

Copper and zinc decontamination from single- and binary-metal solutions using hydroxyapatite

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Abstract

Toxic metals contamination of waters, soils and sediments can seriously affect plants, animals and human being. The bioavailability of metal ions can be reduced trapping them in minerals with low solubilities. This study investigated the sorption of aqueous Cu and Zn onto hydroxyapatite surfaces. Batch experiments were carried out using synthetic hydroxyapatite. The metals were applied as single or binary species, in a range of metal concentrations ranging from 0 to 8 mmol/L at 25 ± 2 °C. The removal capacity of hydroxyapatite was 0.016–0.764 mmol of Cu/g and 0.015–0.725 mmol of Zn/g. In the Cu–Zn binary system, competitive metal sorption occurred with reduction of the removal capacity by 13–76% and 10–63% for Cu and Zn, respectively, compared to the single-metal systems. The sorption of Cu and Zn was well characterized by the Langmuir model. Heavy metal immobilization was attributed to a two-step mechanism: first rapid surface complexation and secondly partial dissolution of hydroxyapatite and ion exchange with Ca followed by the precipitation of a heavy metal-containing hydroxyapatite.

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1. Introduction

The contamination of water due to heavy metals arising from mining operations, metal plating, textile industries, tannery, etc., is a major environmental problem [1]. The heavy metals are of great concern because of their extreme toxicity even at low concentration and the tendency to accumulate in the food chain [2]. Among the commonly encountered metals of concern copper and zinc are hazardous and have been included in the Priority Pollutants List by United States Environmental Protection Agency (USEPA) [3]. Copper has been reported to cause neurotoxicity, jaundice, and liver toxicity [4]. Moreover, continued inhalation of copper-containing sprays is linked with an increase in lung cancer [5]. Zinc plays an important role in essential biological functions but, at high concentrations, causes gastrointestinal distress and diarrhoea [6]. Therefore, removal of copper and zinc from water and wastewater by an appropriate treatment becomes necessary.

Conventional methods for heavy metal removal from water and wastewater include oxidation, reduction, precipitation, membrane filtration, ion exchange, electrochemical operation, biological treatment, and adsorption. Among all the available technologies, adsorption onto solid substrate materials has been used as one of the most suitable process for the removal of heavy metals from solutions. Several solids have been used for the removal of heavy metals such as biomass, activated carbons, fishbone, zeolites, clays [2,5,7–9]. Among the mineral amendments, phosphate minerals have obtained an increasing attention in the past years. Many studies have been carried out to evaluate the effectiveness of phosphate amendments on remediation of contaminated waters and soils [10–15]. The aim is to remove metals through the formation of metal phosphates with a lower solubility and which are stable under a wide range of environmental conditions.

Hydroxyapatite (HA) $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]$ is a unique inorganic compound because of its high removal capacity for divalent heavy metals ions, and synthetic HA has been used to remove heavy metals such as Pb, Zn, Cu, Cd, Co, and Sb from waters [10,16–22]. The possible reaction mechanisms for metal immobilization include: (a) ion exchange processes

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[18,20,23]; (b) surface complexation [18,19,24]; (c) dissolution of HA and precipitation of new metal phosphates [10,18], and (d) substitution of Ca in HA by other metals during recrystallization (coprecipitation) [18,25]. However, because of the limited knowledge on the relative contribution of each process in removing metals, it seems that the above four mechanisms could all be involved [18]. Thus, the term sorption is used in this paper as a general term to define attachment of metals from a solution to its coexisting HA surfaces.

Wastewaters are multi-component systems and the competition among the heavy metals reduces the efficiency of the amendment affecting the removal of metals from such solutions [26]. However, few studies have evaluated the competitive sorption of heavy metals by synthetic HA [10,18].

The aims of this work were: (a) to investigate the retention of Cu and Zn in aqueous solution by HA both in single-metal and binary-metal systems; (b) to examine the effects of one metal on the sorption of another by HA.

