

# Factors influencing the removal of divalent cations by hydroxyapatite

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## Abstract

The effect of pH, contact time, initial metal concentration and presence of common competing cations, on hydroxyapatite (HAP) sorption properties towards  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Sr}^{2+}$  ions was studied and compared using a batch technique. The results strongly indicated the difference between the sorption mechanism of  $\text{Pb}^{2+}$  and other investigated cations: the removal of  $\text{Pb}^{2+}$  was pH-independent and almost complete in the entire pH range (3–12), while the sorption of  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Sr}^{2+}$  generally increased with an increase of pH; the contact time required for attaining equilibrium was 30 min for  $\text{Pb}^{2+}$  versus 24 h needed for other cations; maximum sorption capacity of HAP sample was found to be an order of magnitude higher for  $\text{Pb}^{2+}$  (3.263 mmol/g), than for  $\text{Cd}^{2+}$  (0.601 mmol/g),  $\text{Zn}^{2+}$  (0.574 mmol/g) and  $\text{Sr}^{2+}$  (0.257 mmol/g); the selectivity of HAP was found to decrease in the order  $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Sr}^{2+}$  while a decrease of  $\text{pH}_{\text{PZC}}$ , in respect to the value obtained in inert electrolyte, followed the order  $\text{Cd}^{2+} > \text{Zn}^{2+} > \text{Pb}^{2+} > \text{Sr}^{2+}$ ; neither of investigated competing cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^{+}$  and  $\text{K}^{+}$ ) influenced  $\text{Pb}^{2+}$  immobilization whereas the sorption of other cations was reduced in the presence of  $\text{Ca}^{2+}$ , in the order  $\text{Sr}^{2+} > \text{Cd}^{2+} \geq \text{Zn}^{2+}$ . The pseudo-second order kinetic model and Langmuir isotherm have been proposed for modeling kinetic and equilibrium data, respectively. The sorption of all examined metals was followed by  $\text{Ca}^{2+}$  release from the HAP crystal lattice and pH decrease. The ion exchange and specific cation sorption mechanisms were anticipated for  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Sr}^{2+}$ , while dissolution of HAP followed by precipitation of hydroxypyromorphite ( $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) was found to be the main operating mechanism for  $\text{Pb}^{2+}$  immobilization by HAP, with the contribution of specific cation sorption.

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## 1. Introduction

The toxicity of solid substances containing heavy metals is closely related to their solubility. For this reason, phosphate stabilization resulting in formation of highly insoluble phosphates which are stable over almost the entire pH range found in the natural environment represents an efficient strategy for reducing heavy metals toxicity by decrease of their mobility and bioavailability [1]. A large number of apatite based materials (mineral phosphates [2–5], synthetic apatite [6–10], bone meal [11,12] and bone char [13]) have been considered as matrixes for remediation of metal contaminated water and soil. Generally, calcium-hydroxyapatite (HAP)  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , has demonstrated the best removal efficiency due to its moderate solubility—between highly insoluble and highly soluble phos-

phate bearing materials such as phosphate rock and phosphate fertilizers, respectively [14].

Reported data indicate that divalent metal sorption capacities on HAP, as well as the sorption mechanisms strongly depend on: (a) type of divalent metal, (b) HAP physico-chemical properties and (c) other factors, such as metal concentration, solution pH, contact time, presence of other ionic species etc. [15,16]. In our previous work the influence of HAP properties on divalent cation retention was investigated [17,18]. HAP powders were synthesized by neutralization method. Preparation conditions, HAP physico-chemical properties and sorption behavior towards heavy metal cations were correlated using the experimental design approach [17]. It was found that among investigated parameters (temperature, reagent concentration, reagent addition rate, mixing speed, inert atmosphere, and aging time) synthesis temperature has the strongest influence on HAP structural and sorption properties. Powders obtained at room temperature, without aging, having small crystallite size, low crystallinity, and high specific surface area exhibit the best

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### Nomenclature

$C_0$	initial metal ion concentration (mmol/dm <sup>3</sup> )
$C_e$	residual metal ion concentration at equilibrium (mmol/dm <sup>3</sup> )
$C_s$	HAP concentration (g/dm <sup>3</sup> )
$h$	initial sorption rate (mmol/g min)
$k_1$	pseudo first order sorption rate constant (min <sup>-1</sup> )
$k_2$	pseudo second order sorption rate constant (g/mmol min)
$pH_{PZC}$	the point of zero charge
$K$	Langmuir sorption constant (kg/mmol)
$q$	amount of metal ion sorbed (mmol/g)
$q_e$	amount of metal ion sorbed at equilibrium (mmol/g)
$q_t$	amount of metal ion sorbed at time $t$ (mmol/g)
$R^2$	regression coefficient
$t$	time of equilibration (min)
$T$	solution temperature (°C)
$X_m$	Langmuir sorption constant (mmol/g)

sorption properties towards Pb<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup> and Sr<sup>2+</sup> [18]. On a larger scale, variations in HAP stoichiometry (Ca/P ratio) and  $pH_{PZC}$  had little effect on the metal sorption.

Although the sorption of heavy metals on HAP has been extensively studied, many questions concerning sorption mechanisms under specific experimental conditions remained unresolved, while comparison of data is difficult because of the differences in origin and physico-chemical properties of the HAP sorbents applied.

In order to investigate factors influencing sorption of Pb<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup> and Sr<sup>2+</sup> ions, the low-crystalline HAP sample, with high specific area was selected. Pb<sup>2+</sup>, Cd<sup>2+</sup> and Zn<sup>2+</sup> ions were chosen as typical heavy metals, with wide presence in surface and ground waters, soils and sediments caused by anthropogenic activity. If these heavy metals occur in nature in ionic form, they easily enter the food chain, causing various toxic effects on living organisms. Sorption of Sr<sup>2+</sup> was investigated as it is a representative of alkaline earth cations, but also because Sr-90 (beta emitter, with  $t_{1/2} = 29.1$  years), the important radioactive isotope in the environment behaves chemically similar to calcium and tends to concentrate in the bones and teeth whose principal inorganic constituent is hydroxyapatite [19]. Besides having different toxicity, the selected sorbates also have different ionic radii and hydrolysis behavior, which makes the comparison of their sorption mechanisms interesting.

