Nanohydroxyapatite and its textures as potential carriers of promising short-lived lead isotopes

A. V. Severin,[a*] *M. A. Orlova,*[a,b] *E. S. Shalamova,*[a] *A. V. Egorov,*[a] *and M. A. Sirotin*[a]

[a]*Chemical Department, M. V. Lomonosov Moscow State University,*
Building 3, 1 Leninskie Gory, 119992 Moscow, Russian Federation.
E-mail: severin@radio.chem.msu.ru
[b]*Russian National Research University,*
1 ul. Ostrovityanova, 117997 Moscow, Russian Federation

The possibility of sorption and cocrystallization binding of lead(II) with nanohydroxyapatite (HAP) acting as a potential carrier of short-lived lead radionuclides ^{211,212}Pb was studied. The peculiarities of the kinetics were revealed, and the isotherms of sorption of lead ions on hydroxyapatite with different textures were constructed. A multistage sorption mechanism accompanied by a change in the structure and morphology of the sorbent was studied. The possibility of the formation of a new phase (hydroxypyromorphite) of lead during the sorption and cocrystallization interaction was shown. The introduction of lead into the synthesis of HAP at the early stages of crystallization exerts the highest effect on its morphology and structure. The optimization of the formation of the HAP—Pb composite over the course of the process will make it possible to use the short-lived ^{211}Pb radionuclide in subsequent experiments.

Key words: hydroxyapatite, lead, sorption, cocrystallization, morphology, texture, radionuclide.

The modern development of nuclear medicine is tightly related to the search for new promising radionuclides for radiopharmaceuticals (RPhs) and methods of their delivery to the site of functioning in the human organism. Among these are some lead isotopes interest in which is being increasing continuously. Radionuclide ^{212}Pb ($\tau_{1/2}$ = 10.64 h, β-decay; daughter radionuclide ^{212}Bi is α-emitter with $\tau_{1/2}$ = 60.5 min) is actively used in preclinical and clinical practice as a therapeutical agent. Anticancer RPh based on this radionuclide conjugated with 1,4,7,10-tetraaza-1,4,7,10-tetra(carbamoylmethyl)cyclododecane (TCMC) and Trastuzumab (antibodies targeting the HER2 receptor and having cytostatic effect) turned out to be an efficient remedy against oncological diseases for patients with hyperexpression of HER2.[1,2] Increased interest of researchers is also given to the shorter-lived isotope: ^{211}Pb ($\tau_{1/2}$ = 36.1 min, β-decay; daughter radionuclide ^{211}Bi is α-emitter with $\tau_{1/2}$ = 2.14 min).[3,4]

The use of inorganic nanoparticles as a transporter is a possible method for medical radionuclide delivery to the site of lesion. Nanohydroxyapatite (HAP) has an undisputable advantage for this purpose over other nanosystems due to its complete biocompatibility, bioresorbability (*i.e.*, capability of fast and full processing by the organism), and bioactivity. Nanohydroxyapatite has been long ago and widely applied in medical practice. The HAP drugs with ^{188}Re are used for the treatment of articulation diseases,[5] HAP granules 20—60 μm in size were successfully approbated as carriers of ^{177}Lu (see Ref. 6) and ^{153}Sm (see Ref. 7) for the treatment of hepatic cancer, and nanodispersed HAP combined with ^{223}Ra is used for therapy of oncological diseases of bone tissue.[8]

There are two main direct methods of radionuclide binding with HAP: sorption and cocrystallization. The both methods have already been applied in our works for the preparation of composites HAP-^{223}Ra,[9] HAP-Zn(^{69m}Zn),[10] and HAP-Cu(^{64,67}Cu).[11] Depending on specific purposes of the preparation of similar materials, one can vary such parameters as the contact duration (which is especially urgent for short-lived radionuclides), concentration of components (for the creation of a necessary therapeutic activity of the drug), and degree of retention of the radionuclide (prevention of desorption). In addition, numerous morphological and texture forms of the HAP itself can be used in the sorption method.

