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Removal of Co^{2+} from aqueous solutions by hydroxyapatite

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ARTICLE INFO

Article history:

Received 23 December 2005

Received in revised form

12 April 2006

Accepted 21 April 2006

Keywords:

Hydroxyapatite

Cobalt removal

Equilibrium isotherm

Kinetics

pH

Desorption

ABSTRACT

A study on the removal of cobalt ions from aqueous solutions by synthetic hydroxyapatite was conducted in batch conditions. The influence of different sorption parameters, such as: initial metal concentration, equilibration time, solution pH and presence of EDTA on the amount of Co^{2+} sorbed was studied and discussed. The sorption process followed pseudo-second-order kinetics with necessary time of 24 h to reach equilibrium. Cobalt uptake was quantitatively evaluated using the Langmuir and Dubinin–Kaganer–Radushkevich (DKR) model. The Langmuir adsorption isotherm constant corresponding to adsorption capacity, X_m , was found to be 20.92 mg/g. Sorption of Co^{2+} is constant in the initial pH range 4–8, because HAP surface buffers these solutions to the constant final pH value of 5.1. In the presence of EDTA, sorption of Co^{2+} decreases due to formation of complex with lower sorption affinities. Cobalt desorption depends on the composition of the extracting solution. The desorbed amount of cobalt decreased continuously with increasing pH, and increased with increasing Ca^{2+} concentration in leaching solution.

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1. Introduction

Cobalt is relatively rare element found in the earth's crust with a concentration of approximately $25 \mu\text{g/g}$ (Hamilton, 1994). Although it occurs naturally in the environment, due to anthropogenic activity excessive amounts of cobalt are released from coal combustion and mining, processing of cobalt-containing ores and the production and use of cobalt chemicals. Cobalt has variety of uses: as a metal in electroplating, because of its hardness and resistance to oxidation, in alloys with iron, nickel and other metals, and also in magnet and stainless steels. Its salts have been used for centuries for the production of blue colors in porcelain, glass, pottery, and enamels, while compounds are used as paint pigments. Radioactive, artificial isotope cobalt-60 is an important gamma-ray source and is used extensively as a tracer and radiotherapeutic agent (Schönfeld et al., 2002).

In small amounts cobalt is essential for human health, because it is a part of vitamin B_{12} . However, higher concentrations of cobalt may damage human health. Soils

near mining and melting facilities may contain very high amounts of cobalt. Once it has entered the environment, it may react with other particles or adsorb on soil and sediments. Under acidic conditions, cobalt becomes mobile causing its accumulation in plants and in animals and humans that eat these plants. Health effects may also be produced by radiation of radioactive cobalt isotopes. ^{60}Co is formed in a nuclear reactor by the (n, γ) reaction of the Co present as an impurity in the metals used, and can also be present in the waste water effluents (ali Khan, 2003).

The sorption studies of Co^{2+} are essential for nuclear and hazardous waste management. Different inorganic and organic sorbents have been considered for Co^{2+} immobilisation: vermiculite (da Fonseca et al., 2005), zeolite (Erdem et al., 2004), kaolinite (Yavuz et al., 2003), hydrous manganese oxide (Granados Correa and Jiménez-Becerril, 2004), activated carbon (Demirba, 2003), marine green alga (Vijayaraghavan et al., 2005a), anaerobic granular sludge (van Hullebusch et al., 2005), etc. Inorganic exchangers have interesting properties such as resistance to decomposition in the presence of

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doi:10.1016/j.watres.2006.04.031

ionizing radiation or at high temperatures, which have made them interesting for the treatment of nuclear waste.

Apatite is a general name for different minerals with the formula $X_5(YO_4)_3$ (OH, F, Cl), where X can be any of several metal cations such as calcium, barium, sodium, lead, strontium, etc., and Y can be phosphorous, vanadium or arsenic (Narasaraju and Phebe, 1996). Hydroxyapatite (HAP) is a member of apatite mineral family, with the formula $Ca_{10}(PO_4)_6(OH)_2$. Apatites 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, especially actinides and heavy metals (Monteil-Rivera and Fedoroff, 2002). Apatites of different origin (mineral, synthetic, and derived from animal and fish bones) have been studied as sorbents (Al-Asheh et al., 1999; Deydier et al., 2003; Chen et al., 1997a,b; Krestou et al., 2004; da Rocha et al., 2002). The mechanisms of the metal cations retention are different and include: ion exchange, adsorption, dissolution/precipitation, and formation of surface complexes (Monteil-Rivera and Fedoroff, 2002). Compared to other heavy metals, little attention has been paid on Co^{2+} removal by HAP. Suzuki et al. (1982) have investigated the cobalt sorption on different synthetic HAP samples and found the sorption capacities in the range from ~ 0.13 to ~ 0.30 mmol/g, depending on the sorbents properties. Recently, a comparative study of the retention of Cd, Zn and Co by calcite and HAP was conducted by batch experiments (Gomez del Rio et al., 2004). Both materials were found to be useful for heavy metal retention, but HAP had better performance for water treatment due to its greater efficiency for the retention of Cd, Zn and Co and its lower solubility in a wide range of pH ($6 < \text{pH} < 9$). The interaction of Co^{2+} with HAP was also studied from the aspect of the catalytic activities of cobalt/calcium exchanged samples for oxidative dehydrogenation of ethane (Elkabouss et al., 2005), and it was found that the global conversion and the ethylene yield increased with temperature and depended upon the cobalt content.