The objectives of the present study were: (i) to investigate the effects of pH, contact time, initial metal concentration and presence of competing cations on the sorption of selected divalent cations by HAP, (ii) to compare HAP sorption properties and selectivity for investigated metal cations, and (iii) to propose the theoretical models for describing equilibrium and kinetic data.

Presented results strongly indicate the difference between sorption mechanism of Pb<sup>2+</sup> and other investigated cations, under all experimental conditions, as well as that buffer proper-

ties of HAP represent an important factor influencing efficacy of immobilization of toxic metals.

## 2. Materials and methods

### 2.1. Starting material

HAP sample used in this study was synthesized by neutralization of Ca(OH)<sub>2</sub> with H<sub>3</sub>PO<sub>4</sub>, at room temperature (20 °C) [17]. Chemical and X-ray diffraction (XRD) analyses have confirmed that the sample is a low-crystalline HAP with Ca/P ratio of 1.60. Specific surface area of 67 m<sup>2</sup>/g was determined by the single point nitrogen adsorption method, after degassing the sample at 250 °C for 2 h, using a Micrometrics ASAP 2000 instrument. The point of zero charge ( $pH_{PZC}$ ) determined by batch technique [17] with 0.1 mol/dm<sup>3</sup> KNO<sub>3</sub> as an inert electrolyte was found to be  $6.2 \pm 0.1$ .

### 2.2. Sorption experiments

Sorption of Pb<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup> and Sr<sup>2+</sup> was studied by batch method, under different experimental conditions. All metal solutions were prepared from their nitrate salts (p.a. purity) and distilled water. Generally, sorption experiments were performed by equilibrating 0.1000 g of sorbent with 20.00 ml of metal solution (solid/liquid ratio 1:200) at room temperature ( $20 \pm 1$  °C). The pH measurements were performed with a glass electrode pH meter (Inolab, WTW), using original WTW buffers (pH 4, 7 and 10) for the calibration of the instrument. The initial pH values were adjusted to  $5.0 \pm 0.1$ , unless otherwise stated, by adding minimum amounts of HNO<sub>3</sub> or KOH solutions, since K<sup>+</sup> and NO<sub>3</sub><sup>-</sup> ions are inert in respect to HAP surface. This particular pH was selected because HAP solubility increases significantly at  $pH < 5$ , while at higher pH values hydrolysis of heavy metal cations may occur. The final pH values were those measured after interaction of HAP with the solution of known initial pH. Due to various processes that may occur at the solid surface/solution interface (preferential dissolution of certain constituents of crystal lattice, ionization of surface groups, physical adsorption of ions or formation of complex compounds between surface groups and ions from the solution) the final pH values differ from the initial ones. The suspensions were equilibrated in acid washed 50 ml PVC flasks, on a horizontal shaker.

- Sorption behavior of Pb<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup> and Sr<sup>2+</sup>, for the same initial concentration ( $2 \times 10^{-3}$  mol/dm<sup>3</sup>) and equilibration time (24 h), was studied as a function of pH. The initial pH values were adjusted from  $\sim 3$  to  $\sim 12$ , using HNO<sub>3</sub> or KOH solutions.
- The influence of contact time on each metal sorption was analyzed from 15 min up to 2 days. Initial metal concentrations were  $2 \times 10^{-3}$  mol/dm<sup>3</sup>.
- Sorption isotherms were obtained for different initial metal concentration in the range  $10^{-4}$  to  $10^{-2}$  mol/dm<sup>3</sup> for Cd<sup>2+</sup>, Zn<sup>2+</sup> and Sr<sup>2+</sup>, and  $10^{-4}$  to  $5 \times 10^{-2}$  mol/dm<sup>3</sup> for Pb<sup>2+</sup>. The contact time in all experiments was 24 h. Initial low-

crystalline HAP and solid residues with the maximum sorbed metal cations (obtained after equilibration of HAP with  $10^{-2}$  mol/dm<sup>3</sup> solutions of Cd<sup>2+</sup>, Zn<sup>2+</sup> and Sr<sup>2+</sup>, and  $5 \times 10^{-2}$  mol/dm<sup>3</sup> of Pb<sup>2+</sup> ions), were analyzed by the Philips PW 1050 XRD with CuK $\alpha_{1,2}$  Ni-filtered radiation. The patterns were registered in the  $2\theta$  range 10–100° with a scanning step size of 0.02° and analyzed by Rietveld methodology [20], using Fullprof software [21], in order to determine cell parameters and crystallite size.

- The effect of common competing cations (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>) on the sorption of divalent metals was studied for the initial competing metal concentration in the range  $5 \times 10^{-4}$  to  $5 \times 10^{-3}$  mol/dm<sup>3</sup>, using their nitrate salts. The initial divalent metal concentration was  $2 \times 10^{-3}$  mol/dm<sup>3</sup>, and equilibration time was 24 h.

Each sorption experiment was followed by filtration of the suspension through blue-band filter paper and the final pH measurement. Determination of exact concentrations of initial metal solutions, metal concentrations after sorption, as well as the concentration of released Ca<sup>2+</sup> ions in the equilibrium solution was performed either by the Perkin-Elmer Analyst 200 Atomic Absorption Spectrometer (AAS) or Perkin-Elmer 6500 Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES), depending on the concentration range.

The amount of heavy metal sorbed,  $q$  (mmol/g) was calculated using the equation:

$$q = \frac{(C_0 - C_e)}{C_s} \quad (1)$$

### 3. Results and discussion

#### 3.1. Effect of pH

As HAP particles exhibit pH dependent surface charge, and the percent of various heavy metal hydrolytic species depend on pH, this parameter significantly influences the sorption processes. The pHPZC of the HAP sample determined by equilibration with inert electrolyte (KNO<sub>3</sub>) was found to be 6.2 (Fig. 1). Fig. 1 also demonstrates the large buffer capacity of HAP, since for initial pH in the range 4–10 final pH values were the same and equal to pHPZC. In the lower initial pH range, the consumption of protons from the solution by the protonation of negatively charged and neutral surface groups results in final pH increase, while in the higher range of initial pH, OH<sup>−</sup> consumption occurs due to deprotonation of positively charged surface sites, resulting in final pH decrease.

Variation in final pH after interaction of HAP with Pb<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup> and Sr<sup>2+</sup> solutions, are also plotted as a function of the initial pH (Fig. 1).