The sorption of lead(II) ions on HAP is well studied, since this sorbent was proposed actively for the decontamination of natural and waste waters from heavy metals and radionuclides.[12—16] Depending on the HAP morphology, the kinetics of lead sorption can differ, and the maximum value of the amount adsorbed ranges from 100 to 500 (mg Pb) (g HAP)$^{-1}$.[13,14] The binding process is multistage, and various mechanisms of the interaction of lead and HAP are possible, including those with the formation of mixed nonstoichiometric phosphates or hydroxypyromorphite.[15,16] The introduction of lead ions into the synthesis of HAP is met much more rarely. There were the works on the synthesis and study of nanoparticles of HAP, fluoroapatite, and strontium hydroxyapatites, which were doped by lead ions, in order to prepare nanocatalysts for the formation of ethylene from methane at 700 °C[17] and to produce specialized sorbents for chromatography of proteins and small biomolecules.[18]

The both methods of composite material preparation were applied in the present work. Two morphological types of HAP were used for comparison in sorption binding: hydroxyapatite synthesized using the known procedure[19] (hereinafter, HAP-0) and hydroxyapatite formed during alkaline hydrolysis of calcium glycerophosphate assisted by the alkaline phosphatase enzyme (hereinafter, eHAP).[20] The procedure of Pb^{2+} introduction into the HAP synthesis was earlier[21] tested in doping hydroxyapatite with iron(III) ions. In this case, an aqueous solution of the cation was introduced into the reaction mixture at different stages of calcium phosphate formation. Special attention was given to the time of binding the cation to HAP, the degree of retention of lead by sorbent particles (no desorption), and physicochemical testing of the structural and morphological changes in the potential carrier of radionuclide. All experiments were carried out with non-radioactive lead salts at room temperature.

Experimental

Synthesis of HAP **for sorption experiments** was conducted by two methods described in detail earlier.[10,11] Hydroxyapatite obtained using the described procedure[19] is designated as HAP-0 and represents an aqueous suspension of nanoparticles with the solid phase content X_m = 5.5% (by weight) having an average size of individual crystals of 70½30½2 nm, and the specific surface area estimated as equal to ~170 m^2 g^{-1}. Hydroxyapatite synthesized by the enzymatic method[20] (eHAP) consists of hollow spherical solid particles of hydroxyapatite with an average diameter of 2.7 μm and a specific surface area of 180 m^2 g^{-1}, which was determined by the thermal desorption of nitrogen on a Micromeritics ASAP 2010M instrument (USA). The results were processed using the Brunauer—Emmett—Teller (BET) method under the following conditions of analysis: temperature –196 °C and relative vapor pressure P/P_0 = 0.2.

C**ocrystallization introduction** of Pb^{2+} ions into HAP was conducted using a known procedure.[11,21] Lead ions were introduced into the synthesis in the form of a solution of lead(II) nitrate, whose concentration was chosen in such a way that the resulting molar ratio Pb : Ca would be 1 : 10. As a result, three samples of suspensions were synthesized: HAP-Pb$_1$ (a lead solution was introduced at the initial stage of HAP formation, X_m = 4.3%), HAP-Pb$_2$ (a lead solution was introduced at the moment of sharp decreasing pH, X_m = 4.4%), and HAP-Pb$_3$ (a lead solution was introduced at the end of the synthesis, X_m = 4.4%). Aliquots of the experimental suspensions were sampled for the subsequent morphological analysis. The samples of mother solutions after the synthesis were selected from the solid phase by centrifugation. The residual content of lead and calcium ions in the solution was determined by spectrophotometry. The solid phase was dried to a constant weight at 70 °C for the subsequent study of its phase composition.

C**hemical analyses** of the content of lead and calcium ions in solutions in all experiments were performed by spectrophotometry on a Shimadzu UV-1280 spectrophotometer (Japan, resolution 1 nm). The content of Pb^{2+} was determined using a solution of sodium ethylenediaminetetraacetate (EDTA)[22] measuring the absorbance of the [Pb(EDTA)]$^{2-}$ complex at the wavelength 240—242 nm. It has previously been shown that a similar Ca^{2+} complex does not impede the determination of lead. The calcium concentration in experiments was determined by a Kal´tsii-KFK analytical set (Agat, Russia) at λ = 575 nm using a procedure recommended by the producer.