The main objective of the present study was to investigate factors influencing Co^{2+} immobilization by low-crystalline HAP powder such as: contact time, aqueous Co^{2+} concentration, solution pH, presence of EDTA, as well as to determine the main sorption mechanisms and to estimate the leachability of Co-exchanged HAP in liquid phases with different pH and calcium contents.

2. Materials and methods

2.1. Preparation and characterization of HAP sorbent

HAP sample was synthesized at room temperature, by neutralization of a $Ca(OH)_2$ suspension with H_3PO_4 (Smičiklas et al., 2005). Sorbent was analyzed by X-ray diffraction (XRD), using a Philips PW 1050 diffraction system, with $CuK\alpha_{1,2}$ Ni-filtrated radiation. The patterns were registered in the 2θ range 10 – 100° with a scanning step size of 0.02° and analyzed by the Rietveld methodology, using the Fullprof software.

The Ca/P ratio was determined by ICP-OES (Perkin-Elmer model ICP/6500), the specific surface area was determined from low-temperature nitrogen adsorption isotherms, using a Micrometrics ASAP 2000 instrument, and the point of zero

charge (pH_{PZC}) was measured by batch equilibration technique, with 0.1 mol/dm^3 KNO_3 as an inert electrolyte.

2.2. Sorption experiments

In order to determine the sorption capacity of HAP for Co^{2+} cations, as well as the influence of the contact time, pH and the presence of complexing agent, sorption experiments were performed by batch equilibration technique. Solutions were prepared from $Co(NO_3)_2 \cdot 6 H_2O$ salt (p.a. purity) and distilled water. Initial pH values of the solutions in the sorption experiments were adjusted to 5.0 ± 0.1 , by adding minimum amounts of 0.01 M HNO_3 or KOH. All experiments were performed at room temperature ($20 \pm 1^\circ \text{C}$). PVC flasks, containing suspensions at a solid to solution ratio 1:200, were placed in a horizontal shaker, and after a specified time the sorbents were separated from the solutions by filtration through the blue-band filter paper (Quant, Grade 391). The initial and the final metal concentrations were determined by a Perkin-Elmer Analyst 200 AAS.

2.2.1. Effect of equilibration time

The suspensions containing HAP and 300 mg/dm^3 Co^{2+} solution were shaken in different time intervals ranging from 15 min to 3 days, filtrated and analyzed to determine the metal cation concentration.

According to literature, several models can be used to express the kinetics of the sorption processes (e.g. first-order, pseudo-first, pseudo-second-order reaction model) (Ho and McKay, 1999). The studies on the kinetics of the various sorption processes have revealed that over a long period of time pseudo-second-order model provides the best correlation (Ho and McKay, 1999). Pseudo-second-order reaction model was applied to our experimental data in order to determine the sorption rate constant, at room temperature. The linear form of pseudo-second order rate expression is

$$t/q_t = 1/k'_2 q_e^2 + 1/q_e t, \quad (1)$$

where q_e and q_t are the amounts of solute sorbed at equilibrium and time t (mg/g), k'_2 is the equilibrium rate constant of pseudo-second-order (g/mgmin). The following expression denotes the initial sorption rate h (mg/gmin):

$$h = k'_2 q_e^2. \quad (2)$$

In addition, the intraparticle diffusion model (Weber and Morris, 1963) was considered in order to determine the participation of this process in the sorption of Co^{2+} by synthetic HAP. According to this model, the plot of uptake (q_t), versus the square root of time ($t^{0.5}$) should be linear if intraparticle diffusion is involved in the overall adsorption mechanism. Furthermore, if this line passes through the origin then the intraparticle diffusion is the rate controlling step of the process.

The initial rate of intra particle diffusion, k_d , can be calculated in the following way:

$$k_d = q_t/t^{0.5}, \quad (3)$$

where q_t is the amount of sorbate on the surface of the sorbent at time t (mg/g), k_p is the intraparticle rate constant ($\text{mg/gmin}^{0.5}$) and t is the time (min).

2.2.2. Effect of initial Co^{2+} concentration

HAP was equilibrated with Co^{2+} solutions of different initial concentrations (5–1000 mg/dm^3) for 24 h. After filtration, the final pH values and the final concentrations of metal in the solutions were measured. The solid residue with the maximum amount of Co^{2+} sorbed was analyzed by XR-diffraction (as it was described in Section 2.1 for the starting HAP sample).