The plateau parts of pH<sub>final</sub> versus pH<sub>initial</sub> plots, corresponding to the pH range where the buffering effect of HAP surface takes place, becomes shorter in the presence of Pb<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup>, while in the case of Sr<sup>2+</sup> plateau part is almost the same as for the inert electrolyte. Also, the pHPZC values of HAP, calculated for divalent metal solutions ( $2 \times 10^{-3}$  mol/dm<sup>3</sup>), were lower than

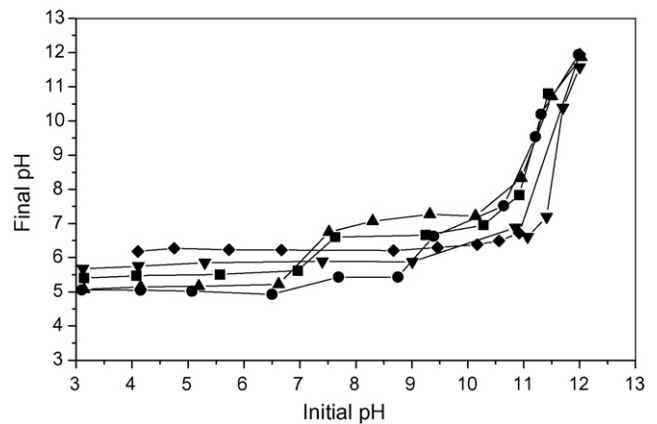


Fig. 1. Relationships between initial and final pH values measured after interaction of HAP with Pb(NO<sub>3</sub>)<sub>2</sub> (■), Cd(NO<sub>3</sub>)<sub>2</sub> (●), Zn(NO<sub>3</sub>)<sub>2</sub> (▲), Sr(NO<sub>3</sub>)<sub>2</sub> (▼) solutions and inert electrolyte (KNO<sub>3</sub>) (◆).

original value determined for inert electrolyte: 5.1, 5.2, 5.5 and 5.8 for Cd<sup>2+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup> and Sr<sup>2+</sup>, respectively. This is in accordance with the theory that the specific cation sorption shifts the pHPZC to lower values [22]. The decrease of pHPZC follows the order: Cd > Zn > Pb > Sr. This sequence matches the sequence of HAP affinity towards examined metals, except for Pb<sup>2+</sup>. Considering the amount of Pb<sup>2+</sup> sorbed by HAP and the corresponding pHPZC value, it can be concluded that the specific sorption has less contribution in the overall sorption mechanism of this cation, in respect to others.

The influence of final pH on Pb<sup>2+</sup> removal from the liquid phase was insignificant, and it was almost complete over the entire pH range (Fig. 2a). Similar results were reported by Chen et al. for Pb sorption on North Carolina mineral apatite [2]. Using a mineral apatite, although the total amount of Pb removed from the solution was pH-independent, the chemical compositions of Pb-bearing solid products were pH-dependent. The formation of pyromorphite-type compounds was found to be the main mechanism of Pb removal under acidic conditions. Under alkaline conditions solubility of apatites decreased leaving less phosphate anions for Pb precipitation, therefore at higher pH values hydrocerussite (Pb<sub>3</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub>) was detected. In our case, with a synthetic HAP, dissolution of a sorbent and precipitation of hydroxypyromorphite (HPY) Pb<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub> is most likely to appear in acidic and neutral, and precipitation of Pb(OH)<sub>2</sub> in alkaline solutions.

Generally, with an increase of pH the concentration of other metals in the liquid phase decreased, to a different extent. Cd and Zn aqueous concentrations diminish rapidly with the increase of final pH, due to both sorption of hydrolytic species and precipitation of insoluble hydroxides. Sr removal from the solution exhibits slower increase with pH, and since it does not hydrolyze, more effective removal at higher pH can be explained by the alteration of HAP surface charge. The HAP surface becomes negatively charged at pH > pHPZC due to adsorption of OH<sup>−</sup> from the solution [10]. Negatively charged surface promotes the sorption of Sr<sup>2+</sup>. In the final pH range ~5 to ~10, the order of HAP affinity towards examined metals was: Pb > Cd > Zn > Sr, however, at final pH > 10 sorption of Zn becomes unfavorable.

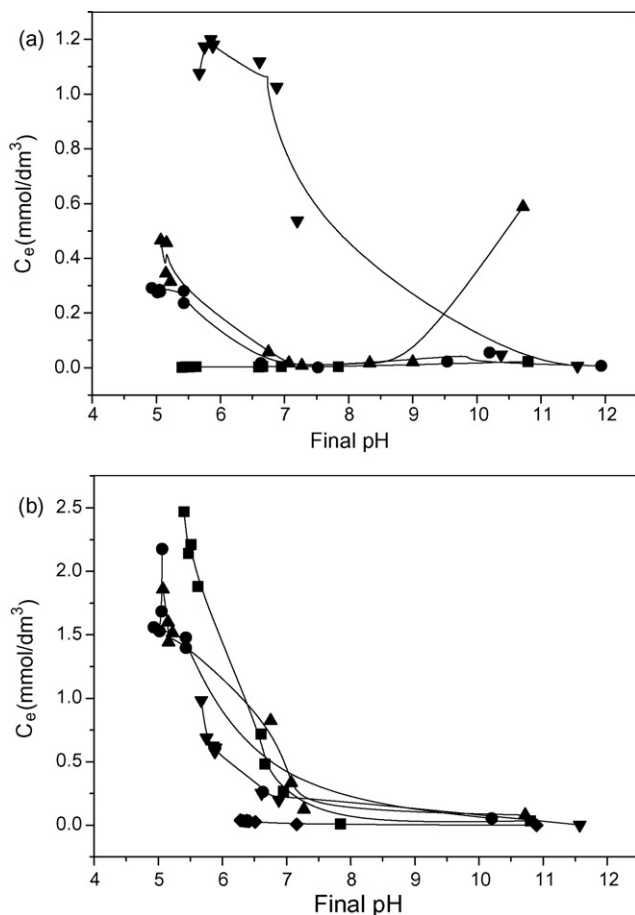


Fig. 2. Equilibrium metal (a) and calcium (b) concentrations as a function of final pH, after interaction of Pb(NO<sub>3</sub>)<sub>2</sub> (■), Cd(NO<sub>3</sub>)<sub>2</sub> (●), Zn(NO<sub>3</sub>)<sub>2</sub> (▲), Sr(NO<sub>3</sub>)<sub>2</sub> (▼) and KNO<sub>3</sub> (◆) solutions with HAP.

