Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.927794

55 (2015) 1825–1831
August

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Adsorption behavior of Zn(II) ions on synthetic hydroxyapatite

L. Pivarčiová*, O. Rosskopfová, M. Galamboš, P. Rajec

Faculty of Natural Sciences, Department of Nuclear Chemistry, Comenius University in Bratislava, Mlynská Dolina, Bratislava 842 15, Slovak Republic, Tel. +421 2 602 96 419; Fax: +421 2 602 96 397; emails: pivarciova@fns.uniba.sk (L. Pivarčiová), rosskopfova@fns.uniba.sk (O. Rosskopfová), galambos@fns.uniba.sk (M. Galamboš), rajec@fns.uniba.sk (P. Rajec)

Received 22 October 2013; Accepted 20 May 2014

ABSTRACT

The adsorption of Zn^{2+} on synthetic hydroxyapatite was investigated using a batch method and a radiotracer technique. The commercial hydroxyapatite and hydroxyapatite of high crystallinity with Ca/P ratio of 1.563:1.688 prepared by a wet precipitation process were used in this study. The adsorption of zinc on hydroxyapatite was pH independent ranging from 4.5 to 6.5 as a result of buffering properties of hydroxyapatite. The adsorption of zinc was rapid and the percentage of Zn adsorption on both samples of hydroxyapatite was >96% during the first 30 min of the contact time. The experimental data for adsorption of zinc have been interpreted in terms of Langmuir isotherm and the values of maximum adsorption capacity of zinc on a commercial hydroxyapatite and hydroxyapatite prepared by wet precipitation process were calculated to be 0.437 and 0.605 mmol g^{-1}, respectively. The competition effect of Fe^{2+} towards Zn^{2+} adsorption was stronger than that of Ca^{2+}, Mg^{2+}, and Sr^{2+} ions. The ability of the bivalent cations to depress the adsorption of zinc on hydroxyapatite was in the following order: $Fe^{2+} > Ca^{2+} > Sr^{2+} \approx Mg^{2+}$.

Keywords: Adsorption; Hydroxyapatite; Zinc; Langmuir isotherm

1. Introduction

Zinc is a trace element, ubiquitous in environment and it is regarded as an essential element of life. It is necessary for development and growth of all species, including humans, and it participates in mineralization in biological systems. It is found in all human tissues, while the major part of the total body zinc is contained in bones. Zinc is also a cofactor for many enzymes and is essential for DNA replication. However, insufficiency as well as excess of zinc can cause diseases. Acute adverse effects of its high intake include nausea, vomiting, and diarrhea. Chronic excess can result in copper deficiency and profound neurological diseases [1].

Human exposure to zinc and its substances present in environment occurs mainly through drinking water and contaminated food. Zinc acts as a micronutrient when it is present in trace amounts but when the permissible limit is exceeded, it can be harmful. The concentration of zinc is usually lower in natural surface water and groundwater than in drinking water, as a result of leaching from pipings and fittings. The daily requirement of zinc for an adult human is 15–20 mg d^{-1}. It is considered, with respect to the recent studies on humans, that the derivation of a recommended level of zinc in drinking water is not required at this time. However, drinking water

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*Corresponding author.

containing zinc at levels above 3 mg L^{-1} has an undesirable astringent taste [2].

Zinc and its compounds are used in many industrial processes such as galvanization, vulcanization, production of some alloys, paints, pigments, cosmetics, and insecticides, which cause increase of its level in environment and, therefore, it represents a serious threat to human health, living, and ecological systems. Due to its extensive application in industry, zinc can be found in effluents, sludge, and solid wastes [3]. The mobility, reactivity, and bioavailability of Zn^{2+} ions are significantly affected by its adsorption properties. In acidic sediments and soils, the majority of zinc is available in ionic forms, and cation exchange processes influence its rate. Interactions with organic ligands are dominant in alkaline soils [4–6].

Various methods are available for the removal of toxic pollutants from water and wastewater including reverse osmosis, ion exchange, precipitation, electrodialysis, and adsorption. The adsorption on the low-cost adsorbent is the most suitable and frequently used method for the treatment of industrial wastewater due to its simplicity and high efficiency. Some low-cost adsorbents have been used for the removal of Zn^{2+} from aqueous media [7–13].