The Langmuir and Dubinin–Kaganer–Radushkevich (DKR) adsorption isotherms, often used to describe the sorption of solutes from a liquid phase, were applied to our experimental results. Linear form of the Langmuir equation can be expressed as follows:

$$C_e/Q_e = 1/X_m K + 1/X_m C_e, \quad (4)$$

where Q_e (mg/g) and C_e (mg/dm^3) denotes the equilibrium concentrations of sorbate in the solid and the liquid phase, X_m (mg/g) is the maximum sorption capacity, and K (dm^3/g) is the Langmuir constant related to the energy of adsorption.

The DKR equation, based on the heterogeneous surface of the adsorbate, has the form:

$$\ln C_{\text{ads}} = \ln X_m - \beta \varepsilon^2, \quad (5)$$

where C_{ads} (mol/g) is the amount of the metal ions adsorbed per unit weight of the adsorbent, X_m (mol/g) is the maximum sorption capacity, β (mol^2/J^2) is the activity coefficient related to the mean sorption energy, and ε is the Polanyi potential. ε can be calculated in the following way:

$$\varepsilon = RT \ln(1 + 1/C_e), \quad (6)$$

where R (8.314 J/molK) is the gas constant and T (K) is the temperature. The saturation limit X_m may represent the total specific micropore volume of the sorbent. The slope of the plot of $\ln C_{\text{ads}}$ versus ε^2 gives β and the intercept yields the sorption capacity, X_m . The mean sorption energy E (kJ/mol) can also be calculated using the following relationship:

$$E = 1/\sqrt{-2\beta}. \quad (7)$$

2.2.3. Effect of pH

The effect of pH was studied in the pH range of 4–12. The initial metal concentration was 300 mg/dm^3 , while the initial pH values were adjusted by adding KOH or HNO_3 solutions. After 24 h of contact, the suspensions were filtrated, and analyzed for final pH and metal concentrations.

2.2.4. Effect of complexing agent

The effect of EDTA on Co^{2+} sorption by HAP was investigated in the EDTA concentration range 50–1000 mg/dm^3 . The initial pH values were adjusted to 5.0, in order to assure the formation of the metal-ligand complexes and to minimize the one of hydroxo-species. Slurries were shaken for 24 h.

2.3. Desorption experiments

In order to estimate the reversibility of Co^{2+} sorption, desorption experiments using solutions with different pH and calcium contents were performed. Firstly, HAP was loaded with Co^{2+} , equilibrating the sorbent with the 1000 mg/dm^3 cobalt solution (at a solid/solution ratio 1:200).

Solid residue was thoroughly washed several times with distilled water, and dried at 105 °C. Secondly, 0.1000 g of the obtained solid phase was treated with the 20 cm^3 of each leaching solution, on a horizontal shaker, for 24 h. Four extracting solutions of varying pH values were prepared. Two acidic solutions were prepared from acetic acid at pH 2.93 ± 0.05 and 4.93 ± 0.05 following the technique for preparation of extraction fluids for toxicity characteristic leaching procedure (TCLP) (USEPA, 1999). The other two solutions were neutral and alkaline, prepared from distilled water and NaOH, while the last three solutions used in this study were prepared using different amounts of $\text{Ca}(\text{NO}_3)_2$ salt.

3. Results and discussion

3.1. Characteristics of sorbent

The physico-chemical analysis of the HAP sample has confirmed a low-crystalline product, with the specific surface area of 67 m^2/g , and the point of zero charge (pH_{PZC}) 6.1 ± 0.1 . The Ca/P molar ratio was found to be 1.60, instead of 1.67 characteristic for stoichiometric HAP. The slight calcium deficiency is common for the samples obtained by the wet methods (Narasaraju and Phebe, 1996).

3.2. Sorption kinetics

The effect of equilibration time on the sorption of Co^{2+} by HAP was investigated for time periods from 15 min up to 3 days. As shown in Fig. 1(a), the removal of cobalt ions by HAP takes place in two distinct steps: a relatively fast phase (first 3 h), followed by a slow increase until the state of equilibrium is reached. The necessary time to reach the equilibrium is about 24 h. Since an increase of time to 72 h did not show any notable effects, the contact time of 24 h was chosen for further experiments.

The application of the linear form of pseudo-second-order kinetic model on our experimental results is presented in Fig. 1(b). Both constants k'_2 and h were calculated from the intercept and slope of the line obtained by plotting t/q_t against t . The value of pseudo-second-order rate constant k'_2 is 2.74×10^{-3} g/mgmin , while the value of initial sorption rate h is 0.280 mg/gmin . Calculated and experimentally obtained amounts of solute sorbed at equilibrium are 10.11 mg/g and 9.92 mg/g , respectively.

Excellent agreement exists between the model and our experimental results ($R = 0.999$). Furthermore, theoretically predicted equilibrium sorption is close to that determined experimentally. The same kinetic model was used to define the sorption kinetics of metal cations on different apatites: Cr^{3+} on natural apatite derived from animal bones (Chojnacka, 2004), and Pb^{2+} on low-grade mineral phosphate (Abu Al-Rub, 2004).