This can be explained on the basis of Zn ionic species distribution with pH. Formation of negatively charged Zn(OH)<sub>3</sub><sup>-</sup> species begins at pH > 10, therefore repulsive forces are likely to appear between them and the negatively charged HAP surface.

The solubility of HAP itself decreases with the increase of the solution pH [23], consequently the equilibrium Ca<sup>2+</sup> concentrations, after interaction of HAP with inert electrolyte or divalent metal solutions, also decreased with final pH increase (Fig. 2b). The total amounts of released Ca<sup>2+</sup> were higher in divalent metal solutions where sorption takes place, than in the inert electrolyte, and followed the order of HAP selectivity: Pb > Cd > Zn > Sr. Comparing the results presented in Fig. 2a. and b, it can be concluded that the amounts of divalent cations removed from the solution increased, whereas the amounts of desorbed Ca<sup>2+</sup> decreased with pH. This supports the fact that at higher pH instead of ion-exchange and dissolution/precipitation, depending of the type of cation, sorption of hydrolytic species, precipitation of insoluble hydroxides or attractive electrostatic forces become the dominant mechanisms of cation removal.

### 3.2. Effect of contact time-kinetic modeling

The results of sorption studies, carried out as a function of contact time, for different divalent metals are presented in

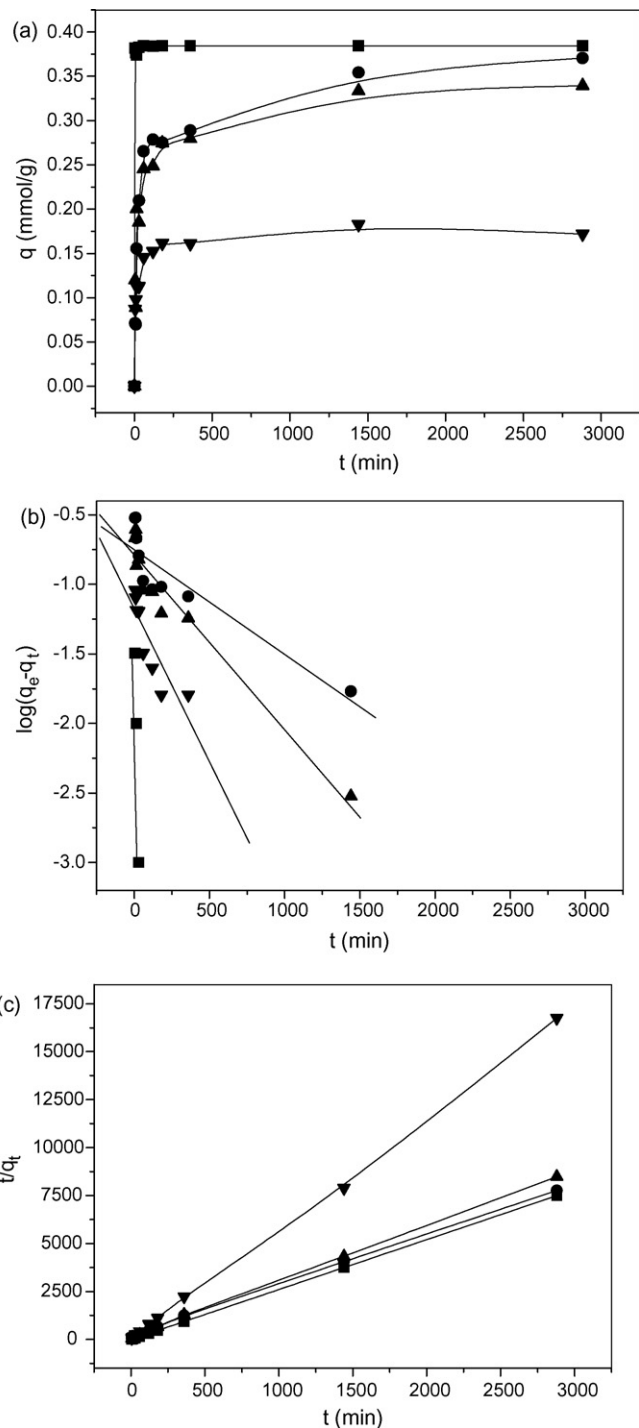


Fig. 3. Variation of sorbed amounts of metal cations (Pb<sup>2+</sup>—■, Cd<sup>2+</sup>—●, Zn<sup>2+</sup>—▲ and Sr<sup>2+</sup>—▼) on HAP, with time (a) and the linear fitting of experimental data using pseudo-first order (b) and pseudo second order (c) kinetic model.

Fig. 3a. A contact time of approximately 30 min was required for attaining the sorption equilibrium for Pb<sup>2+</sup>, thus it was the most rapid uptake in respect to other cations. Rapid sorption in the first 6 h, followed by a slower phase was observed for Cd<sup>2+</sup>, Zn<sup>2+</sup> and Sr<sup>2+</sup>. For Zn<sup>2+</sup> and Sr<sup>2+</sup> the equilibrium was reached in 24 h. Though a very slow increase of sorbed Cd<sup>2+</sup> existed after the first day of equilibration, a con-

tact time of 24 h was assumed sufficient for further experiments.

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. Generally, the reaction rate is defined as the change of reactants or products per unit of time. The Lagergren pseudo-first order equation can be expressed as [24]:

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad (2)$$

Integrating this for the boundary conditions  $t=0$  to  $t=t$  and  $q_t=0$  to  $q_t=q_t$ , the above equation can be rearranged for linearized data plotting as:

$$\log(q_e - q_t) = \log q_e - (k_1/2.303)t \quad (3)$$

A 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.

The pseudo-second order rate model, based on sorbent capacity [25], can be expressed as a differential equation:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (4)$$

Integrating this for the same boundary conditions, the Eq. (4) can be rearranged in the following linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

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 min), when  $t \rightarrow 0$ , can also be calculated as follows:

$$h = k_2 q_e^2 \quad (6)$$

Fig. 3b and c show the results of fitting the experimental data using linear forms of pseudo-first and pseudo-second order kinetic equations. Rate constants, calculated  $q_e$  values and regression coefficients for pseudo-first and pseudo-second order kinetic models are presented in Table 1.