Hydroxyapatite (HA), $Ca_{10}(PO_4)_6(OH)_2$, is most commonly found in nature in phosphate rocks as a member of the apatite mineral group. It can undergo a series of cationic and anionic isomorphous substitutions, leading to the formation of isomorphous substances. In addition, hydroxyapatite is an important component of bones and teeth of vertebrates [14]. Generally, hydroxyapatite is a suitable sorbent for heavy metals and radionuclides due to its low water solubility, high stability under reducing and oxidizing conditions, high specific surface area, and good buffering properties. The mechanisms of the metal cations retention by HA are different and include ion exchange processes, adsorption, dissolution–precipitation, and substitution of Ca^{2+} ions in HA by other metals during co-precipitation [15]. Several studies have focused on successful use of HA of different origins in removing zinc ions from the solution [16–20].

This work was aimed to study influence of the contact time, effect of pH, and effect of competitive cations on adsorption of zinc ions. The adsorption of zinc on the synthetic hydroxyapatite as a function of zinc concentration in aqueous phase was studied. The data were fit to the Langmuir isotherm equation. The study was performed in order to test the possibility of the synthetic HA utilization for the removal of radioactive Zn^{2+} cations from simulated aqueous solutions.

2. Experimental

2.1. Reagents

All chemicals used in experiments were analytical reagent-grade pure materials from supplies company Slavus, s.r.o., Bratislava SR. Radioisotope of ^{65}Zn (Czech Metrological Institute, Prague, Czech Republic) with volume activity 1.6 MBq mL^{-1} was used as a radio indicator.

2.2. Preparation and characterization of hydroxyapatite

The samples of hydroxyapatite used were synthetic hydroxyapatites, grade puriss from Sigma-Aldrich Chemie GmbH, Germany (HA1) and the hydroxyapatite (HA2) was prepared by precipitation according to the method of Tiselius et al. [21].

An EDX analyzer fitted with a Si(Li) detector with a resolution of 130 eV coupled to a JEOL JXA-840A scanning electron microscope was used for chemical composition analysis of the sample of hydroxyapatite. Characterization of hydroxyapatite samples HA1 and HA2 with SEM micrographs, TEM images, and EDX spectrum is described in detail in previous work [22].

2.3. Adsorption experiments

Adsorption of zinc on the sample of hydroxyapatite was studied by radioisotope indication method using radioisotope ^{65}Zn (γ-radiation energy 1.116 MeV, half-life 244 d). A batch method was used in static arrangement of experiment under aerobic conditions at laboratory temperature. Adsorption parameters were determined after adding 3 mL of Zn^{2+} ions in aqueous phase to 30 mg of hydroxyapatite in a plastic tube with a tap, and both the phases were mixed in an orbital shaker at a constant speed of mixing. After adsorption of zinc, the suspension was centrifugated at 6,000 rot min^{-1} for 10 min and an aliquot of the supernatant was measured on the Gamma Counter 1470 Wizard using NaI(Tl) detector. The statistical error of the measurement was below 1%.

The influence of contact time on the zinc adsorption was analyzed from 3 to 480 min with the concentration of Zn^{2+} ions in aqueous phase 1×10^{-4}, 5×10^{-4}, and 1×10^{-3} mol dm^{-3}.

Adsorption behavior of zinc was studied as a function of pH. The initial solution was distilled water with pH values that were adjusted from ≈3 to ≈8, using HCl or NaOH solutions and labeled with a stock solution of ^{65}Zn with zinc carrier concentration of 3.7×10^{-5} mol dm^{-3}. The final concentration of Zn^{2+} ions in aqueous phase was 3.7×10^{-7} mol dm^{-3}. The pH measurements were performed using pH meter

CPH 51 from Fisher Scientific Co., before the experiment (initial pH) and after the interaction of HA with the solution at the equilibrium time (final pH).

Adsorption experiments were carried out using an initial concentration of Zn^{2+} ions in aqueous phase ranging from 1×10^{-5} to 1×10^{-1} mol dm^{-3}. The solutions of Zn^{2+} with different concentrations were prepared from its chloride salt in distilled water and the tracer ^{65}Zn was added.

