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Removal of aqueous lead ions by hydroxyapatites: Equilibria and kinetic processes

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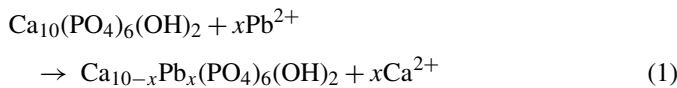
Abstract

The capacity of hydroxyapatite (HAp) to remove lead from aqueous solution was investigated under different conditions, namely initial metal ion concentration and reaction time. The sorption of lead from solutions containing initial concentrations from 0 to 8000 mg/L was studied for three different HAp powders. Soluble Pb and Ca monitoring during the experiment allows characterizing the mechanism of lead uptake. Dissolution of calcium is followed by the formation of a solid solution, $Pb_xCa_{10-x}(PO_4)_6(OH)_2$, with a Ca/P ratio decreasing continuously. Langmuir–Freundlich classical adsorption isotherms modeled adsorption data. The adsorption capacities calculated from this equation vary from 330 to 450 mg Pb/g HAp for the different solids. Modeling of the sorption process allows to determine theoretical saturation times and residual lead concentrations at equilibrium.

Keywords: Hydroxyapatite; Lead; Adsorption

1. Introduction

Calcium hydroxyapatite (HAp), $Ca_{10}(PO_4)_6(OH)_2$, is used for the removal of heavy metals from contaminated soils, wastewater and fly ashes [1–7]. Among heavy metals, lead was particularly studied with an aim to establish the mechanisms of lead capture by HAp. An ion exchange mechanism was proposed by Takeuchi et al. [8] in which lead ions are first adsorbed on the HAp surface and substitution with Ca occurs as described by the following equation:



The mass balance of lead is given by:

$$mq = V(C_0 - C) \quad (2)$$

where m is the weight of HAp (g), q the amount of lead removed by unit of weight of HAp (mg Pb/g HAp), V the volume of lead solution (l), C_0 the initial lead concentration of solution (mg Pb/l) and C is the concentration of lead at the time t of adsorption (mg Pb/l). After a long time, C and q will reach equilibrium value C_e and q_e . As the exchange reaction between Pb^{2+} and Ca^{2+} described by Eq. (1) is very fast and seems to take place at the surface of HAp particles, the following rate equation can be given by

$$\frac{\partial q}{\partial t} = K_F a_p (C - C_s) \quad (3)$$

where K_F is the Takeushi constant and a_p is the specific surface area of the particles. The initial conditions and equilibrium relation can be written as:

$$C = C_0 \quad \text{and} \quad q = 0 \quad \text{at} \quad t = 0, \quad \text{and} \quad q_e = \text{constant} \quad (4)$$

$$q = \left(\frac{q_e}{C_e} \right) C_s \quad (5)$$

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The interaction of HAp with heavy metals may form relatively insoluble metal phosphates and/or result in the sorption of heavy metal on HAp, thus significantly reducing aqueous metal concentrations. The study of the equilibrium will help to determine the adsorption capacity of the hydroxyapatite powders used. This capacity is an important parameter to design a pilot plant which could be used for wastewater treatment.

Adsorption isotherms are used to determine the affinity of HAp for lead. The lead concentration at equilibrium (C_e) helps to calculate the amount of lead (q_e) removed by unit weight of HAp at the end of the experiment. This quantity is defined as follows:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (6)$$

An isotherm model such as the Freundlich–Langmuir model is generally used to describe the sorption of heavy metals by natural adsorbents [9–12]

$$q_e = Q_0 \frac{k_{FL} C_e^{1/n_{FL}}}{1 + k_{FL} C_e^{1/n_{FL}}} \quad (7)$$

where Q_0 is lead concentration on solid surface in equilibrium with the initial liquid concentration (mg Pb²⁺/g HAp), k_{FL} is related to the kinetics of adsorption (mg Pb²⁺/g HAp) and C_e is the equilibrium concentration of lead (mg/l).

2. Materials and methods

Two series of experimental measurements were carried out: (1) batch sorption measurements to determine kinetic parameters and the effect of pH on lead removal and (2) adsorption measurements to define the adsorption efficiency of HAp for lead. All experiments were carried out with three different HAPs synthesized at room temperature by precipitation from solution [13]. The solids obtained were dried at 105 °C during 1 day and ground to obtain monomodal powders.

