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Full Length Research Paper

Potential of nano crystalline hydroxyapatite for lead (II) removal from aqueous solutions: Thermodynamic and Adsorption isotherm study

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The potential of the synthesized nano hydroxyapatite to remove Pb (II) from aqueous solutions was investigated in batch reactor under different experimental conditions. The study also investigates the effects of process parameters such as initial concentration of Pb (II) ion, temperature and adsorbent mass. Various thermodynamic parameters, such as $\Delta G°$, $\Delta H°$ and $\Delta S°$ have been calculated. The thermodynamics of Pb (II) ion onto nano HAp system indicates spontaneous and endothermic nature of the process. Lead uptake was quantitatively evaluated using the Langmuir, Freundlich and Dubinin–Kaganer–Radushkevich (DKR) model. The adsorption data follow the Langmuir model better than the Freundlich and DKR model and the adsorption equilibrium was described well by the Langmuir isotherm model with maximum adsorption capacity of 714.286 mg/g of Pb (II) ions on nano HAp.

Key word: Adsorption, nano crystalline hydroxyapatite, Pb (II), thermodynamic parameters, adsorption isotherms.

INTRODUCTION

The presence of heavy metals in aqueous waste streams has become a problem due to its harmful effects on human health and to the fauna and flora of receiving water bodies. It is known that legal standards on environment control are becoming strict and as a result, the discharge of heavy metals into aquatic bodies and sources of potable water is being rigorously controlled. The US EPA allows solutions containing heavy metals to be discharged if the concentration is usually less than 5.0 mg L^{-1} (Sahin et al., 2005).

Lead is one of the most ubiquitous contaminants in the soil and aqueous environments. A severe environmental Pb contamination can often be found at shooting ranges where the soil Pb concentration sometimes exceeds 10000 mg kg^{-1} because of spent lead bullets. In Iran, many shooting ranges are generally located in mountainous regions and suffer from the degradation of natural vegetation due to Pb toxicity, which may have the potential to augment the Pb contamination via soil erosion. Therefore, development of cost-effective technologies is necessary to reduce the mobility and bioavailability of Pb in soil and water environments (Vangronsveld et al., 1995).

Calcium hydroxyapatite (HAp), $Ca_{10}(PO_4)_6(OH)_2$, is used for the removal of heavy metals from contaminated soils, wastewater and fly ashes (Chen et al., 1997; Laperche et al., 1996; Ma et al., 1993,1994; Mavropoulos et al., 2002; Nzihou et al., 2002; Takeuchi et al., 1990). Calcium hydroxyapatite (CaHAp) is a principal component of animal hard tissues and has been of interest in industry and medical fields. Its synthetic particles find many applications in bioceramics, chromatographic adsorbents to separate protein and enzyme, catalysts for dehydration and dehydrogenation of alcohols, methane oxidation, and powders for artificial teeth and bones paste germicides (Elliott, 1994). These properties relate to various surface characteristics of HAp, e.g., surface functional groups, acidity and basicity, surface charge, hydrophilicity and porosity. It has been found that CaHAp surface possesses 2.6 groups nm^{-2} of P–OH groups acting as sorption sites (Tanaka et al., 2005). The sorption properties of HAp are of great importance for both environmental processes and industrial purposes

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Hydroxyapatite is an ideal material for long-term containment of contaminants because of its high sorption capacity for actinides and heavy metals, low water solubility, high stability under reducing and oxidizing conditions, availability, and low cost (Helferrich, 1962). It was conducted in stabilization of a wide variety of metals (e.g., Cr, Co, Cu, Cd, Zn, Ni, Pu, Pb, As, Sb, U and V) by many investigators (Krestou et al., 2004; Czerniczyniec et al., 2003; Vega et al., 1999; Reichert et al., 1996; Leyva et al., 2001; Fuller et al., 2002; McGrellis et al., 2001). They reported that the sorption take place through ionic exchange reaction, surface complexation with phosphate, calcium and hydroxyl groups and/or co-precipitation of new partially soluble phases.

The objective of this study was to investigate the possible use of nano crystalline hydroxyapatite as an alternative adsorbent material for removal of Pb (II) ions from aqueous solutions. The Langmuir, Freundlich and D-K-R models were used to fit the equilibrium isotherm. The dynamic behavior of the adsorption was investigated on the effect of initial metal ion concentration, temperature, adsorbent mass and pH of solution. The thermodynamic parameters were also evaluated from the adsorption measurements.