Phase compositions (**X-ray diffraction analysis**, **XR**D) of the studied samples were monitored using a DRON-3 automated X-ray diffractometer focused in the Bragg—Bretano geometry with a graphite monochromator on the diffracted beam controlled by the EXPRESS computer program. The measurements were performed on a Co-Kα detector at the radiation wavelength 0.179021 nm in the step-to-step scan mode in the angle range 2θ = 10—80° with an increment of 0.1—0.05°. The exposure time per point was 3—5 s.

Morphology and texture of the samples were examined by transmission electron microscopy (TEM, JEM-1011B microscope, Japan, resolution 0.3 nm) and scanning electron microscopy (SEM, CamScan microscope, Japan, resolution 10 nm). In addition, some samples were studied using high-resolution TEM (HR-TEM) on a Jeol JEM-2100 F microscope with the possibility of local X-ray dispersive analysis.

Kinetics of lead sorption on HAP-0 **and** eHAP. A solution (5 mL) of lead (5 mg mL^{-1}), distilled water (4 mL), and a suspension of HAP-0 (1 mL) were mixed in ten polyethylene 10-mL tubes (Sarstedt, Germany). The tubes were stirred on a Multi Bio RS-24 programmed rotator (Latvia). The stirring duration was varied from 10 s to 180 min. After the end of the necessary time period, the suspension was centrifuged for 1.5 min (3000 *g*, MLW T.51.1 centrifuge, German Democratic Republic). The lead and calcium content in the mother liquor was determined as described above. An experiment on establishing the dependence of the pH of the HAP suspension on the duration of sorption of Pb^{2+} ions was additionally carried out. For this purpose, distilled water (16 mL), a solution (20 mL) of Pb (5 mg mL^{-1}), and a suspension of HAP-0 (4 mL) were mixed. Immediately after the suspension was prepared, its stirring with an MLW-RH3 magnetic stirrer (German Democratic Republic) was started, and the change in pH of the mixture was detected during the whole experiment (ELIT 3305 pH meter, Great Britain).

When the kinetics of lead sorption on eHAP was studied, an exact weighed sample of the dry powder (Shimadzu AX200 analytical balance, Japan, accuracy 0.0001 g) was preliminarily mixed with distilled water (5 mL) in polyethelene 10-mL tubes, and the tubes were kept for 16 h for the complete wetting of the samples with water. Then a solution of lead (5mg mL^{-1}) was added to the mixture, and stirring on a Multi Bio RS-24 programmed rotator (Latvia) was started. The stirring duration was varied from 10 s to ~300 h. After the end of a specified period, the suspension was centrifuged for 2 min (3000 *g*, MLW T.51.1 centrifuge, German Democratic Republic) and the lead and calcium contents were determined in the mother liquor.

Isotherm of lead sorption on HAP-0 **and** eHAP. In order to construct the isotherm of lead sorption on HAP-0, we prepared ten samples in polyethylene 10-mL tubes in which a suspension of HAP-0 (1 mL) was mixed with solutions containing various amounts of lead ions. The samples were stirred for 3 h on a Multi Bio RS-24 programmed rotator after which the tubes were centrifuged for 5 min at 3000 *g*, the mother liquor was separated, and the lead and calcium concentrations were measured in the samples as described earlier.

In the case of eHAP, the eHAP powder (20 mg) was placed in each polyethylene 10-mL tube, distilled water (5 mL) was added, the tubes were kept for the time necessary for the complete wetting of the solid phase, and solutions with various contents of lead ions were introduced. The reaction mixture was stirred for 5 days on a Multi Bio RS-24 programmed rotator after which the solid and liquid phases were separated by centrifugation at 3000 *g* for 5 min, and the contents of lead and calcium were determined as described previously.

Samples of the solid phase and suspension were taken during the study for analyses by X-ray diffraction, SEM, TEM, and HR-TEM. All sorption experiments were carried out at 22±1 °C.

All experiments were conducted three times. The experimental error was found from the accuracy of spectrophotometric determination of the concentration of the main cations (5—7%) by the statistical data processing at $p = 0.95$. The accuracy of pH determination was 10—12%.