X-ray powder diffraction measurements (XRD), were carried out with Cu K α radiation from 20 to 50° (Siemens D5000). The phases present were determined by comparing the patterns with JCPDS standards. The XRD pattern of powder calcined at 1000 °C during 15 h shows that HAP₁ is composed of hydroxyapatite and tricalcium phosphate (TCP) with a Ca/P ratio of 1.6004. HAP₂ is a stoichiometric HAp, Ca₁₀(PO₄)₆(OH)₂ with a Ca/P ratio of 1.6669. HAP₃ is composed of hydroxyapatite and lime (CaO) with a Ca/P ratio of 1.7275. The specific surface area of the particles was determined by nitrogen adsorption using a BET method (MICROMERITICS Gemini Vacprep 061). The bulk density of the powder was measured by helium pycnometry (MICROMERITICS Accupyc 1330). The powder particles size distribution was determined with a MALVERN Laser Mastersizer Hydro 2000. The particles were placed in an ethanol suspension shaken by ultrasound. This characterization of the three HAP powders gave the following results (Table 1).

Aqueous solutions containing Pb²⁺ ions of concentration (1000, 2000, 3000, 5000, 6000 and 8000 mg/l) were prepared from lead nitrate. The initial pH of the suspension varied from 3 to 5 depending on the concentration of lead in the solution.

Table 1
Hydroxyapatite properties

	HAP ₁	HAP ₁	HAP ₁
Ca/P molar ratio	1.60	1.67	1.73
Specific surface area (m ² /g)	41	50	104
Bulk density (g/cm ³)	2.97	2.92	2.80
d(50) (μm)	11	16	18

Four grams of HAp were introduced in a stirred-tank reactor containing 400 ml of the prepared solution after 10 min of equilibration time. The stirring speed of the agitator was 400 rpm. The temperature of the suspension was maintained at 25 °C.

The lead and calcium concentrations in the solution during the run were determined by an atomic absorption photometer (VARIAN Spectra AA 400). After 24 h of reaction, the sample was filtered and dried at 105 °C during 2 h.

3. Results and discussion

The evolution of lead concentrations during the batch sorption experiment for HAP₂ is presented in Fig. 1. The curves show a swift decrease of lead concentration during the first minutes. The final concentration corresponds to the equilibrium or to the entire consumption of lead.

Both the Pb²⁺ concentration evolutions and the pH decreases observed in Figs. 1 and 2 for the first few minutes can be explained by surface complexation. In fact, Mavropoulos et al.

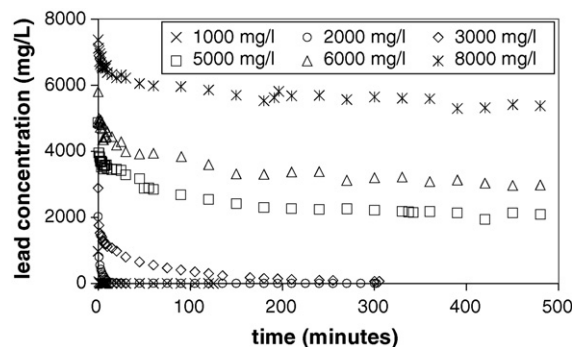


Fig. 1. Batch sorption kinetic measurements for HAP₂.

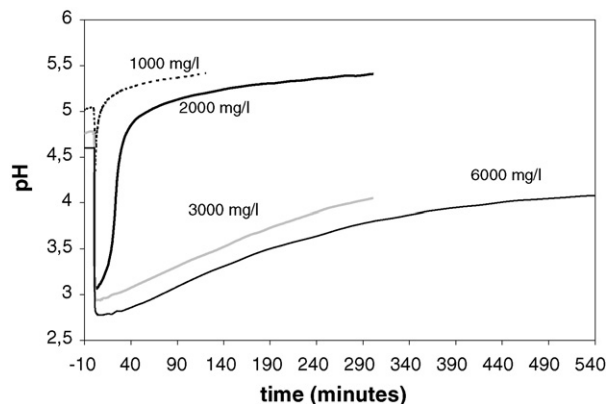


Fig. 2. Effect of Pb sorption on the pH of the solution for HAP₂.

