Chemical Engineering Journal 160 (2010) 503–510

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Aqueous Pb sorption by synthetic and natural apatite: Kinetics, equilibrium and thermodynamic studies

T. Kaludjerovic-Radoicic[a,*], S. Raicevic[b]

[a] *Chemical Engineering Department, Faculty of Technology and Metallurgy, University of Belgrade, 11001 Belgrade, Serbia*
[b] *Radiation and Environmental Protection Laboratory, VINCA Institute for Nuclear Sciences, Box 522, 11001 Belgrade, Serbia*

ARTICLE INFO

Article history:
Received 1 October 2009
Received in revised form 22 March 2010
Accepted 25 March 2010

Keywords:
Hydroxyapatite
Natural apatite
Lead
Sorption kinetics
Mechanism

ABSTRACT

Natural apatites represent a cost effective soil amendment, which can be used for *in situ* reduction of lead bioavailability and mobility. In our previous work, we selected Lisina apatite (LA) as a promising natural mineral for lead immobilization based on theoretical predictions. This study investigated the adsorption equilibrium and kinetics of aqueous Pb sorption onto Lisina apatite and synthetic hydroxyapatite (HAP) at different temperatures. XRD analysis indicated that LA consists of three minerals: fluorapatite, quartz and muscovite. After reaction with a Pb solution, only FA peaks were changed, confirming that fluorapatite present in LA is responsible for Pb sorption. Sorption experiments confirmed that both LA and HAP are effective in Pb removal. Langmuir, Freundlich, Temkin, Koble–Corrigan and Redlich–Peterson isotherm models were applied to experimental data. The kinetics of the sorption process on both minerals was well characterized by the pseudo-second order reaction rate. Results indicate that Pb immobilization by HAP is a two-step process: the first rapid phase, possibly surface complexation and secondary dissolution of HAP and precipitation of pyromorphite. The sorption of Pb by Lisina apatite is also a two-step process, but the reaction mechanisms are more complicated and need further research as the results indicate that different mechanisms dominate at different temperatures. The values of thermodynamic equilibrium constants and Gibbs free energy were also calculated. The values of ΔG^0 obtained confirm the feasibility of both HAP and LA as effective sorbents of the Pb ion.

1. Introduction

Contamination due to the presence of heavy metals in soils, surface and ground waters represents a major environmental problem. Most heavy metals are extremely toxic, non-biodegradable and tend to accumulate in living organisms.

Lead is one of the most widespread heavy metals present in the environment due to historical use of Pb-containing products such as paint, petrol and pesticides [1]. The main sources of lead contamination are mining, processing and smelting operations, metal plating and other industries. Pb leaching from contaminated soils is a constant source of surface and ground water contamination. Lead is highly toxic to humans, especially young children even at low concentrations because of its bioaccumulation in the food chain [2]. Therefore, constant efforts are being made to remediate Pb contaminated sites.

Until recently, the main basis for environmental risk assessment was the total concentration of an element [3]. According to that concept, efforts were made to eliminate Pb from the contaminated site. Some classical methods of soil lead remediation consist of contaminated soil removal followed by physical and/or chemical treatment such as: solidification, vitrification, washing, leaching and particle size separation [4,5]. These conventional engineering type remedial approaches have proven economically prohibitive and at times ecologically unfriendly.

In the new approach, only the bioavailable fraction of the total contaminant concentration is considered when risk assessment is made. On the basis of this approach, assisted natural remediation processes were proposed [3]. These *in situ* immobilization techniques use abundant, rather inexpensive natural substances for transforming the contaminants to more insoluble phases, thus preventing them from accumulating in the biosphere [6].

This approach can be used for Pb contamination as, in most cases, Pb is present in the environment in the form of highly soluble minerals such as PbO, $Pb(CO_3)_2$ and $PbSO_4$ [7]. For remediation of Pb contamination, phosphate minerals, especially apatites, were suggested [8–10]. The apatites investigated include synthetic hydroxyapatite (HAP) [11–14], apatites of biological origin such as bone meal [15] and Apatite II^{TM} [16,17], and naturally occurring apatite minerals (phosphate rock) [18–28]. Naturally occurring apatite minerals can represent a low cost alternative to synthetic HAP. The stability of the reaction product is of the high-

---

* Corresponding author. Tel.: +381 11 3303 744; fax: +381 11 3370 387.
E-mail address: tanjak@tmf.bg.ac.rs (T. Kaludjerovic-Radoicic).

1385-8947/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2010.03.061

Table 1
HAP and LA properties.

Name	Ca/P molar ratio	Surface area, $m^2 g^{-1}$	X^- group
HAP	1.67	21.0	OH^-
LA	1.5	4.49	F^-

est importance when using *in situ* remediation techniques, as the contaminant is not removed from the environment [29]. Therefore, before the use of any natural mineral for *in situ* remediation of contaminated sites, it is important to investigate in detail the mechanisms involved.

The present work involves experimental investigation and computer modeling of Pb retention by two minerals: synthetic HAP and Lisina apatite from the phosphate ore deposit in south Serbia (denoted hereafter as LA). The sorption properties of HAP and LA were investigated using various two-parameter and three-parameter sorption isotherms. The kinetics of the reaction of Pb immobilization was investigated using pseudo-first and pseudo-second order kinetic models. XRD analysis was performed on synthetic HAP and Lisina apatite and on the reaction products of these minerals with a solution of lead-nitrate. The systems were modeled using the Visual MINTEQ computer program. Visual MINTEQ was used to calculate which minerals could precipitate in Pb-HAP and Pb-LA systems. The experimental results were compared with the computer simulation.

2. Materials and methods

2.1. Materials (apatites)

Two sorbents were used in this study: stoichiometric hydroxyapatite (HAP) and natural apatite from the phosphate ore deposits in Lisina (LA), near Bosilegrad (Serbia).

Stoichiometric HAP was synthesized in the laboratory by a slow titration of the $Ca(OH)_2$ solution with H_3PO_4 at an elevated temperature (95 °C) in a nitrogen atmosphere, following a previously described procedure [30]. Chemical analysis confirmed that the product was stoichiometric hydroxyapatite with the formula $Ca_{10}(PO_4)_6(OH)_2$, having a Ca/P ratio 1.67 ± 0.02 and surface area $21.0\,m^2\,g^{-1}$, as determined by the application of the B.E.T. method. SEM micrographs show that the solid phase consists of spherical aggregates, around 10 μm in diameter. The spherical aggregates are composed of smaller particles, about 100–200 nm in diameter.

