Chemical Engineering Journal 148 (2009) 80–88

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

The influence of equilibration conditions and hydroxyapatite physico-chemical properties onto retention of Cu^{2+} ions

M. Šljivić*, I. Smičiklas, I. Plećaš, M. Mitrić

The Vinča Institute of Nuclear Sciences, P.O. Box 522, 11001 Belgrade, Serbia

ARTICLE INFO

Article history:
Received 2 November 2007
Received in revised form 28 July 2008
Accepted 1 August 2008

Keywords:
Hydroxyapatite
Cu^{2+}
Sorption
Desorption

ABSTRACT

The influence of equilibration conditions and hydroxyapatite (HAP) physico-chemical properties onto retention of Cu^{2+} ions was studied in batch conditions. The amount of cation removed from the solution increased with increasing pH, reaching almost 100% at pH 3, 4 and 7 for 5×10^{-4}, 10^{-3} and 5×10^{-3} mol/dm^3 solutions, respectively. Contact time necessary for reaching equilibrium was found to increase with the increase of Cu^{2+} concentration. Kinetic and equilibrium data were best described by pseudo-second-order kinetic model and Langmuir theoretical model. The calculated values of separation factors and Gibbs free energy change confirmed that the sorption was spontaneous and thermodynamically feasible at room temperature. The experiments conducted using HAP samples with different physico-chemical characteristics have revealed that the amounts of sorbed Cu^{2+} depended mainly on the specific surface area and crystallinity of the applied powders. Desorption of Cu^{2+} was more efficient in acidic conditions than in the solution of competing cation—Ca^{2+}. The samples with higher sorption capacities also demonstrated higher stability; consequently, from the aspects of both higher sorption and lower desorption, utilization of low-crystalline HAP samples with high specific surface area was superior for immobilization of Cu^{2+} ions. Taking into account molar Cu/Ca ratios, observed final pH changes, copper speciation in the function of pH and the results of X-ray diffraction analyses, conclusions about sorption mechanisms at different experimental conditions were derived.

1. Introduction

Copper is a heavy metal widespread in the environment, with the average concentrations in the earth's crust and soil of 24–55 and 20–30 mg/kg, respectively [1]. However, due to various human activities, the amount of Cu^{2+} in the environment increases every year. The largest sources of copper pollution are metal mining and manufacturing, as well as petroleum refining, coal mining and manufacturing of cement, lime, concrete, paper, wood, glass and ceramic products.

In small concentrations this element is essential for living organisms. Furthermore copper deficiency may cause various effects on human health such as anemia, osteoporosis, decreased glucose tolerance, arthritis, cardiac arrhythmias and neurological problems [2]. On the other hand, excess copper in cells causes toxicity, as the redox properties, essential for its function in cuproenzymes, can also result in marked reactive oxygen species formation that can damage lipids, nucleic acids and proteins [3]. Therefore, Cu^{2+} containing effluents from various industries require special treatment before their discharge into receiving waters.

Sorption technologies, as a method for the removal of heavy metals from wastewaters, have gained much attention in the last decade due to their simplicity, low cost and high efficiency [4]. Various mineral sorbents have been evaluated as potential Cu^{2+} removal agents from aqueous media, such as clinoptilolite [5], bentonite [6], palygorskite [7], kaolinite [8], aluminum hydroxide and oxyhydroxides [9]. Furthermore, a potential application of various organic materials: activated carbon [10], peanut hull pellets [11], dried sunflower leaves [12], sugar beet pulp [13], Capsicum annuum seeds [14], etc., for Cu^{2+} removal has been considered as well.

Apatite materials of different origin (mineral, biological and synthetic) were fund to be potential sorbents for numerous heavy metals and radionuclides [15,16]. Ion-exchange with Ca^{2+} from apatite crystal lattice, dissolution/precipitation and specific cation sorption were identified as main removal mechanisms, depending on the cation type. In comparison to other divalent, toxic, heavy metals such as Pb^{2+}, Cd^{2+} and Zn^{2+}, much less attention has been paid to Cu^{2+} immobilization by apatites in the scientific literature. The understanding of Cu^{2+} interaction with apatite is not only important for finding better ways to treat contaminated sites, but it is also useful for understanding the processes which occur at

---

* Corresponding author. Tel.: +381 11 8066439; fax: +381 11 2455 943.
E-mail address: marijasljivic@vin.bg.ac.yu (M. Šljivić).

1385-8947/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2008.08.003

the phosphate rock–Cu^{2+} solution interface, and phenomena that take place when this cation interacts with bones and teeth which consist mainly of apatite [17]. Cu^{2+} sorption was studied using: carbonate hydroxyapatite derived from eggshell waste [18], bone char [19], spent animal bones [20], phosphate rocks [21] and synthetic powder [22]. Although apatite sorbents were, in general, evaluated as promising agents for Cu^{2+} removal from aqueous media, the comparison of sorption capacities and main operating sorption mechanisms is difficult due to the presence of various apatites and other solid phases in phosphate rocks and bone materials.

The understanding of the removal mechanism is fundamental in properly designing and operating sorption processes, therefore in this study synthetic calcium hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAP) samples were used as Cu^{2+} sorbents. The aims of this study were to investigate both the influence of equilibration conditions (contact time, pH and Cu^{2+} concentration) as well as HAP physico-chemical properties on Cu^{2+} sorption, in order to evaluate main sorption mechanisms at different experimental conditions, and to estimate the reversibility of Cu^{2+} immobilization by HAP using leaching tests. Presented results have potential application in optimization of HAP matrix, as well as equilibrium conditions, for Cu^{2+} immobilization.

2. Materials and methods

2.1. HAP sorbents

As sorbents, synthetic HAP samples were used (denoted in this study as HAP1-8). They were prepared by neutralization of $Ca(OH)_2$ with H_3PO_4 [23], at various temperatures, mixing speeds, concentrations of reactants, H_3PO_4 addition rates, and with/without inert atmosphere and precipitate aging, in order to produce powders with different physico-chemical characteristics. In addition, the commercial HAP (DNA grade Bio-Gel HTP) supplied by Bio Rad laboratory, Richmond, CA, was used (denoted as HAP9).

2.2. Bach sorption procedure

2.2.1. Influence of the sorption conditions

The influence of pH, contact time and initial cation concentration on Cu^{2+} removal from aqueous solutions was studied in a batch system, using one of the HAP samples denoted as HAP5. Solutions of Cu^{2+} ions were prepared by dissolving an adequate mass of $Cu(NO_3)_2 \cdot 3H_2O$ (Merck, p.a.) in distilled water. PVC flasks, containing 20 ml of Cu^{2+} solution and 0.1 g of HAP sample were agitated on a horizontal shaker with a constant speed of 120 rpm, at room temperature (20 ± 1 °C). The sorption experiments were carried out in systems without pH control; more precisely, only initial pH values were adjusted (adding 0.1 mol/dm^3 HNO_3 and KOH), thus equilibrium pH values were governed mainly by a buffering capacity of the sorbent itself. The conditions under which experiments were conducted are given in Table 1.

After sorption, the solid phase was separated from the solution using the blue-band filter paper (Quant, Grade 391). The exact initial Cu^{2+} concentrations, as well as the Cu^{2+} and Ca^{2+} concentrations after the sorption were measured by PerkinElmer Analyst 200 Atomic Absorption Spectrometer (AAS). The flame type was air/acetylene, while absorption wavelengths were 327.4 and 422.7 nm for Cu^{2+} and Ca^{2+}, respectively. Initial and final pH values were measured with a glass electrode pH meter (Inolab, WTW). The amount of the sorbed Cu^{2+} was calculated as the difference between the solution concentrations before and after the sorption. The relative standard deviations of AAS measurements were less than 3%.