Calculated  $q_e$  values, obtained using the Lagergren pseudo-first order equation, are substantially different from the experimental ones. According to regression coefficients and calculated values of equilibrium concentrations, the pseudo-second order model was more appropriate, suggesting that the rate limiting step in divalent metal sorption on HAP involves valence

forces through sharing or exchange of electrons between the sorbent and sorbates [25]. It should be mentioned that although sorption mechanism of  $\text{Pb}^{2+}$  by HAP is assumed to be different from the mechanism characteristic for other investigated cations, the same kinetic model (pseudo-second-order) was successfully applied to all experimental data. In the literature, this model was found to be appropriate for describing kinetics of metal sorption by different apatite materials:  $\text{Cr}^{3+}$  by animal bones [26],  $\text{Cd}^{2+}$  by bone char [27],  $\text{Pb}^{2+}$  by soil amended with HAP [28] and uranium by low-cost rock phosphate [29], where  $\text{Pb}^{2+}$  and uranium are sorbed via dissolution/precipitation mechanism. Therefore, the significant correlation between experimental data and a simple kinetic model, such as this one, is useful for the purpose of comparison and  $q_e$  prediction, but is unlikely to describe the actual sorption mechanism, especially for the systems where various transport and chemical phenomena take place on the solid/liquid interface, simultaneously [30].

The amounts of metal ions sorbed at equilibrium decreased in the order:  $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Sr}^{2+}$  (Table 1). A significantly higher  $k_2$  and  $h$  values calculated for  $\text{Pb}^{2+}$  in respect to other cations, confirmed the difference in  $\text{Pb}^{2+}$  sorption mechanism, whose driving force is rapid dissolution of HAP followed by precipitation of less soluble HPY. The rate constants and the initial sorption rates were similar for Cd and Zn, while somewhat higher for the sorption of  $\text{Sr}^{2+}$ . This may be explained by considering the hydrated ionic radii of cations;  $\text{Sr}^{2+}$  (4.12 Å),  $\text{Cd}^{2+}$  (4.26 Å) and  $\text{Zn}^{2+}$  (4.30 Å). Since  $\text{Sr}^{2+}$  ions have the smallest hydrated ionic radii, it is possible that with fewer and more weakly bonded water molecules they tend to move faster to potential adsorption surface sites.

### 3.3. Effect of initial metal concentrations-equilibrium modeling

Sorption studies over a large initial concentration range ( $10^{-4}$  to  $10^{-2}$  mol/dm<sup>3</sup> for  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Sr}^{2+}$ , and  $10^{-4}$  to  $5 \times 10^{-2}$  mol/dm<sup>3</sup> for  $\text{Pb}^{2+}$ ) were performed in order to determine the HAP sorption capacity towards examined metal cations. Generally, the uptake of metals increased with increasing solution concentrations, however, the shape of the sorption isotherm obtained for  $\text{Pb}^{2+}$  differs from the others (Fig. 4).

For initial metal concentrations from  $10^{-4}$  up to  $10^{-2}$  mol/dm<sup>3</sup>, the residual concentrations of  $\text{Pb}^{2+}$  in the solution were nearly the same. Isotherms with similar equilibrium concentrations obtained from different initial metal concentrations indicate a precipitation mechanism according to Echeveirra

Table 1  
Comparison between experimental and calculated amounts of metal 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

Sorbate	$q_{e,\text{exp}}$ (mmol/g)	Pseudo-first order model			Pseudo-second order model			
		$k_1 \times 10^3$ (min <sup>-1</sup> )	$q_{e,\text{cal}}$ (mmol/g)	$R^2$	$k_2$ (g/mg min)	$q_{e,\text{cal}}$ (mmol/g)	$h$ (mmol/g min)	$R^2$
$\text{Pb}^{2+}$	0.384	26.370	0.070	0.994	25.495	0.384	3.759	1.000
$\text{Cd}^{2+}$	0.371	1.762	0.180	0.927	0.061	0.373	0.008	0.999
$\text{Zn}^{2+}$	0.336	2.786	0.153	0.946	0.088	0.342	0.010	0.999
$\text{Sr}^{2+}$	0.177	4.997	0.065	0.740	0.646	0.174	0.019	0.999

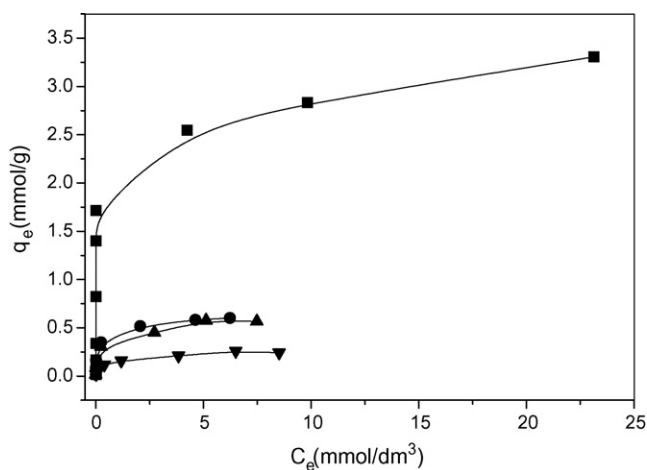


Fig. 4. The sorption isotherms of  $\text{Pb}^{2+}$  (■),  $\text{Cd}^{2+}$  (●),  $\text{Zn}^{2+}$  (▲) and  $\text{Sr}^{2+}$  (▼) on HAP (initial metal concentration range  $10^{-4}$  to  $10^{-2}$  mol/dm<sup>3</sup> for  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Sr}^{2+}$ , and  $10^{-4}$  to  $5 \times 10^{-2}$  mol/dm<sup>3</sup> for  $\text{Pb}^{2+}$ ).

et al. [31]. Sorption isotherms of  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Sr}^{2+}$  are similar in shape, all showing a gradual increase of sorption with an increase of initial metal concentration although the sorption capacities were different. The shape of these isotherms reflects surface adsorption or a more complex sorption mechanism [31].