Effect of competitive cations on the adsorption of zinc was studied with its concentration 1×10^{-5} mol dm^{-3}, while the concentration of competitive ions was in the range of 1×10^{-5} to 5×10^{-2} mol dm^{-3}.

Adsorption properties of hydroxyapatite were calculated by the following Eqs. (1)–(4) [23]:

$$\text{Distribution coefficient } K_d = \frac{c_0 \cdot c_{eq}}{c_{eq}} \cdot \frac{V}{m} = \frac{a_0 \cdot a}{a} \cdot \frac{V}{m} (\text{cm}^3\,\text{g}^{-1}) \tag{1}$$

$$\text{Adsorption percentage } R = \frac{100 \cdot K_d}{K_d + \frac{V}{m}} (\%) \tag{2}$$

$$\text{Adsorption capacity } \Gamma = K_d \cdot c_{eq} (\text{mol}\,\text{g}^{-1}) \tag{3}$$

$$\text{Equilibrium concentration } c_{eq} = \frac{c_0 \cdot a}{a_0} (\text{mol}\,\text{dm}^{-3}) \tag{4}$$

where c_0 is the initial concentration (mol dm^{-3}), c_{eq} is the equilibrium concentration (mol dm^{-3}), V is the volume of aqueous phase (cm^3), m is the mass of sorbent (g), a_0 is the volume activity of initial solution (Bq cm^{-3}), and a is the equilibrium volume activity of solution (Bq cm^{-3}).

3. Results and discussion

3.1. Contact time

The influence of contact time was investigated in the range of 3–480 min at initial pH 4, for three initial Zn^{2+} concentrations of 1×10^{-4}, 5×10^{-4}, and 1×10^{-3} mol dm^{-3}. The percentage of zinc adsorption on HA1 and HA2 was more than 96% during 1 h for the initial Zn^{2+}concentrations of 1×10^{-4} and 5×10^{-4} mol dm^{-3}. The influence of contact time on the adsorption of zinc on hydroxyapatite HA1 and HA2 is presented in Fig. 1. The equilibrium time of 2 h was chosen for further experiments.

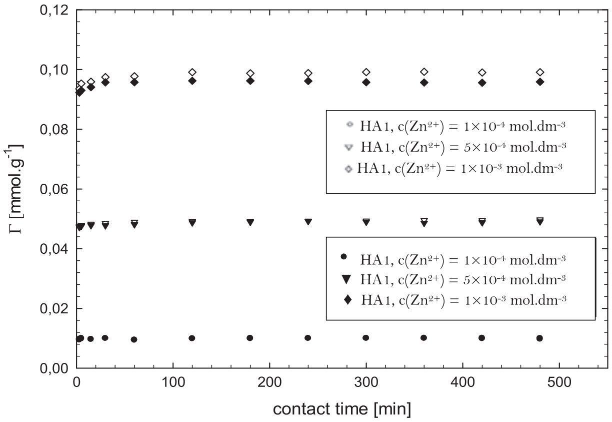

Fig. 1. The dependency of zinc sorption on the time for the sample of hydroxyapatite.

3.2. pH dependence

The pH of a solution is an important parameter that controls adsorption process because of ionization of the surface functional groups and alteration of the solution composition. It is well known that a synthetic hydroxyapatite exhibits excellent buffering properties in the initial pH range of 4–10 [24,25]. The buffering capacity of HA is the result of acid–base reactions of accessible chemical groups on the surface. Adsorption of zinc on the hydroxyapatite was studied using the initial pH ranging from 3.2 to 8.2. After 2 h of contact time, final pH value and the activity of ^{65}Zn of solutions were measured. The results are presented in Fig. 2. In the initial pH range of 4.5–6.5, final pH values are the same. The percentage of zinc adsorption was constant in the whole examined range of pH. The zinc ionic species that predominate at a specific solution pH may play an important role in the adsorption of zinc on hydroxyapatite. Zn(II) is present in the forms of Zn^{2+}, $Zn(OH)^+$, $Zn(OH)_2^0$, $Zn(OH)_3^-$, and $Zn(OH)_4^{2-}$ at various pH values (Fig. 3). Upto pH 6.5, zinc is present in the solution mainly in the form of