The kinetic results were also subjected to analysis by the Weber and Morris model. The plot of q_t versus $t^{0.5}$ (Fig. 1c) has demonstrated that two types of mechanisms are operating in the removal of Co^{2+} . Due to the varying extent of adsorption in the initial and final stages of the experiment two straight lines with different slopes were obtained.

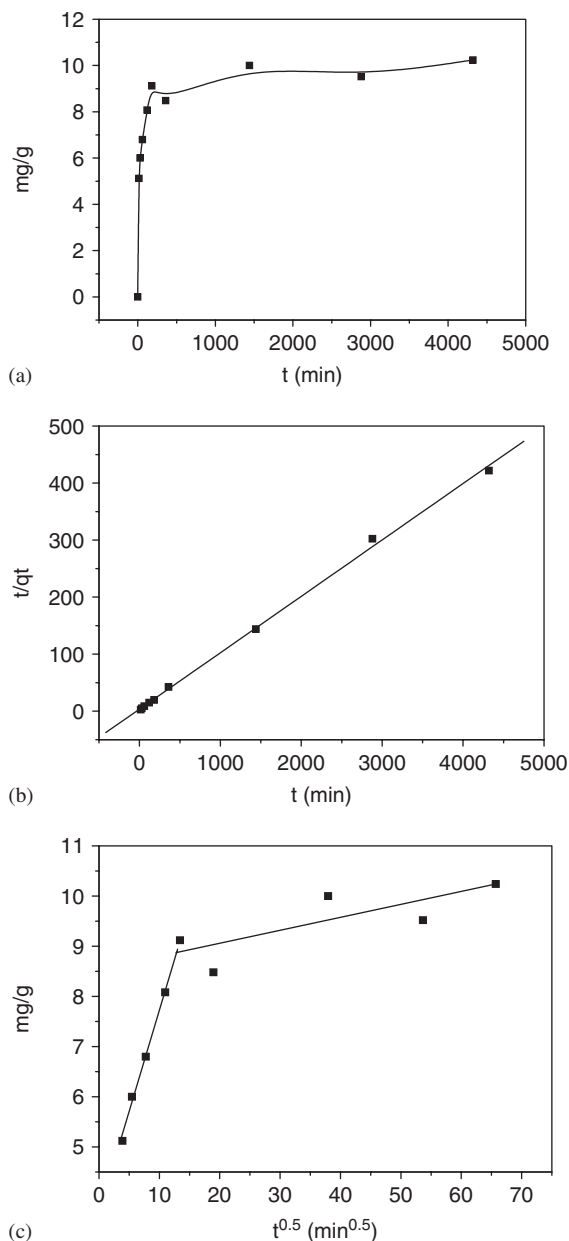


Fig. 1 – (a) The influence of contact time on the amount of Co²⁺ sorbed by HAP, (b) linear fit of experimental data obtained using pseudo-second order kinetic model and (c) the amount of Co²⁺ sorbed versus square root of time.

The initial rapid uptake can be attributed to the boundary layer effects. After the external surface loading was completed, the intraparticle diffusion takes place. The second linear part of the plot presented in Fig. 1(c), for contact times 180 min–72 h, corresponds to the transportation of Co²⁺ within HAP particles, thus Eq. (3) was applied to these adsorption data. The calculated rate constant for intraparticle diffusion k_d , was found to be $2.5 \times 10^{-2} \text{ mg/g min}^{0.5}$. However, the plot indicated that the intraparticle diffusion was not the rate-controlling step because it did not pass through the origin.

3.3. Sorption isotherms

Taking into account all the investigated initial concentrations of cobalt (5–1000 mg/dm³), the corresponding concentrations of nitrate anions and pH 5, the negative values of the log saturation indices were found for possible Co solid phases, by the visual MINTEQ software. This reinforced the fact that, under applied experimental conditions, cobalt exists in the form of Co²⁺ ions, therefore its removal from the solution is a result of the sorption process by HAP. The plot of Co²⁺ sorbed by HAP (mg/g) against metal concentrations in the equilibrated solutions (mg/dm³) is presented in Fig. 2.

The sorption of Co²⁺ increases as its initial concentration in the solution increases, until the equilibrium is reached. The linear fits of our experimental data obtained by Langmuir and DKR isotherms are presented in Fig. 3.

The correlation factors R (0.994 and 0.996 for Langmuir and DKR model, respectively) confirm good agreement between both theoretical models and our experimental results. The maximum sorption capacity, X_m , calculated from Langmuir equation is 20.92 mg/g (0.354 mmol/g), while Langmuir constant K is 0.019 dm³/g. The values of sorption constants, derived from DKR model are: 0.501 mmol/g for X_m , $-4.05 \times 10^{-9} \text{ mol}^2/\text{J}^2$ for β and 11.11 kJ/mol for E .