Based on theoretical predictions the natural apatite from the phosphate ore deposits in Lisina (LA), near Bosilegrad (Serbia) was selected for the sorption experiment [31]. This phosphate ore contains 43.3% apatite. This sample has the following chemical composition: $Ca_{2.94}Na_{0.03}K_{0.05}Al_{1.38}Fe_{0.22}Si_6P_{1.96}S_{0.16}Cl_{0.04}F_{0.11}O_{22.28}$ [31]. A surface area of $4.49\,m^2\,g^{-1}$ was determined using the B.E.T. method. The sample was ground to fine powder with a particle size lower than 200 μm and was used without further modifications.

The comparison of HAP and LA properties is given in Table 1.

2.2. Sorption experiments

2.2.1. Batch sorption studies

The sorption and kinetic properties of lead removal by HAP and LA apatite samples were determined in batch experiments. 0.2 g of HAP/LA was held in contact with 50 mL of solution containing $2.415/0.4826\,mmol\,L^{-1}$ Pb (as nitrate salt). The suspensions were agitated using a reciprocal shaker (150 rpm) under constant temperature. The initial pH of suspensions was 5.1 for HAP and 5.6 for LA and it was not further modified during these experiments in order to simulate the real environmental conditions, where the pH control is either not applicable or very difficult to achieve. After the corresponding time interval, the suspensions were sampled through direct filtration, using a 0.45 μm membrane filter. The filtrates were analyzed for Pb and Ca content using a Shimadzu AA-6501 F atomic absorption (flame) Spectrometer. Detection limits for Pb and Ca were $10\,\mu g\,L^{-1}$. The amount of lead sorbed on HAP/LA at a specific time (q) could be calculated by the obtained data using the mass balance equation.

According to the mass balance equation, the total number of moles of lead ions in the solution at time $t = 0$ plus the number of moles adsorbed on apatite at $t = 0$ is equal to the number of moles left in the solution plus the number of moles adsorbed on HAP/LA:

$$m(q_0 - q) = V(c - c_0) \qquad (1)$$

As HAP/LA at $t = 0$ did not contain any lead ions, $q_0 = 0$.

Therefore:

$$q = \frac{V}{m}(c_0 - c) \qquad (2)$$

where V is the volume of the solution (L); m is the mass of HAP/LA (g); c_0 is the initial concentration of lead in solution ($mmol\,L^{-1}$); c is the lead ion concentration in the solution at a given time ($mmol\,L^{-1}$); q_0 is the initial lead concentration in the adsorbent ($mmol\,g^{-1}$ HAP/LA); q is the amount of lead sorbed on HAP/LA at a given time ($mmol\,g^{-1}$ HAP/LA).

2.2.2. XRD analysis

Two sorption batch experiments were carried out, especially designed to provide samples for XRD analysis. 2 g of HAP or LA samples were mixed with 100 mL of $Pb(NO_3)_2$ solution, containing $4.826\,mmol\,L^{-1}$ of Pb. The suspensions were thermostated at 25 °C and agitated at 150 rpm for 5.5 h, i.e. for enough time to achieve equilibrium, according to the respective kinetic data. The suspension was subsequently filtered and solid phases were dried at room temperature for 2 days, and then stored for XRD analysis.

X-ray diffractometry (XRD) was performed by a Siemens Model D500 PC diffraction system with Cu Kα radiation at 35 kV and 20 mA. Measurements were made using a step scanning technique with a fixed time of 4 s per 0.05° 2θ. The XRD patterns were obtained from 10 to 80° 2θ.

2.3. Adsorption isotherms

To examine the relationship between sorbed and aqueous concentration at equilibrium, various two-parameter (Langmuir, Freundlich and Temkin) and three-parameter (Redlich–Peterson and Koble–Corrigan) sorption isotherms were used to describe the equilibrium between the Pb sorbed onto HAP/LA and Pb in the solution. To determine the best-fit model for the sorption system, experimental results were substituted into equilibrium isotherm model equations and the values of equations parameters were obtained using non-linear regression analysis. To assess the adequacy of the fit, the analysis of variance (ANOVA) was performed on all the isotherm models used in non-linear regression analysis. *F*-Ratios from ANOVA analysis are defined as the ratio of the respective mean-square-effect and the mean-square-error. The large values of F and the small values of Prob > F indicate the significance of the model. Apart from these values, the correlation coefficient (R^2), the residual sum of squares error (SSE) and the standard error (S.E.) of the fit were also reported for each model. SSE can be defined as:

$$\mathrm{SSE} = \sum_{i=1}^{m}(q_{c,i} - q_i)^2 \qquad (3)$$

Standard error can be defined as:

$$\text{S.E.} = \sqrt{\frac{1}{m-p}\sum_{i=1}^{m}(q_{c,i}-q_i)^2} \tag{4}$$

where q is the experimental and q_c calculated value of the amount of lead adsorbed onto HAP/LA, m is the number of experimental points and p is the number of parameters in the model.

The equations representing five adsorption isotherm models used in this study are reported in Appendix A.

2.4. Kinetic studies

In order to determine the rate constants, the two most widely used kinetic models in sorption processes (pseudo-first and pseudo-second order models) have been applied to experimental data.

2.4.1. The pseudo-first order equation

The Lagergren pseudo-first order equation can be expressed as:

$$\frac{dq}{dt} = k_1(q_e - q) \tag{5}$$

where q is the amount of metal sorbed at time t, q_e is the amount of metal sorbed at equilibrium and k_1 is the sorption rate constant.

Integrating Eq. (5) for the boundary conditions $t = 0$ to $t = t$ and $q = 0$ to $q = q_t$, and rearranging it for linearized data plotting, the following equation is obtained:

$$\log(q_e - q) = \log\ q_e - \frac{k_1}{2.303}t \tag{6}$$

This model can be applied if $\log(q_e - q_t)$ versus t gives a straight line, in which case q_e and k_1 can be calculated from the intercept and slope of the plot.