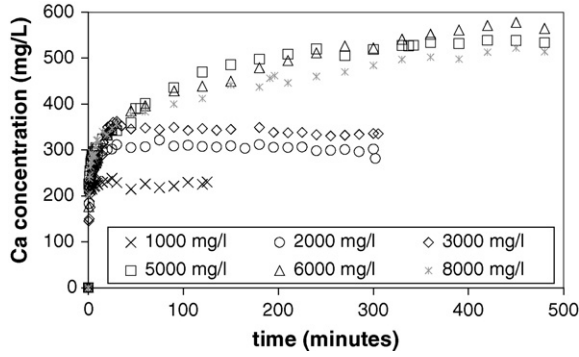


Fig. 3. Ca^{2+} released into the solution for HAp₂.

[5] postulated that surface $\equiv\text{POH}$ sites of hydroxylapatite in neutral water are transformed into $\equiv\text{POPb}^+$ sites, which leads to proton leaching and consequently explains the initial pH decrease and calcium dissolution observed in Fig. 3. The progressive return towards initial pH values depends on the initial lead concentration, with higher concentrations responding more slowly.

Fig. 4 establishes the relation between Pb^{2+} uptake and Ca^{2+} release. The slope of this curve is approximately equal to unity suggesting that the reaction mechanism corresponds to equimolar exchange of lead and calcium yielding $\text{Ca}_{10-x}\text{Pb}_x(\text{PO}_4)_6(\text{OH})_2$, where x can vary from 0 to 10 depending on the reaction time and experimental conditions. Similar results were obtained with HAp₁ and HAp₃. The proposed mechanism for lead removal by Hap comprises two steps: firstly, rapid surface complexation of the lead on the $\equiv\text{POH}$ sites of the HAp which causes the decrease of the pH and secondly, partial dissolution of calcium followed by the precipitation of an apatite with formula: $\text{Pb}_x\text{Ca}_{10-x}(\text{PO}_4)_6(\text{OH})_2$. Fig. 5 shows the adsorption isotherms for the three HAPs. For C_e above 500 mg/l, the amount of sorbed lead, q_e , does not increase significantly. This plateau corresponds to the saturation of the HAP surface which can be modeled with the Langmuir–Freundlich Eq. (7). Table 2 lists the values of the resulting parameters.

The results confirm the large affinity of lead for all the HAPs studied. HAp₁ and HAp₂ have same specific surface areas, but HAp₁ has the higher adsorption capacity. As HAp₁ is a deficient HAP ($\text{Ca}/\text{P} < 1.67$), the cation deficiency can be compensated by lead ions in order to obtain a stoichiometric apatite

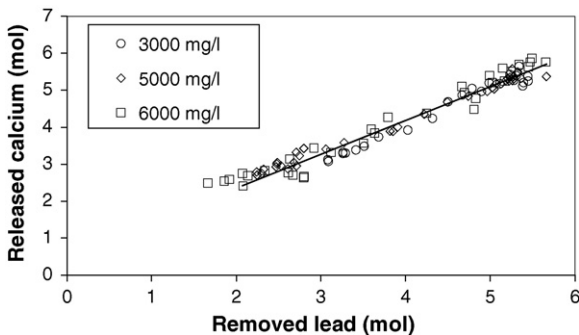


Fig. 4. Moles of Ca^{2+} released into the solution as function of moles of Pb^{2+} removed from the solution.

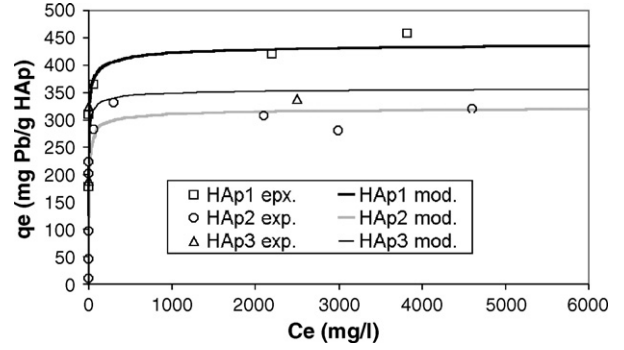


Fig. 5. Adsorption isotherms for the three hydroxyapatites.

Table 2
Langmuir–Freundlich parameters

	HAp ₁	HAp ₂	HAp ₃
n_{LF}	2.6	2.5	2
$k_{LF} [(\text{mg Pb/l})^{-1/n_{LF}}]$	1	1	1
$q_{max} (\text{mg Pb/l})$	450	330	360

(i.e. $(\text{Ca} + \text{Pb})/\text{P} = 1.67$). The calculated theoretical formulas of the solid phosphates formed have the molar ratios presented in Table 3.