The Langmuir model is basically developed to describe the sorption processes where no interaction between sorbate species occur on sites having the same sorption energies independent of surface coverage. Maximum sorption capacity represents the monolayer coverage of sorbent with sorbate. Considering differences in physico-chemical properties of applied sorbents, maximum sorption capacity of 0.30 mmol Co²⁺ per gram of synthetic HAP reported by Suzuki et al. (1982), is very close to our experimental data obtained using the Langmuir equation (20.92 mg/g or 0.354 mmol/g). X_m value obtained by DKR model is higher, while calculated sorption energy E of 11.11 kJ/mol lies in the range of energies (8–16 kJ/mol) characteristic for the ion-exchange mechanisms (Erdem et al., 2004).

Generally, HAP selectivity towards divalent metal cations is a result of the ion-exchange process with Ca²⁺ ions (Monteil-Rivera and Fedoroff, 2002). Crystal radius of cobalt (0.72 Å)

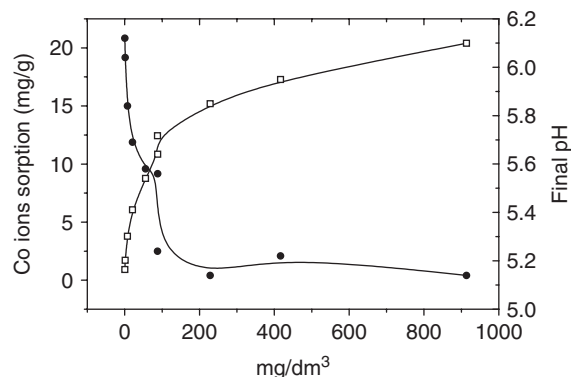


Fig. 2 – Relationship between equilibrium metal concentrations, amounts of Co²⁺ sorbed (□) and final pH values (●).

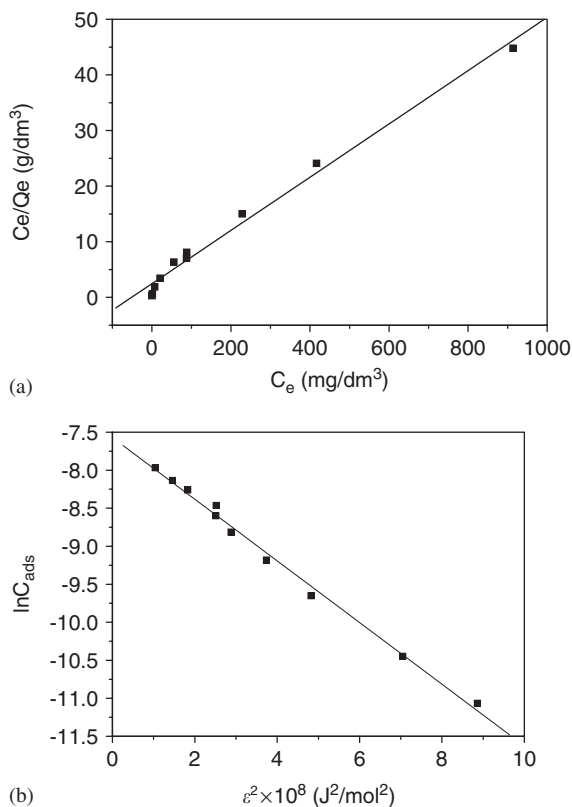


Fig. 3 – Linear fits of experimental data obtained using (a) Langmuir and (b) DKR sorption isotherms.

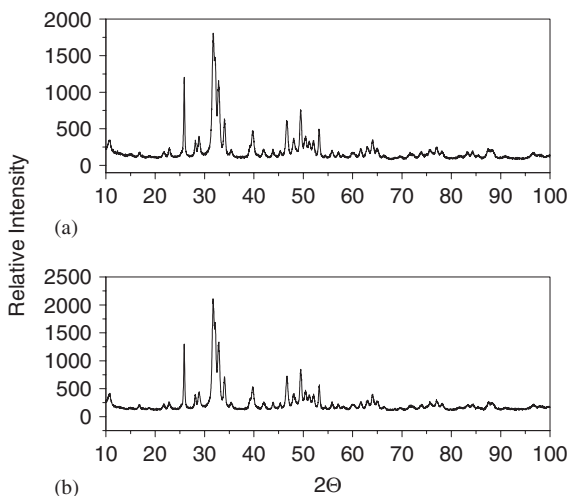
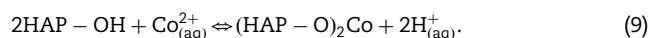
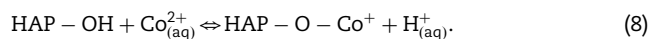


Fig. 4 – XRD patterns of (a) original synthetic low-crystalline HAP, and (b) solid residue with maximum amount of sorbed Co^{2+} .