The Langmuir adsorption isotherm, often used for sorption of solutes from a liquid phase, can be expressed as:

$$q_e = \frac{X_m K C_e}{1 + K C_e} \quad (7)$$

The above equation can be rearranged to the following linear form:

$$\frac{C_e}{q_e} = \frac{1}{X_m K} + \frac{C_e}{X_m} \quad (8)$$

The constants  $K$  and  $X_m$  can be determined from the slope and the intercept of the linear plot  $C_e/q_e$  as a function of  $C_e$ . The constants derived from Langmuir modeling represent the combined effects of all solution and surface reactions that contribute to the sorption under experimental conditions, and they are convenient for the general characterization of the sorbing system and for comparing different systems. The constant  $K$  is related to the energy of adsorption, while the constant  $X_m$  represents the maximum sorption capacity. The Langmuir isotherm was applied to our experimental data (Fig. 3b) and the corresponding values of sorption constants, maximum capacities and regression coefficients ( $R^2$ ) are summarized in Table 2.

Table 2

Values of maximum sorption capacities  $X_m$ , the constants  $K$  and the regression coefficients  $R^2$ , obtained from the linear Langmuir equation, for  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Sr}^{2+}$  sorption on HAP

Sorbate	Linear form of Langmuir isotherm	$X_m$ (mmol/g)	$K$ (dm <sup>3</sup> /mmol)	$R^2$
$\text{Pb}^{2+}$	$C_e/q_e = 0.107 + 0.306C_e$	3.263	2.848	0.994
$\text{Cd}^{2+}$	$C_e/q_e = 0.185 + 1.662C_e$	0.601	8.969	0.996
$\text{Zn}^{2+}$	$C_e/q_e = 0.323 + 1.741C_e$	0.574	5.393	0.990
$\text{Sr}^{2+}$	$C_e/q_e = 1.684 + 3.883C_e$	0.257	2.310	0.992

A good correlation, which was observed between experimental data and the Langmuir equation (for all examined metals the values of  $R^2$  were  $>0.990$ ), indicates that the sorption occurs on a set of sites having the same sorption energies independent of surface coverage. The highest maximum sorption capacity was calculated for  $\text{Pb}^{2+}$ , followed by  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Sr}^{2+}$  (Table 2). According to Suzuki et al. [32] HAP most selectively sorbs metal cations with high electronegativity and ionic radii in the range 0.90–1.30 Å (the ionic radius of  $\text{Ca}^{2+}$  is 0.99 Å). Our results support this theory: out of investigated metal cations  $\text{Pb}^{2+}$  has the ionic radii in the preferred range (1.20 Å), the highest electronegativity (2.33) and the highest sorption capacity was obtained for this cation.  $\text{Cd}^{2+}$  ions also have the proper radii (0.97 Å), but lower electronegativity (1.69), which makes its sorption capacity lower. On the other hand, the remaining two cations meet only one of the requirements:  $\text{Zn}^{2+}$  has the electronegativity of 1.65 (close to  $\text{Cd}^{2+}$ ) but ionic radii out of the preferred range (0.74 Å), while the  $\text{Sr}^{2+}$  although with suitable ionic radii (1.12 Å) exhibit significantly lower electronegativity (0.95) and was the least sorbed. Generally, the similarity between crystallographic radii of an exchangeable cation from the sorbent crystal lattice and a cation from the solution is the most important factor influencing the ion-exchange component of the sorption mechanism. On the other hand, a specific cation sorption mechanism is enhanced by increased electronegativity of the cation.

During sorption, the reaction system was free of acidity control, in order to better simulate real environmental conditions, and to conclude what occurs with the protons at the end of metal sorption. Therefore, the initial pH of all metal solutions was adjusted to 5 and the final pH values were measured, as well as the concentrations of  $\text{Ca}^{2+}$  ions in equilibrium solutions (Fig. 5). Interaction of HAP with metal solutions caused changes in the final pH (Fig. 5a).

For the lowest metal concentrations, due to HAP buffer properties, the pH was increasing from the initial pH 5 to final values which were close to the HAP  $\text{pH}_{\text{PZC}}$  (6.2). For higher metal concentrations, the final pH values were decreasing with an increase of the amount of metals sorbed: comparing only final pH values at the maximum amount of sorbed metals, decrease in solution pH by 0.53 units for  $\text{Sr}^{2+}$ , 1.48 units for  $\text{Zn}^{2+}$  and 1.69 pH units for  $\text{Cd}^{2+}$  was observed. These metals followed a general trend: the greater sorption capacity, the greater final pH decrease. The simple ion-exchange process between  $\text{Ca}^{2+}$  and  $\text{Me}^{2+}$  ions from the solution would not cause any pH changes. Since examined metal ions are not inert in respect to the HAP surface, their specific sorption leads to pH decrease [22]. Therefore, divalent cation sorption may cause: (a) the ion-exchange with  $\text{H}^+$  of protonated HAP surface groups, or (b)  $\text{OH}^-$  sorption on positive charges produced by  $\text{Me}^{2+}$  adsorption on HAP surface.

However, it should be noted that this final pH decrease is still very small compared to other sorbents, due to good HAP buffer property [10]. The final pH profile for  $\text{Pb}^{2+}$  was more complex. Compared to other metals, in the initial concentration range  $10^{-4}$  to  $10^{-2}$  mol/dm<sup>3</sup>, pH decreased by 1.25 units which is a small drift considering the amount of sorbed  $\text{Pb}^{2+}$ . This is