2.4.2. The pseudo-second order equation

Since the introduction of the pseudo-second order model in 1999, it has been widely applied in liquid-phase adsorption systems [32]. The pseudo-second order rate model is based on sorbent capacity and can be expressed as a differential equation:

$$\frac{dq}{dt} = k_2(q_e - q)^2 \tag{7}$$

Integrating Eq. (7) for the same boundary conditions, it can be rearranged in the following linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{8}$$

A plot of t/q_t versus t should give a straight line with a slope of $1/q_e$ and intercept of $1/k_2 q_e^2$. Furthermore, the initial sorption rate h (mmol g^{-1} min^{-1}), when $t \to 0$, can also be calculated as follows:

$$h = k_2 q_e^2 \tag{9}$$

2.5. Sorption thermodynamics

The thermodynamic equilibrium constant K_e^0 was obtained from calculating the apparent equilibrium constant, (K_e') at different initial concentrations of Pb^{2+} and extrapolating to zero. K_e' was calculated using the following expression:

$$K_e' = \frac{c_S}{c_e} \tag{10}$$

where c_s is the concentration of Pb^{2+} sorbed on apatite (HAP or LA) at equilibrium (mmol L^{-1}) and c_e is the equilibrium concentration of Pb^{2+} in the solution (mmol L^{-1}). The Gibbs free energy for the adsorption process was obtained using the formula:

$$\Delta G^0 = -RT\ln K_e^0 \tag{11}$$

where R is the ideal gas constant (8.315 kJ kmol^{-1} K^{-1}) and T is the temperature (K).

2.6. Visual MINTEQ program simulation

Equilibrium modeling was conducted using a thermodynamic program, Visual MINTEQ ver. 2.50 [33] to compare the results with various possible precipitates that may control Pb solubility. The input data for modeling (Pb^{2+}, NO_3^- and HAP or LA concentration and solution pH) were chosen from the experiment where 50 mL of the 2.415/0.4826 mg L^{-1} $Pb(NO_3)_2$ solution was equilibrated with 0.2 g HAP/LA. In Visual MINTEQ the degree of saturation with respect to a specific solid phase SI (saturation index) is defined as:

$$\text{SI} = \log\left(\frac{\text{IAP}}{K_{sp}}\right) \tag{12}$$

where IAP is the ion activity product and K_{sp} is the solubility product. A SI < 0 indicates that the solution is undersaturated while a SI > 0 indicates that the solution is supersaturated with respect to a given solid phase. A SI = 0 indicates that the solution is in equilibrium with a given solid.

3. Results and discussion

3.1. Equilibrium isotherm models

The analysis of equilibrium data is essential to understand the sorption process and to be able to compare different sorbents under different operational conditions. In this paper, two-parameter (Langmuir, Freundlich and Temkin) and three-parameter (Redlich–Peterson and Koble–Corrigan) isotherm models were applied to the experimental data [31]. The results of these five isotherm models applied to the Pb-HAP and Pb-LA systems are shown in Fig. 1(a) and (b). The isotherm constants, ANOVA analysis values (F and Prob > F), correlation coefficients (R^2), the residual sum of squares errors (SSE) and the standard errors (S.E.) for these models are presented in Table 2.

The ANOVA statistical analysis shows that all of the presented models have very low values of Prob > F. The values of Prob > F are all less than 0.0001, except for the Temkin isotherm in the Pb-LA system, where Prob > F is 0.0005. From the data presented in Table 2 it can be concluded that four of the tested isotherms can be used to describe the sorption of aqueous lead by HAP and LA. These isotherms are the Langmuir, Freundlich, Koble–Corrigan and Redlich–Peterson isotherm. The Temkin isotherm model had the lowest values of F and R^2 and the highest values of SSE and S.E. in both systems (Pb-HAP and Pb-LA), therefore it could not be used for modeling of Pb sorption by HAP and LA.

Both Langmuir and Freundlich models described the sorption processes with similar accuracy. The Freundlich isotherm fit had a slightly higher value of R^2 and lower values of SSE and S.E. in both systems. The slightly higher F-values from the ANOVA statistical analysis also indicate that the Freundlich isotherm model represents the experimental data a little better. Although both systems can be accurately described by the Langmuir isotherm model, the value of the parameter R_L (Table 2) indicates the different shapes of the isotherms. The values of the R_L parameters are in the favorable range for both systems, but at the opposite ends: for Pb-HAP system $R_L = 0.0144$, which is near the value for the irreversible isotherm, while the value for the Pb-LA system is 0.80, which approaches the

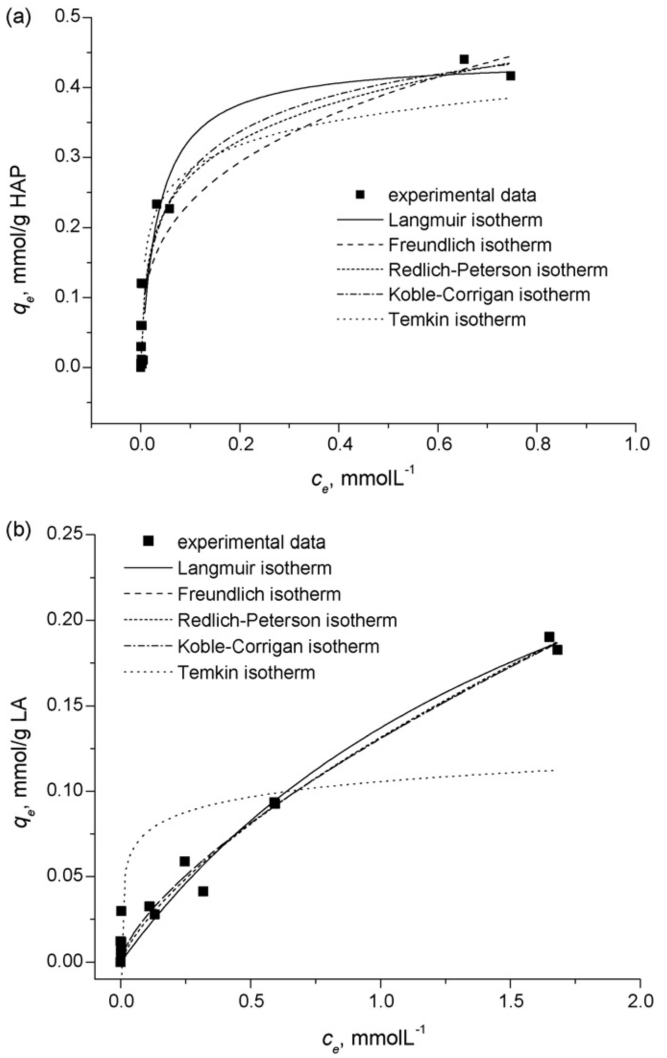

Fig. 1. Different sorption isotherm models applied to (a) Pb sorption by HAP and (b) Pb sorption by LA.