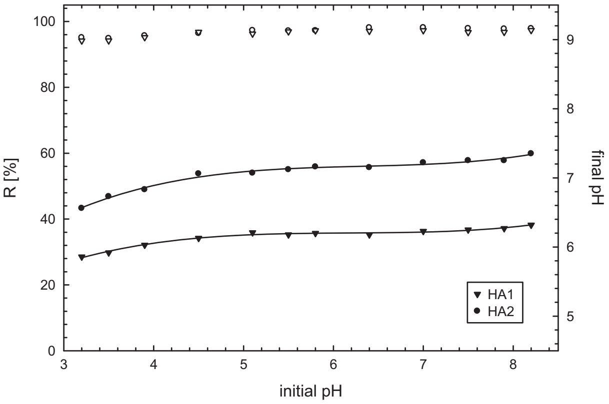

Fig. 2. The percentage of the zinc sorption (*open symbols*) and final pH (*solid symbols*) vs initial pH.

Zn^{2+} ions and the adsorption is guided by ion exchange process with hydroxyapatite. The positively charged $Zn(OH)^+$ hydrolytic product appears in the pH range of 6–10, while $Zn(OH)_2$ starts to precipitate at pH 7.

The mechanisms of the metal cations retention are different and include ionic exchange reactions at the surface or co-precipitation of low-soluble metal phosphate phases [26]. Hydroxyapatite could provide phosphates by dissolution in acidic environment by Eq. (5). These phosphates can react with metal ions to precipitate low-soluble metal phosphate crystals with an apatitic structure according to Eq. (6):

$$\begin{aligned}&Ca_{10}(PO_4)_6(OH)_2 + 14H^+\\&\rightarrow\ 10Ca^{2+} + 6H_2PO_4^- + 2H_2O\end{aligned} \tag{5}$$

$$\begin{aligned}&10Me^{2+} + 6H_2PO_4^- + 2H_2O\\&\rightarrow\ Me_{10}(PO_4)_6(OH)_2 + 14H^+\end{aligned} \tag{6}$$

According to the exchange theory, metal ions adsorbed onto the surface of the hydroxyapatite particle will substitute Ca^{2+} ions from the apatite lattice by diffusion process by Eq. (7).

$$\begin{aligned}&Ca_{10}(PO_4)_6(OH)_2 + xMe^{2+}\\&\rightarrow (Ca_{10-x})Me_x(PO_4)_6(OH)_2 + xCa^{2+}\end{aligned} \tag{7}$$

The adsorption of zinc on hydroxyapatite can be divided into two steps. The first represents a rapid complexation of zinc on specific sites of the HA surface, displacing partially the H^+ ions, resulting in pH reduction and calcium release. The second step is attributed to an ion exchange with Ca^{2+} and the partial dissolution of HA followed by the precipitation of a metal-containing hydroxyapatite formation [17]. In the substitution with Zn^{2+}, the surface phase of hydroxyapatite contains only a small part of zinc ions incorporated in the particles. The replacement of Ca^{2+} with Zn^{2+} should make the crystal structure of HA unstable because of the considerably smaller radii of Zn^{2+} (0.074 nm) than that of Ca^{2+} (0.099 nm). Zn^{2+} ions introduced into the hydroxyapatite lattice by ion exchange process could support the conversion of the amorphous hydrated surface layer [27]. The formation of a new crystalline phase of $Zn_3(PO_4)_2{\cdot}4H_2O$ (hopeite) on the HA surface is observed at higher zinc concentrations [28].