2. Materials and methods

2.1. Materials

The HA used in this study was commercially synthesized by Alfa Aesar. The chemical composition was determined as: Ca (38.3%), P (16.8%), Mg (0.3%), Si (0.3%), Cd (1 ppm), Cu (4 ppm), Zn (5 ppm), Pb (1 ppm), Ca/P ratio 1.76 ± 0.2 and surface area $50 \text{ m}^2/\text{g}$ determined by the BET-method (adsorption gas N_2 , carrier gas He, heating temperature 150°C). X-ray diffraction (XRD) analysis confirmed the mineralogical identity and the crystallinity of HA (ICDD 9-432) [27]. Scanning electron microscopy (SEM) analyses showed that the starting material comprised of spherical-like particles and energy dispersive spectroscopy (EDS) analyses showed only Ca and P.

All reagents were of analytical grade and double distilled water was used to prepare all solutions and suspensions. Single- and binary-metal aqueous solutions of Cu(II) and Zn(II) were prepared from their nitrate salts. All the experiments were run in duplicate.

No solution pH adjustment was imposed during the experiments of this study in order to mimic the conditions existing during the remediation of wastewater, where the pH control is either not applicable, or not necessary or very difficult to be realized. For the same reason a background electrolyte was not applied.

2.2. Sorption procedure

Sorption experiments were carried out in batch. The HA (0.2 g) was equilibrated in high-density polyethylene beakers (Nalgene) with 200 mL of the heavy metal solutions with concentration ranging from 0 to 8 mmol/L. The HA suspensions and appropriate blanks were shaken at 300 rpm at $25 \pm 2^\circ\text{C}$ for 24 h, which was considered to be necessary to attain apparent equilibrium based on our preliminary kinetic experiments (Fig. 1a) as well as according to the literature data [20,21].

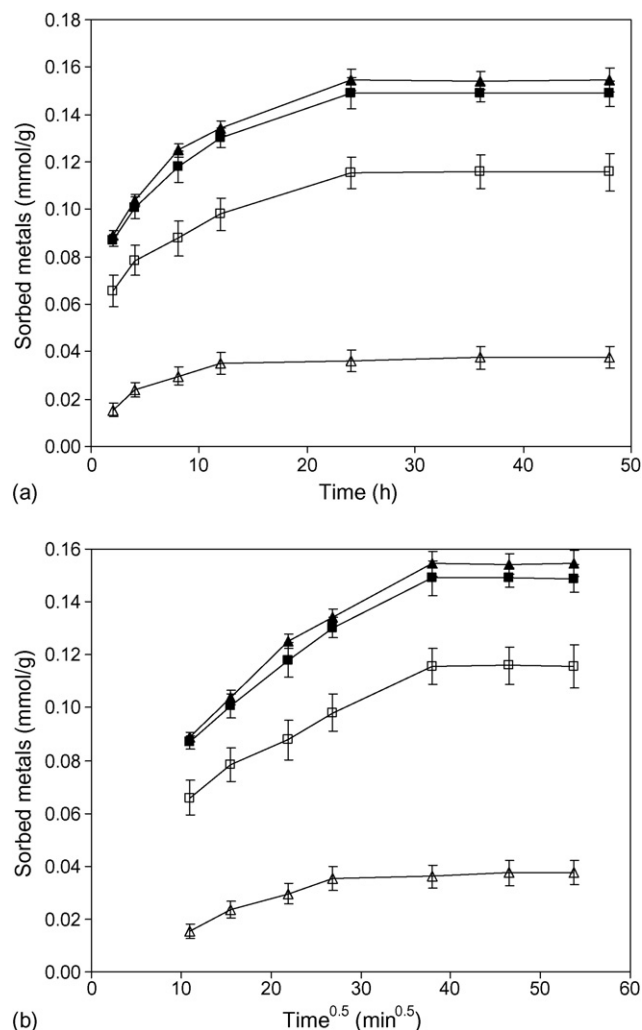


Fig. 1. Kinetics of copper and zinc sorption on HA (a) ($[\text{Cu}^{2+}] = 1.57 \text{ mmol/L}$, $[\text{Zn}^{2+}] = 1.53 \text{ mmol/L}$, amount of HA = 0.2 g, $T = 25 \pm 2^\circ\text{C}$) and the amount of sorbed metals versus square root of time (b). \blacktriangle Cu; \blacksquare Zn; \triangle Cu(+Zn); \square Zn(+Cu).