linear isotherm shape. Based on the q_m value of the Langmuir model (Table 2) hydroxyapatite has greater sorption capacity for aqueous lead than Lisina apatite. The other Langmuir model constant, K_L, indicates the affinity for the binding of aqueous lead. Based on this constant HAP has much greater affinity for Pb sorption than LA. The applicability of the Langmuir model for synthetic and natural apatite minerals was also confirmed by other authors [13,23]. The value of the Freundlich model constant K_F, which is a measure of sorption capacity, is also higher for Pb sorption by synthetic HAP than for Lisina apatite.

Based on R^2 values, it could be concluded that the introduction of the third parameter in Koble–Corrigan and Redlich–Peterson isotherms improved the fit for the Pb-HAP system. The Koble–Corrigan model also has the lowest values of SSE and S.E. This is in accordance with the data of Baillez et al. [12] who found that the Koble–Corrigan isotherm (also called the Freundlich–Langmuir isotherm) modeled the Pb-HAP system well. However, the F-values from the ANOVA statistical analysis show that significance of regression surface in the Pb-HAP system is greatest for the Freundlich model. Based on these data it can be concluded that the Freundlich, Koble–Corrigan and Redlich–Peterson models fit equally well. Given the fact that the Freundlich model is the only two-parameter equation among these models, it could be considered the best model in the Pb-HAP system.

Table 2
Isotherm constants for lead ions on HAP and LA.

Isotherm	Model parameter	HAP	LA
Langmuir	K_L (L mmol^{-1})	28.2	0.521
	q_m (mmol g^{-1})	0.442	0.400
	R_L	0.0144	0.80
	R^2	0.876	0.941
	SSE	0.0309	0.00266
	S.E.	0.053	0.0149
	F-Value	93.2	210
	Prob > F	<0.0001	<0.0001
Freundlich	K_F (L mmol^{-1})	0.487	0.131
	n	3.17	1.46
	R^2	0.887	0.947
	SSE	0.0280	0.0024
	S.E.	0.0505	0.0141
	F-Value	103	234
	Prob > F	<0.0001	<0.0001
Temkin	A	0.399	0.106
	B	0.0507	0.0129
	R^2	0.802	0.536
	SSE	0.0493	0.0209
	S.E.	0.067	0.0417
	F-Value	56.1	21.6
	Prob > F	<0.0001	0.0005
Koble–Corrigan	A	1.92	0.131
	B	3.26	0.00251
	n	0.554	0.686
	R^2	0.891	0.942
	SSE	0.0246	0.0024
	S.E.	0.050	0.0148
	F-Value	78.9	156
	Prob > F	<0.0001	<0.0001
Redlich–Peterson	A	38.7	0.532
	B	82.6	3.05
	g	0.797	0.410
	R^2	0.895	0.948
	SSE	0.0272	0.0025
	S.E.	0.0521	0.0151
	F-Value	71.2	241
	Prob > F	<0.0001	<0.0001

In the Pb-LA system, the Freundlich model has the smallest values of SSE and S.E, while R^2 and F-values from the ANOVA statistical analysis are almost the same for the Freundlich and Redlich–Peterson model. Based on these facts, the overall best isotherm model in the Pb-LA system is the Freundlich model. This may be an indication that the sorption of lead by natural Lisina apatite is a heterogeneous process, during which the stronger binding sites are occupied first and the binding strength decreases with the increase of degree of site occupation.

3.2. Kinetics of Pb sorption by HAP and LA

The results of the kinetics of Pb removal and Ca release by HAP and LA at 37 °C are shown in Fig. 2(a) and (b). A rapid kinetic reaction of Pb removal by both sorbents occurred in the first 5 min. After that, in the second stage, the reaction rate slows down and the amount of sorbed Pb slowly increases to a steady-state value. After ≈120 min of reaction, pseudo-equilibrium is achieved, with sorption capacities of 0.379 mmol g^{-1} HAP and 0.056 mmol g^{-1} LA. This result is in accordance with experiments of other authors [13,14] who also observed a two-phase reaction with a rapid first step and a slower second phase. Sorption capacity of LA was significantly lower than that of synthetic HAP. This can partially be attributed to the fact that LA consists of 43.3% apatite, but can also indicate different mechanisms involved in these two systems. The results for the Ca release show a similar trend: the aqueous Ca concentration increases very fast during the first stage of reaction, while this