The Ca/P molar ratios of the HAPs at the end of the experiments are higher than 1.67. Based on the experimental concentration–decay curves, the mass balance was solved using a Runge–Kutta Telling equation [14], assuming diffusion in the macropores is rate determining and that the equilibrium relationship is given by Langmuir–Freundlich isotherms at any specified radial position. If the hydroxyapatite particles are spherical and their dimension and porosity are uniform, the differential mass balance on a spherical shell element is:

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r^2 D_{ef} \frac{\partial C}{\partial r} \right) = \frac{\partial C}{\partial t} + \left(\frac{1 - \varepsilon_p}{\rho} \right) \frac{\partial q}{\partial t} \quad (8)$$

The tortuosity, τ of the adsorbent was taken equal to 4 referring to other natural adsorbent tortuosities varying from 2 to 6 [9]. The macropore diffusivity was taken as independent of concentration, with ε_p is the porosity of the HAP particles (0.49), q the adsorbate quantity per gram of HAP and D_{ef} is the effective diffusivity, related to the molecular diffusivity D_M by the relation:

$$D_{ef} = \frac{\varepsilon_p}{\tau} D_M \quad (9)$$

Assigning a value of $D_M = 2.6 \times 10^{-7}$ m/s, the effective diffusivity D_{ef} of lead in the liquid phase inside micropores is then

Table 3
Hydroxyapatite formula before and after lead removal

	At the beginning		At the end	
	Formula	Ca/P	Formula	(Ca + Pb)/P
HAp ₁	$\text{Ca}_{9.6}(\text{PO}_4)_6(\text{OH})_2$	1.6	$\text{Pb}_{2.13}\text{Ca}_{8.12}(\text{PO}_4)_6(\text{OH})_2$	1.71
HAp ₂	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	1.67	$\text{Pb}_{1.5}\text{Ca}_9(\text{PO}_4)_6(\text{OH})_2$	1.75
HAp ₃	$\text{Ca}_{10.38}(\text{PO}_4)_6(\text{OH})_2$	1.73	$\text{Pb}_{1.71}\text{Ca}_{8.59}(\text{PO}_4)_6(\text{OH})_2$	1.72

Table 4
Comparison between experimental and model results

$C_{0,\text{exp}}$ (g Pb/M ³)	$C_{e,\text{exp}}$ (g Pb/M ³)	$t_{c,\text{exp}}$ (s)	C_e (g Pb/M ³)	t_c (s)
2000	0	1.5	0	1.3
5000	2000	5	8	2400
6000	3200	11.5	30	28000

3.1×10^{-8} m/s. Using normal initial and boundary conditions, the characteristic time t_c corresponding to the time required for the saturation of the hydroxyapatite is then deduced as:

$$t_c = \frac{(1 - \varepsilon_p)C_e r_p^2}{D_{\text{ef}}C_0} \quad (10)$$

Based on the experimental concentration–decay curves such as those shown in Fig. 1, the mass balance was solved for our experimental conditions and yielded the theoretical saturation times t_c and equilibrium concentrations C_e . The comparison between the experimental and model results is summarized in Table 4. We observe that adsorption takes a very long time before attaining saturation with extremely low values of residual lead concentrations in water. The results show that even after a few hours, when the adsorption kinetics become very slow, the sorption capacity remains very high.

Modeling of the reaction kinetics shows that after 24 h (time limit of our experiments) the reaction is not finished but is in fact very slow. So, with longer contact times, higher sorption capacity could be obtained.

4. Conclusions

Isothermal batch adsorption results show that hydroxyapatite is able to remove important quantities of lead (between 330 and 450 mg Pb/g HAp for the three studied hydroxyapatites). Experimental and theoretical considerations show that a high specific surface area and a large porosity are favorable parameters for lead adsorption. The kinetic results show that the lead uptake by hydroxyapatite proceeds with a rapid surface complexation of the lead on the $\equiv\text{POH}$ site before the formation of a pyromorphite compound of formula $\text{Ca}_{10-x}\text{Pb}_x(\text{PO}_4)_6(\text{OH})_2$. The model results predict that hydroxyapatite may be an effective sorbent to remove dilute lead from aqueous solutions for long time periods before reaching saturation. The phase purity or Ca/P ratio of the adsorbent is not of critical importance for the

material's capacity. This leads to interesting prospects for the use of hydroxyapatites in water purification.

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