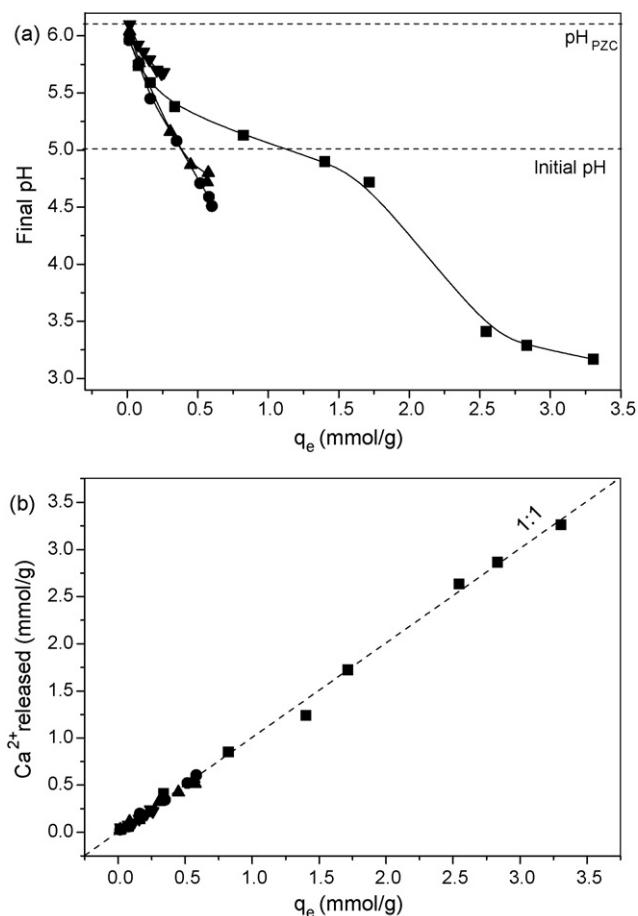


Fig. 5. Variations between the amounts of sorbed Pb<sup>2+</sup> (■), Cd<sup>2+</sup> (●), Zn<sup>2+</sup> (▲) and Sr<sup>2+</sup> (▼) and final pH (a), and between the amounts of metals sorbed and Ca<sup>2+</sup> released from HAP crystal lattice (b).

another clear indication of a different sorption mechanism. At the maximum amount of sorbed Pb<sup>2+</sup>, the final pH decreased by 3.03 units.

A linear relationship exists between the amount of metal sorbed and the amount of Ca<sup>2+</sup> released from the HAP crystal lattice (Fig. 5b). Although the Ca<sup>2+</sup>/Me<sup>2+</sup> ratios are close to unity, the final pH decrease which promotes HAP dissolution (i.e. Ca<sup>2+</sup> release), indicates the existence of other sorption mechanisms instead of pure ion-exchange or a dissolution–precipitation. According to both kinetic and equilibrium data, it can be concluded that the sorption mechanism of Cd<sup>2+</sup>, Zn<sup>2+</sup> and Sr<sup>2+</sup> is complex involving at least: ion-exchange, adsorption and/or surface complexation.

Contrary to that, both kinetic and equilibrium data suggest that the mechanism of Pb<sup>2+</sup> sorption by HAP is quite different. Fast sorption reaction for Pb<sup>2+</sup> (Table 1), an order of magnitude higher quantity of sorbed Pb<sup>2+</sup> (Table 2) and specific pH dependence (Fig. 5a), strongly indicate that dissolution–precipitation is a dominant mechanism of Pb<sup>2+</sup> retention by HAP.

XRD-analysis of solid residues with the maximum sorbed metal cations confirmed the differences in sorption mechanisms (Fig. 6). An XRD pattern of initial HAP material before the sorption is given in the same figure for comparison.

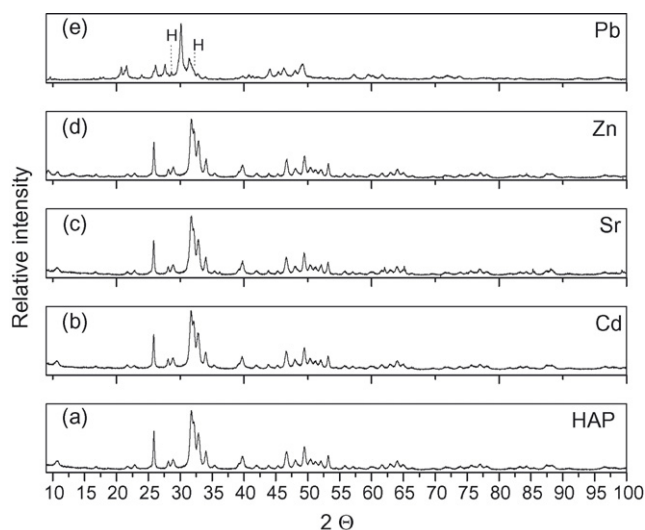


Fig. 6. XRD patterns of initial low-crystalline HAP (a), products of the reaction of HAP with 10<sup>-2</sup> mol/dm<sup>3</sup> Cd<sup>2+</sup> (b), Zn<sup>2+</sup> (c), Sr<sup>2+</sup> (d), and solid residues obtained after equilibration of HAP with 5 × 10<sup>-2</sup> mol/dm<sup>3</sup> of Pb<sup>2+</sup> ions (e); the major HAP peaks are labeled “H”, while other peaks belong to hydroxyapatite.

According to Fig. 6, Cd<sup>2+</sup>, Zn<sup>2+</sup> and Sr<sup>2+</sup> exchanged powders represent monophasic solid systems, isomorphous with the original calcium–HAP. All of the samples belong to the hydroxyapatite hexagonal structural type, with the space group P6<sub>3</sub>/m. On the other hand, the product obtained after interaction of HAP with Pb<sup>2+</sup> solution, represents a two phase system. This sample was dominated by HPY, with minor amounts of Pb-exchanged HAP. The calculated unit cell parameters  $a=b$  and  $c$ , as well as crystallite size are presented in Table 3. In mixed cadmium-, zinc-, strontium- and lead-hydroxyapatite, the concentrations of these cations in solid phase are too small to induce significant modifications of cell parameters. A slight decrease of unit cell parameters were observed in cadmium and zinc substituted HAP, and slight increase in the lead substituted sample. This is in accordance with smaller ionic radii of Cd<sup>2+</sup> and Zn<sup>2+</sup> and larger ionic radius of Pb<sup>2+</sup> in respect to Ca<sup>2+</sup>. The unit cell parameters obtained for precipitated HPY are close to values of synthetic sample ( $a=b=9.877$  and  $c=7.427$ ) [8].

The products of HAP reaction with aqueous Pb<sup>2+</sup> have smaller particle size, which may be a consequence of rapid dissolution of original HAP and precipitation of numerous small nuclei of HPY in solution [33].

Table 3  
Unit cell parameters  $a$  and  $c$ , and crystallite size along the 002 and 300 plane, of HAP and products of the reaction of HAP with divalent metal solutions.