2.2.2. Influence of the physico-chemical properties of the sorbent

A single point sorption experiments were conducted to provide a comparison of the sorptive capacity of 9 HAP sorbents. In order to assure that HAP properties are the only system variable, all experiments were performed at the same time, using the same Cu^{2+} solution (initial Cu^{2+} concentration 10^{-2} mol/dm^3, initial pH 5). The batches containing 0.1 g of different sorbents, and 20 ml of solution were shaken for 24 h with the agitation speed of 120 rpm. Sorption experiments were conducted in duplicate, and the average values of Cu^{2+} sorbed, Ca^{2+} released and final pH are presented.

X-ray diffraction (XRD) analyses of different HAP-Cu products were performed to determine the structural changes after metal cation sorption. A Philips PW 1050 instrument, with Cu K$\alpha_{1,2}$ Ni-filtered radiation was used, while the patterns were registered in the 2Θ range 10–60° with a scanning step size of 0.05°.

2.3. Batch desorption procedure

Desorption of Cu^{2+} ions from HAP was investigated as a function of the quantity of Cu^{2+} sorbed, as well as a function of HAP characteristics. For that purpose, solid residues obtained after Cu^{2+} sorption from the solutions of different initial concentrations by HAP5, and the residues derived after sorption on different HAP samples were considered. Solids were rinsed with distilled water and dried at 105 °C for 24 h. As apatite materials are known for their excellent buffering properties, aggressive acid leaching solution, TCLP 2 (pH 2.93) proposed by EPA, was used [24]. In addition, reversibility of Cu^{2+} sorption by various HAP samples was investigated using 10^{-2} mol/dm^3 $Ca(NO_3)_2$ solution, at initial pH 5.

The Cu-loaded powders were placed into the PVC flasks containing 20 ml of the leaching solution and shaken for 24 h, at room temperature. The suspensions were than filtered and the final pH values and Cu^{2+} concentrations in the liquid phase were quantified.

3. Results and discussion

3.1. Physico-chemical properties of HAP samples

The major physico-chemical properties of HAP powders are listed in Table 2 [23].

The variation of the synthesis parameters caused variation in physico-chemical properties of obtained samples. The values of specific surface area (Sp) were in the range from 24 to 72 m^2/g. As molar Ca/P ratio of 1.67 is characteristic for pure stoichiometric HAP, results from Table 2, indicated that all samples, except HAP4 and HAP8, were calcium deficient. The fractions of crystalline phase (X_c) ranged from 0.19 to 0.9, while the points of zero charge (pH_{PZC}) of all nine samples varied between 6.1 and 6.6.

Table 1
Experimental conditions for the study of the effect of process parameters onto Cu^{2+} sorption

	pH	Contact time	Initial Cu^{2+} concentration (mol/dm^3)
Effect of pH	2–10	24 h	5×10^{-4}, 10^{-3}, 5×10^{-3}
Effect of contact time	5	15 min to 48 h	5×10^{-4}, 10^{-3}, 5×10^{-3}
Effect of initial Cu^{2+} concentration	5	24 h	10^{-4} to 10^{-2}

Table 2
Physico-chemical properties of HAP powders [23]

Sample	Sp ($\pm 1\ m^2/g$)	Ca/P (± 0.03)	pHpzc (± 0.1)	X_c
1	41	1.59	6.1	0.69
2	72	1.62	6.4	0.28
3	67	1.60	6.2	0.36
4	60	1.67	6.5	0.72
5	58	1.59	6.6	0.63
6	72	1.55	6.5	0.19
7	47	1.65	6.6	0.72
8	24	1.70	6.6	0.90
9	64	1.53	6.6	0.28

Investigation of the influence of various sorption parameters was conducted using one representative sample—HAP5. This powder was selected as it was slightly Ca-deficient, like most of the samples prepared from aqueous solutions. Furthermore, given that the major differences between samples were observed comparing the values of specific surface areas and crystallinity, we picked HAP5, which exhibited moderate Sp and X_c values.

3.2. *Effect of pH*

One of the most important parameters influencing sorption processes is pH, which controls not only dissociation of sorbent surface sites, but also the solution chemistry and the speciation of the metal cations.

The excellent buffering properties of synthetic HAP powders are well known, i.e. the addition of HAP will increase the pH of acidic and decrease pH of alkaline solutions to the constant final value (pH_{PZC}), as a result of sorption of either H^+ or OH^- ions from the solution by surface active sites [25]. For the solutions of electrolytes (such as KNO_3) which are inert in respect to HAP surface, the buffering pH range of synthetic samples is 4–10 [23,26]. The pH_{PZC} value of sample HAP5, determined in KNO_3 solution was 6.6 (Table 2). Practical meaning of pH_{PZC} is that the sorbent will be positively charged for pH values below PZC, and negatively for pH above PZC.

Metal cations in aqueous solution convert to different hydrolysis products, depending on the solution pH. In the case of copper, a major difficulty in predictions of the chemical behavior with respect to complexation, adsorption, and precipitation processes is a lack of convincing equilibrium data for the second hydrolysis equilibrium. According to the experimental work of Vuceta and Morgan [27] a hydrolysis constant for the formation of $Cu(OH)_2$ is closer to the value proposed by Spivakovski and Makovskaya $\log\beta = -13.7$ [28] than to the value proposed by Mesmer and Baes $\log\beta = -17.3$ [29]. Using the value of $\log\beta = -13.7$, the dominant species in the pH range 2–5 are Cu^{2+} ions. At pH 6 there are three species in equilibrium: Cu^{2+} (in large quantity) and $CuOH^+ = Cu(OH)_2$ (in small quantity), while at pH > 6 insoluble hydroxide $Cu(OH)_2$ is dominant.

Final pH values, amounts of Cu^{2+} sorbed and Ca^{2+} released after interaction of Cu^{2+} with HAP sorbent are presented in Fig. 1a–c, respectively.

In respect to the pH_{PZC} value of the sample determined in inert electrolyte, the pH_{PZC} values obtained as points where pH_{final} vs. pH_{inital} plots crosses the line $pH_{final} = pH_{initil}$, were lower for Cu^{2+} solutions and decreased from ~5.8 to ~4.6 with the increase of Cu^{2+} concentration from 5×10^{-4} to $5 \times 10^{-3}\ mol/dm^3$ (Fig. 1a). The decrease of pH_{PZC} value was caused by the specific sorption of positively charged species on protonated sorbent active sites from which H^+ ions were liberated into the solution [30].

Furthermore, plateau parts of pH_{final} vs. $pH_{initial}$ plots became shorter (~4 to ~6) when compared to inert electrolyte [23], suggesting that the buffering capacity of HAP became less significant in Cu^{2+} solutions. The sharp increase in final pH was observed for initial pH 6–7, followed by a slow increase at higher initial pH values.

Fig. 1b, demonstrates the quantity of Cu^{2+} removed in the presence of HAP vs. solution pH. For lower initial Cu^{2+} concentrations removal rate was slightly suppressed at pH 2–3, while relatively constant and pH independent in the range of 4–10. In pH range 2–3 lower sorption of Cu^{2+} ions was caused by the competing effect of H^+ ions, and the increased solubility of the HAP sorbent. For the highest metal concentration studied, sorbed amount of Cu^{2+} increased from pH 2 to 4, remained constant in the range of 4–6, significantly increased from pH 6 to 7 and than remained constant to pH 10.

