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REMOVAL OF LEAD (Pb) BY HYDROXYAPATITE SORBENT

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The capacity of hydroxyapatite (HA) for removal of lead from aqueous solution was investigated under different conditions, namely initial metal ion concentration and reaction time. The sorption of lead solution by synthetic hydroxyapatite was investigated with initial concentration in the solution containing Pb^{2+} varying from 1000 to 8000 mg l^{-1}. Pb and Ca analysis in the solutions, X-ray diffractometry associated with SEM-WDS and XPS analysis characterized the mechanisms of lead uptake. It was shown that the dissolution of hydroxyapatite is followed by the formation of hydroxypyromorphite, a solid solution of $Pb_{10-x}Ca_x(PO_4)_6(OH)_2$ formula, with Pb ions mostly occupying Ca(II) sites, and that the Ca/P molar ratio of this solid solution decreases continuously. Classical adsorption isotherms were used to describe adsorption data. The adsorption capacity, k_{LF}, of 320 mg Pb g^{-1} HA and the adsorption intensity, n_{LF}, of 2.5 were calculated from Langmuir–Freundlich. This isotherm was at an initial pH 5 and 25°C for 16 μm mean particle size. This shows significant affinity of HA to Pb^{2+} according to literature data.

Keywords: kinetics of sorption; ion exchange; dissolution-precipitation; surface characterization; isotherms.

INTRODUCTION

Heavy metals are toxic to human life. Their ubiquitous nature, their toxicity even in trace quantities, their tendency to bioaccumulate in the food chain, and the stricter environmental regulations related to heavy metal discharges justify the development of processes for heavy metal removal from both wastewater and landfill leachates (Ma *et al.*, 1994; Rengaraj *et al.*, 2001).

Hydroxyapatite, HA, can accept a series of cationic and anionic substitution inside its structure (Elliot, 1994). Consequently, it was proposed for the removal of heavy metals from contamined soils and wastewater (Chen *et al.*, 1997; da Rocha *et al.*, 2002). Thus, the understanding of the effect of these substitutions on HA structure and properties like dissolution, crystallinity, surface activity and thermal stability have motivated a number of fundamental works (Laperche *et al.*, 1996; Mavropoulos *et al.*, 2002; da Rocha *et al.*, 2002).

In particular, the sorption of heavy metals such as Pb by HA was extensively studied because of its high toxicity. The main aim of the studies was related to the mechanisms of lead capture by HAP. Takeuchi *et al.* (1998) and Mavropoulos *et al.* (2002) proposed that the ion exchange reaction is responsible for the formation of the solids, whereas Ma *et al.* (1993) concluded that the dissolution of hydroxyapatite followed by the precipitation of pyromorphites is the mechanism responsible for reducing Pb concentration below regulatory limits.

This controversy is certainly related to insufficient understanding of the physicochemical properties of the HA surface. However, such studies are very difficult due to hydroxyapatite's strong variability in crystallinity, morphology, texture, stability and solubility when synthesized. Because of the limited knowledge of the mechanisms for removing heavy metals from solution by apatites, the term sorption is herein used loosely as a general term to describe the attachment of heavy metals from a solution to its coexisting apatite surfaces.

Three types of reactions may control Pb immobilization by HA: surface adsorption, cation substitution or precipitation. According to Takeuchi *et al.* (1998) Pb was first adsorbed on the surface of HA, and then cation substitution (ion exchange) with Ca occurred as described by the following equation:

$$Ca_{10}(PO_4)_6(OH)_2 + xPb^{2+} \longrightarrow xCa^{2+} + Ca_{10-x}Pb_x(PO_4)_6(OH)_2 \quad (1)$$

They concluded that this process was controlled by liquid-film diffusion and took place at the surface of the HA particles.

This reaction cannot explain changes in P concentrations during the Pb immobilization process or the associated changes in solution pH. The major evidence for the cation substitution theory was that the molar ratio of Pb removed/Ca released stayed at an approximate value of 1 in their experiments. However, this phenomenon can also be explained in

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terms of dissolution/precipitation. In other words, 10 mol of Pb are consumed with each 1 mol of HP precipitated, and 1 mol of HA has to be dissolved to supply P, and thus 10 mol of Ca are released to the solution.