slightly differ from that of Ca^{2+} (0.99 Å), and it can substitute Ca^{2+} in the HAP crystal lattice. Fig. 4 presents the XRD patterns of the original HAP powder and Co^{2+} -loaded sample. No structural changes of HAP were detected by the powder X-ray diffraction analysis of the solid residue with maximum amount of sorbed metal, obtained after interaction of HAP with 1000 mg/dm^3 Co^{2+} solution. The samples were indexed in the hexagonal system with space group $\text{P6}_3/\text{m}$. The unit

cell parameters of the starting Ca-HAP were $a = b = 0.9433$ nm and $c = 0.6881$ nm, while values of $a = b = 0.9428$ nm and $c = 0.6876$ nm were calculated for the Co-exchanged sample. The slight decrease in unit cell parameters is in agreement with the lower ionic radii of the Co^{2+} ion. These data strongly support the ion-exchange mechanism for Co^{2+} sorption by HAP.

However, in comparison to the HAP pH_{PZC} (6.1), the sorption process of Co^{2+} (Fig. 2), caused the decrease of the final pH values in the range from 6.1 to 5.1 (for lowest and highest Co^{2+} concentrations, respectively). The drop in equilibrium pH suggests that H^+ ions are liberated from the solid surface into the aqueous phase as a result of the exchange with metal cations:



Therefore, decreases in final pH values suggest that formation of surface complexes contributes, to some extent, to the overall sorption mechanism.

Table 1, shows the comparison of cobalt sorption capacities for various sorbents, found in literature. From Table 1 it can be concluded that HAP exhibits moderate sorption capacity toward Co^{2+} ions, which is between the values characteristic for highly selective cation exchange resins, natural vermiculite, marine green alga, and the range of other organic and inorganic sorbents: anaerobic sludge, activated carbon, zeolite, kaolinite and crab shell.

3.4. Effect of pH

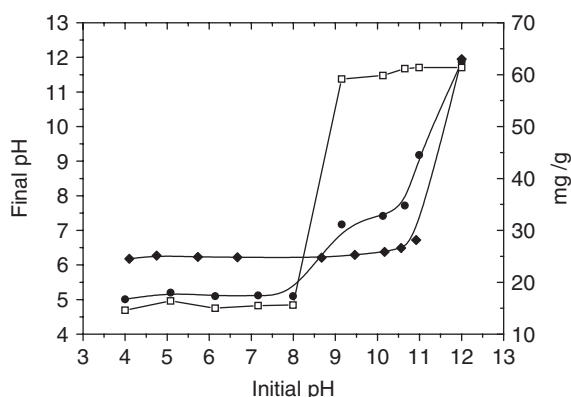
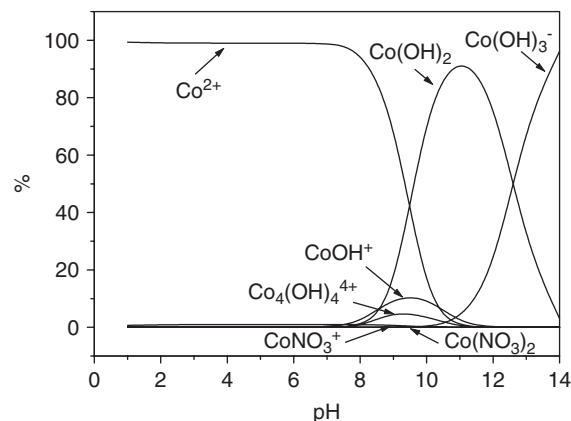
Sorption of cobalt by HAP was studied using the initial pH range 4–12. After 24 h of contact time, equilibrium pH (pH_f) values were measured, as well as the residual metal concentrations and the results are presented in Fig. 5. In the same figure, the pH_f vs. pH_i plot, obtained by equilibrating HAP powder with inert electrolyte (KNO_3) for pH_{PZC} determination, was also included. As it was mentioned in our earlier paper (Smičiklas et al., 2000), synthetic HAP exhibits excellent buffering properties. If no specific sorption from the solution occurs, acidic, as well as basic solutions (in the initial pH range 4–10) are buffered after the reaction with HAP to its pH_{PZC} value. The buffering characteristics of HAP are the result of the acid-base reactions of the reactive surface sites. According to Wu et al. (1991), the reactions responsible for the surface properties of HAP in aqueous solutions are:



In the range of the lower initial pH values (below pH_{PZC}) consumption of protons from the solution by the protonation of surface $\equiv \text{PO}^-$ and $\equiv \text{CaOH}^0$ groups results in a final pH increase. The positively charged $\equiv \text{CaOH}_2^+$ and neutral $\equiv \text{POH}^0$ sites prevail on HAP surface in acidic solutions, making surface charge of HAP in this pH region positive. On the other hand, final pH decrease takes place in the range of higher initial pH (above pH_{PZC}) due to OH^- consumption via deprotonation of surface $\equiv \text{CaOH}_2^+$ and $\equiv \text{POH}^0$ sites. Thus

