones and teeth, besides its biomedical applications, proved to be an excellent candidate for removing many heavy metals ions such as *Pb, Cd, Zi, Ni, Co* and *U* form aqueous solutions due to its remarkable biocompatibility, lack of toxicity, biodegradability, moderate stability and adsorption properties [5-8].

In order to improve the properties (specific surface area, porosity, etc.) of the HAp nanopowders, often a polymer coating is used [9-12].The purpose of this study is to prepare a novel compound based on dextran coated hydroxyapatite (DHAp) nanoparticles as a sorption material for lead removal in aqueous solutions. The prepared dextran coated hydroxyapatite (DHAp) nanoparticles were characterized by X-Ray Diffraction (XRD), scanning electron microscopy (SEM) and Fourier transforms infrared (FTIR) spectroscopy.

2. Materials and methods

2.1. Materials section

All the reagents for synthesis including ammonium dihydrogen phosphate [$(NH_4)_2HPO_4$] (Alfa Aesar) and calcium nitrate [$Ca(NO_3)_2 \cdot 4H_2O$] (Alpha Aesar) were purchased without further purification. Dextran, $H(C_6H_{10}O_5)_xOH$, (MW ~ 40,000) was purchased from Merck. Dextran coated hydroxyapatite nanoparticles were obtained by setting the Ca/P ratio at 1.67. De-ionized water was used in the synthesis of nanoparticles, and for rinsing of clusters. Lead nitrate [$Pb(NO_3)_2$] and HCl solution of extra pure grade were used for adjusting the initial Pb^{2+} ion concentration and pH value in aqueous solutions, respectively.

2.2. Synthesis of dextran coated hydroxyapatite nanoparticles

Nanocrystalline hydroxyapatite coated with dextran was performed by setting the atomic ratio of Ca/P as 1.67. The $Ca(NO_3)_2 \cdot 4H_2O$ was dissolved in deionised water to obtain 250 ml solution. On the other hand, the $(NH_4)_2HPO_4$ was dissolved in deionised water to make 250 ml solution. The 250 ml $Ca(NO_3)_2 \cdot 4H_2O$ solution was dropped into dextran (10 g dextran in 100 ml of water) at room temperature. The [Ca^+ dextran] solution was put into a Berzelius and stirred for 30 minutes. The pH of $(NH_4)_2HPO_4$ solution was adjusted to 10 with NH_3 and stirred continuously for 30 minutes. The $(NH_4)_2HPO_4$ solution was added drop by drop into the [Ca^+ dextran] solution and stirred for 2h and the pH was constantly adjusted and kept at 10 during the reaction. After the reaction, the deposited mixtures were washed several times with deionised water. The resulting material (DHAp) was dried at room temperature for 96 h.

2.3. Removal experiment of Pb^{2+} ion in aqueous solution

Removal experiments of Pb^{2+} ions were carried out in aqueous solutions (500 ml) with controlled Pb^{2+} concentrations in 5g of hydroxyapatite and pH value of 6 in accord with Suk Hyun Jang et al. [13]. The initial Pb^{2+} ion concentrations in aqueous solutions were 100 mg/l by dissolving lead nitrate [$Pb(NO_3)_2$] in deionized water. The pH value of aqueous solutions with a controlled initial Pb^{2+} ion concentration was adjusted to 6 by adding 0.1M HCl standard solution in deionized water. Furthermore, batch studies were performed to analyze the pH effect on the capacity of DHAp-NPs to remove lead ions from aqueous solutions. In order to achieve this, batch experiments similar to those performed at pH 6 were conducted for the value of pH equal to 3.

2.4. Characterization

The X-ray diffraction measurements for DHAp samples were recorded using a Bruker D8 Advance diffractometer, with nickel filtered Cu K_α (λ=1.5405 Å) radiation. The diffraction patterns were collected in the 2θ range 20^o – 60^o, with a step of 0.02^o and 34 s measuring time per step. TEM studies were conducted using a FEI Tecnai 12 equipped with a low-dose digital camera from Gatan. The samples used for TEM imaging investigations were obtained from DHAp nanoparticle suspensions by adding a droplet on a carbon-coated 200-mesh copper grid. Scanning electron microscopy (SEM) study was performed on a HITACHI S2600N-type microscope equipped with an energy dispersive X-ray attachment (EDAX/2001 device). The functional groups present in the prepared powder were identified by FTIR (Spectrum BX Spectrometer). For this 1% of the powder was mixed and ground with 99% KBr. Tablets of 10 mm diameter for FTIR measurements were prepared by pressing the powder mixture at a load of 5 tons for 2 min and the spectrum was taken in the range of 400 to 4000 cm^{-1} with resolution 4 and 128 scans.