The intraparticle diffusion model [28] was applied in order to discriminate the contribution of this process in the sorption of the metals. According to the model, a linear plot of sorbed metal amounts versus the square root of time suggests the involvement of intraparticle diffusion in the sorption mechanism. Moreover, a plot passing through the origin means that the diffusion is the rate-controlling step of the process.

In the binary-metal sorption tests mixtures of Cu and Zn were used. In these suspensions the initial and final pH was measured but not adjusted [14,18,29].

2.3. Analytical methods

After the reaction periods, the HA suspensions and blanks were filtered through $0.20 \mu\text{m}$ Nucleopore polycarbonate membrane filters and the Cu, Zn, and Ca concentrations were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES) with a Varian Vista RL CCD Simultaneous ICP-AES spectrometer. Analytical detection limits for Cu, Zn

and Ca were 0.3, 0.6 and 0.3 $\mu\text{mol/L}$, respectively. Analytical errors were estimated to be of the order of 3%. The amount of Cu and Zn removed from the solutions per gram of HA was calculated using the equation:

$$q = (C_0 - C_e) \times V/M \quad (1)$$

where q is the amount of contaminant removed from solution (mmol/g), C_0 denotes the concentration of the heavy metal in the solution before mixing with HA (mmol/L), C_e is the equilibrium concentration of the contaminant left in the solution after the experiment (mmol/L), V is the volume of the solution and M denotes the mass of HA.

Selected solid residues were examined with an X-ray diffractometer Seifert MZ IV using Cu- α at 35 kV and 20 mA. Scans were made from 5 to 60° with a rate of 2 s/0.05° 2 θ . The solid phases were also examined with a Zeiss MD 940 scanning electron microscope operating at 25 kV equipped with X-ray energy dispersive spectroscopy (EDS).

FTIR analyses were executed in selected solid samples after being dispersed in KBr excess (sample/KBr ratio about 1/100) at ambient temperature using the DRIFT (diffuse reflectance infrared Fourier transform) technique with an Interferometer Equinox 55 Bruker having the sample compartment carefully purged. Spectra were taken at a resolution of 1 cm^{-1} or better, cumulating at least 200 scans.

The initial and final pH was measured using a pH 510 Eutech pH-meter at different initial metal concentrations to obtain information about the change in hydrogen ion concentration during the metal sorption.

3. Results and discussion

3.1. Solid examinations

The XRD results did not detect new crystalline phases, neither a significant broadening in the XRD diffraction peaks has been observed. However, as XRD cannot normally detect phases at concentration lower than 1% of the sample matrix, the precipitation of a new crystalline phase cannot be excluded on the basis of the measurements.

SEM analysis did not show any morphological differences in the solid residues with respect to the starting HA. Detailed EDS analysis was unable to identify new solid phases on the surface of HA grains, whereas uniform coverage of Cu and Zn was detected. The solid residues show white zones spread on the HA grains, corresponding to the sorbed heavy metals [30].

Fig. 2 shows the infrared spectra of HA before and after interaction with Cu and Zn in the 4000–400 cm^{-1} region. FTIR spectra of the solid residues are comparable to those of the original HA, suggesting no other phases formed during the heavy metal sorption. The bands ν_3 near 1027 cm^{-1} and ν_4 near 575 cm^{-1} represent the vibration mode of the tetrahedral PO_4^{3-} [31]. The band at 3566 cm^{-1} confirmed the presence of OH^- groups [19,32]. The adsorption band at 2916 cm^{-1} could be due to a stretching mode of the P–O–H group [33]. The band at 1984 cm^{-1} corresponds to overtones and combinations ($2\nu_3$,