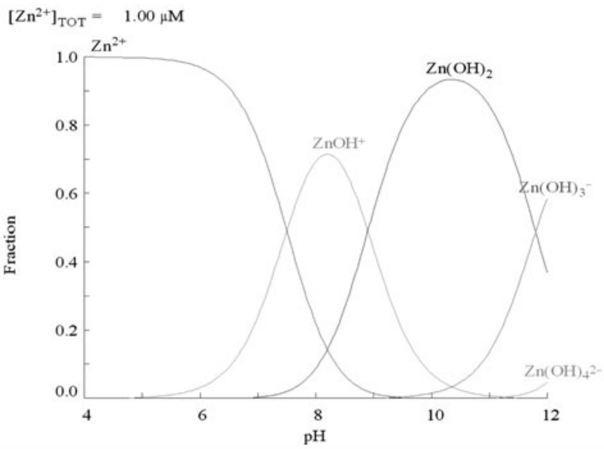

Fig. 3. Distribution diagram for the Zn(II) species as a function of pH (using the program Medusa).

3.3. Adsorption isotherms

The percentage of zinc adsorption on synthetic hydroxyapatite HA1 and HA2 showed nearly no change with increase in concentration of Zn^{2+} in solution up to 1×10^{-4} mol dm^{-3}. Further increase of Zn^{2+} concentrations in solution decreased the adsorption of zinc (Fig. 4(a)). The amount of zinc adsorbed on hydroxyapatite increased along with the increase in concentration of Zn^{2+} in solution, until the equilibrium was achieved.

The Langmuir isotherm has been proposed for modeling experimental data. The Langmuir isotherm model is a theoretical model for monolayer adsorption:

$$\Gamma = \frac{\Gamma_{\max}{\cdot}b.c_{eq}}{(1 + b{\cdot}c_{eq})} \tag{8}$$

where Γ is the adsorption capacity (mol g^{-1}), $\Gamma_{\max}$ is the maximum of the adsorption capacity corresponding to site saturation (mol g^{-1}), c_{eq} is the equilibrium concentration (mol dm^{-3}), and b is the ratio of adsorption/desorption rates.

The results of the measurements of zinc adsorption on synthetic HA are plotted according to the Langmuir equation (Eq. (8)) in Fig. 4(b). The calculated values of maximum adsorption capacity of zinc on HA1 and HA2 were 0.437 and 0.605 mmol g^{-1}, respectively.

Several inorganic ion-exchange materials, either naturally occurring or synthetic, can be used in a remediation of soil and water from industrial and nuclear wastes due to their ability to retain a variety of ionic species. The maximum zinc uptakes for the different materials are listed in Table 1. Langmuir isotherm model was used to fit the data of experiments,

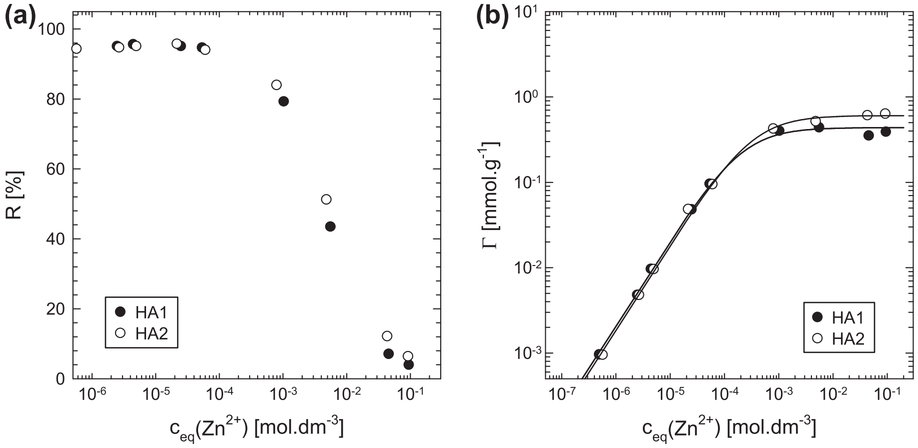

Fig. 4. The percentage of the zinc sorption (a) and the amount of zinc adsorbed on hydroxyapatite modeled by Langmuir isotherm (b) in the presence of Zn^{2+} ions.