The aqueous solutions used in the Pb^{2+} removal experiments were analyzed by atomic absorption spectrometry (AAS) using a Hitachi Z-8100 spectrophotometer. Flame spectrometer was used to measure Pb^{2+} concentrations ranging from 0 to 19.98 mg/l. From measuring the pollutant concentration in solution before and after interaction with our samples, the amount of pollutant was quantified [14]. Due to the narrow range (0-19.98 mg/l) of the atomic absorption spectrophotometer the quantification of the pollutant amount in aqueous solution was obtained from the measurement performed on the diluted solution recovered after the batch experiments. All samples and control tubes were tested in triplicate for statistical purposes.

3. Results and discussions

Fig. 1 presents the X-ray diffraction patterns of dextran coated hydroxyapatite powder before (DHAp) and after removal experiment of Pb^{2+} at pH6 (DHAp_Pb).

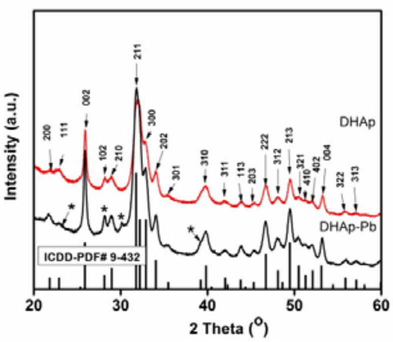


Fig. 1. XRD patterns of hydroxyapatite coated with dextran before (DHAp) and after removal experiment of Pb^{2+} at pH6 (DHAp_Pb). The asterisk indicates the reflection peaks from DHAp_Pb.

All the diffraction peaks of DHAp powders are assigned to the standard characteristic peaks of hexagonal hydroxyapatite, indicating that the phase of the samples was of pure HAp [15]. The diffraction patterns support the facts that HAp nanoparticles were successfully coated with dextran without any structural changes. HAp coated with dextran composite is transformed into DHAp_Pb via the adsorption of Pb^{2+} ions followed by the cation exchange reaction [13]. The diffraction patterns of the samples obtained after Pb^{2+} removal experiments (DHAp_Pb sample) revealed a mixture of HAp and $Pb_5(PO_4)_3(OH)$ [16].

Fig. 2 displays the TEM image of the hydroxyapatite coated with dextran sample, exhibiting an uniform rod-like morphology.

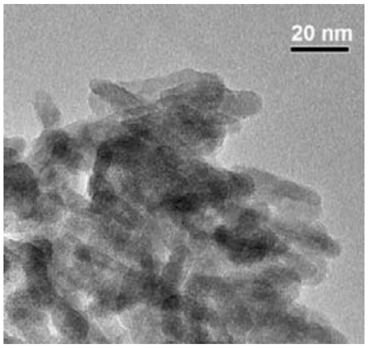


Fig. 2. Bright Field TEM image of DHAp composite

On the other hand, the particles exhibit nanometric size, as observed on the Bright Field micrograph.

In Fig. 3 is shown the SEM micrograph of HAp prepared by the precipitation method. We can clearly see that DHAp particles have a small long morphology. The mean size of DHAp particles is about 50 nm. The DHAp particles formed agglomerates due to flocculation.

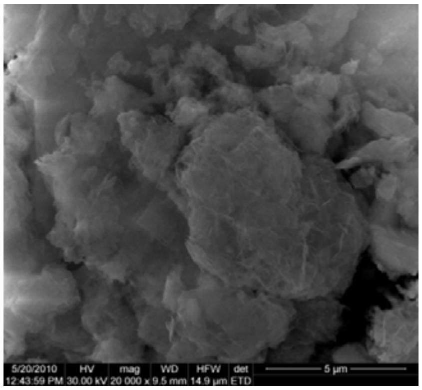


Fig. 3. SEM image of hydroxyapatite coated with dextran composite prepared by precipitated method.

Fig. 4 displays the EDAX spectrum of dextran coated hydroxyapatite powder which confirmed the presence of calcium (Ca), phosphorus (P), and oxygen (O) in the samples.