Ma *et al.* (1994) showed that HA dissolution and HP precipitation were the main mechanisms for Pb immobilization by HA in the absence of other metals. These chemical reactions can be described as follows:

$$Ca_{10}(PO_4)_6(OH)_2 + 14H^+ \xrightarrow{\text{dissolution}} 10Ca^{2+} + 6H_2PO_4^- + 2H_2O \quad \log k = 28.92 \tag{2}$$

$$10Pb^{2+} + 6H_2PO_4^- + 2H_2O \xrightarrow{\text{percipitation}} 14H^+ + Pb_{10}(PO_4)_6(OH)_2 \quad \log k = -8.28 \tag{3}$$

The interaction of apatites with heavy metals may form relatively insoluble metal phosphates and/or result in the sorption of heavy metals on apatite, thus significantly reducing aqueous metal concentrations. For instance, studies pusblished (Ma *et al.*, 1993; Laperche *et al.*, 1996) have suggested that the reaction of synthetic hydroxyapatite with aqueous Pb can result in the formation of lead apatites [or hydropyromorphites, $Pb_{10}(PO_4)_6(OH)_2$].

Finally, the objective of the present study is to elucidate the mechanism of lead immobilization by apatite during batch sorption experiments because no clear mechanisms are proposed in the literature. The presented results are focussed on the evaluation of:

- the effect of initial concentration of lead on hydroxyapatite uptake capacity;
- the sorption kinetics and mechanism;
- the adsorption efficiency.

MATERIALS AND METHODS

Preparation of Material

All experiments were carried out with a stoichiometric hydroxyapatite HA, $Ca_{10}(PO_4)_6(OH)_2$, synthesized at room temperature by precipitation in solution according to reaction (4):

$$10Ca(NO_3)_2 + 6(NH_4)_2HPO_4 + 8NH_4OH \longrightarrow Ca_{10}(PO_4)_6(OH)_2 + 20NH_4NO_3 + 6H_2O \tag{4}$$

Adsorption Experiments

Aqueous solutions containing Pb^{2+} ions [obtained by dissolution of $Pb(NO_3)_2$] of various concentrations was prepared. A 4 g sample of hydroxyapatite was put into a stirred-tank reactor containing 400 ml of the prepared solution. The temperature of the suspension was maintained at 25°C. An atomic absorption photometer (Varian Spectra AA 400) measured lead and calcium concentrations in the solution during the runs. After 24 h of reaction, the sample was filtered and dried at 105°C for 2 h.

Analysis of Powder

The structure and the composition (Ca/P molar ratio) of the dried particles were determined and quantified using an X-ray powder diffractometer (Siemens D5000). XRD measurements were carried out with CuK_α radiation from 20 to 50°. The comparison of experimental patterns with JCPDS standards determined the crystalline phases (Nzihou and Bailliez, 2003).

XPS analyses were carried out using a SIA Riber Cameca UHV device. The photoelectron emission spectra were recorded using an Al-Kα source ($h\nu = 1486.6$ eV) after ionic sputtering of the films surfaces with an Ar^+ ion beam accelerated under 0.5 keV. The ion flux was fixed at about 0.5 $\mu A\,cm^{-2}$ in order to remove only the contaminant species. The sputtering time was around 5 min. The kinetic energy of the photoelectrons was measured using a Riber Cameca MAC 2 spectroscopic two stages spectrometer. The analyser resolution was fixed at 1 eV. XPS spectra were recorded in direct N(Ec). The peak positions were normalized to the position of C 1s peak (carbon contamination) located at 285 eV (Wagner *et al.*, 1979; Bêche *et al.*, 1995). The surface atomic concentrations were determined from photoelectron peaks areas corrected by the atomic sensitivity factors reported by Scofield (1976) and by the transmission function of the analyser. Spectrometer energy calibration was performed with the Au $4f^{7/2}$ and Cu $2p^{3/2}$ photoelectron lines, respectively, at 83.8 and 932.8 eV.