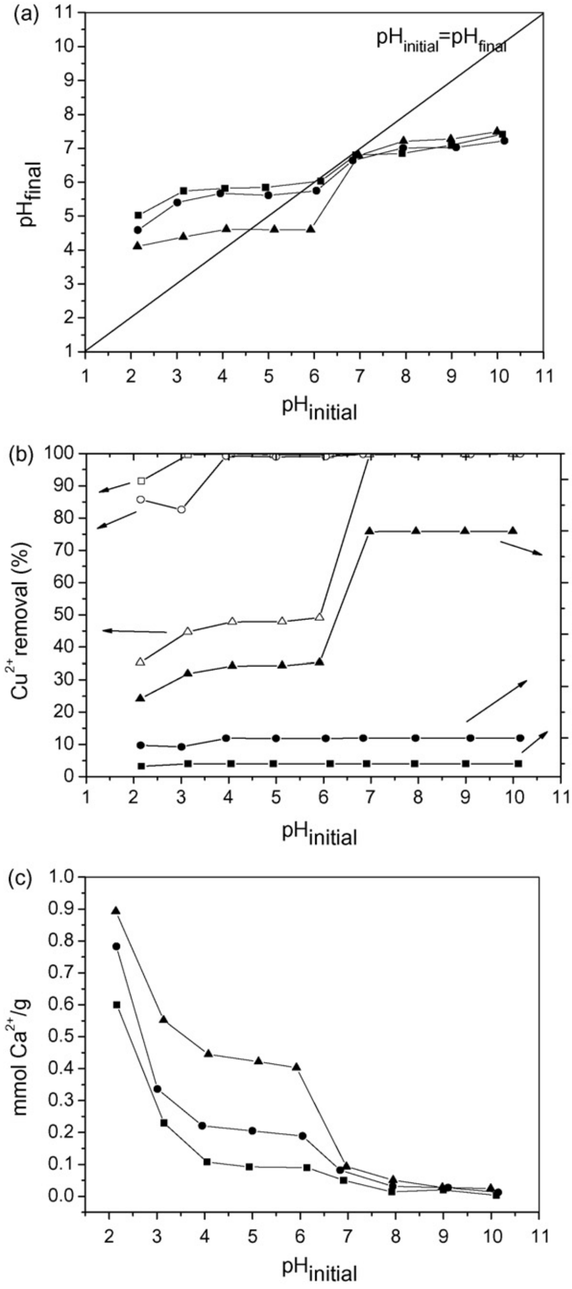

Fig. 1. Effect of initial pH on (a) final pH values, (b) amounts Cu^{2+} sorbed by HAP5 and (c) amounts of Ca^{2+} released. *Experimental conditions*: $5 \times 10^{-4}\ mol/dm^3$ (■), $10^{-3}\ mol/dm^3$ (●) and $5 \times 10^{-3}\ mol/dm^3$ (▲) $Cu(NO_3)_2$, contact time 24 h, solid/solution ratio 1:200.

In the presence of HAP, nearly 100% of Cu^{2+} removal was achieved at pH 3, 4 and 7 for 5×10^{-4}, 10^{-3} and 5×10^{-3} mol/dm^3 solutions, respectively.

Another important factor for estimation of Cu^{2+} sorption mechanism is the quantity of Ca^{2+} ions released from HAP crystal lattice. The amounts of Ca^{2+} desorbed increased with the increase of Cu^{2+} initial concentration, while decreased with initial pH increase (Fig. 1c).

Taking into account molar Cu/Ca ratios, observed final pH changes and copper speciation in the function of pH, conclusions about sorption mechanism can be derived.

In the initial pH interval 2–4, the Cu/Ca molar ratios for all investigated sorbate concentrations were <1, suggesting that, due to enhanced HAP dissolution, more cations were released in respect to the amount of cations sorbed. In the buffering pH range (4–6) the Cu/Ca ratios were ~1. As Cu^{2+} cations were dominant species up to pH 6, ion-exchange or dissolution of HAP and precipitation of Cu-bearing solid phase could be anticipated as dominant mechanisms, whereas final pH decrease in respect to PZC value confirmed existence of another bonding mechanism-specific cation sorption. For pH > 6, the Cu/Ca molar ratios were >1. Because of increased HAP stability in alkaline solutions [31], ion exchange or dissolution/precipitation sorption mechanisms were insignificant, while precipitation of $Cu(OH)_2$ became the main reason for enhanced Cu removal at pH > 6.

In order to avoid precipitation of copper at pH > 6, or HAP dissolution at pH < 4, the initial pH 5 was chosen for further experiments.

3.3. *Effect of contact time*

The influence of contact time was investigated in the range of 15 min to 48 h, for different initial Cu^{2+} concentrations (5×10^{-4}, 10^{-3} and 5×10^{-3} mol/dm^3). After separation of solid from liquid phase, final pH values, Cu^{2+} and Ca^{2+} concentrations in the solution were measured as the dependent variables of time. This functionality is presented in Fig. 2.

The kinetics of Cu^{2+} removal by HAP was a two-step process (Fig. 2a). At the beginning of the sorption, the number and availability of HAP surface active sites, as well as the highest driving force for the mass transfer, caused the rapid Cu^{2+} uptake. This rapid phase of Cu^{2+} sorption was followed by a slower increase of the amount of cation sorbed, where, due to gradual occupancy of active sites and decreasing Cu^{2+} concentration in the liquid phase, sorption became less efficient. The time necessary for achieving equilibrium increased with the initial Cu^{2+} concentration increase: 180 min for 5×10^{-4}, 360 min for 10^{-3} and approximately 24 h for 5×10^{-3} mol/dm^3, respectively. The amounts of Cu^{2+} sorbed at equilibrium increased with the increase of initial Cu^{2+} concentration as well. Practical residence times in water purification processes are significantly shorter than the equilibrium times, observed under experimental conditions applied in this study. Therefore, additional optimization of stirring conditions (type of agitation device, agitation speed, etc.) is required, to improve the kinetic feasibility of Cu^{2+} removal by HAP.

Along with the Cu^{2+} sorption, release of Ca^{2+} cations from HAP crystal lattice was observed (Fig. 2a). The molar Cu/Ca ratios were ~1 for the lower Cu^{2+} concentration (5×10^{-4} and 10^{-3} mol/dm^3) and slightly above 1 for 5×10^{-3} mol/dm^3 of Cu^{2+}. These data confirmed that Cu^{2+} sorption by HAP included either ion-exchange with Ca^{2+} or dissolution/precipitation.

The pH of the solution also varied with time (Fig. 2b). Compared to the initial pH 5, general increase of final pH was observed for lower Cu^{2+} concentrations (5×10^{-4} and 10^{-3} mol/dm^3) reaching equilibrium values of 5.87 and 5.72, respectively. Conversely, for the initial concentration of 5×10^{-3} mol/dm^3, pH decrease was detected with the equilibrium value of 4.57. However, all final pH values were lower then pH_{PZC} value of the HAP sample, verifying that the replacement of superficial H^+ ions with Cu^{2+} contributed to the overall sorption mechanism, especially for high metal concentrations.