MATERIALS AND METHODS

Preparation of nano crystalline hydroxyapatite sorbents

All chemicals used in this work were of analytical grade and the aqueous solutions were prepared using double distilled water. Nanocrystalline hydroxyapatite compounds were prepared by a solution-precipitation method (Mobasherpour et al., 2007) using $Ca(NO_3)_2.4H_2O$ (Analar No.10305) and $(NH_4)_2HPO_4$ (Merck No. 1205) as starting materials and ammonia solution as agents for pH adjustment. A suspension of $Ca(NO_3)_2.4H_2O$ was vigorously stirred and its temperature was maintained at 25°C. A solution of $(NH_4)_2HPO_4$ was slowly added dropwise to the $Ca(NO_3)_2.4H_2O$ solution. In all experiments the pH of $Ca(NO_3)_2.4H_2O$ solution by ammonia solution was 11. The precipitin HAp was removed from solution by the centrifuge method at a rotation speed of 3000 rpm. The resulting powder was dried at 100°C.

Transmission electron microscopy (TEM) was used to characterize the particles of HAp. For this purpose, particles were deposited onto Cu grids, which support a ''holey'' carbon film. The particles were deposited onto the support grids by deposition from a dilute suspension in acetone or ethanol. The crystalline shapes and sizes were characterized by diffraction (amplitude) contrast and for crystalline materials, by high resolution (phase contrast) imaging. The specific surface area was determined from N_2 adsorption isotherm by the BET method using a micromeritics surface area analyzer model ASAP 2010.The particles thus synthesized were characterized by the following methods. The crystal phase was identified by powder X-ray diffraction (XRD) using Siemens (30 kV and 25 mA) X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5404 A^{\circ}$) and XPERT software.

Sorption study

Aqueous solutions containing Pb (II) ions of concentration 100, 200, 300 and 400 mg/L were prepared from Lead nitrate ($Pb(NO_3)_2$, Merck No.7397). 0.1 g of nano HAp was introduced in a stirred tank reactor containing 500 ml of the prepared solution. The stirring speed of the agitator was 300 rpm. The temperature of the suspension was maintained at 20±1°C. The initial pH of the solution was adjusted to the value 5.5 by adding NH_3 and HCl.

Samples were taken after mixing the adsorbent and Pb (II) ion bearing solution at pre determined time intervals (5, 10, 20, 30, 60, and 120 min) for the measurement of residual metal ion concentration in the solution and to ensure equilibrium was reached. After specified time the sorbents were separated from the solution by centrifuge and filtration through the filter paper (Whatman grade 6). The exact concentration of metal ions was determined by AAS (GBC 932 Plus atomic absorption spectrophotometer). All experiments were carried out twice. The mass balance of lead is given by:

$$mq = V\ (C_0\text{-}C) \quad (1)$$

Where m is the weight of nano-HAp (g), q the amount of lead removed by unit of weight of HAp (Uptake capacity: mg Pb/g HAp), V the volume of lead solution (L), C_0 the initial lead concentration of solution (mg Pb/L) and C is the concentration of lead at the time t of adsorption (mg Pb/L). After a long time (120 min), C and q will reach equilibrium value Ce and qe. The percent removal (%) and distribution ratio (K_d) were calculated using the equations.

$$\%\,\mathrm{Re}\,moval = \frac{(C_i - C_f)}{C_i} \times 100 \quad (2)$$

Where C_i and C_f are the concentrations of the metal ion in initial and final solutions (after 120 min) respectively, and

$$K_d = \frac{amount\ \ of\ \ metal\ \ in\ \ adsorbent}{amount\ \ of\ \ metal\ \ in\ \ solution} \times \frac{V}{m} \quad (3)$$

Where V is the volume of the solution (mL) and m is the weight of the adsorbent (g).

RESULTS AND DISCUSSION

Characteristics of adsorbent

TEM micrograph of the HAp powders after drying is seen in Figure 1. The microstructure of the HAp crystalline after drying is observed be almost like irregular circular plates, with size in the range 8 to 10 nm. The crystal structure analysis of HAp particles was performed, using X-ray diffraction and the obtained diffractograms are represented in Figure 2. The produced reflection patterns match the ICDD standards (JCPDS) for HAp.

The patterns show only the peaks characteristic to the synthesized HAp with no obvious evidences on the presence of other additional phases. The broadened peaks indicate that the crystallites are very tiny in size. XRD grain size has been calculated by scherrer method. The apparent size of hydroxyapatite crystallites obtained from XRD profile analysis by Scherrer method is 7.75 nm