Ca, Pb, O and P distribution inside the particle was analysed using an SEM-WDS microprobe (Cameca 'Microbeam' operating at 15 kV and 10 nA).

RESULTS AND ANALYSES

Batch Sorption Kinetics and Structural Characterization

The reaction kinetic of lead removal was studied for initial lead concentration of 1000, 2000, 3000, 5000, 6000 and 8000 $mg\,l^{-1}$. The change of lead concentration in the solution is presented in Figure 1. The curves show a rapid decrease of lead concentration during the first minutes then the slope decreases and the final concentration corresponds to the equilibrium or the entire consumption of lead.

Both Pb^{2+} concentration and pH decreases observed in Figure 2 can be explained by surface complexation (Mavropoulos *et al.*, 2002). The $=POH$ site of hydroxyapatite transforms into a $=POPb^+$ site, which leads to a proton leaching and, consequently, to pH decreases.

The slow decrease of Pb^{2+} concentration in the solution corresponds to a slow increase of the calcium concentration in the solution as shown in Figures 1 and 3.

Figure 4 establishes the relation between Pb^{2+} taken up and Ca^{2+} released. The slope of the curve equal to unity, as a consequence the reaction mechanism, corresponds to equimolar exchange of lead and calcium. This ion exchange may be the result of the hydroxyapatite dissolution and the precipitation of the apatite $Ca_{10-x}Pb_x(PO_4)_6(OH)_2$. In this formula x can vary from 1 to 10 depending on the reaction time and experimental conditions as suggested by Takeuchi *et al.* (1998), Ma *et al.* (1994) and Mavropoulos *et al.* (2002). The experimental amount of Pb^{2+} uptake was 0.00149 $mol\,g^{-1}$ of HA and the amount of calcium removed from the solution was 0.00851 $mol\,g^{-1}$ of HA; the phosphorous amount was constant. Consequently the apatite formula corresponding to the dissolution-precipitation mechanism followed by ion exchange is $Ca_{8.51}Pb_{1.49}(PO_4)_6(OH)_2$.

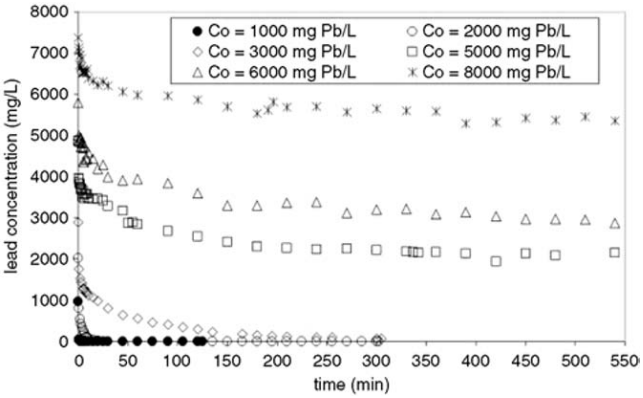

Figure 1. Batch sorption kinetic measurements.

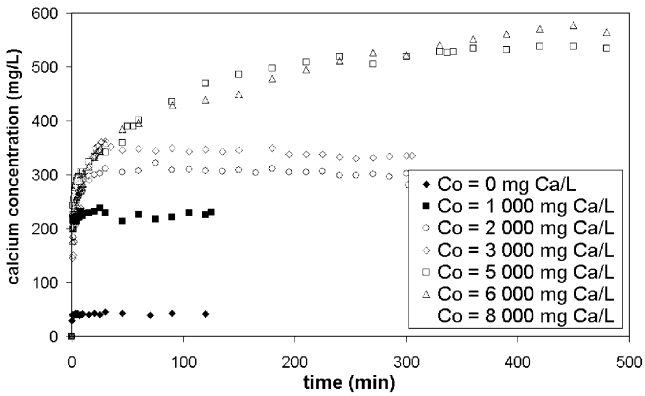

Figure 3. Ca^{2+} released to the solution.