Solid phase	Unit cell parameters (Å)		Crystallite size (Å)	
	$a$	$c$	L <sub>002</sub>	L <sub>300</sub>
HAP	9.433 (2)	6.881 (2)	390.29	150.83
Cd–HAP	9.428 (2)	6.874 (2)	351.79	146.52
Zn–HAP	9.432 (2)	6.877 (2)	355.14	151.48
Sr–HAP	9.434 (3)	6.881 (2)	362.68	156.24
Pb–HAP	9.438 (4)	6.884 (4)	143.05	119.65
HPY	9.853 (4)	7.405 (4)	123.60	109.77

These results are in accordance with experimental data reported by other authors [33–36], as well as theoretical predictions based on a molecular modeling [37], confirming that the main mechanism of Pb immobilization is dissolution of HAP followed by precipitation of a new, more stable Pb-phosphate phase belonging to the pyromorphite family.

### 3.4. Effect of competing cations

The effects of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$ , on divalent metal sorption by HAP were studied as a function of competing cation concentrations. As it is shown in Table 4, the selectivity of HAP towards investigated cations remains the same in the presence of all competing cations ( $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Sr}^{2+}$ ). Under applied experimental conditions, neither of them influenced  $\text{Pb}^{2+}$  immobilization (99.9% sorbed). Monovalent metals, as well as  $\text{Mg}^{2+}$  had little effect on the removal of other cations (88.2–90.9% of  $\text{Cd}^{2+}$ , 82.6–84.1% of  $\text{Zn}^{2+}$  and 39.2–43.3% of  $\text{Sr}^{2+}$  was sorbed over the entire concentration range of  $\text{Na}^+$  and  $\text{K}^+$  and  $\text{Mg}^{2+}$ ). Finally, sorption of  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Sr}^{2+}$  was reduced in the presence of  $\text{Ca}^{2+}$ . Sorption of  $\text{Sr}^{2+}$  was the most effected. With an increase of  $\text{Ca}^{2+}$  concentration from  $5 \times 10^{-4}$  to  $5 \times 10^{-3} \text{ mol/dm}^3$ ,  $\text{Sr}^{2+}$  sorption decreased by  $\sim 13\%$ , while sorption of  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  was reduced by  $\sim 9$  and  $\sim 8\%$ , respectively. These results confirm that HAP selectively and efficiently removes investigated divalent metals from the solutions of competing cations, commonly present in the environment.

Previous investigations of the sorption of alkaline and earth alkaline cations on HAP showed a combination of ion-exchange and specific cation sorption, with the binding affinity in the order  $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$  [38]. It would be reasonable to expect

Table 4  
The effect of the competing cation on the percent of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Sr}^{2+}$  sorbed by HAP

Competing cation ( $\text{mol/dm}^3$ )	% of metal cation sorbed			
	$\text{Pb}^{2+}$	$\text{Cd}^{2+}$	$\text{Zn}^{2+}$	$\text{Sr}^{2+}$
$\text{Ca}^{2+}$				
$5 \times 10^{-4}$	99.9	89.2	79.1	37.6
$1 \times 10^{-3}$	99.9	84.7	76.3	36.3
$2.5 \times 10^{-3}$	99.9	82.2	73.0	29.1
$5 \times 10^{-3}$	99.9	80.1	71.0	24.0
$\text{Mg}^{2+}$				
$5 \times 10^{-4}$	99.9	88.9	82.9	40.2
$1 \times 10^{-3}$	99.9	88.9	83.0	39.2
$2.5 \times 10^{-3}$	99.9	88.7	83.1	40.0
$5 \times 10^{-3}$	99.9	88.2	82.6	39.9
$\text{Na}^+$				
$5 \times 10^{-4}$	99.9	90.1	84.1	42.5
$1 \times 10^{-3}$	99.9	89.9	83.1	43.0
$2.5 \times 10^{-3}$	99.9	89.9	84.1	42.5
$5 \times 10^{-3}$	99.9	89.7	82.6	40.5
$\text{K}^+$				
$5 \times 10^{-4}$	99.9	90.7	82.9	42.0
$1 \times 10^{-3}$	99.9	89.9	83.4	43.3
$2.5 \times 10^{-3}$	99.9	90.9	83.9	42.3
$5 \times 10^{-3}$	99.9	90.2	82.9	41.2

that these cations will affect (in the same order) the sorption of other species that compete for the same active sites. Once more, the dissolution/precipitation mechanism of  $\text{Pb}^{2+}$  removal by HAP was confirmed, since sorption of this cation was not influenced by the presence of examined co-ions.  $\text{Ca}^{2+}$ , as a parent cation of HAP, exhibits more affinity for the HAP surface sites than  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$ , thus reducing the sorption of  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Sr}^{2+}$ . As a consequence of the lowest sorption affinity and the major chemical similarity with  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  sorption was reduced the most.

## 4. Summary

The influence of equilibration conditions on divalent Pb, Sr, Zn and Cd uptake from aqueous solutions by low-crystalline HAP powder was investigated. All experimental data have confirmed the differences in the  $\text{Pb}^{2+}$  sorption mechanism in respect to the mechanism of  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Sr}^{2+}$  sorption. The removal of  $\text{Pb}^{2+}$  from the solution was almost complete at the entire initial pH range (3–12). Sorption of other cations generally increased with increase of pH. Uptake of  $\text{Pb}^{2+}$  was the most rapid—30 min was required for attaining the sorption equilibrium, while for other cations 24 h was necessary. Kinetic data were well fitted by the pseudo-second order equation. Sorption isotherms were well-characterized by a linear form of the Langmuir equation, from which maximum sorption capacities were calculated: 3.263 mmol  $\text{Pb}^{2+}/\text{g}$ , 0.601 mmol  $\text{Cd}^{2+}/\text{g}$ , 0.574 mmol  $\text{Zn}^{2+}/\text{g}$  and 0.257 mmol  $\text{Sr}^{2+}/\text{g}$ . Metal uptake was followed by final pH decrease and linear increase of a  $\text{Ca}^{2+}$  aqueous concentration. HAP selectively sorbes investigated metals from the solutions of cations commonly present in the environment ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$ ). Neither of them influenced  $\text{Pb}^{2+}$  immobilization, while presence of  $\text{Ca}^{2+}$  slightly reduced sorption of other cations in the order  $\text{Sr}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}$ . The dissolution/precipitation mechanism was found to be the dominant mechanism of  $\text{Pb}^{2+}$  immobilization by HAP, while for  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Sr}^{2+}$  the existence of ion-exchange and specific sorption mechanisms was confirmed. The observed good buffer properties of HAP are particularly important for its possible practical application (treatment of acid rock drainage, acid mine drainage and wastewater from chemical processing).

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