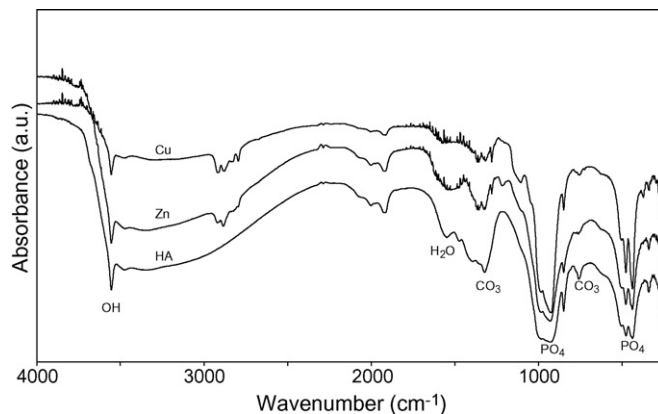


Fig. 2. FTIR spectra before and after copper and zinc sorption on HA.

$\nu_3 + \nu_1$, $2\nu_1$) [34]. The band at 1635 cm^{-1} could be assigned to water [35]. The ν_2 and ν_3 peaks of CO_3^{2-} are located near 875 cm^{-1} and near 1400 cm^{-1} [19].

3.2. Sorption of Cu and Zn in single-metal and binary-metal systems

The sorption kinetics (Fig. 1a) is characterized by two stages: a first step of rapid metal immobilization followed by a slower step before the equilibrium was reached. Fig. 1b shows for both single- and binary-metal systems for the metals two straight lines with almost different slopes, indicating that intraparticle diffusion was involved in the overall sorption process.

In single-metal tests Cu sorption was slightly higher than that of Zn. The amount of sorbed metals ranged from 0.016 ($C_0 = 0.157$ mmol/L) to 0.764 mmol ($C_0 = 7.85$ mmol/L) of Cu and from 0.015 ($C_0 = 0.153$ mmol/L) to 0.725 mmol ($C_0 = 7.65$ mmol/L) of Zn per gram of HA. In the Cu–Zn system, competitive sorption between the aqueous heavy metals affected retention of metals by HA. Cu sorption was lower than that of Zn, with values of sorbed metal ranging from 0.008 to 0.217 mmol for Cu and from 0.006 to 0.546 mmol for Zn per gram of HA. The competitive effects between the two metals has reduced the amount of sorbed metals by 13% ($C_0 = 0.0314$ mmol/L)–76% ($C_0 = 0.157$ mmol/L) and 10% ($C_0 = 0.459$ mmol/L)–63% ($C_0 = 0.153$ mmol/L) for Cu and Zn, respectively, compared to the single-metal systems. In this view, according to Chen et al. [36], in single-metal sorption the heavy metals could be retained by HA with only internal competition (competition between ions of the same metal) and they were in competition with H^+ for adsorption sites. On the contrary, in the binary-metal sorption there was internal competition, competition with H^+ and competition among each other for precipitation and for adsorption sites.

The metal sorption produced a pH decrease from 6.58 to 5.27 for Cu and from 6.67 to 5.35 for Zn.

Heavy metal sorption by HA has been analyzed using the Langmuir model, probably the most popular isotherm model due to its simplicity and its good agreement with experimental data. The model is based on the assumption that a monomolecular layer is formed on a surface containing a finite number of