The concentrations of Pb^{2+} found at the end of the treatment are reported in Table 1 for initial concentrations from 1000 to 8000 mg l^{-1}. For concentrations less than 3000 mg l^{-1}, the removal of lead was complete, as shown in Table 1. The mechanism of the Pb^{2+} removal for these concentration is discussed below. For concentrations higher than 3000 mg l^{-1}, precipitation was observed and affects the amount of Pb^{2+} removed from the solution (Table 1). The mechanism of precipitation and removal in these conditions was proposed by Bailliez *et al.* (2003).

For the initial concentration of Pb^{2+} below 3000 mg l^{-1}, the end of lead consumption corresponded to an increase of pH. Lead was incorporated into the matrix instead of calcium and site $\equiv POPb^{+}$ ions changed back to the initial form, $\equiv POH$, which causing the pH increase.

This mechanism was confirmed by SEM-WDS analysis. Figure 5 illustrates the results of the Ca, Pb, P and O distribution (element mapping). We observe that the powder surface was not homogenous and that the sites of the HA powder had different affinities to the species. It seems that some sites have better affinity with lead. In addition, Figure 5 shows that the areas containing Pb^{2+} were deficient in Ca^{2+}. This confirms the substitution between calcium from hydroxyapatite and Pb^{2+} from the solution. The results also show the affinity between Ca and P.

To complete these analyses, XPS measurements determined the atomic percentage of the major elements: Pb, Ca, P and O. For increasing values of initial Pb concentration, the surface composition of calcium decreased with increasing surface composition of Pb.

Figure 6 shows the variations of the atom fraction (atomic percent) of Ca and Pb for various initial Pb concentrations. The atom fractions of P ($13 \pm 1\%$) and O ($60 \pm 1\%$) do not change in the range 0–8000 mg l^{-1} of Pb^{2+}.

Ca^{2+} ions were released from the HA surface to the solution and the Pb^{2+} ions were taken up from the solution to the HA surface. This is an ion exchange mechanism. P and O do not participate in this mechanism.

The results presented in Figures 4–6 correlated well. They confirm that Ca^{2+} ions are removed by Pb^{2+} at the hydroxyapatite surface from the solution by an ion exchange mechanism.

Adsorption Isotherms

The adsorption isotherms were used to determine the affinity of hydroxyapatite to lead. The lead concentration at equilibrium C_e was used to calculate the amount of lead q_e (mg Pb^{2+} g HA^{-1}) removed by a unit weight of hydroxyapatite at the end of the experiment. This quantity was defined as follows:

$$q_e = \frac{(C_o - C_e)V}{m} \tag{5}$$

where C_o is the initial concentration of lead (mg l^{-1}), C_e is the equilibrium concentration of lead (mg l^{-1}), V is, the

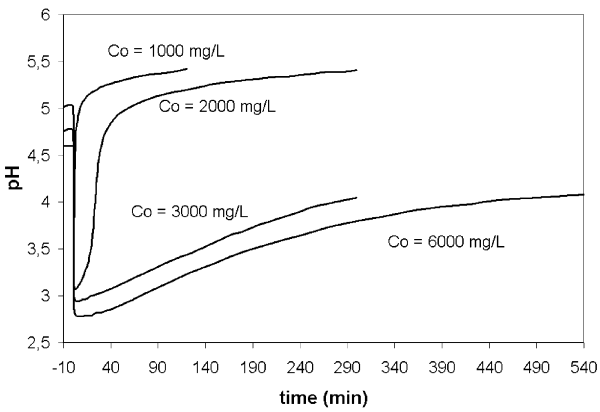

Figure 2. Effect of sorption on the pH of the solution.