Results and Discussion

An analysis of the mother liquor to the residual content of lead and calcium ions after the synthesis of HAP doped with Pb^{2+} ions showed that the lead concentration in all samples did not exceed $(1.1\pm0.1)\cdot10^{-5}$ mol L^{-1}, indicating its complete transition to the solid phase. The content of Ca^{2+} in the mother liquor (mol L^{-1}) was as follows: HAP-Pb_1, $(3.1\pm0.1)\cdot10^{-2}$; HAP-Pb_2, $(3.2\pm0.1)\cdot10^{-2}$, and HAP-Pb_3, $(3.3\pm0.1)\cdot10^{-2}$. Based on these data, one can present the following conventional scheme for the formation of the solid phase of the prepared nanocomposite:

Equation.

The diffraction patterns obtained by the XRD method (Fig. 1) demonstrated the absence of reflections of foreign phases, a decrease in the relative intensity, and peak broadening for the HAP-Pb_3 sample; *i.e.*, amorphization of this sample is possible.

Fig. 1

According to the TEM results, the experimental samples contain indeed amorphized particles of the solid phase (Fig. 2, *a*). In addition, it is found that the HAP-Pb_1 sample exhibits the destruction of some HAP crystals when they decompose to component-subnanoparticles (Fig. 2, *b*).

Fig. 2

The distribution functions of the studied nanocrystals over length and width were calculated from the data obtained (Fig. 3). Figure 3 shows that lead ions exert the maximum effect on the morphology and size of the formed crystals were the ions are introduced at the initial stage of HAP formation. The HAP-Pb_2 and HAP-Pb_3 samples are characterized by the formation of more extended and narrow crystals compared to those of HAP-0. The presence of partially decomposed crystals in the first sample can be explained by the initial acidification of the system by the introduction of a lead solution and the presence of the salt background. The character of changing the HAP morphology upon the introduction of lead ions is similar to that for doping hydroxyapatite by transition metal ions, such as Zn^{II} and Cu^{II}.[10,11]

Fig. 3

The peculiarities of the occurrence of sorption processes when HAP-0 and eHAP were used as sorbents manifested themselves already for the kinetics of sorption. For sorption on HAP-0, the quasi-equilibrium was achieved within nearly 3 h. In the case of sorption on eHAP, the process of achieving quasi-equilibrium lasted almost 300 h, and the quasi-equilibrium was reached within ~5 days. However, in the case of the task of preparing RPhs with short-lived lead radionuclides, especially ^{211}Pb, which completely decay within ~6 h, it is necessary to restrict the duration of the process. Therefore, in this work we chose the contact duration equal to 3 h in order to compare the sorption kinetics on HAP-0 and eHAP (Fig. 4). For sorption in eHAP, this time corresponds to the time of achieving the quasi-stationary state in which the system exists for subsequent ~10 h.

Fig. 4

In the chosen time interval, both kinetic curves are well described by the Langrene model for the pseudo-second order[13]

Equation,

$$\frac{dm}{dt} = k_2(m_e - m)^2 \qquad (1)$$

or after integration,

Equation, $$\frac{t}{m} = \frac{1}{k_2 m_e^2} + \frac{1}{m_e} t \quad (2)$$

where m is the weight of the sorbate sorbed to the time t, and m_e is the weight of the sorbate sorbed to the moment of equilibrium achievement. Constructing the plot of the dependence $t/m = f(t)$ (Fig. 5), we can find the values of m_e (or the maximum amount adsorbed Γ_e) and estimate the rate constant of the pseudo-second order k_2 (Table 1).

Fig. 5

Table 1

In addition, in both cases of lead sorption, an equivalent amount of calcium ions transits to the mother liquor (Fig. 6), indicating that an ion-exchange process can occur.

Fig. 6

To describe the sorption isotherms of lead ions on HAP-0 and eHAP (Fig. 7), we applied the models similar to the Langmuir and Freundlich models. However, in both cases, the experimental results were described by latter much more badly. Only the Langmuir model was used for comparison of the calculated sorption parameters. The data are presented in Table 2.