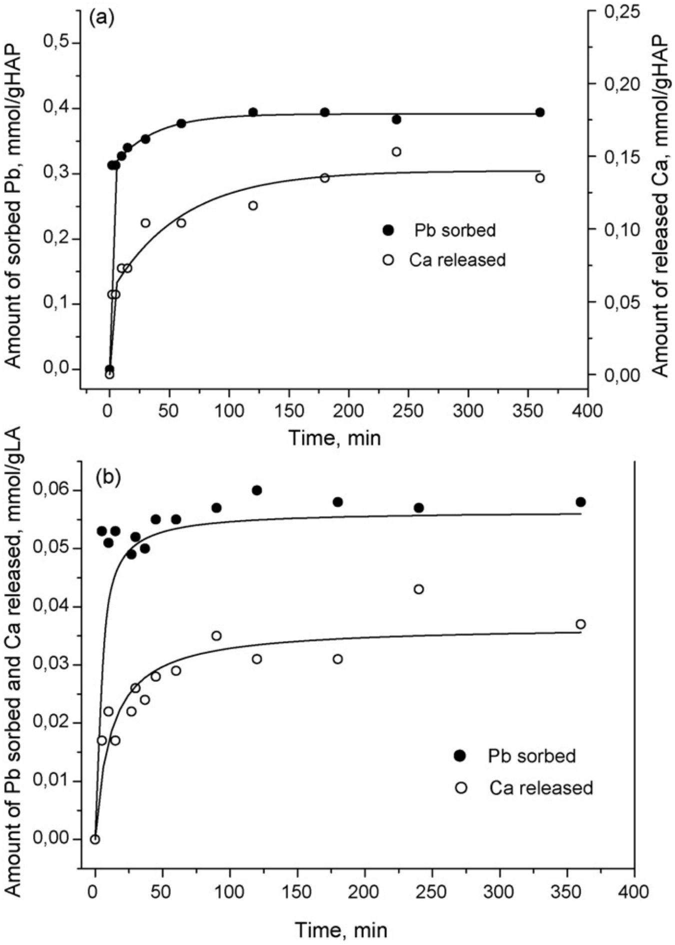

Fig. 2. Kinetics of Pb removal and Ca release at 37 °C: (a) using hydroxyapatite (HAP) and (b) using Lisina apatite (LA).

increase slows down in the second stage and reaches a steady-state value.

Lagergren pseudo-first order and pseudo-second order rate equations were applied to experimental data for Pb-HAP and Pb-LA systems at temperatures 25 °C [31], 37 °C and 50 °C. Rate constants, calculated q_e values and regression coefficients (R^2) for pseudo-first and pseudo-second order kinetic models are presented in Table 3. Calculated q_e values, obtained using the Lagergren pseudo-first order equation, are substantially different from the experimental ones, while q_e values obtained from pseudo-second order equation agree well with experimental values. Based on q_e and R^2 the pseudo-second order model was chosen as more appropriate for both systems at all the temperatures investigated. The pseudo-second order model assumes that two reactions are occurring in the process, the first one is fast and reaches equilibrium quickly and the second is a slower reaction that can continue for long time periods [34].

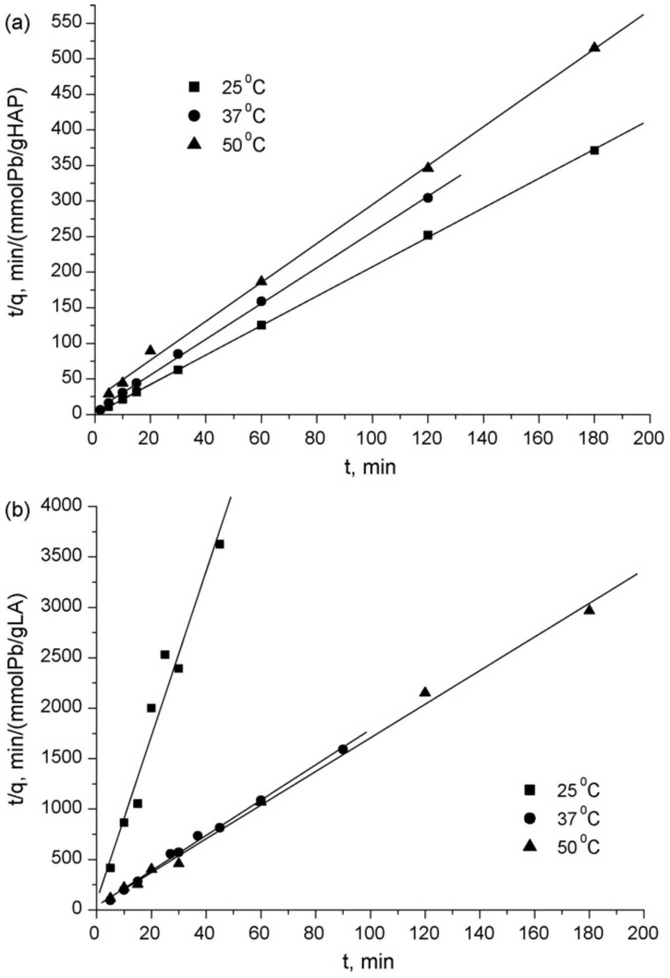

Fig. 3. Results of pseudo-second order model experimental data fitting for (a) Pb-HAP system and (b) Pb-LA system.

The results for the pseudo-second order rate model for Pb-HAP and Pb-LA systems are shown in Fig. 3(a) and (b). Contrary to the similar shape of kinetic curves, the influence of temperature on these two systems is completely different. The rate constant of the sorption reaction in the Pb-HAP system gradually decreases with increase of temperature: k_2 (25 °C) > k_2 (37 °C) > k_2 (50 °C). In the case of the Pb-LA system, the results are different and more complicated to explain as k_2 (25 °C) > k_2 (37 °C) ≈ k_2 (50 °C). These values of rate constants could indicate that two different mechanisms are involved in Pb sorption by LA: one of them dominates at 25 °C, while at elevated temperatures the other mechanism controls the process. Based on our previous work [31] and present data we postulate

Table 3
Experimental and calculated amounts of Pb sorbed at equilibrium (q_e), sorption rate constants (k_1 and k_2) and corresponding regression coefficients (R^2), for pseudo-first and pseudo-second order kinetic models.

	Temp.	$q_{e,exp}$, mmol Pb g^{-1}	Pseudo-first order model			Pseudo-second order model			
			k_1, min^{-1}	$q_{e,cal.}$, mmol Pb g^{-1}	R^2	k_2, g mmol^{-1} Pb min^{-1}	$q_{e,cal.}$, mmol Pb g^{-1}	h, mmol Pb g^{-1} min^{-1}	R^2
HAP	25 °C	0.480	0.220	0.119	0.870	11.0	0.480	2.56	1
	37 °C	0.379	0.0409	0.126	0.718	1.19	0.398	0.188	0.999
	50 °C	0.351	0.0390	0.251	0.984	0.346	0.366	0.0462	0.999
LA	25 °C	0.053	0.0614	0.0983	0.667	73.8	0.0522	0.0110	0.953
	37 °C	0.056	0.0271	0.0140	0.584	7.97	0.0570	0.0260	0.996
	50 °C	0.060	0.0966	0.0347	0.781	7.42	0.0599	0.0266	0.996

Table 4
Thermodynamic equilibrium constant (K_e^0) and Gibbs free energy ΔG^0 at 25 °C for Pb sorption on HAP and LA.