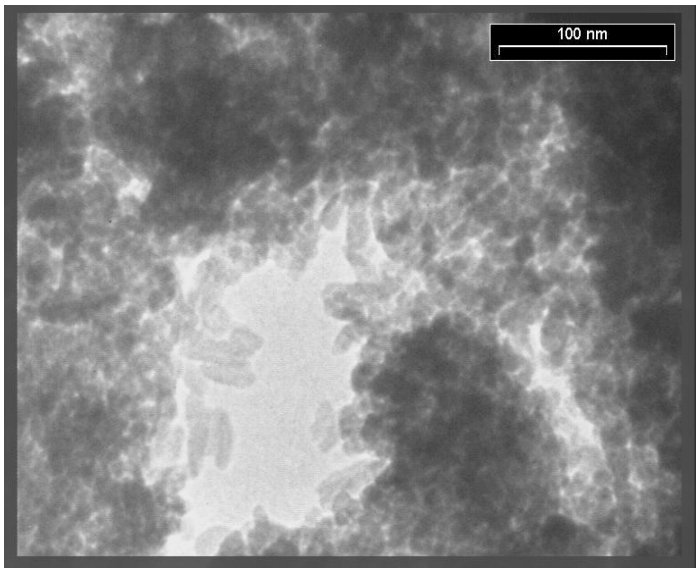

Figure 1. TEM micrograph of the nanocrystalline hydroxyapatite after drying at 100°C.

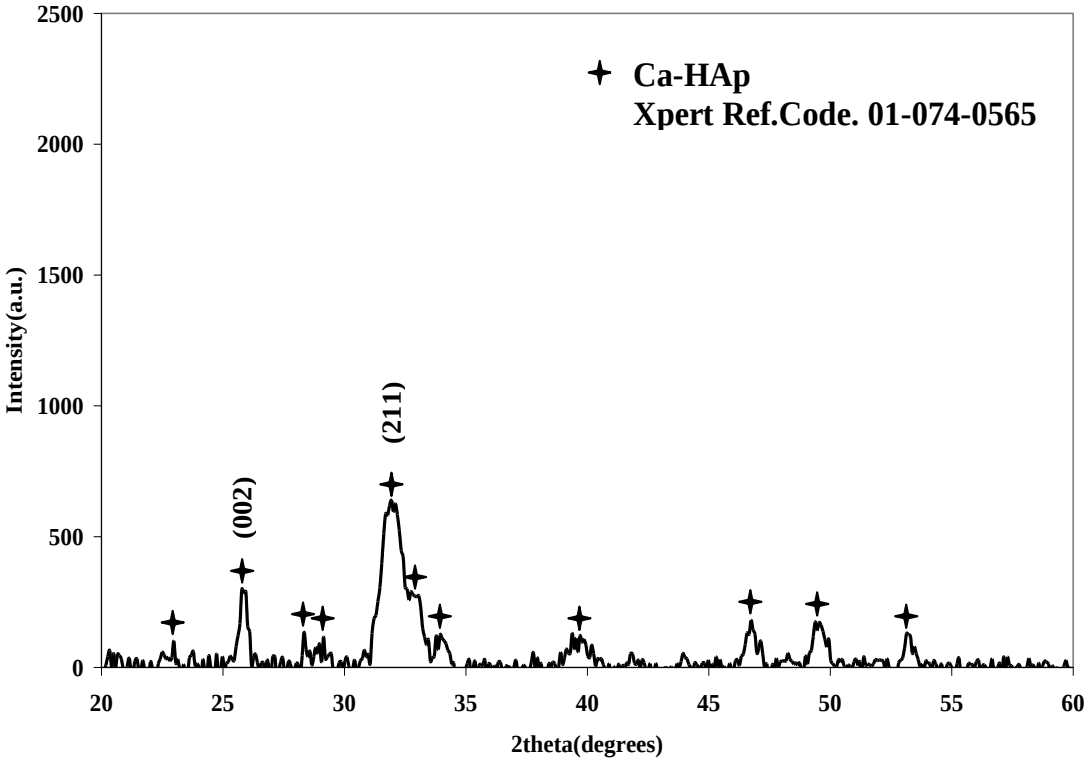

Figure 2. XRD pattern of calcium nanocrystalline hydroxyapatite powders after drying at 100°C.

(Mobasherpour et al., 2007). This TEM observation on the shape of particles agrees with our earlier XRD studies. The analysis of the HAp sample has confirmed a low-crystalline product, with the specific surface area 94.9 m^2/g.

Effect of adsorbent dosage and initial Pb (II) concentration

The sorption of Pb (II) ions was carried out at different initial lead ion concentrations ranging from 200 to 400