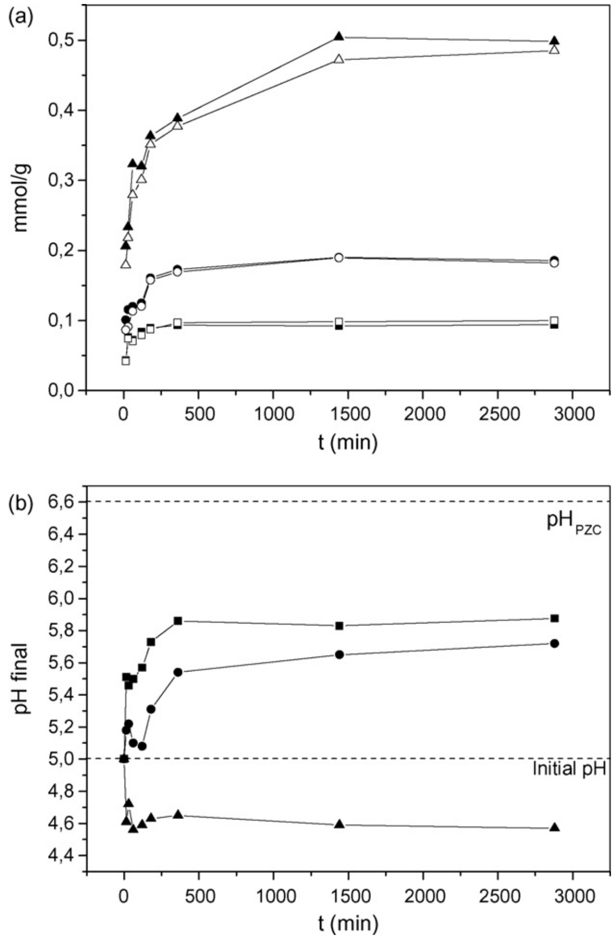

Fig. 2. Effect of contact time on (a) amounts of Cu^{2+} sorbed and Ca^{2+} released (hollow symbols) and (b) final solution pH. *Experimental conditions*: initial pH 5, solid/solution ratio 1:200, initial pH 5, Cu^{2+} concentrations 5×10^{-4} mol/dm^3 (■), 10^{-3} mol/dm^3 (●) and 5×10^{-3} mol/dm^3 (▲).

The contact time of 24 h was chosen for the further sorption experiments.

3.3.1. *Kinetic modeling*

The experimental results were analyzed using two most widely applied kinetic models for fitting sorption kinetic data: pseudo-first-order equation proposed by Lagergren [32] and pseudo-second-order model proposed by Ho and McKay [33]. The detailed derivations of these equations are described in the cited literature, while the linear forms of pseudo-first- and pseudo-second-order equations are given by following equations:

$$\log(q_e - q_t) = \log(q_e) - k_1 \times \frac{t}{2.303} \qquad (1)$$

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

where t (min) is the contact time, q_e and q_t (mmol/g) are amounts of sorbed Cu^{2+} at equilibrium and time t, and k_1 (1/min) and k_2 (g/mmol min) are the rate constants of pseudo-first- and pseudo-second-order kinetics, respectively.

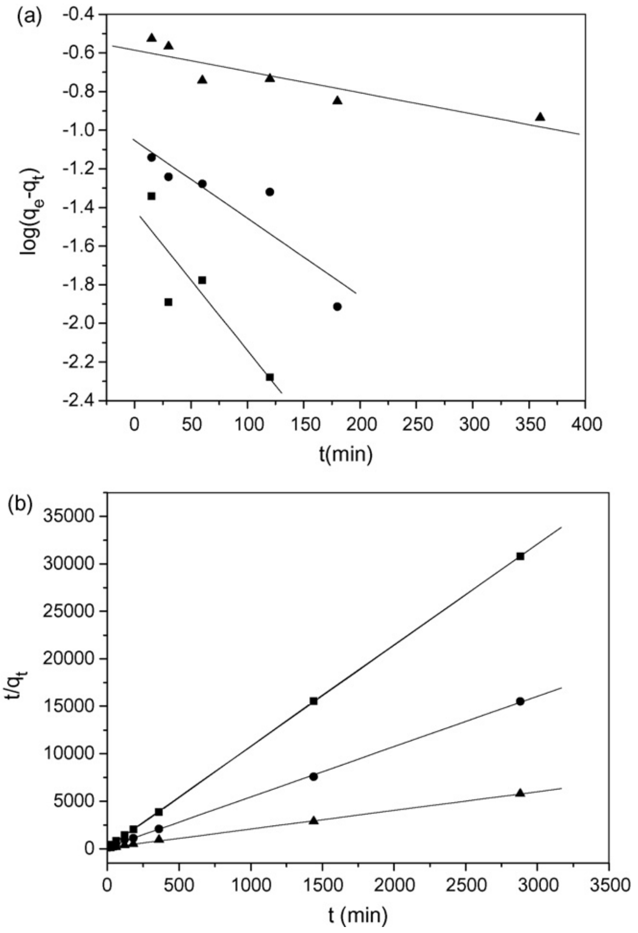

Fig. 3. Linear fitting of the kinetic data by (a) pseudo-first-order kinetic model and (b) pseudo-second-order kinetic model. Cu^{2+} concentrations 5×10^{-4} mol/dm^3 (■), 10^{-3} mol/dm^3 (●) and 5×10^{-3} mol/dm^3 (▲).

The initial sorption rate h (mmol/g min) can be obtained using calculated values of pseudo-second-order constant and equilibrium sorbed amounts, by the following expression:

$$h = k_2 \times q_e^2 \tag{3}$$

From the slopes and intercepts of the linear dependencies which are presented in Fig. 3a and b, rate constants and the amounts of Cu^{2+} sorbed at equilibrium, were calculated (Table 3).

Comparing the results of kinetic data fitting (Table 3) it can be concluded that for Cu^{2+} sorption by HAP pseudo-second-order model provided better correlation coefficients, and more realistic q_e values—closer to the values obtained experimentally. Pseudo-first-order model correlation factors were lower, while calculated equilibrium amounts of the sorbed Cu^{2+} presented only about 50% of the real value.

The calculated k_2 values decreased from 0.884 to 0.037 g/mmol min, with the increase of sorbate concentration (Table 3) whereas initial sorption rates were constant (0.007 mmol/g min) for 5×10^{-4} and 10^{-3} mol/dm^3 and increased to 0.009 mmol/g min for the highest Cu^{2+} concentration (5×10^{-3} mol/dm^3).

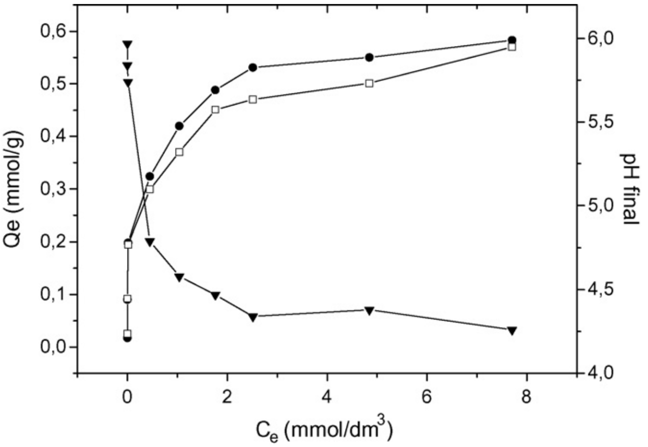

Fig. 4. Sorption isotherm for Cu^{2+} onto HAP5—the functionality between equilibrium Cu^{2+} solution concentration and amounts of Cu^{2+} sorbed (●), Ca^{2+} released (□) and final pH values (▼). *Experimental conditions*: pH initial 5, equilibration time 24 h, solid/solution ratio 1:200.

Processes that were found to comply with the pseudo-second-order kinetic model include different sorption mechanisms such as surface complexation, ion-exchange and dissolution/precipitation [34–36], therefore, the significant correlation between experimental data and a pseudo-second-order kinetic model is useful for the purpose of comparison and q_e prediction, but is unlikely to describe the actual sorption mechanism. According to the literature, the fact that the pseudo-second-order kinetics is the best fit model for certain sorbent/sorbate system indicates that the sorption rate depends on the concentration of sorbate at the sorbent surface and that chemical sorption is the rate-controlling step [37].

3.4. *Effect of initial solute concentration*

The influence of the initial solute concentration on the sorption process was presented by a sorption isotherm (Fig. 4) which described the relationship between equilibrium concentration of Cu^{2+} at HAP surface (Q_e) and equilibrium concentration of Cu^{2+} in the solution (C_e).