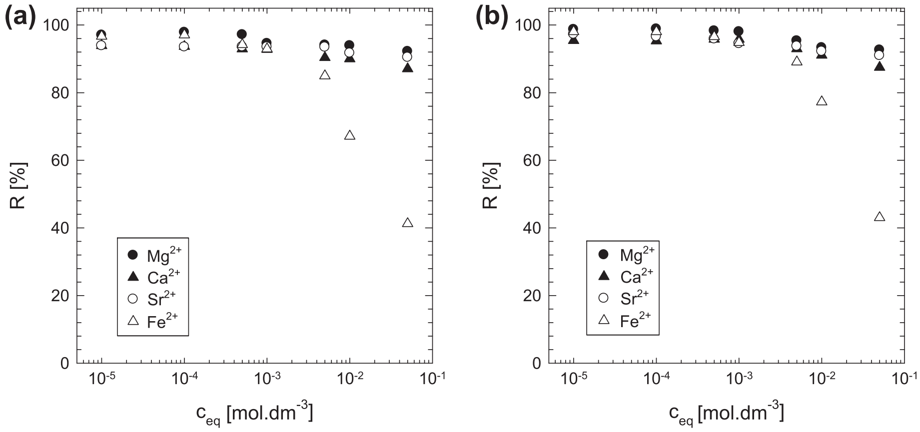

Fig. 5. The percentage of the zinc sorption on HA1 (a) and HA2 (b) as dependency on the concentration of competitive ions in solution.

Table 1
Literature data of Γ_{max} for zinc and various samples of natural and synthetic sorbents

Sorbent	Γ_{max} (mmol g^{-1})	Reference
Synthetic HA	0.437, 0.605	Our results
Synthetic HA	0.574	[29]
Natural HA	1.051–1.562	[30]
Bone char	0.505	[19]
Animal bones	0.181–0.210	[20]
Phosphate rock	0.667	[31]
Natural zeolite	0.134	[32]
Synthetic zeolite A	2.53	[33]
Bentonite	0.538	[34]

but the adsorption mechanism depends on the ionic species of zinc, the nature of the sorbent, and experimental conditions.

3.4. Competitive ions

The metal ions of interest in wastewater usually coexist with various ions. The foreign ions can compete for the binding sites on sorbent. The influence of competitive cations (Ca^{2+}, Mg^{2+}, Sr^{2+}, Fe^{2+}) on the zinc adsorption was studied. Ca^{2+} exhibits more affinity for the surface sites of hydroxyapatite than Sr^{2+} and Mg^{2+} [35]. Under applied experimental conditions, the presence of Mg^{2+}, Ca^{2+}, and Sr^{2+} ions had little effect on the adsorption of Zn^{2+}. With an increase of Ca^{2+} concentration from 1×10^{-3} to 5×10^{-2} mol dm^{-3}, the adsorption of zinc decreased by approximately 6%. The zinc adsorption on hydroxyapatite was significantly decreased with an increasing concentration of Fe^{2+} ions in solution with concentration above 1×10^{-3} mol dm^{-3}. The competition effect of Fe^{2+} towards Zn^{2+} adsorption is obviously stronger than that of Ca^{2+} ions. Fig. 5(a) and (b) shows that the percentage of the zinc adsorption on HA1 and HA2 as dependency on the concentration of competitive ions. The selectivity of hydroxyapatite for bivalent ions is in the following order: $Fe^{2+} > Ca^{2+} > Sr^{2+} \approx Mg^{2+}$. In the case of Fe^{2+}, the oxidation of Fe^{2+} to Fe^{3+} could be expected at $pH > 5$ under aerobic conditions. The precipitate of iron hydroxides, eventually the iron (hydr)oxides, was observed.