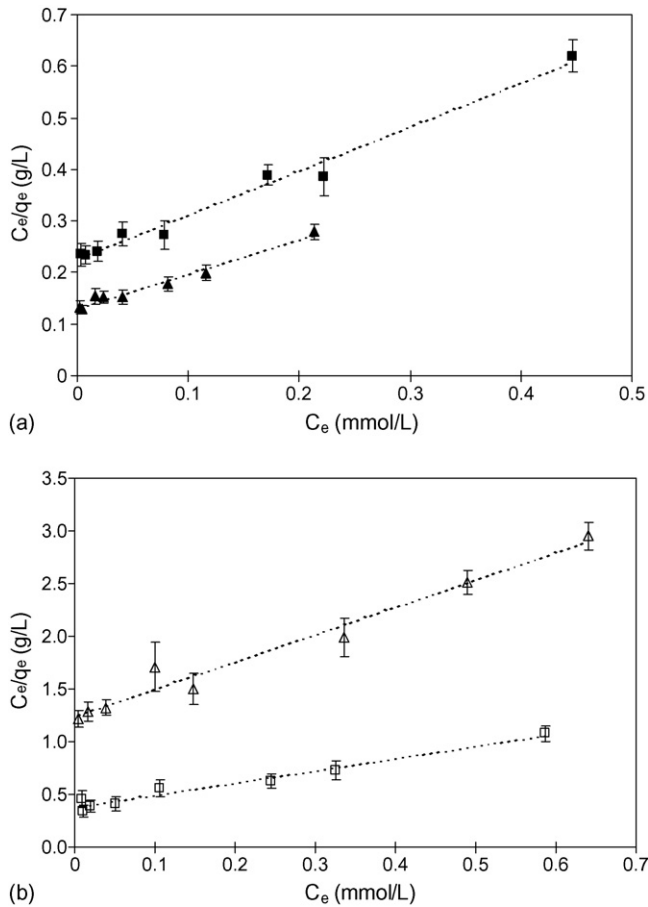


Fig. 3. Langmuir sorption isotherms of copper and zinc in (a) single-metal and (b) binary-metal systems. Symbols as in Fig. 1.

binding sites of uniform energies of adsorption. The Langmuir equilibrium equation is:

$$C_e/q_e = C_e/q_m + 1/bq_m \quad (2)$$

where C_e is the equilibrium aqueous metal ions concentration (mmol/L), q_e the amount of Cu or Zn sorbed per gram of HA (mmol/g), q_m (mmol/g) and b (L/mmol) the Langmuir constants related to the maximum sorption capacity and energy of sorption, respectively. The linearity of the plots C_e/q_e versus C_e (Fig. 3) showed that Langmuir model adequately described the sorption data for the metal ions in single- as well as in binary-systems. The values of q_m and b were determined from the slopes and intercepts of the plots (Table 1).

Sorption parameters for HA showed variability between the two metals. However, the values of q_m and b were higher in single-metal than in competitive sorption in agreement with

the results of previous studies [2,14]. The experimental data showed that HA retained more Cu than Zn in single-metal system whereas in binary-metal system Zn is more removed than Cu. In binary-metal sorption, competition between the two metals produced a reduction of the q_m values by about 75% for Cu and 26% for Zn, compared to the single-metal system.

The main characteristics of Langmuir isotherm is its dimensionless constant separation factor R_L defined by

$$R_L = 1/(1 + bC_0)$$

The value of R_L indicates the shape of the isotherm as follows

R_L value	Type of isotherm
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

The values of R_L (Table 1) were found to be less than one and greater than zero indicating the favourable sorption of Cu and Zn on HA in both single- and binary-metal systems [37].

The competitive effects between Cu and Zn in the binary-system could be represented by the ratio of the maximum sorption capacity for the metal in the binary-metal system (q_{mix}) to the maximum sorption capacity for the same metal in the single-metal system (q_m). When the value of the ratio is greater than one, the sorption is promoted by the presence of the other metals; when $q_{mix}/q_m = 1$ no competitive effects are observable; when the value of the ratio is less than one, the sorption is reduced by the presence of other metal ions.

Our values of the ratio (Table 1) were less than one, confirming the effects of the competitive sorption in the binary-metal system.

The experimental q_m values are different from those of previous studies [18,20,38] suggesting HA sorption capacity varies according to the conditions of sample preparation. However, normalizing our data in respect to BET surface area of our HA, the values, ranging from $7.6 \mu\text{mol}/\text{m}^2$ to $2.3 \times 10^{-2} \text{ mmol}/\text{m}^2$, are closer to those of the above studies. Therefore, according to Da Rocha et al. [39], the maximum sorption capacity per specific surface area could be almost a constant value for any HA.