The amounts of sorbed metal cations increased with the increase of initial solution concentrations until the equilibrium was achieved. After that, the removal of Cu^{2+} became independent of the initial cation concentration, due to occupancy of all active sites on HAP surface. The experimentally derived maximum sorption capacity of HAP5 sample was 0.582 mmol/g.

The sorption of Cu^{2+} from the solutions of different initial concentrations, was followed by Ca^{2+} aqueous concentration increase (Fig. 4), however, the Cu/Ca molar ratios for initial Cu^{2+} concentrations higher than 10^{-3} mol/dm^3 were slightly lower than 1.

Table 3
Amounts of Cu^{2+} sorbed at equilibrium (q_e), sorption rate constants (k_1 and k_2) and corresponding correlation coefficients (R^2), for pseudo-first- and pseudo-second-order kinetic models

Cu^{2+} (mol/dm^3)	Peudo-first-order			Pseudo-second-order				$q_{e,exp.}$ (mmol/g)
	R^2	q_e (mmol/g)	k_1 (min^{-1})	R^2	q_e (mmol/g)	k_2 (g/mmol min)	h (mmol/g min)	
5×10^{-4}	0.763	0.039	1.67×10^{-2}	0.999	0.094	0.884	0.007	0.094
1×10^{-3}	0.811	0.088	9.26×10^{-3}	0.999	0.189	0.189	0.007	0.185
5×10^{-3}	0.811	0.260	2.53×10^{-3}	0.998	0.509	0.037	0.009	0.498

Table 4
Correlations coefficients and sorption parameters obtained using Langmuir, DKR and Freundlich model

Model	Equation	Sorption Parameters	
Langmuir	$\frac{C_e}{Q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L}$	R^2	0.998
		q_m (mmol/g)	0.585
		K_L (L/mmol)	5.062
DKR	$\ln Q_e = \ln q_m - \beta \times \varepsilon^2$	R^2	0.855
	$\varepsilon = R \times T \times \ln\left(1 + \frac{1}{C_e}\right)$	q_m (mmol/g)	0.902
		β (mol^2/J^2)	2.621×10^{-9}
Freundlich	$\ln Q_e = \ln K + n \times \ln C_e$	R^2	0.828
		K (mmol^{1-n} dm^{3n} g^{-1})	0.392
		n	0.296

Final pH values decreased with the increase of Cu^{2+} concentration. This sorbate concentration dependant relationship between a sorbed metal quantity, a pH change and a quantity of released Ca^{2+}, confirmed the presence of two sorption mechanisms: specific cation sorption and displacement of Ca^{2+} ions from HAP crystal lattice.

3.4.1. Equilibrium data modeling

The experimental equilibrium data were fitted using Langmuir, DKR and Freundlich models (Table 4). Sorption parameters are as follows: q_m (mmol/g) is the maximum sorption capacity, K_L (dm^3/mmol) the Langmuir constant related to the energy of adsorption, β (mol^2/kJ^2) the DKR constant related to adsorption energy, ε (kJ/mol) the Polanyi potential, and K (mmol^{1-n} dm^{3n} g^{-1}) and n are the Freundlich constants related to the capacity and intensity of the sorption process. Graphical illustration of the linear data fitting is given in Fig. 5, while calculated sorption parameters and the degree of correlation between the sorption data and applied models are given in Table 4.

It is obvious from Table 4, that the highest correlation coefficient was obtained using Langmuir model, suggesting that the Cu^{2+} ions were sorbed by HAP in a monolayer. Furthermore, the q_m value calculated by this equation corresponded well with the experimentally obtained sorption capacity. Langmuir isotherm was approved to be useful for calculation of the theoretical sorption capacity in many mineral sorbent/metal ion systems [38–40].

Knowing the Langmuir constant, K_L, the dimensionless separation factor (R_L) can be derived using the expression [41]:

$$R_L = \frac{1}{1 + K_L \times C_0} \tag{4}$$

where C_0 (mol/dm^3) denotes the initial solution concentration.

R_L values indicate that the sorption process is: unfavorable for $R_L > 1$, linear for $R_L = 1$, favorable for $0 < R_L < 1$, or irreversible for $R_L = 0$.

For initial Cu^{2+} concentration range 10^{-4} to 10^{-2} mol/dm^3, used in this study, calculated R_L values were between 0.665 and 0.019, which indicated that the Cu^{2+} sorption by HAP5 sample was favorable.

Furthermore, the value of Gibbs free energy change (ΔG°) points out if the process is feasible and unforced. ΔG° can be calculated using the equation:

$$\Delta G^\circ = -R \times T \times \ln K_L \tag{5}$$

where ΔG° (kJ/mol) is standard free energy change, R (8.314 J/mol K) the universal gas constant, and T (K) is absolute temperature.

For the Cu^{2+}/HAP system, negative value of ΔG° (−21.132 kJ/mol) indicated that the process was thermodynamically feasible and spontaneous. The obtained ΔG° value was in the range of magnitudes, characteristic for ion-exchange processes and comparable to the results of Cu^{2+} sorption on various ion-exchangers: natural kaolinite −20.16 kJ/mol [8], natural vermiculate −29.29 kJ/mol [40] and synthesized zeolite −23.23 kJ/mol [42].

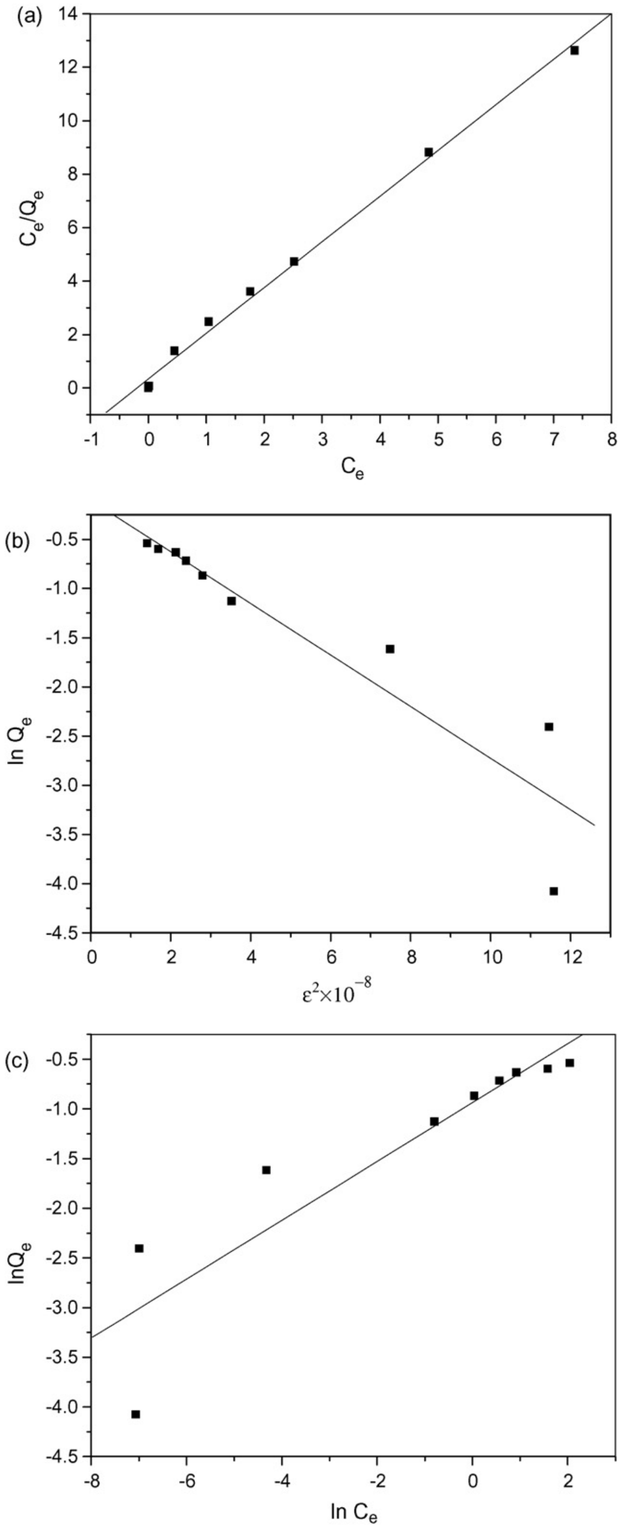

Fig. 5. Experimental data fitting using linear forms of Langmuir (a), DKR (b) and Freundlich (c) isotherms.