Fig. 7

Table 2

The experimental data on the dynamics of pH changing during sorption (Fig. 8) show that the adsorption interaction between lead and HAP proceeds *via* several consecutive stages with the possible change in the interaction mechanism.

Fig. 8

The kinetics of pH changing in the system shows that the sorption of lead is a prolonged process for both eHAP and HAP-0. The following chemical reaction can occur at the earliest stages[16]:

Equation.

The pH value of the solution (see Fig. 8) decreases sharply and then increases when the lead complex with hydroxyl groups on the hydroxyapatite surface decomposes and other processes begin to occur.

Under our conditions, processes of ion exchange, physical adsorption, and chemisorption occur, most likely, during lead sorption. Unstable mixed calcium—lead apatite $Pb_{10-x}Ca_x(PO_4)_6(OH)_2$ (for experiments on cocrystallization, $x = 1$) can be formed first and then is dissolved and transformed into hydroxypyromorphite ($Pb_5(PO_4)_6(OH)$). After this, the sorption of lead ions on HAP is significantly retarded because of the appearance of difficulties of lead access to the hydroxyapatite surface. In our opinion, the prolonged sorption kinetics and changes in the pH of the system in the case of HAP-0 are related to this fact. A similar sequence of stages of the process is proved by both the published data[13,16,23] and the XRD patterns of the HAP samples after sorption (Fig. 9), which distinctly demonstrate the formation of a new phase. The influence of peculiarities of the texture of the sample is additionally observed in the case of eHAP. The sorption of Pb^{2+} on this sorbent is impeded because of the branched system of nanopores, the access to which takes much more time.

Fig. 9

The change in the morphology of HAP-0 and eHAP nanoparticles after sorption (Fig. 10) can be considered as one more proof. In the first case, extended crystals are formed (the same tendency is observed for the cocrystallization method of binding). In the second case, the spherical particles of the sorbent decompose in part (according to the SEM data, see Fig. 10, *b*, *d*). The HR-TEM and X-ray dispersive analysis results (Fig. 11) confirm the formation of the phase containing lead on the HAP surface. The mapping of the nanoparticle surface over elements showed that lead was distributed uniformly as the main elements of HAP (Fig. 12). The HR-TEM data for the cocrystallization sample HAP-Pb_1 demonstrated the formation of the lead subnanophase (Fig. 13) on the surface of formed hydroxyapatite as in the case of sorption binding (see Fig. 11). The diffraction patterns of the HAP-Pb_{1-3} samples contain no peaks of foreign phases, which is related, most likely, to small amount of the introduced cation.

Figs 10—13

The experiment on lead desorption performed in the present work showed an almost complete absence of desorption, which indirectly confirms our assumptions.

To conclude, it was found that for both sorption and cocrystallization lead can form mixed and individual phosphates (of the hydroxypyromorphite type) strongly bound to the HAP nanoparticles regardless the method of preparation. Further, when developing RPhs based on short-lived lead isotopes and hydroxyapatite, the peculiarities of the kinetics of the sorption interaction of Pb^{2+} and HAP should be taken into account. For example, the duration of the process in the sorption method should be restricted by 3 h, since the system reaches the quasi-stationary state within this time. The sorbent based on HAP-0 (see Fig. 4) within this time will bind a larger amount of lead than eHAP, although the maximum amount adsorbed on eHAP is more than three times higher. A similar behavior is primarily related to peculiarities of the texture and morphology of the used sorbent.

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Graphical Abstract

Nanohydroxyapatite and its textures as potential carriers of promising short-lived lead isotopes

A. V. Severin, M. A. Orlova, E. S. Shalamova,
A. V. Egorov, and M. A. Sirotin
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Authors′ Figure

Partially destroyed crystals of nanohydroxyapatite (HAP) of the HAP-Pb_1 sample (*a*) and the formation of the lead subnanophase in the HAP-Pb_1 sample (*b*).