4. Conclusion

The adsorption of zinc on hydroxyapatite was studied using batch techniques. The samples of hydroxyapatite used in the adsorption experiments were commercial synthetic hydroxyapatite and the hydroxyapatite prepared by a wet precipitation process. The adsorption of zinc was carried out through radioisotope indication using ^{65}Zn as the radiotracer. The time required for achievement of the adsorption equilibrium, the effect of pH and of foreign ions on the adsorption of zinc on the samples of HA were studied. The percentage of zinc adsorption in the observed initial pH range was constant. The highest values of percentage zinc adsorption on HA1 and HA2 were achieved at the lowest concentration of the zinc ions in solution. Adsorption isotherm was well characterized by Langmuir equation and the value of maximum adsorption capacity of zinc on hydroxyapatite HA1 and HA2 was calculated to be 0.437 and $0.605\,mmol\,g^{-1}$, respectively. The competition effect of Fe^{2+} towards Zn^{2+} adsorption is obviously stronger than that of Ca^{2+} ions. Mg^{2+} and Sr^{2+} ions have no apparent effect on zinc adsorption on synthetic hydroxyapatite. The ability of the bivalent cations present in the environment to depress the adsorption of zinc on hydroxyapatite is in the following order: $Fe^{2+} > Ca^{2+} > Sr^{2+} \approx Mg^{2+}$. This study showed that this is a promising candidate for the removal of radio zinc from aqueous solutions.

References

[1] S.P. Nations, P.J. Boyer, L.A. Love, M.F. Burritt, J.A. Butz, G.I. Wolfe, L.S. Hynan, J. Reisch, J.R. Trivedi, Denture cream: An unusual source of excess zinc, leading to hypocupremia and neurologic disease, Neurology 71 (2008) 639–643.

[2] WHO, Zinc in Drinking-water. Guidelines for Drinking-water Quality, WHO/SDE/WHS/03.04/17, World Health Organization, Geneva, 2003.

[3] E. Chmielewská, J. Kuruc, Odpady. Nakladanie s tuhým neaktívnym a rádioaktívnym odpadom [Wastes. Loading with solid inactive and radioactive waste], Univerzita Komenského Bratislava, Bratislava, 2008.

[4] D. Wenming, G. Zhijun, D. Jinzhou, Z. Liying, T. Zuyi, Sorption characteristics of zinc(II) by calcareous soil-radiotracer study, Appl. Radiat. Isot. 54 (2001) 371–375.

[5] D.H. Mu, J.Z. Du, D.J. Li, H.Q. Song, S.P. Yan, Y.J. Gu, Sorption/desorption of radio zinc on the surface sediments, J. Radioanal. Nucl. Chem. 267 (2006) 585–589.

[6] M. Nakayama, D. Mitsutaka, R. Fujiyoshi, S. Sawamura, Sorption of manganese(II) and zinc(II) to soils alluvial in origin using a radiotracer technique, J. Radioanal. Nucl. Chem. 254 (2002) 331–334.

[7] F. Fu, Q. Wang, Removal of heavy metal ions from wastewaters: A review, J. Environ. Manage. 92 (2011) 407–418.

[8] P.C. Mishra, R.K. Patel, Removal of lead and zinc ions from water by low cost adsorbents, J. Hazard. Mater. 168 (2009) 319–325.

[9] J.A. Gómez del Río, P.J. Morando, D.S. Cicerone, Natural materials for treatment of industrial effluents: Comparative study of the retention of Cd, Zn and Co by calcite and hydroxyapatite. Part I: Batch experiments, J. Environ. Manage. 71 (2004) 169–177.

[10] C.W. Cheung, J.F. Porter, G. McKay, Sorption kinetics for the removal of copper and zinc from effluents using bone char, Sep. Purif. Technol. 19 (2000) 55–64.

[11] A.K. Bhattacharya, S.N. Mandal, S.K. Das, Adsorption of Zn(II) from aqueous solution by using different adsorbents, Chem. Eng. J. 123 (2006) 43–51.

[12] E. Pehlivan, S. Cetin, B.H. Yanik, 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.

[13] Y. Dong, Z. Liu, L. Chen, Removal of Zn(II) from aqueous solution by natural halloysite nanotubes, J. Radioanal. Nucl. Chem. 292 (2012) 435–443.

[14] T.S.B. Narasaraju, D.E. Phebe, Some physico-chemical aspects of hydroxylapatite, J. Mater. Sci. 31 (1996) 1–21.

[15] A. Nzihou, P. Sharrock, Role of phosphate in the remediation and reuse of heavy metal polluted wastes and sites, Waste Biomass. Valor. 1 (2010) 163–174.

[16] Y. Xu, F.W. Schwartz, S.J. Traina, Sorption of Zn^{2+} and Cd^{2+} on hydroxyapatite surfaces, Environ. Sci. Technol. 28 (1994) 1472–1480.