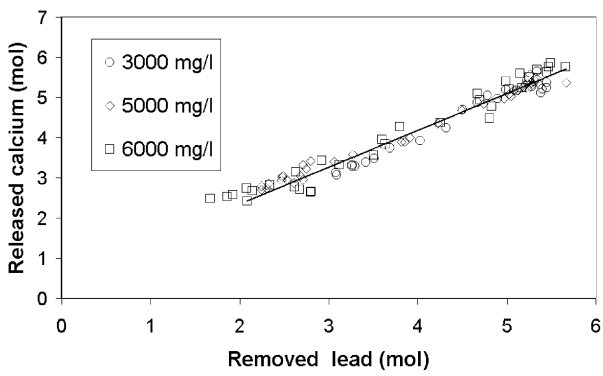

Figure 4. Moles of Ca^{2+} released to the solution as function of moles of Pb^{2+} removed from the solution.

Table 1. Equilibrium values.

C_o (mg l^{-1})	1000	2000	3000	5000	6000	8000
C_e (mg l^{-1})	0	0	0	2160	2900	5400
t_e (min)	2	15	350	550	550	550
Percentage Pb removed	100	100	100	57	52	32

volume of the solution (l) and m is the weight of hydroxyapatite (g).

Three isotherm equations were used to describe the sorption of lead into HA:

- the Langmuir equation used generally for high concentrated solution,

$$q_e = q_{max} \frac{k_L C_e}{1 + k_L C_e} \tag{6}$$

where q_{max} is Pb concentration in solid phase at the initial liquid concentration (mg Pb^{2+} g HA^{-1}), k_L is the first coefficient related to the energy of adsorption (l mg^{-1}) and C_e is the equilibrium concentration of lead (mg l^{-1});

- the Freundlich equation also adapted for high concentrated solution,

$$q_e = k_F C_e^{1/n_F} \tag{7}$$

where k_F is the first coefficient related to the energy of adsorption ([mg Pb^{2+}]$^{1-(1/n_F)}$ l$^{1/n_F}$ g^{-1}HA) and n_F is a coefficient;

- the Freundlich–Langmuir equation.

Because of the limited success of the Langmuir equation in predicting mixture equilibria at very low concentrations, several authors have modified the Langmuir equation by