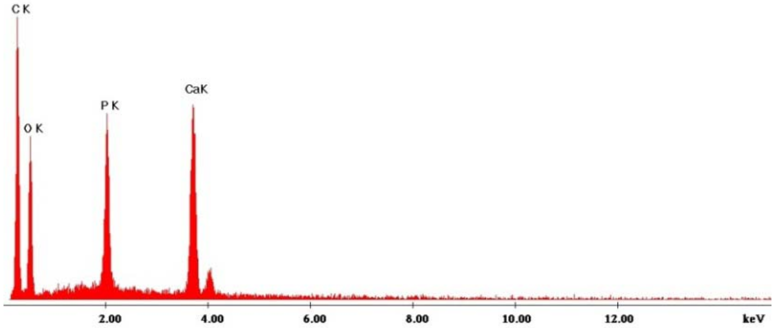


Fig. 4. EDAX spectrum of DHAp

The element mapping (Fig. 5) confirms that Pb was incorporated into the matrix of hydroxyapatite.

Fig. 5 presents the results of the O, Ca, P and Pb distribution. We have also observed that the powder surface was homogenous.

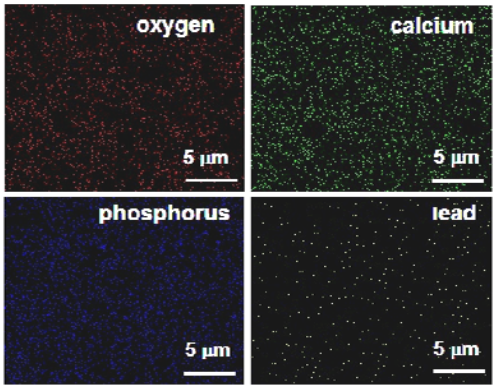


Fig. 5. The element mapping of DHAp_Pb.

The FTIR spectrum displayed in Fig. 6 confirms the formation of hydroxyapatite phase in the synthesized DHAp nanocomposite. The data clearly reveals the presence of various vibrational modes corresponding to phosphate and hydroxyl groups. For all the samples, the presence of strong OH vibration peak could be noticed. The peak observed at 634 cm^{-1} is attributed to the characteristic stretching and vibrational modes of structural OH groups [17]. The band at 1630 cm^{-1} corresponds to the adsorbed H_2O [18]. The broad bands in the regions 1580-1700 cm^{-1} and 3200-3600 cm^{-1} correspond to H-O-H bands of water lattice [19-22]. Bands characteristics of PO_4^{3-} tetrahedral apatite's structure are clearly observed at 563 cm^{-1}, 603 cm^{-1}, 960 cm-1, and 1095-1033 cm^{-1} [23-26]. The peaks at 563 cm^{-1} and 603 cm^{-1}belong to PO_4 (ν_4). The peak at 960 cm^{-1} is attributed to PO_4 (ν_1) and the peaks at 1095-1033 cm^{-1}, to PO_4(ν_3). For the prepared DHAp nanocomposites, one can observe the band at 1434 cm^{-1} that may occur due to C-OH deformation vibration with contributions of O-C-O symmetric stretching vibration of carboxylate group [27].

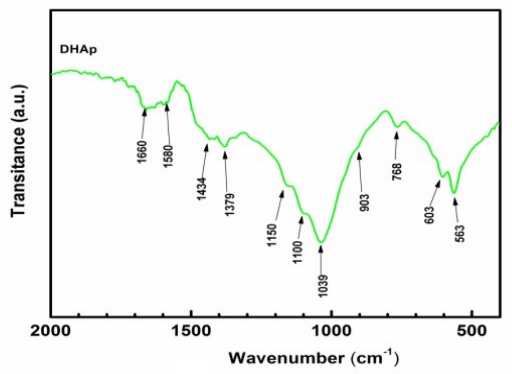


Fig. 6. Infrared spectra of dextran coated hydroxyapatite (DHAp).