[17] 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.

[18] 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.

[19] K.K.H. Choy, G. McKay, Sorption of metal ions from aqueous solution using bone char, Environ. Int. 31 (2005) 845–854.

[20] F. Banat, S. Al-Asheh, F. Mohai, Batch zinc removal from aqueous solution using dried animal bones, Sep. Purif. Technol. 21 (2000) 155–164.

[21] A. Tiselius, S. Hjertén, Ö. Levin, Protein chromatography on calcium phosphate columns, Arch. Biochem. Biophys. 65 (1956) 132–155.

[22] O. Rosskopfová, M. Galamboš, L. Pivarčiová, M. Čaplovičová, P. Rajec, Adsorption of nickel on synthetic hydroxyapatite from aqueous solutions, J. Radioanal. Nucl. Chem. 295 (2013) 459–465.

[23] M. Marhol, Měniče iontů v chemii a radiochemii [Ion exchangers in chemistry and radiochemistry], Academia, Československá akademie věd, Praha, 1976.

[24] Å. Bengston, A. Shuchukarev, P. Persson, S. Sjöberg, A solubility and surface complexation study of a non-stoichiometric hydroxyapatite, Geochim. Cosmochim. Acta 73 (2009) 257–267.

[25] I. Smičiklas, S. Dimović, I. Plećaš, M. Mitrić, Removal of Co^{2+} from aqueous solutions by hydroxyapatite, Water Res. 40 (2006) 2267–2274.

[26] C. Stötzel, F.A. Müller, F. Reinert, F. Niederdraenk, J.E. Barralet, U. Gbureck, Ion adsorption behaviour of hydroxyapatite with different crystallinities, Colloid Surf., B 74 (2009) 91–95.

[27] S. Hayakawa, K. Ando, K. Tsuru, A. Osaka, E. Fujii, K. Kawabata, C. Bonhomme, F. Babonneau, Structural characterization and protein adsorption property of hydroxyapatite particles modified with zinc ions, J. Am. Ceram. Soc. 90 (2007) 565–569.

[28] Y.J. Lee, E.J. Elzinga, R.J. Reeder, Sorption mechanisms of zinc on hydroxyapatite: Systematic uptake studies and EXAFS spectroscopy analysis, Environ. Sci. Technol. 39 (2005) 4042–4048.

[29] I. Smičiklas, A. Onjia, S. Raičević, Đ. Janaćković, M. Mitrić, Factors influencing the removal of divalent cations by hydroxyapatite, J. Hazard. Mater. 152 (2008) 876–884.

[30] R. Bazargan-Lari, M.E. Bahrololoom, A. Nemati, Dependence of equilibrium, kinetics and thermodynamics of Zn(II) ions sorption from water on particle size of natural hydroxyapatite extracted from bone ash, World Acad. Sci. Eng. Technol. 61 (2012) 1117–1122.

[31] M. Prasad, H. Xu, S. Saxena, Multi-component sorption of Pb(II), Cu(II) and Zn(II) onto low-cost mineral absorbent, J. Hazard. Mater. 154 (2008) 221–229.

[32] E. Erdem, N. Karapinar, R. Donat, The removal of heavy metal cations by natural zeolites, J. Colloid Interface Sci. 280 (2004) 309–314.

[33] A.M. El-Kamash, A.A. Zaki, M. Abed El Geleel, Modeling batch kinetics and thermodynamics of zinc and cadmium ions removal from waste solutions using synthetic zeolite A, J. Hazard. Mater. 127 (2005) 211–220.

[34] G. Purna Chandra Rao, S. Satyaveni, A. Ramesh, K. Seshaiah, K.S.N. Murthy, N.V. Choudary, Sorption of cadmium and zinc from aqueous solutions by zeolite 4A, zeolite 13X and bentonite, J. Environ. Manage. 81 (2006) 265–272.

[35] A. Yasukawa, M. Higashijima, K. Kandori, T. Ishikawa, Preparation and characterization of cadmium–calcium hydroxyapatite solid solution particles, Colloid Surf., A 268 (2005) 111–117.