Table 5
The amounts of Cu^{2+} sorbed, Ca^{2+} released and pH values after metal sorption on different HAP samples

Sample	Final pH	Cu (mmol/g)	Ca (mmol/g)	Cu (mmol/m^2)
1	4.20 ± 0.04	0.436 ± 0.006	0.338 ± 0.001	0.011
2	4.38 ± 0.10	0.795 ± 0.031	0.714 ± 0.007	0.011
3	4.38 ± 0.01	0.651 ± 0.025	0.651 ± 0.044	0.010
4	4.42 ± 0.01	0.593 ± 0.011	0.600 ± 0.009	0.010
5	4.40 ± 0.07	0.582 ± 0.018	0.570 ± 0.014	0.010
6	4.32 ± 0.07	0.792 ± 0.018	0.742 ± 0.014	0.011
7	4.40 ± 0.06	0.486 ± 0.020	0.470 ± 0.001	0.010
8	4.42 ± 0.05	0.270 ± 0.013	0.275 ± 0.002	0.011
9	4.24 ± 0.01	0.792 ± 0.015	0.686 ± 0.006	0.012

Table 6
Correlation between HAP physico-chemical properties and Cu^{2+} sorption

HAP physico-chemical properties	Correlation with Cu^{2+} sorption (R)
Sp	0.959
Ca/P	−0.706
pHpzc	0.014
X_c	−0.934

3.5. Correlation between HAP properties and Cu^{2+} sorption

In order to establish the influence of HAP physico-chemical properties on the Cu^{2+} sorption process, equilibrium experiments on 9 HAP samples under the same experimental conditions were performed. The values of Cu^{2+} sorbed, Ca^{2+} released and final pH with deviations from average value obtained by working in duplicate (Table 5), showed differences in HAP powders sorption properties.

While the initial pH of Cu^{2+} solution was 5, after the metal sorption, decrease of final pH was observed (4.20–4.42). The sorption capacities of different synthetic HAP samples ranged from 0.270 to 0.795 mmol/g. Real comparison of HAP samples efficiency in Cu^{2+} removal to the literature data on other sorbent materials is difficult, due to dissimilar experimental conditions applied (pH, solid/solution ratio, temperature, etc.). For example, reported capacities of various commercial carbons are 0.410–0.964 mmol/g [10], bone char 0.709 mmol/g [19], phosphate rock 0.114 mmol/g [43], zeolites 0.404 mmol/g [44], kaolinite 0.234 mmol/g [8], sunflower leaves 1.407 mmol/g [12] and peanut pellets 0.189 mmol/g [11].

Along with the variation of the amount of Cu^{2+} sorbed by HAP samples, variation of released Ca^{2+} was also observed (0.275–0.742 mmol/g). The ratios between sorbed and desorbed metal cations (Cu/Ca), ranged from 0.98 to 1.29, for various samples, confirming that the release of Ca^{2+} ions was a part of the sorption mechanism.

Three HAP samples with different physico-chemical properties were chosen for the structure analysis. The XRD patterns of samples HAP2, HAP5 and HAP8, after interaction with 10^{-2} mol/dm^3 Cu^{2+} solution, are presented in Fig. 6. Unchanged crystal structure of synthetic HAP after Cu^{2+} sorption [22] as well as the appearance of peaks attributed to a new solid phase—libethenite, $Cu_2(PO_4)(OH)$ [21], were reported in the literature. In Fig. 6, the positions of the most characteristic libethatite peaks are marked. In the case of HAP2 sample (0.759 mmol Cu^{2+}/g), approximately 5% of the libethenite was detected. Due to broad HAP5 XRD peaks and lower sorption capacities of HAP5 and HAP8 samples (0.582 and 0.275 mmol Cu^{2+}/g, respectively), it was unfeasible to detect libethenite. However, as XRD cannot normally detect phases at concentration of approximately 1% of the sample matrix, the precipitation of a new crystalline phase could not be excluded. Therefore, beside ion-exchange with Ca^{2+} ions, Cu^{2+} may be sorbed via dissolution/precipitation mechanism.

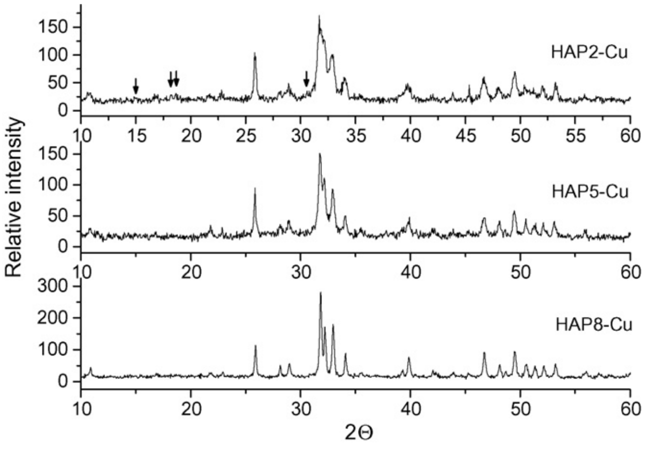

Fig. 6. XRD patterns of Cu-loaded samples HAP2, HAP5 and HAP8 (unmarked peaks belong to HAP phase; arrows denotes the position of major libethenite $Cu_2(PO_4)(OH)$ peaks).

The relationships between physico-chemical properties of HAP powders and Cu^{2+} sorption capacities were examined by correlation analysis. The linear correlation coefficients are presented in Table 6.

A good agreement existed between sorbed amount of Cu^{2+} ions and specific surface area ($R = 0.959$) as well as HAP crystallinity ($R = -0.934$). The Cu^{2+} uptake was directly proportional to the specific surface area and inversely to the sorbent crystallinity. The highest Cu^{2+} sorption capacities were obtained for the powders HAP2 and HAP6, which exhibited highest Sp and lowest X_c values (Table 2). The quantity of Cu^{2+} sorbed per square meter of HAP (Table 5) was almost constant (0.011 ± 0.001 mmol/m^2). The variations in HAP stoichiometry (Ca/P ratio) and especially pH_{PZC} values, in the investigated ranges, did not show notable correlation with the metal sorption. High correlation coefficients between sorption and HAP specific surface area, were also determined for Cd^{2+}, Zn^{2+} and Sr^{2+} cations [45]. The results implied that parameters of HAP synthesis, for this specific application, should be chosen in order to produce powders with high Sp (i.e. low reaction temperature; no aging of precipitate [23]).

3.6. Desorption

The results of leaching experiments are presented in Figs. 7 and 8. The percentages of desorption are relative vales calculated in respect to the amount of Cu^{2+} sorbed. Desorption of bonded Cu^{2+} ions depended on the amount of metal cation previously sorbed, HAP characteristics and the leaching solution composition.

Desorption from the same sample (HAP5), loaded with Cu^{2+} at different levels (Fig. 7), has shown that the percentages of Cu^{2+} released in acidic solution increased from 20 to 50% with the increase of sorbed amount of metal from 0.017 to 0.601 mmol/g.