The stronger peaks appear at 1150-900 cm^{-1} mainly attributed to the stretching vibration of C-O-C [28-29] and ν(C-O) vibrations [30] are hidden by the overlapping with the vibration bands characteristic to PO_4^{3-} (ν_1) and PO_4^{3-} (ν_3). The peak at 1379 cm^{-1} in the IR spectrum of DHAp is attributed to the stretching vibration δ H-C-OH [31]. On the other hand, a CO_3^{2-} band occurred in the spectra at 1452-1400 cm^{-1} [24].The results for the adsorption capacity of Pb^{2+} ions from aqueous solutions at different pH values (pH 3 and pH 6) quantified by the atomic absorption spectrophotometer are presented in table 1.The adsorption capacity (qt), which represents the metal amount retained on the unit mass of the sorbent at a time t, was calculated using the following equation:

$$q_t = \frac{(C_i - C_f)\times V}{m} (mg\ metal\ ion\ /g\ DHAp),$$

and the percentage of the Pb^{2+} ions removed from the solution at equilibrium was calculated according to :

$$\text{Removal (\%)} = 100 \times \frac{C_i - C_e}{C_i}$$

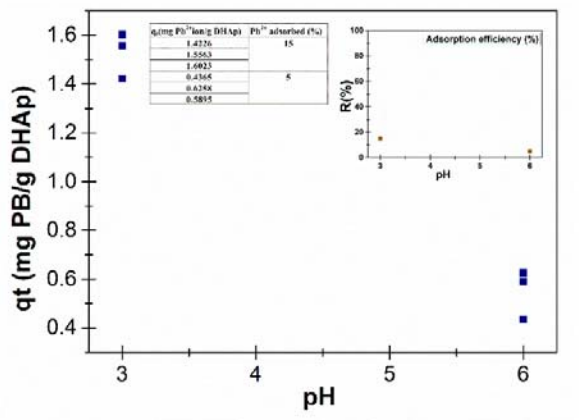
where C_i and C_f are the metal concentration (initial and final) in the aqueous solution (mg/L), C_e is the concentration of the solution at equilibrium (mg/L), V represents the volume of the aqueous solution (L), and m represents the amount of DHAp nanopowders used in the experiments (g).

Table 1

The Pb^{2+} ions adsorption from aqueous solution at different pH values after 24 h of exposure

	Pb^{2+}adsorbed (mg/L)	$\overline{\text{Pb2 + adsorbed(mg/L)}}$
pH 3	14.226	15.27
	15.563	
	16.023	
pH 6	4.365	5.506
	6.258	
	5.895	

The data quantified revealed that the pH of the aqueous solution has a great influence on the capacity of DHAp-NPs to remove lead ions. As it can be seen in Table 1, the amount of adsorbed lead by DHAp nanopowders increased from 5% to 15% when pH of DHAp solution decreased to pH 3. The values of the adsorption capacity of DHAp nanopowders regarding Pb^{2+} ions as well as the percentage of the Pb^{2+} ions removed from the aqueous solutions are presented in Fig. 7.



q_t(mg Pb^{2+}ion/g DHAp)	Pb^{2+} adsorbed (%)
1.4226	15
1.5563	
1.6023	
0.4365	5
0.6258	
0.5895	

Fig 7. The adsorption capacity (qt) of the DHAp nanopowders and the Pb^{2+} adsorption efficiency (R) of the DHAp nanopowders at pH 3 and pH 6.

4. Conclusions

In this study aqueous co-precipitation synthesis was used for the preparation of calcium hydroxyapatite coated with dextran. It was observed that the typical XRD pattern of DHAp powder perfectly covers the peaks for HAp. The diffraction patterns support the fact that HAp powder was successfully incorporated into dextran without any structural changes. The TEM investigations revealed nanometric particles with uniform distribution and rod-like morphology.

The AAS results demonstrate that the dextran coated hydroxyapatite nanocomposite can be used as an adsorbent for removing Pb^{2+} ions from aqueous solutions. In addition, it has been found that the pH of the solution has a great influence on the capacity of adsorption. These results show that the composite materials based on hydroxyapatite may have interesting applications in water purification.

Acknowledgments

The financial and encouragement support provided by the Ministery of Educations of Romania under the project IFA-CEA C2-06.

R E F E R E N C E S

[1]. Agency for Toxic Substances and Disease Registry (ATSDR), "Toxicological Profile for Lead", Atlanta, GA, 2007

[2]. *N.Gupta, A.K.Kushwaha, M.C.Chattopadhyaya*, "Adsorptive removal of Pb^{2+}, Co^{2+} and Ni^{2+} by hydroxyapatite/chitosan composite from aqueous solution", Journal of the Taiwan Institute of Chemical Engineers, **vol. 43**, no. 1, 2012, pp. 125-131

[3]. *M.A.A.Zaini, Y.Amano, M.Machida*, "Adsorption of heavy metals onto activated carbons derived from polyacrylonitrile fiber", Journal of Hazardous Materials, **vol. 180,** no. 1-3,