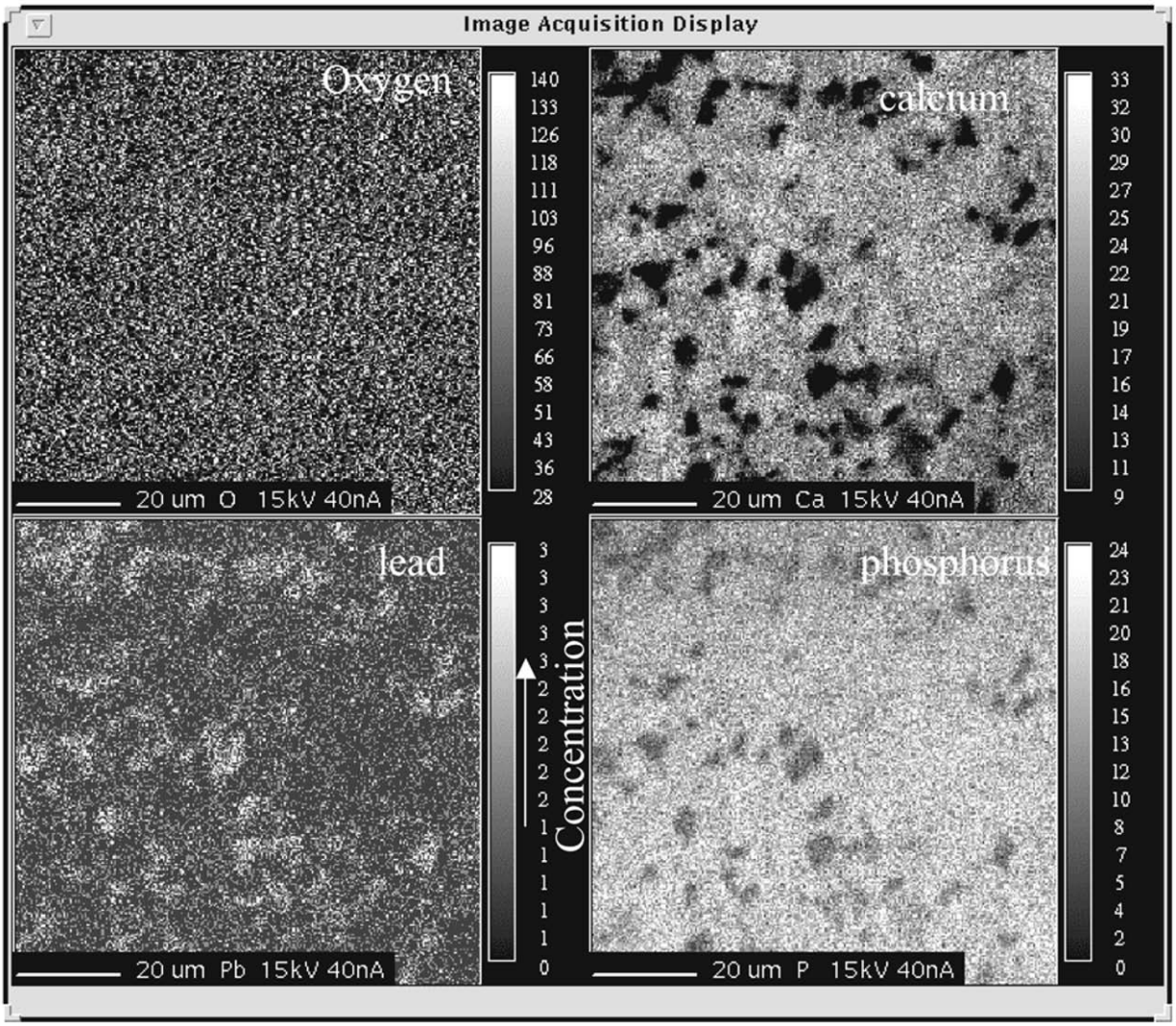

Figure 5. WDS microprobe analysis of the experiment with initial lead concentration of 5000 mg l^{-1}.

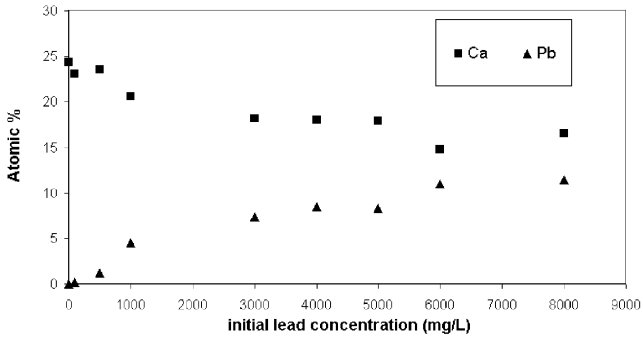

Figure 6. Surface atomic percentage of lead removed and calcium released.

introducing a power law expression, which is a combination of the two first equations (Ruthven, 1984):

$$q_e = q_{max} \frac{k_{LF} C_e^{1/n_{LF}}}{1 + k_{LF} C_e^{1/n_{LF}}} \quad (8)$$

This equation can be used both for high and low solution concentrations. Although not thermodynamically consistent, this expression has been shown to provide a reasonably good empirical correlation of binary mixture for a number of adsorbents and is widely used for design purposes (Yon and Turnock, 1971; Morer, 1980).

The three equations fit experimental data. All these models fit experimental trends. Figure 7 shows a plateau that is evident for the series of data. It corresponds to the HA saturation and the three equations are able to account qualitatively for this effect. However, only the Freundlich–Langmuir equation describes well the behaviour of the system at low concentrations of lead in the liquid phase. In the left part of Figure 7, for equilibrium concentrations of lead (C_e) less than 200 mg l^{-1}, only the Langmuir–Freundlich curve matches the experimental data. This can be clearly observed with the enlargement of the curve, which is not presented in this paper and with the correlation coefficient, r^2, of 98 for Langmuir–Freundlich curve and 70 for Freundlich and for Langmuir curves. Both Langmuir and Langmuir–Freundlich do not account the fact that, below $C_e = 200$ mg l^{-1}, all the lead is removed (i.e. $q_e \approx 0$ mg l^{-1}). Consequently, in this paper, the adsorption efficiency is evaluated using the Freundlich–Langmuir equation.