The absolute amounts of metal desorbed increased in the same way from 1.11 to 96.65 mg/dm^3. The buffering properties of the sorbent participated in the desorption process, as well as in the sorption. In comparison with initial pH of TCLP solution, pH values after desorption were in the range of 4.16–3.95.

The desorption processes was dependant on the physico-chemical properties of the sorbents. These results are shown in Fig. 8.

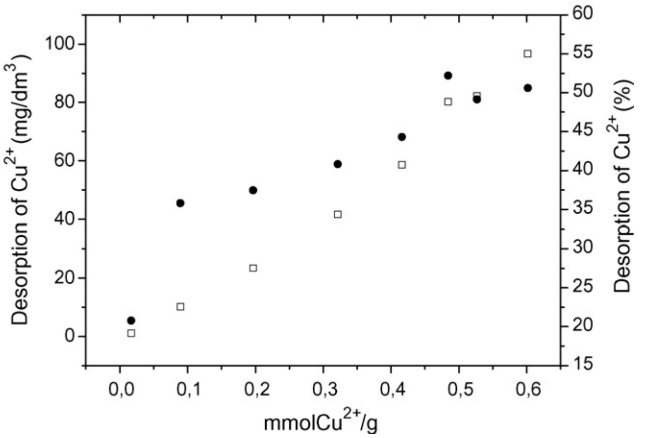

Fig. 7. Desorption of Cu^{2+} ions from variously loaded HAP5 sample: aqueous Cu^{2+} concentrations (□); relative percentages (●). Leaching solution—TCLP2.

Stability of the HAP-Cu products was higher in the solutions of competing cation, than in acidic media. In the TCLP2 solution 48–57% of Cu^{2+} ions were removed from different HAP samples, while leaching experiments with 10^{-2} mol/dm^3 $Ca(NO_3)_2$ showed that the Cu^{2+} desorption was only 8–16% in respect to the quantity of the sorbed cation. The equilibrium pH values were in the range of 4.02–4.11 and 5.04–5.47, for TCLP2 and $Ca(NO_3)_2$ solutions, respectively.

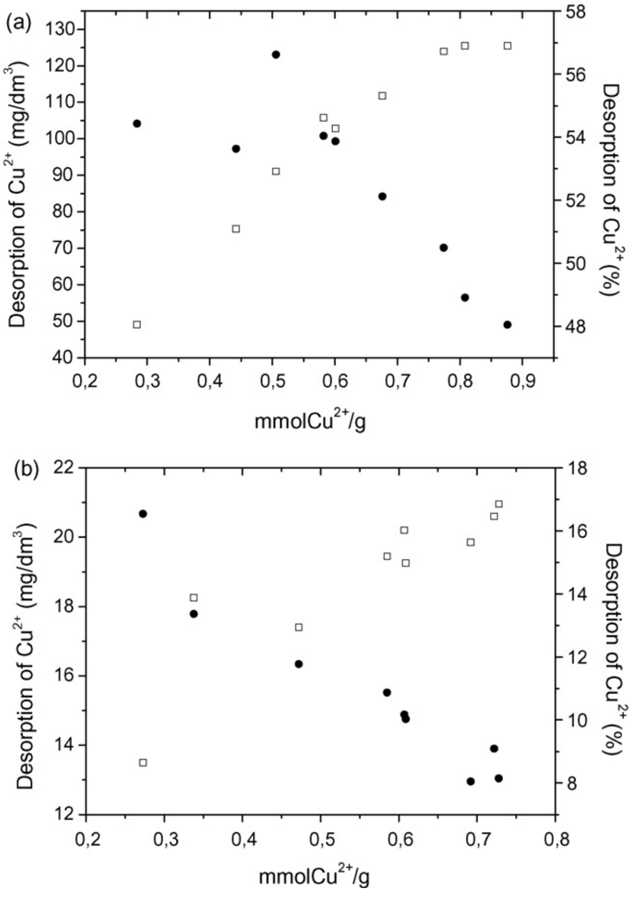

Fig. 8. Desorption of Cu^{2+} ions (aqueous Cu^{2+} concentrations (□) and relative percentages (●)) from various HAP samples: (a) leaching solution—TCLP2; (b) leaching solution—10^{-2} mol/dm^3 $Ca(NO_3)_2$.

Generally, the absolute amounts of Cu^{2+} released increased with the increase of the quantity initially sorbed by HAP, whereas desorption percentages decreased (Fig. 8a and b). The results implied that samples with higher sorption capacities also demonstrated higher stability, consequently the utilization of low-crystaline HAP samples, with high Sp values, was superior for immobilization of Cu^{2+} ions.

4. Conclusions

Sorption of Cu^{2+} ions by HAP depended on equilibration conditions as well as on HAP properties. Presented experimental results have shown that:

1. Sorbed amount of Cu^{2+} generally increased with the increase of pH reaching near 100% at pH 3, 4 and 7 for 5×10^{-4}, 10^{-3} and 5×10^{-3} mol/dm^3 solutions, respectively. The pH_{PZC} value of HAP sorbent decreased with the increase of initial Cu^{2+} concentration.
2. Contact time necessary for reaching sorption equilibrium increased with the increase of initial Cu^{2+} concentration. Experimental data were well characterized by pseudo-second-order model. Calculated values of pseudo-second rate constant decreased with the increase of Cu^{2+} concentration, while equilibrium sorbed amounts of Cu^{2+} and initial sorption rates increased.
3. The sorption isotherm was well defined by Langmuir theoretical model, while the values of separation factors and Gibbs free energy change of sorption indicated that the process is spontaneous and thermodynamically feasible at room temperature.
4. Cu^{2+} sorption was positively correlated with HAP specific surface area, and negatively with HAP crystallinity. The influence of Ca/P molar ratios and pH_{PZC} values of HAP powders on Cu^{2+} sorption was less significant.
5. Obtained HAP-Cu products were more stable in the solution of competing cation, than in acidic environment (8–16 and 48–57% desorbed, respectively).
6. Sorption of Cu^{2+} by HAP was followed by Ca^{2+} release and final pH decrease, therefore the sorption mechanism was complex, including at least ion-exchange and formation of surface complex compounds. Dissolution of HAP followed by a precipitation of libethenite may have also contributed to the overall sorption mechanism.

Acknowledgements

This work was supported by the Ministry of Science and Environmental Protection of the Republic of Serbia, under Project No. 142050G.

References

[1] D.E. Baker, J.P. Senft, Copper, in: B.J. Alloway (Ed.), Heavy Metals in Soils, second ed., Blackie Academic and Professional, London, 1995, pp. 179–205.
[2] R. Mehta, D.M. Templeton, P.J. O'Brien, Mitochondrial involvement in genetically determined transition metal toxicity. II. Copper toxicity, Chem. Biol. Interact. 163 (2006) 77–85.
[3] B. Halliwell, J.M. Gutteridge, Role of free radicals and catalytic metal ions in human disease: an overview, Methods Enzymol. 186 (1990) 1–85.
[4] G. McKay, Use of Adsorbents for the Removal of Pollutants From Wastewater, CRC Press Inc., Tokyo, 1996.
[5] M. Sprynskyy, B. Buszewski, A.P. Terzyk, J. Namiesnik, Study of the selection mechanism of heavy metal (Pb^{2+}, Cu^{2+}, Ni^{2+} and Cd^{2+}) adsorption on clinoptilolite, J. Colloid Interf. Sci. 304 (2006) 21–28.
[6] M.H. Al-Qunaibit, W.K. Mekhemer, A.A. Zaghloul, The adsorption of Cu(II) ions on bentonite—a kinetic study, J. Colloid Interf. Sci. 283 (2005) 316–321.
[7] T.H. Chen, S.C. Peng, H.F. Xu, X.L. Shi, C.H. Huang, X.L. Shi, C.H. Huang, Mechanism for Cu^{2+} sorption on palygorskite, Pedosphere 15 (2005) 334–340.
[8] X.S. Wang, J. Wang, C. Sun, Removal of copper(II) ions from aqueous solutions using natural kaolinite, Adsorpt. Sci. Technol. 24 (2006) 517–530.