Adsorbent	Equilibrium constant (K_e^0)	Gibbs free energy, ΔG^0, kJ mol^{-1}
HAP	36.6	−8.92
LA	6.97	−4.81

Table 5
Lattice parameters of HAP, FA and FA-Pb.

	a, Å	*c*, Å	*L*, nm
HAP	9.43	6.90	36.7
FA	9.38	6.89	44.9
FA-Pb	9.37	6.89	43.1

that the mechanism of Pb sorption by HAP is surface complexation in the first rapid phase and dissolution of HAP followed by precipitation of pyromorphite in the second slower phase. The reaction of Pb sorption by Lisina apatite is also a two-step process: the rapid first phase could be attributed to surface complexation followed by the incorporation of Pb ions into the LA lattice. This was additionally supported by the increase of concentration of the released Ca more than the amount of sorbed Pb while the phosphate concentration remains below the detection limit. However, in this case further research is needed as the temperature dependence of rate constants suggests that different mechanisms might be dominant at different temperatures.

3.3. Sorption thermodynamics

The results of thermodynamic equilibrium constants and Gibbs free energy are summarized in Table 4. The Gibbs free energy values indicate the degree of spontaneity of a process, a more negative value indicating a more energetically favorable process. HAP shows values of ΔG^0 greater than that for LA indicating the larger affinity for Pb removal as was also shown by the greater value of the sorption capacity of synthetic hydroxyapatite. The values of ΔG^0 obtained confirm the feasibility of both HAP and LA as effective sorbents for the Pb ion.

3.4. XRD analysis

XRD analysis was used for phase identification as well as for lattice parameter calculation. Crystallite size was obtained from broadening of diffraction peaks using the Scherer equation.

XRD patterns of HAP and LA before reaction with Pb are shown in Fig. 4. It can be seen that synthetic HAP is pure hydroxyapatite with lattice parameters shown in Table 5. Lattice parameters *a* and *c* are in accordance with literature data for synthetic hydroxyapatite [35].

Lisina apatite consists of three minerals: fluorapatite (FA), quartz (Q) and muscovite $KAl_2(Si_3Al)O_{10}(OH, F)_2$ (M). Lattice parameters *a* and *c* for fluorapatite are shown in Table 5.

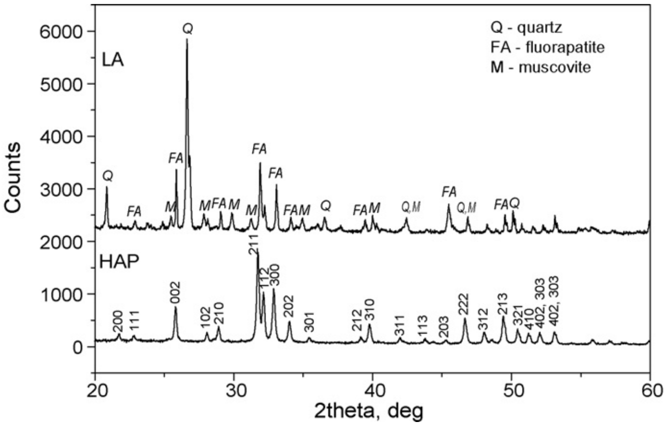

Fig. 4. XRD patterns of hydroxyapatite (HAP) and Lisina apatite (LA) before reaction with Pb.

The XRD pattern of solid residue of the HAP reaction with the Pb solution $c = 4.826$ mmol L^{-1} for 5.5 h did not show any new solid phase formation (data not shown). According to many authors [2,11,37] hydroxypyromorphite should form in this reaction. The reason that HPM was not detected in our experiment could be its low concentration in the solid phase or the poor crystallinity of the newly formed solid phase.

XRD patterns of LA before and after the reaction with the Pb solution are shown in Fig. 5. Fig. 5 shows the 2θ range from 25° to 35°. Lattice parameters *a* and *c* for apatite peaks of the Lisina mineral after reaction with the Pb solution are shown in Table 5.

The XRD patterns of quartz and muscovite did not change after the reaction with the Pb solution, while there was significant change in FA peaks. The greatest changes occurred to the 0 0 2, 2 1 0 and 2 2 2 peaks (47.2, 31.1, and 24.5%, respectively). The reduced intensity of FA peaks after reaction with Pb might be an indication of PR dissolution [36]. This dissolution could be induced by removal of soluble phosphates from the solution in the presence of Pb through precipitation reactions. Reduced FA peaks could also indicate increased sorption of metals onto LA. Increased sorption of metals onto mineral surfaces can also be responsible for reduced intensity of XRD peaks because of the increased mass absorption coefficient of X-rays upon adsorption of metals. A similar reduction in FA peak intensities was attributed to the formation of the solid solution of Ca and Pb apatites [24]. Lattice parameters of FA after reaction with the Pb solution are of approximately the same values as values for FA before the reaction (Table 5). No new solid phase was detected by XRD measurements. A small decrease in the crystallite size was observed after the reaction.

3.5. Visual MINTEQ computer program simulations

The Visual MINTEQ program was run to simulate the experiment in which 0.2 g of HAP/LA reacted with the solution containing 0.483 mmol L^{-1} Pb^{2+} as nitrate salt. XRD has shown that fluorapatite was the main constituent of Lisina apatite. The Visual MINTEQ database value of the fluorapatite solubility product is $K_{sp} = -58.6$. In some investigations, however, it was shown that the real solubility product for natural (mineral) fluorapatites is lower than this

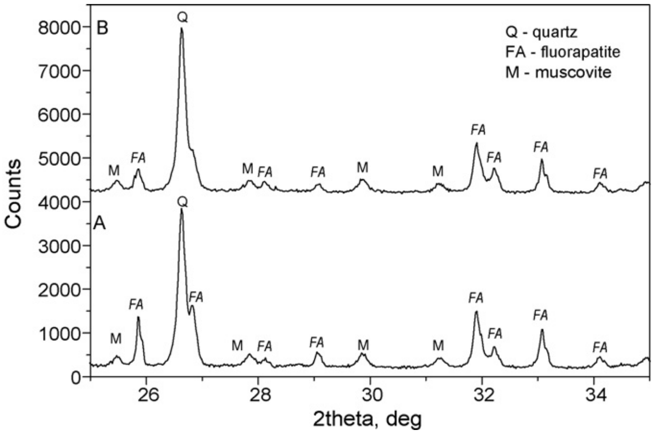

Fig. 5. XRD patterns of Lisina apatite: (A) before reaction with Pb and (B) after reaction with 4.826 mmol L^{-1} of Pb for 5.5 h.

database value. The value reported by Valsami-Jones et al. [37] for mineral apatite is −70. When using the value $K_{sp} = -58.6$ calculations have shown a high amount of phosphates present in the solution. In our work the phosphates were below the detection limit (data not shown). Based on the comparison of this and other experimental data with Visual MINTEQ calculations, it was concluded that this K_{sp} is not appropriate for Lisina apatite. In further calculations the Visual MINTEQ database was modified and the value of $K_{sp} = -70$ was added as the value of the solubility product of mineral fluorapatite.