Running title

Figure Captions

Fig. 1. Diffraction patterns of the reference HAP-0 sample (*1*) and HAP samples doped with lead ions: HAP-Pb$_1$ (*2*), HAP-Pb$_2$ (*3*), and HAP-Pb$_3$ (*4*).
/град /deg
Fig. 2. Amorphized particles in the HAP-Pb$_3$ sample (*a*) and partially destroyed crystals of the HAP-Pb$_1$ sample (*b*).
/нм /nm
Fig. 3. Distribution functions of HAP-Pb particles over length (*a*) and width (*b*): HAP-0 (*1*), HAP-Pb$_1$ (*2*), HAP-Pb$_2$ (*3*), HAP-Pb$_3$ (*4*), and subnanoparticles in the HAP-Pb$_1$ sample (*5*).
/нм /nm
Fig. 4. Kinetics of sorption of Pb^{2+} ions on HAP-0 (*1*) and eHAP (*2*) during the occurrence of the process (180 min).
/мг Pb•(г ГАП)$^{-1}$ /(mg Pb) (g HAP)$^{-1}$
/мин /min
Fig. 5. Linearization of the kinetics of lead sorption on HAP-0 (*1*) and eHAP (*2*) according to the pseudo-first-order model; *1*: $y = 0.0044x + 0.0348$ ($R^2 = 0.9866$); *2*: $y = 0.0096x + 0.0032$ ($R^2 = 0.999$).
/мин•г ГАП•(мг Pb)$^{-1}$ /min (g HAP) (mg Pb)$^{-1}$
/мин /min
Fig. 6. Number of calcium ions (N(Ca)) transferred to the mother liquor during sorption *vs* number of lead ions N(Pb) sorbed on HAP-0 (*1*) and eHAP (*2*).
/ммоль /mmol
Fig. 7. Isotherms of sorption of Pb^{2+} ions on HAP-0 (*1*) and eHAP (*2*); C_e is the equilibrium concentration of Pb^{2+} ions.
/мг Pb•(г ГАП)$^{-1}$ /(mg Pb) (g HAP)$^{-1}$
/мг Pb•мл$^{-1}$ /(mg Pb) mL^{-1}
Fig. 8. Change in the pH during lead sorption on HAP-0, inset: data for the initial stage of the process.
/ч /h
Fig. 9. Diffraction patterns of the HAP samples before lead sorption on HAP-0 (*1*), after lead sorption on HAP-0 (*2*), and after lead sorption on eHAP (*3*). Inset: diffraction patterns of pure HAP (*1*) and after lead sorption on HAP for 1 min (*2*), 1 h (*3*), 1 day (*4*), and 9 days (*5*) accompanied by the formation of hydroxypyromorphite (P).[23]
/град /deg
Fig. 10. Changes in the morphology of particles of the sorbents HAP-0 (*a*) and eHAP (*b*) after lead sorption (*c* and *d*, respectively).
/нм /nm
/мкм /μm
Fig. 11. Results of local X-ray dispersive analysis of the chosen aggregate of crystals (*a*) and the obtained spectra of the chosen region on the image (*b*—*d*).
/нм /nm
/кэВ /keV
(имп.) (pulse)
Fig. 12. Mapping of the sample of HAP-0 nanoparticles (*a*) after the sorption of lead ions for the main cations: Ca (*b*) and Pb (*c*).
/нм /nm
Fig. 13. Formation of the lead subnanophase in the HAP-Pb$_1$ sample (*a*, indicated by arrow) and local X-ray dispersive analysis results for aggregates of nanoparticles of this sample (*b*—*e*).
/кэВ /keV
(имп.) (pulse)

Tables

Table 1. Parameters of the pseudo-second-order model for the kinetics of lead sorption on HAP-0 and eHAP (t = 180 min) (accuracy 5—7%)
Sample k_2 Γ_e R^2
/(g HAP) ((mg Pb) min^{-1})$^{-1}$/(mg Pb) (g HAP)$^{-1}$
ГАП-0 HAP-0
фГАП eHAP
Table 2. Parameters of lead adsorption on HAP-0 and eHAP calculated using the Langmuir model (accuracy 5—7%)
Sorbent Γ_{max}/(mg Pb) (g HAP)$^{-1}$$K_L$/mL (mg Pb)$^{-1}$ R^2
ГАП-0 HAP-0
фГАП eHAP