[9] M.B. McBridge, Cu^{2+}-adsorption characteristics of aluminum hydroxide and oxyhydroxides, Clays Clay Miner. 30 (1982) 21–28.

[10] K. Wilson, H. Yang, C.W. Seo, W.E. Marshall, Select metal adsorption by activated carbon made from peanut shells, Biores. Technol. 97 (2006) 2266–2270.

[11] P.D. Johnsona, M.A. Watsona, J. Browna, I.A. Jefcoat, Peanut hull pellets as a single use sorbent for the capture of Cu(II) from wastewater, Waste Manage. 22 (2002) 471–480.

[12] H. Benaıssa, M.A. Elouchdi, Removal of copper ions from aqueous solutions by dried sunflower leaves, Chem. Eng. Process. 46 (2007) 614–622.

[13] E. Pehlivan, S. Cetin, B.H. Yanık, Equilibrium studies for the sorption of zinc and copper from aqueous solutions using sugar beet pulp and fly ash, J. Hazard. Mater. B 135 (2006) 193–199.

[14] A. Özcan, A.S. Özcan, S. Tunali, T. Akar, I. Kiran, Determination of the equilibrium, kinetic and thermodynamic parameters of adsorption of copper(II) ions onto seeds of Capsicum annuum, J. Hazard. Mater. B 124 (2005) 200–208.

[15] F. Monteil-Rivera, M. Fedoroff, Sorption of inorganic species on apatites from aqueous solutions, in: Encyclopedia of Surface and Colloid Science, Marcel Dekker Inc., New York, 2002, pp. 1–26.

[16] B.M. Thomson, C.L. Smith, R.D. Busch, M.D. Siegel, C. Baldwin, Removal of metals and radionuclides using apatite and other natural sorbents, J. Environ. Eng. 129 (2003) 492–499.

[17] R.Z. LeGeros, Calcium Phosphates in Oral Biology, Karger, Basel, 1991.

[18] W. Zheng, X. Li, Q. Yang, G. Zeng, X. Shen, Y. Zhang, J. Liu, Adsorption of Cd(II) and Cu(II) from aqueous solution by carbonate hydroxylapatite derived from eggshell waste, J. Hazard. Mater. 147 (2007) 534–539.

[19] D.C.K. Ko, C.W. Cheung, K.K.H. Choy, J.F. Porter, G. McKay, Sorption equilibria of metal ions on bone char, Chemosphere 54 (2004) 273–281.

[20] S. AlAsbeb, F. Banat, F. Mobai, Sorption of copper and nickel by spent animal bones, Chemosphere 39 (1999) 2087–2096.

[21] 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. Br. Chem. Soc. 16 (2005) 62–68.

[22] A. Corami, S. Mignardi, V. Ferrini, Copper and zinc decontamination from single- and binary-metal solutions using hydroxyapatite, J. Hazard. Mater. 146 (2007) 164–170.

[23] I. Smičiklas, A. Onjia, S. Raičević, Experimental design approach in the synthesis of hydroxyapatite by neutralization method, Sep. Purif. Technol. 44 (2005) 97–102.

[24] USEPA, Test methods for evaluating solid waste, Laboratory Manual Physical/Chemical Methods, SW-846, 3rd ed., U.S. Gov. Print. Office, Washington, DC, 1999.

[25] L. Wu, W. Forsling, P.W. Schindler, Surface complexation of calcium minerals in aqueous solutions. 1. Surface protonation of fluoroapatite water interfaces, J. Colloid Interf. Sci. 147 (1991) 178–185.

[26] Đ. Janaćković, I. Janković, R. Petrović, Lj. Kostić-Gvozdenović, S. Milonjić, D. Uskoković, Surface properties of HAP particles obtained by hydrothermal decomposition of urea and calcium-EDTA chelates, Key Eng. Mater. 240–242 (2003) 437–440.

[27] J. Vuceta, J. Morgan, Hydrolysis of Cu(II), Limnol. Oceanogr. 22 (1977) 742–746.

[28] V.B. Spivakovski, G.V. Makovskaya, Copper(II) hydroxide chlorides, hydroxide and hydroxo-complexes. A new version of the method of three variables, Russ. J. Inorg. Chem. 13 (1968) 815–819.

[29] R.E. Mesmer, C.F. Baes, The hydrolysis of cations: a critical review of hydrolytic species and their stability constants in aqueous solution, Part 3, Oak Ridge Natl. Lab. ORNL-NSF-EATC-3, 1974.

[30] A. Onjia, S. Milonjić, Influence of background electrolyte on the point of zero charge of chromium(III)-oxide, Mater. Sci. Forum 413 (2003) 87–94.

[31] G.J. Levinskas, W.F. Neuman, The solubility of bone mineral. I. Solubility studies of synthetic hydroxyapatite, J. Phys. Chem. 59 (1959) 164–168.

[32] S. Lagergren, Zur theorie der sogenannten adsorption gelöster stoffe, K. Sven. Vetenskapsakad. Handl. 24 (1898) 1–39.

[33] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem. 34 (1999) 451–465.

[34] K. Chojnacka, Equilibrium and kinetic modeling of chromium(III) sorption by animal bones, Chemosphere 59 (2004) 315–320.

[35] N. Bektas, S. Kara, Removal of lead from aqueous solutions by natural clinoptilolite: equilibrium and kinetic studies, Sep. Purif. Technol. 39 (2004) 189–200.

[36] S. Saxena, M. Prasad, S.F. D'Souza, Radionuclide sorption onto low-cost mineral adsorbent, Ind. Eng. Chem. Res. 45 (2006) 9122–9128.

[37] H. Chen, A. Wang, Kinetic and isothermal studies of lead ion adsorption onto palygorskite clay, J. Colloid Interf. Sci. 307 (2007) 309–316.

[38] E. Alvarez-Ayuso, A. Garcia-Sanchez, Sepiolite as a feasible soil additive for the immobilization of cadmium and zinc, Sci. Total Environ. 305 (2003) 1–12.

[39] A. Naeem, S. Mustafa, N. Rehana, B. Dilara, S. Murtaza, The sorption of divalent metal ions on AlPO$_4$, J. Colloid Interf. Sci. 252 (2002) 6–14.

[40] M.G. da Fonseca, M.M. De Oliveira, L.N.H. Arakaki, J.G.P. Espinola, C. Airoldi, Natural vermiculite as an exchanger support for heavy cations in aqueous solutions, J. Colloid Interf. Sci. 285 (2005) 50–55.

[41] K.R. Hall, L.C. Eagleton, A. Acrivos, T. Vermeulen, Pore and solid diffusion kinetics in fixed bed adsorption under constant pattern conditions, Ind. Eng. Chem. Fundam. 5 (1966) 212–215.

[42] T. Mishra, S.K. Tiwari, Studies on sorption properties of zeolite derived from Indian fly ash, J. Hazard. Mater. B 137 (2006) 299–303.

[43] 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.

[44] M. Sprynskyy, B. Buszewski, A.P. Terzyk, J. Namiesnik, Study of the selection mechanism of heavy metal (Pb^{2+}, Cu^{2+}, Ni^{2+}, and Cd^{2+}) adsorption on clinoptilolite, J. Colloid Interf. Sci. 304 (2006) 21–28.

[45] I. Smičiklas, A. Onjia, J. Marković, S. Raičević, Comparison of hydroxyapatite sorption properties towards cadmium, lead, zinc and strontium ions, Mater. Sci. Forum 494 (2005) 405–410.