Aug. 2010, pp. 552–560

[4]. *J.Jeanjean, J.Rouchaud, L.Tran, M.Fedoroff,* "Sorption of uranium and other heavy metals on hydroxyapatite", Journal of Radioanalytical and Nuclear Chemistry, **vol. 201**, no. 6, 1995, pp. 529–539

[5]. *I.Smiciklas, A.Onjia, S.Raicevic, kovic Janac, M.Mitric*, "Factors influencing the removal of divalent cations by hydroxyapatite", Journal of Hazardous Materials, **vol. 152,** no.2, Apr. 2008, pp. 876–884

[6]. *S.Bailliez, A.Nzihou, E.Beche, G.Flamant*, "Removal of Lead (Pb) by hydroxyapatite sorbent", Process Safety and Environmental Protection, **vol. 82**, no. 2, 2004, pp. 175–180

[7]. *I.Smiciklas, S.Dimovic, I.Plecas, M.Mitric*, "Removal of Co^{2+} from aqueous solutions by hydroxyapatite", *Water Research*, **vol. 40**, no. 12, Jul. 2006, pp. 2267–2274

[8]. *R.Zhu, R.Yu, J.Yao, D.Mao, C.Xing, D.Wang*, "Removal of Cd^{2+} from aqueous solutions by hydroxyapatite", Catalysis Today, **vol. 139**, 2008, pp. 94–99

[9]. *J.Jovanovic, B.Adnadjevic, M.Kicanovic, D.Uskokovic*, "The influence of hydroxyapatite modification on the cross-linking of polydimethylsiloxane/HAp composites", Colloids and Surfaces B: Biointerfaces, **vol. 39**, 2004, pp. 181–186

[10]. *A.Groza, A.Surmeian, C.Diplasu, M.Ganciu, P.Chapon, I.I.Popescu*, "Substrate oxide distribution in polydimetylsiloxane polymers generated in negative and positive corona discharges", Journal of Optoelectronic and Advanced Materials, **vol. 12**, no. 11, 2010, pp. 2311-2314

[11]. *A.Groza, A.Surmeian, C.Diplasu, C.Luculescu, P.Chapon, A.Tempez, M.Ganciu*, "Physico-chemical processes occurring during polymerization of liquid polydimethylsiloxane films on metal substrates under atmospheric pressure air corona discharges", Surface & Coatings Technology, **vol. 212**, Nov. 2012, pp. 145–151

[12]. *A.Groza*, "Review of the processes identified during the polymerization of organic and organosilicon liquid films in atmospheric pressure air corona discharges", Romanian Reports in Physics, **vol. 64**, Supplement, 2012, pp. 1227–1242

[13]. *Suk Hyun Jang, Young Gyu Jeong, Byung Gil Min, Won Seok Lyoo, Sang Cheol Lee*, "Preparation and lead ion removal property of hydroxyapatite/polyacrylamide", Journal of Hazardous Materials, **vol. 159**, no. 2-3, Nov. 2008, pp. 294–299

[14]. *Lijing Dong, Zhiliang Zhua, Yanling Qiub, Jianfu Zhao*, "Removal of lead from aqueous solution by hydroxyapatite/magnetite composite adsorbent", Chemical Engineering Journal, **vol. 165**, no.3, Dec. 2010, pp. 827–834

[15]. *C.S.Ciobanu, E.Andronescu, D.Predoi*, "Bet and XRD Studies on The Hydroxyapatite and Europium Doped Hydroxyapatite", Digest Journal of Nanomaterials and Biostructures, **vol. 6**, no. 3, 2011, pp. 1239-1244

[16]. *F. Zhang, Z. Zhao, R. Tan, W. Xu, G. Jiang, W. Song,* "Efficient and selective immobilization of Pb^{2+} in highly acidic wastewater using strontium hydroxyapatite nanorods", Chemical Engineering Journal, **vol. 203**, 2012, pp. 110–114.