Table 1 – The comparison of Co^{2+} sorption capacities for various sorbents

Sorbent	Sorption capacity (mg/g)	Reference
Marine green alga	46.1	(Vijayaraghavan et al., 2005a)
Anaerobic granular sludge	12.34	(van Hullebusch et al., 2005)
Cation exchange resins		
IRN77	86.17	(Rengaraj and Moon, 2002)
SKN1	69.44	
Activated carbon	13.88	(Demirba, 2003)
Natural vermiculite	49.49	(da Fonseca et al., 2005)
Natural zeolites	14.38	(Erdem et al., 2004)
Kaolinite	0.919	(Yavuz et al., 2003)
Crab shell	20.47	(Vijayaraghavan et al., 2005b)
Synthetic HAP	17.67	(Suzuki et al., 1982)
Synthetic HAP	20.19	This study

**Fig. 5 – Relationships between initial pH, final pH values obtained after equilibration of HAP with inert electrolyte (◆) and Co^{2+} solution (●), and the amount of cobalt sorbed (□).****Fig. 6 – The distribution of cobalt ionic species as a function of pH.**

neutral $\equiv\text{CaOH}^0$ and negatively charged $\equiv\text{PO}^-$ species predominate in alkaline solutions, causing HAP surface to become negatively charged in alkaline solutions.

If a specific cation sorption occurs, pH_{PZC} is shifted to the lower values. This was confirmed for HAP-Co system. The plateau part of the pH_f vs. pH_i plot, corresponding to the pH range where the buffering effect of HAP surface takes place, becomes shorter in the presence of Co^{2+} , while pH_{PZC} of HAP decreases from 6.1 to 5.1. For the initial pH range 4–8, final pHs are the same and as a consequence, the sorption of cobalt is constant in that pH range. A further increase of the solution pH from 8 to 12 leads to almost a 100% removal of cobalt. Fig. 6 presents the relationship between the relative amounts of cobalt ionic species and solution pH, calculated for the total cobalt concentration of 300 mg/dm^3 and corresponding 631.16 mg/dm^3 of NO_3^- , by visual MINTEQ software. Up to pH 8, cobalt is present in the solution mainly in the form of Co^{2+} ions. The positively charged $\text{Co}(\text{OH})^+$ and $\text{Co}_4(\text{OH})_4^{4+}$ hydrolytic products appear in the pH range 7–12, while neutral $\text{Co}(\text{OH})_2$ particles start to precipitate at pH 8 and become predominant at pH 11. From Figs. 5 and 6, it can be concluded that in the initial pH range 4–8 cobalt is removed from the solution in the form of Co^{2+} through ion exchange process with HAP, while the sharp decrease of aqueous cobalt concentration in the

initial pH range 8–12 is mainly due to precipitation of $\text{Co}(\text{OH})_2$. In addition to that, HAP surface, which is negatively charged in the higher pH region, may contribute to the overall removal process by the sorption of positively charged hydrolytic species $\text{Co}(\text{OH})^+$ and $\text{Co}_4(\text{OH})_4^{4+}$.

3.5. Effect of EDTA addition

Organic chelating agents have a great practical importance as constituents of the chemical decontamination agents, which are used to remove toxic or radioactive metal contaminants from different surfaces types. As a consequence, liquid waste arising from decontamination activities contains large amounts of these agents that may affect further processes of wastewater treatments (such as sorption). One of the most frequently used chelating agent is ethylenediaminetetraacetic acid (EDTA). In agriculture, EDTA complexes have been used as commercial soil amendments to improve micronutrient availability, and it is also widely utilized for various industrial purposes. The influence of EDTA on Co^{2+} sorption by HAP is presented in Fig. 7.

The greater the concentration of EDTA, the smaller is the percentage of Co^{2+} sorbed. The calculation made by visual MINTEQ software have shown that at pH 5, EDTA appears mainly in the form of $\text{H}_2\text{EDTA}^{2-}$ which reacts with Co^{2+}

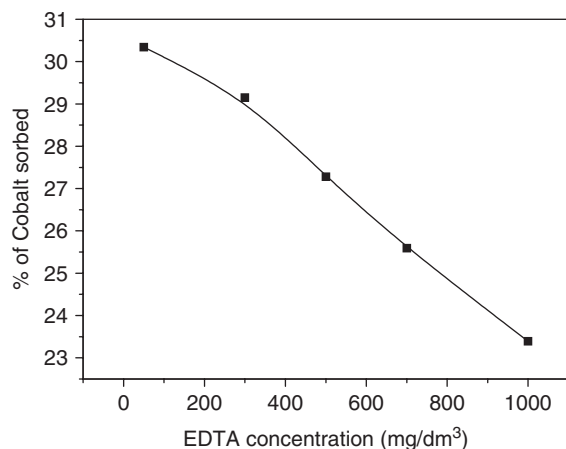


Fig. 7 – The effect of different concentration of EDTA, on Co^{2+} sorption by HAP.