3.3. Sorption mechanisms

The sorption patterns (Fig. 1a) are similar to those observed in previous studies [13,20,39]. According to these authors, the sorption process can be divided in two steps. The first represents a rapid complexation on specific sites of the HA surface. The second step is attributed either to a metal diffusion into

Table 1
Langmuir parameters for the sorption of Cu and Zn in single- and binary-metal systems on HA

	Single-metal				Binary-metal				
	q_m (mmol/g)	b (L/mmol)	R^2	R_L	q_m (mmol/g)	b (L/mmol)	R^2	R_L	q_{mix}/q_m
Cu	1.51	5.06	0.976	0.18	0.38	2.13	0.972	0.29	0.25
Zn	1.17	3.81	0.984	0.21	0.87	3.03	0.968	0.24	0.75

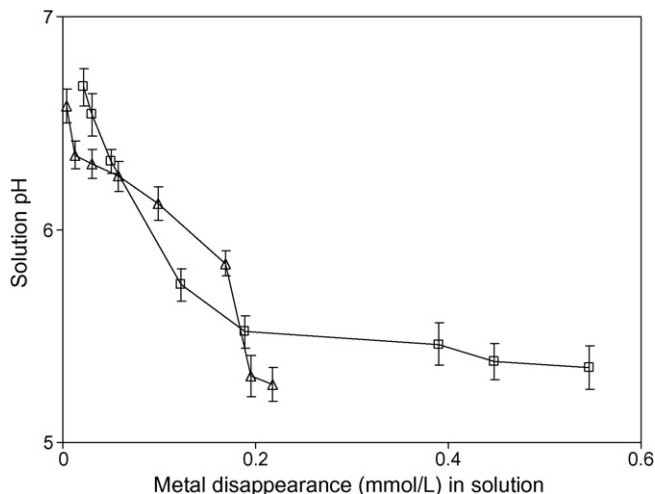


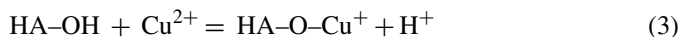
Fig. 4. Final solution pH as a function of solution metal disappearance. Symbols as in Fig. 1.

the HA structure or to a heavy metal-containing hydroxyapatite formation.

Information about the sorption mechanisms have been inferred by the values of molar ratios (Q_s) of cations bound by HA to Ca desorbed from HA, the pH decrease, the relation between metal uptake and Ca^{2+} release, as well as the results of XRD and FTIR analysis. When $Q_s = 1$, the amounts of sorbed and released cations are equal, indicating the possibility of ion exchange of cations between the HA and the solution. When $Q_s > 1$, the quantity of sorbed metal ions is larger than that of the released ones, which suggests surface complexation was the main sorption mechanism. When $Q_s < 1$, dissolution of HA and precipitation of new phosphate phase with lower cation to phosphate molar ratio occurs. Generally, our Q_s values were greater than one; however, some values are close to one. These results are compatible with both surface complexation and ion exchange.

Metal uptake produced a decrease of solution pH (Fig. 4). Similar pH decrease was observed in previous studies [14,40] and attributed to the release of H^+ ions by HA surface groups during the metal sorption.

In agreement with the results of previous studies [14,18,41] when aqueous Cu and Zn were mixed with HA, surface complexation of the heavy metals occurred on the HA surface displacing partially the H^+ ions, resulting in pH reduction and calcium release (Fig. 5). With Cu (or Zn) in solution, the following reaction may occur:



Therefore, the observed pH decrease further suggests that surface complexation contributed, to some extent, to the overall sorption process.

The identical X-ray diffraction patterns and FTIR spectra, as well as the unchanged morphology of the solid particles, observed in our SEM-EDS analysis support the contribution of surface complexation to the metal sorption.