[17].*C.S.Ciobanu, E.Andronescu, A.Stoicu, O.Florea, P.Le Coustumer, S.Galaup, A.Djouadi, J.Y Mevellec, I.Musa, F.Massuyeau, A.M.Prodan, K.Lafdi, R.Trusca, I.Pasuk, D.Predoi*, "Influence of annealing treatment of nano-hydroxyapatite bioceramics on the vibrational properties", Digest Journal of Nanomaterials and Biostructures, **vol. 6**, no. 2, 2011, pp. 609-624

[18]. *C.S.Ciobanu, E.Andronescu, B.S.Vasile, C.M.Valsangiacom, R.V.Ghita, D.Predoi*, "Looking fornew synthesis of hydroxyapatite doped with europium", Optoelectronics And Advanced Materials-Rapid Communications, 4(10), 2010, pp. 1515-1519

[19]. *C.S.Ciobanu, S.L.Iconaru, P.Le Coustumer, L.V.Constantin, D.Predoi*, "Antibacterial activity of silver-doped hydroxyapatite nanoparticles against gram-positive and gram-negative bacteria", Nanoscale Research Letters, **vol. 7**, no. 1,324, 2012

[20]. *S.M.Barinow, J.V.Rau, S.Nunziante Cesaro, J.Ďurišin, I.V.Fadeeva, D.Ferro, L.Medvecky, G.Trionfetti*, "Carbonate release from carbonated hydroxyapatite in the wide temperature range", Journal of Materials Science*:* Materials in Medicine, **vol. 17**, no.7, 2006, pp. 597–604

[21]. *D.Predoi, R.A.Vatasescu-Balcan, I.Pasuk, R.Trusca, M.Costache*, "Calcium phosphate ceramics for biomedical applications", Journal of Optoelectronics and Advanced Materials, **vol. 10**, no. 8, Aug. 2008, pp. 2151-2155

[22]. *D.Predoi, M.Barsan, E.Andronescu, R.A.Vatasescu-Balcan, M.Costache*, "Hydroxyapatite-iron oxide bioceramic prepared using nano-size powders", Journal of Optoelectronics and Advanced Materials, **vol. 9**, no. 11, 2007, pp. 3609-3613

[23]. *C.S.Ciobanu, F.Massuyeau, L.V.Constantin, D.Predoi*, "Structural and physical properties of antibacterial Ag doped nano- hydroxyapatite synthesized at 100 degrees C", Nanoscale Research Letters, **vol. 6**:613, 2011

[24. *C.S.Ciobanu, S.L.Iconaru, F.Massuyeau, L.V.Constantin, A.Costescu, D.Predoi*, "Synthesis, Structure, and Luminescent Properties of Europium-Doped Hydroxyapatite Nanocrystalline Powders", Journal of Nanomaterials, 2012

[25]. *M.Birsan, D.Predoi, C.Birsan, C.E.Secu, E.Andronescu*, "Characterisation of magnetic iron oxide in hydroxyapatite", Journal of Optoelectronics and Advanced Materials, **vol. 9**, no. 6, Jun. 2007, pp. 1829-1832

[26]. *C.Birsan, D.Predoi, E.Andronescu*, "IR and thermal studies of iron oxide nanoparticles in a bioceramic matrix", Journal of Optoelectronics and Advanced Materials, **vol. 9**, no. 6, 2007, pp. 1821-1824

[27]. *R.M.Silverstein, G.Clayton Bassier, T.C.Morrill*, "Spectrometric Identification of Organic Compounds", New York: Wiley, 1991

[28]. *K.Lammers, G.Arbuckle-keil, J.Dighton,* "FT-IR study of the changes in carbohydrate chemistry of three New Jersey pine barrens leaf litters during simulated control burning", Soil Biology and Biochemistry, **vol. 41**, no. 2, Feb. 2009, pp. 340-347

[29]. *C.S.Ciobanu, S.L.Iconaru, E.Gyorgy, M.Radu, M.Costache, A.Dinischiotu, P.Le Coustumer, K.Lafdi, Daniela Predoi*, "Biomedical properties and preparation of iron oxide-dextran nanostructures by MAPLE technique", Chemistry Central Journal, **vol. 6**, no. 17, 2012

[30]. *D.Predoi, C.S.Ciobanu, M.Radu, M.Costache, A.Dinischiotu, C.Popescu, E.Axente, I.N.Mihailescu, E.Gyorgy*, "Hybrid dextran-iron oxide thin films deposited by laser techniques for biomedical applications", Materials Science and Engineering, C32, 2012, pp. 296–302

[31]. *D.Predoi*, "A study on iron oxide nanoparticles coated with dextrin obtained by coprecipitation", Digest Journal of Nanomaterials and Biostructures, **vol. 2**, no. 1, 2007, pp. 169-173