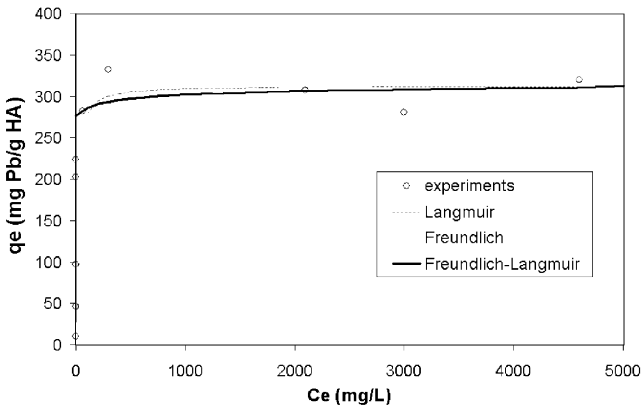

Figure 7. Isotherm (25°C) of Pb^{2+} sorption by hydroxyapatitie.

The adsorption capacity (q_{max}) is 320 mg Pb g HA^{-1}, the adsorption intensity (n_{LF}) is equal to 2.5 and the Langmuir–Freundlich constant (k_{LF}) is equal to 1 $l^{1/n_{LF}}$ (mg $Pb^{2+})^{-1/n_{LF}}$. These values indicate a greater affinity of hydroxyapatite for lead, as reported in the literature (Chiarle *et al.*, 2000; Panayotova, 2001; da Rocha *et al.*, 2002; Mavropoulos *et al.*, 2002; Ruthven, 1984). In most papers in the literature related to adsorption capacity based on isotherms, the efficiency is evaluated using the adsorption capacity k_{LF} and the adsorption intensity n_{LF}. It is assumed that higher is this parameter, higher is the adsorption capacity. For hydroxyapatite adsorbents, high adsorption capacity is assumed for $k_{LF} > 150$ mg Pb g HA^{-1} (Mavropoulos *et al.*, 2002; Ruthven, 1984). This value is also assumed for a number of adsorbents. On the other, and where the adsorption intensity is more precisely defined, high affinity is assumed for $n_{LF} = 1$–10. Many examples are available in the literature (Ruthven, 1984).

CONCLUSIONS

Batch sorption experiments determined the capacity of hydroxyapatite in removing Pb from solution. The results show that the reaction of lead uptake by hydroxyapatite involves dissolution of Ca_{10} $(PO_4)_6$ $(OH)_2$ followed by precipitation of pyromorphite structure $Ca_{8.51}$ $Pb_{1.49}$ $(PO_4)_6$ $(OH)_2$ by ion exchange between Ca and Pb ions. The lead content in this solid increases with time. The exchange is not completed, whereas all Pb^{2+} available in the solution was removed at the surface of HA. This means that part of lead uptake is immobilized by other surface mechanisms such as adsorption and complexation. Additional studies are in progress in order to characterize these mechanisms.

HA was effective in removing lead in aqueous solution from HA exchange sites. The immobilization process was rapid (60 min). Results of batch experiments, SEM-WDS and XPS analysis strongly support the mechanism of dissolution of HA/precipitation of pyromorphite. The pH also plays a role since it determines hydroxyapatite solubility. HA does not only supply P to immobilize Pb, but also provides Ca for replacement from exchange sites.

The uptake process by hydroxyapatite obeys the kinetic equation describing adsorption. This, together with the correlation found between lead uptake and the amount of calcium release into the solution, confirms that ion exchange is the basic mechanism of uptake.

The equilibrium is well described by the Freundlich–Langmuir isotherm. The adsorption capacity (q_{max}) is 320 mg Pb g HA^{-1} and the adsorption intensity (n_{LF}) is 2.5. According to the literature, these values indicate a strong affinity of hydroxyapatite for lead.

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