During the second step of the sorption process, after the surface complexation was completed, the intraparticle diffusion process occurred as suggested by the linear part of the plot in

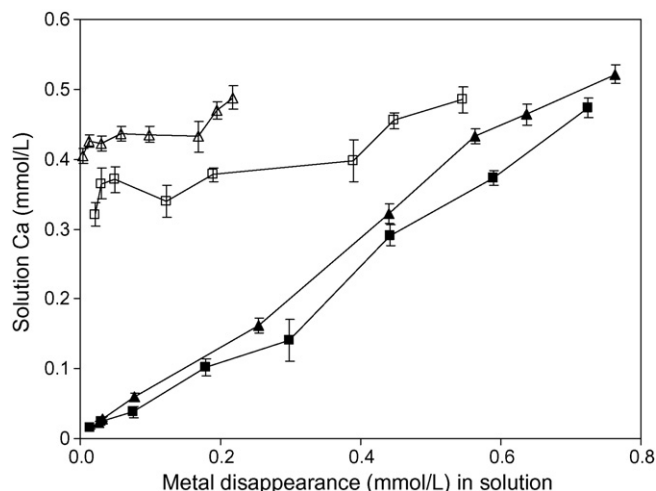
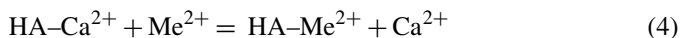


Fig. 5. Relation between metal disappearance and total Ca concentrations in the final solution. Symbols as in Fig. 1.

Fig. 1b for contact times 24–48 h. However, as the plot does not pass through the origin, the diffusion process was not the rate-controlling step.

Fig. 5 shows that solution Ca increased with increasing metal disappearance. The greatest increase was found for Cu sorption. Correlation between the amounts of Ca desorbed in single-metal systems and the amounts of Cu and Zn removed by HA was apparently linear and correlation coefficients for both Cu and Zn were greater than 0.98. For binary-metal sorption, a positive linear correlation between the amount of Ca released and the amount of metal sorbed was still observed. Nevertheless, the correlation coefficients were lower than those in single-metal sorption due to competitive complexation [36]. The linear relationship between Ca and sorbed Cu and Zn appears to be consistent with the ion exchange mechanism between the metals and Ca. The ion exchange mechanism could be described by the following general reaction:



However, slopes for Cu and Zn in single-metal systems were 0.70 and 0.64, respectively, and 0.27 and 0.25 in binary-metal systems, suggesting a non-equimolar exchange of metals and calcium. The less amounts of desorbed Ca in the single-metal systems compared to the binary systems at the corresponding C_0 , suggest the heavy metal-containing superficial layer limited the HA dissolution as the layer isolated almost the whole surface of the grains [42]. Whereas, in the binary systems the competitive sorption reduced the amounts of sorbed metals resulting a less extent of the superficial layer which allowed a larger HA dissolution causing more Ca in solution. The contribution of the ion exchange process to the metal immobilization is difficult to determine as part of Ca is due to HA dissolution produced by the decrease in pH. The substitution of Ca by other cations in HA crystal structure is a result of the ion exchange process [43]. In this view, according to the results of previous studies [13,44], the proposed mechanism for the second step of the overall sorption process involves either the ion exchange with Ca^{2+} and the partial dissolution of HA followed by the

precipitation of a heavy metal-containing hydroxyapatite with formula $\text{Me}_x\text{Ca}_{10-x}(\text{PO}_4)_6(\text{OH})_2$.

The results obtained in our study suggest that the final product of the overall sorption of Cu and Zn sorption would be a heavy metal-containing hydroxyapatite.

4. Conclusions

Hydroxyapatite is able to substantially remove Cu and Zn from aqueous solutions. The removal efficiency ranged from 97.3 to 98.6% and from 94.2 to 97.7% of Cu and Zn, respectively. Binary-metal addition induced competitive sorption among the metals with reduction of the removal capacity by 13–76% and 10–63% for Cu and Zn, respectively, compared to the single-metal sorption. The Cu and Zn immobilization mechanism was through a two-step process: the first step is the surface complexation on specific sites of HA surface; the second step is either a ion exchange with Ca^{2+} and the precipitation of a heavy metal-containing hydroxyapatite. The reduced efficiency of HA in binary-systems should be carefully considered for practical environmental applications processing wastewater containing heavy metals.

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