species in 1:1 molar ratio forming the negatively charged Co(II)EDTA^{2-} complex. For the applied initial EDTA and Co^{2+} concentrations (50–1000 mg/dm^3 and 300 mg/dm^3 , respectively) EDTA/Co molar ratio varies in the range 0.026–0.527. Therefore, cobalt is present in the solution as a mixture of Co^{2+} and Co(II)EDTA^{2-} complex. According to Zachara et al. (1995), adsorption of Me(II)EDTA^{2-} complexes on -SOH sites of sorbents at lower pH can be explained by surface coordination using the following reaction:



With the previously mentioned increase of EDTA/Co molar ratio, cobalt sorption by HAP decreases nearly 7%, so we can conclude that cobalt is sorbed on HAP in the form of both Co^{2+} and Co(II)EDTA^{2-} species, via ion-exchange and surface-coordination mechanisms, respectively. However, Co(II)EDTA^{2-} complex have a lower sorption affinity for the HAP surface. This is consistent with previous studies on divalent metal sorption onto various solid phases (Zachara et al., 1995; ali Khan et al., 1995; Ma, 1996). The presence of EDTA reduces the effectiveness of the sorption process, thus increasing the mobility of Me^{2+} and the potential for metal pollution of the environment.

3.6. Desorption

In order to evaluate the reversibility of cobalt sorption onto HAP, desorption characteristics were also determined. Cobalt desorption from synthetic HAP depends on the composition of the extracting solution (Table 2). The amounts desorbed from acidic solutions were highest, although increases of final pH values, due to HAP buffering properties, were noticed (Table 2). Under alkaline extracting conditions, sorbed metal remained more stable. The desorbed amount of cobalt decreased continuously with increasing pH, with only trace amounts being desorbed above pH 7. This is in accordance with increased HAP stability at higher pH. Furthermore, the amount of Co^{2+} desorbed increased with the increase of the Ca^{2+} concentration. Ca^{2+} , as a parent cation of HAP, is a strong competing cation, which makes application of synthetic HAP for Co^{2+} removal less effective in hard waters.

Table 2 – The characteristics of leaching solutions and percents of Co^{2+} desorbed

Solution No.	Composition	Initial pH	Final pH	Desorbed Co^{2+} %
1	TCLP 2	2.93	4.20	30.36
2	TCLP 1	4.93	5.13	23.80
3	Distilled water	7.12	6.30	1.28
4	NaOH solution	12.70	12.72	0.07
5	Ca 0.001 M	5.62	5.47	11.12
6	Ca 0.005 M	5.66	5.39	13.47
7	Ca 0.01 M	5.58	5.40	16.89

4. Conclusion

In this study, sorption of Co^{2+} on synthetic hydroxyapatite was investigated as a function of equilibration time, initial metal concentration, pH and EDTA content. The experiments have shown that:

- Sorption in the investigated system follows a pseudo-second-order kinetics with a contribution of intraparticle diffusion. The contact time of approximately 24 h was required to reach the equilibrium.
- The sorption isotherm can be well defined by either Langmuir or DKR equation. Under defined experimental conditions (solid/solution ratio = 1:200, room temperature, initial pH = 5, initial metal concentration range 5–1000 mg/dm^3), the calculated capacity per gram of hydroxyapatite, obtained by Langmuir equation is 20.92 mg Co^{2+} . The results of XRD analysis strongly support the ion-exchange as a main mechanism for Co^{2+} removal by HAP. However, the decrease of equilibrium pH after cobalt sorption implies that formation of surface complexes contributes to the overall sorption mechanism.
- The HAP surface buffers solutions of the inert electrolyte in the pH range 4–10 to the constant final value of 6.1 (pH_{PZC}). In the presence of Co^{2+} ions, the buffering range of HAP becomes shorter (pH 4–8), the pH_{PZC} value decreases to 5.1, and as a consequence of constant final pH sorption of Co^{2+} is constant. The increase of final pH starts at initial $\text{pH} > 8$, so does the percentage of cobalt removed from the solution. In the initial pH range 8–12, cobalt is mainly precipitated as Co(OH)_2 and, in a lesser degree, sorbed on HAP in the form of positively charged hydrolytic species Co(OH)^+ and $\text{Co}_4(\text{OH})_4^{4+}$.
- The percentage of cobalt, removed from the solution by HAP, decreases with an increase of EDTA concentration. Under applied experimental conditions ($\text{pH } 5, 0.026 < \text{EDTA/Co} < 0.527$) cobalt is sorbed in the form of both Co^{2+} and Co(II)EDTA^{2-} species, via ion-exchange and surface-coordination mechanisms, respectively. Nevertheless, Co(II)EDTA^{2-} complex has lower sorption affinity for HAP surface.

- The desorbed amount of cobalt depended on the leaching solution pH and its composition; decreased continuously with increasing pH, with only trace amounts being desorbed at $\text{pH} > 7$, and increased with increasing Ca^{2+} concentration.

Acknowledgments

This work was supported by the Ministry of Science and Environmental Protection of the Republic of Serbia, under Project No. 1985.

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