Visual MINTEQ calculations show that in the Pb-HAP system the percentage of Pb removed from the solution is 99.97%, while the experimental value was 99.6%. The calculations show that at the end of the reaction when equilibrium is reached, there would be two solids present: pyromorphite (HPM) and hydroxyapatite. According to this, HAP dissolved to form HPM until there were Pb ions present in the solution. Only 0.03% of the Pb initial concentration remained in the solution. This indicates that according to the Visual MINTWQ calculations the main mechanism of Pb removal from the solution is dissolution of HAP followed by HPM precipitation. Our experimental data, however, did not show any new solid phase formation. As discussed in Section 3.4 the reason for this could be the low concentration of HPM or the poor crystallinity of the newly formed solid phase. According to Visual MINTEQ calculations synthetic HAP is an appropriate sorbent for Pb removal.

In the case of the Pb-LA system, there is significant difference between calculated and experimental values of percentage of Pb removed from the solution (99.95% calculated versus 41.6% experimental). Visual MINTEQ predicts two solids at equilibrium: fluorapatite and pyromorphite. The calculations show that ≈100% lead would be precipitated, i.e. that LA dissolved to provide ${PO_4}^{3-}$ ions for HPM formation. Fluoride ions that would be produced remained in the solution, as HPM is a more stable phase than fluoropyromorphite, $Pb_{10}(PO_4)_6F_2$. The dissolution–precipitation mechanism suggested by the Visual MINTEQ model cannot describe the process of Pb sorption by Lisina apatite because of the large discrepancy between experimental and calculated values of the percentage of Pb removed from the solution.

Two different mechanisms of Pb immobilization by HAP and some mineral apatites were previously suggested [31]. Immobilization of Pb by HAP leads to encapsulation of HAP particles by insoluble pyromorphite, preventing the further process of Pb immobilization. In contrast, some mineral apatites form the apatite/Pb solid solution instead of the pyromorphite. This allows the diffusion of Pb from the surface into the HAP particle resulting in slow but continual sorption of Pb. Results presented here strongly support the existence of these two mechanisms and point out some advantages of mineral apatites as matrix for barriers and amendments for the assisted natural remediation of Pb.

4. Conclusions

In order to determine the most appropriate adsorption isotherm for lead sorption by synthetic and natural apatite, the experimental data were substituted into five isotherm models. The most appropriate model for Pb sorption by synthetic hydroxyapatite as well as by Lisina apatite is the Freundlich isotherm model. The kinetics of the sorption reaction was studied using the pseudo-first and pseudo-second order rate model. It was determined that the pseudo-second order model described the kinetic data in both systems (Pb-HAP and Pb-LA) accurately. The kinetics of Pb removal by these two sorbents is a two-phase process, with a rapid first phase and a slower second phase, which leads to pseudo-equilibrium. The calculated values of the Gibbs free energy ($\Delta G^0 < 0$) indicate that the processes of lead sorption from the aqueous solution by HAP and LA are spontaneous. The results of this study show that natural apatite from Lisina ore deposit in south Serbia can be an effective way for Pb contamination treatment. Synthetic hydroxyapatite used in this study has a larger sorption capacity and affinity to Pb than Lisina apatite, but based on the greater cost of synthetic mineral, the use of Lisina apatite can be suggested.

Acknowledgments

This work was supported by the Ministry of Science and Technological Development of the Republic of Serbia (Project No. 142014 and Project No. 142050).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2010.03.061.

References

[1] D.W. Hardison, L.Q. Ma, T. Luongo, W.G. Harris, Lead contamination in shooting range soils from abrasion of lead bullets and subsequent weathering, Sci. Total Environ. 328 (2004) 175–183.
[2] N. Arnich, M.C. Lanhers, F. Laurensot, R. Podor, A. Montiel, D. Burnel, In vitro and in vivo studies of lead immobilization by synthetic hydroxyapatite, Environ. Pollut. 124 (2003) 139–149.
[3] D.C. Adriano, W.W. Wenzel, J. Vangronsveld, N.S. Bolan, Role of assisted natural remediation in environmental cleanup, Geoderma 122 (2004) 121–142.
[4] United States Environmental Protection Agency (USEPA), Abstracts of Remediation Case Studies, EPA-542-R-95-001, United States Environmental Protection Agency (USEPA), Washington, USA, 1995.
[5] C.N. Mulligan, R.N. Yong, B.F. Gibbs, Remediation technologies for metal-contaminated soils and groundwater: an evaluation, Eng. Geol. 60 (2001) 193–207.
[6] United States Environmental Protection Agency (USEPA), Recent Development for In Situ Treatment of Metal Contaminated Soils, EPA-542-R-97-004, United States Environmental Protection Agency (USEPA), Washington, USA, 1997.
[7] X. Cao, L.Q. Ma, S.P. Singh, O. Zhou, Phosphate-induced lead immobilization from different lead minerals in soils under varying pH conditions, Environ. Pollut. 152 (2008) 184–192.
[8] T. Suzuki, K. Ishigaki, N. Ayuzawa, Removal of toxic Pb^{2+} ions by synthetic hydroxyapatites, Chem. Eng. Commun. 34 (1985) 143–151.
[9] Q.Y. Ma, S.J. Traina, T.J. Logan, J.A. Ryan, In situ lead immobilization by apatite, Environ. Sci. Technol. 27 (1993) 1803–1810.
[10] A.S. Knox, D.I. Kaplan, M.H. Paller, Phosphate sources and their suitability for remediation of contaminated soils, Sci. Tot. Environ. 357 (2006) 271–279.
[11] M. Manecki, P.A. Maurice, S.J. Traina, Kinetics of aqueous Pb reaction with apatites, Soil Sci. 165 (2000) 920–933.
[12] S. Baillez, A. Nzihou, D. Bernache-Assolant, E. Champion, P. Sharrock, Removal of aqueous lead ions by hydroxyapatites: equilibria and kinetic processes, J. Hazard. Mater. 139 (2007) 443–446.
[13] Y. Hashimoto, T. Sato, Removal of aqueous lead by poorly-crystalline hydroxyapatites, Chemosphere 69 (2007) 1775–1782.
[14] H.Y. Xu, L. Yang, P. Wang, Y. Liu, M.S. Peng, Kinetic research on the sorption of aqueous lead by synthetic carbonate hydroxyapatite, J. Environ. Manage. 86 (2008) 319–328.
[15] I.R. Sneddon, M. Orueetxebarria, M.E. Hodson, P.F. Schofield, E. Valsami-Jones, Use of bone meal amendments to immobilize Pb, Zn and Cd in soil: a leaching column study, Environ. Pollut. 144 (2006) 816–825.
[16] J.L. Conca, Phosphate-Induced Metal Stabilization (PIMS), Final Report to the U. S. Environmental Protection Agency #68D60023, U.S. Environmental Protection Agency, Research Triangle Park, 1997.
[17] J.L. Conca, J. Wright, An apatite II permeable reactive barrier to remediate groundwater containing Zn, Pb and Cd, Appl. Geochem. 21 (2006) 1288–1300.
[18] Q.Y. Ma, T.J. Logan, S.J. Traina, Lead immobilization from aqueous solutions and contaminated soils using phosphate rocks, Environ. Sci. Technol. 29 (1995) 1118–1126.
[19] X. Chen, J.V. Wright, J.L. Conca, L.M. Peurrung, Evaluation of heavy metal remediation using mineral apatite, Water Air Soil Pollut. 98 (1997) 57–78.
[20] X.B. Chen, J.V. Wright, J.L. Conca, L.M. Peurrung, Effects of pH on heavy metal sorption on mineral apatite, Environ. Sci. Technol. 31 (1997) 624–631.
[21] L.Q. Ma, A.L. Choate, G.N. Rao, Effects of incubation and phosphate rock on lead extractability and speciation in contaminated soils, J. Environ. Qual. 26 (1997) 801–807.
[22] M. Prasad, S.S. Amritphale, S. Saxena, N. Chandra, Separation of lead ions on francolite surfaces, Sep. Sci. Technol. 35 (2000) 2431–2442.
[23] M. Prasad, S. Saxena, S.S. Amritphale, N. Chandra, Kinetics and isotherms for aqueous lead adsorption by natural minerals, Ind. Eng. Chem. Res. 39 (2000) 3034–3037.

[24] E. Mavropoulos, N.C.C. da Rocha, J.C. Moreira, L.C. Bertolino, A.M. Rossi, Pb^{2+}, Cu^{2+} and Cd^{2+} ions uptake by Brazilian phosphate rocks, J. Braz. Chem. Soc. 16 (2005) 62–68.

[25] M. Mouflih, A. Aklil, N. Jahroud, M. Gourai, S. Sebti, Removal of lead from aqueous solutions by natural phosphate, Hydrometallurgy 81 (2006) 219–225.

[26] S. Saxena, S.F. D'Souza, Heavy metal pollution abatement using rock phosphate mineral, Environ. Int. 32 (2006) 199–202.

[27] X. Cao, L.Q. Ma, D.R. Rhue, C.S. Appel, Mechanisms of lead, copper, and zinc retention by phosphate rock, Environ. Pollut. 131 (2004) 435–444.

[28] S.P. Singh, L.Q. Ma, W.G. Harris, Heavy metal interactions with phosphatic clay: sorption and desorption behavior, J. Environ. Qual. 30 (2001) 1961–1968.

[29] C.E. Martinez, A.R. Jacobson, M.B. Mcbride, Lead phosphate minerals: solubility and dissolution by model and natural ligands, Environ. Sci. Technol. 38 (2004) 5584–5590.

[30] I.D. Smičiklas, S.K. Milonjić, P. Pfendt, S. Raičević, The point of zero charge and sorption of cadmium(II) and strontium(II) ions on synthetic hydroxyapatite, Sep. Purif. Technol. 18 (2000) 185–194.

[31] S. Raicevic, T. Kaludjerovic-Radoicic, A.I. Zouboulis, In situ stabilization of toxic metals in polluted soils using phosphates: theoretical prediction and experimental verification, J. Hazard. Mater. 117 (2005) 41–53.

[32] F.C. Wu, R.L. Tseng, S.C. Huang, R.S. Juang, Characteristics of pseudo-second-order kinetic model for liquid-phase adsorption: a mini-review, Chem. Eng. J. 151 (2009) 1–9.

[33] J.P. Gustafsson, Visual Minteq 2.30, 2000 [online] Available at http://www.lwr.kth.se/english/OurSoftWare/Vminteq/index.htm, verified September 2009.

[34] Y. Khambhaty, K. Mody, S. Basha, B. Jha, Kinetic, equilibrium and thermodynamic studies on biosorption of hexavalent chromium by dead fungal biomass of marine *Aspergillus niger*, Chem. Eng. J. 145 (2009) 489–495.

[35] S.K. Lower, P.A. Maurice, S.J. Traina, Simultaneous dissolution of hydroxylapatite and precipitation of hydroxypyromorphite: direct evidence of homogeneous nucleation, Geochim. Cosmochim. Acta 62 (1998) 1773–1780.

[36] G.M. Hettiarachchi, G.M. Pierzynski, M.D. Ransom, *In situ* stabilization of soil lead using phosphorus, J. Environ. Qual. 30 (2001) 1214–1221.

[37] E. Valsami-Jones, K.V. Ragnarsdottir, A. Putnis, D. Bosbach, A.J. Kemp, G. Cressey, The dissolution of apatite in the presence of aqueous metal cations at pH 2–7, Chem. Geol. 151 (1998) 215–233.