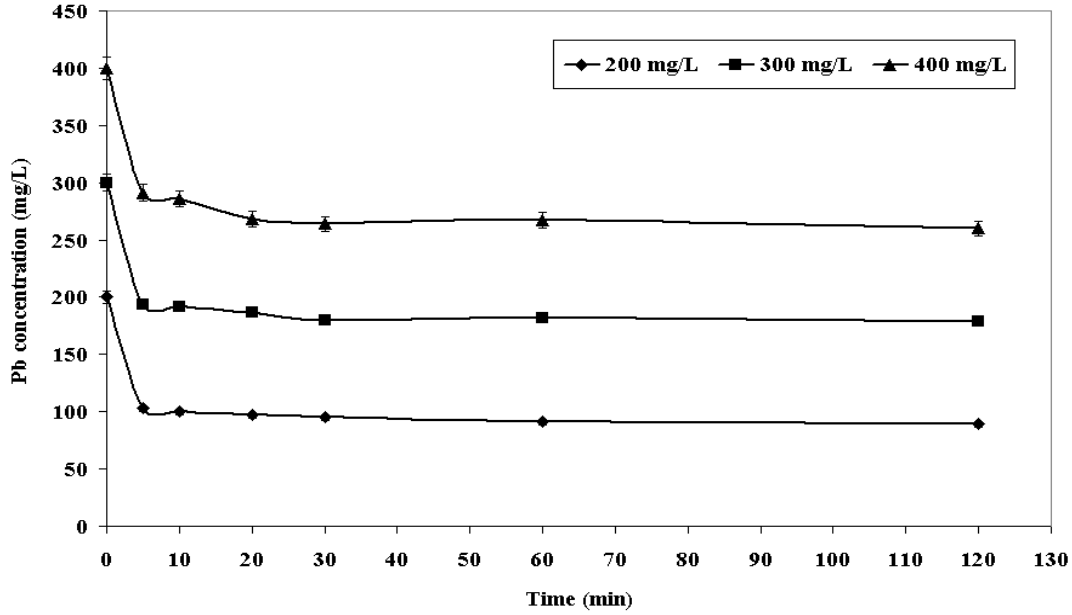

Figure 3. Time dependent concentration of aqueous Pb (II) by nano hydroxyapatite sorbents (pH 5.5, adsorbent dosage=0.2 gr/L, 300 rpm agitating rate).

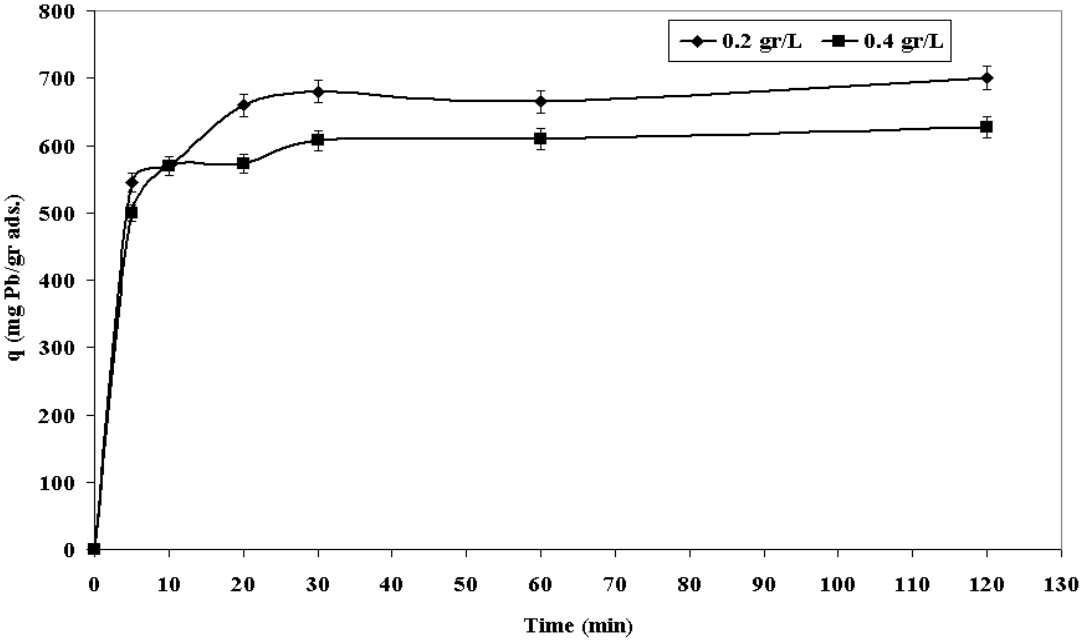

Figure 4. Effect of adsorbent dosage on removal of Pb (II) by nano hydroxyapatite (pH 5.5, initial metal concentration = 400 mg/L, 300 rpm agitating rate).

mg/L, at pH 5.5, at 300 rpm with 120 min of contact time using nano-HAp. A rapid kinetic reaction of Pb removal by sorbent occurred within the first 5 min (Figure 3.). The aqueous Pb concentration at 5 min decreased to 103, 194 and 291 mg/L by nano-HAp for 200, 300 and 400 mg/L initial concentration, respectively. Our findings on rapid kinetic reaction of synthesized nano-HAp agreed with those described elsewhere (Aklil et al., 2004; Chaturvedi et al., 2006; Prasad et al., 2004). The effect of nano-HAp dosage is presented in Figure 4. It is evident that adsorption increases with the increase in the mass of sorbent and the uptake capacity of Pb (II) decreased from

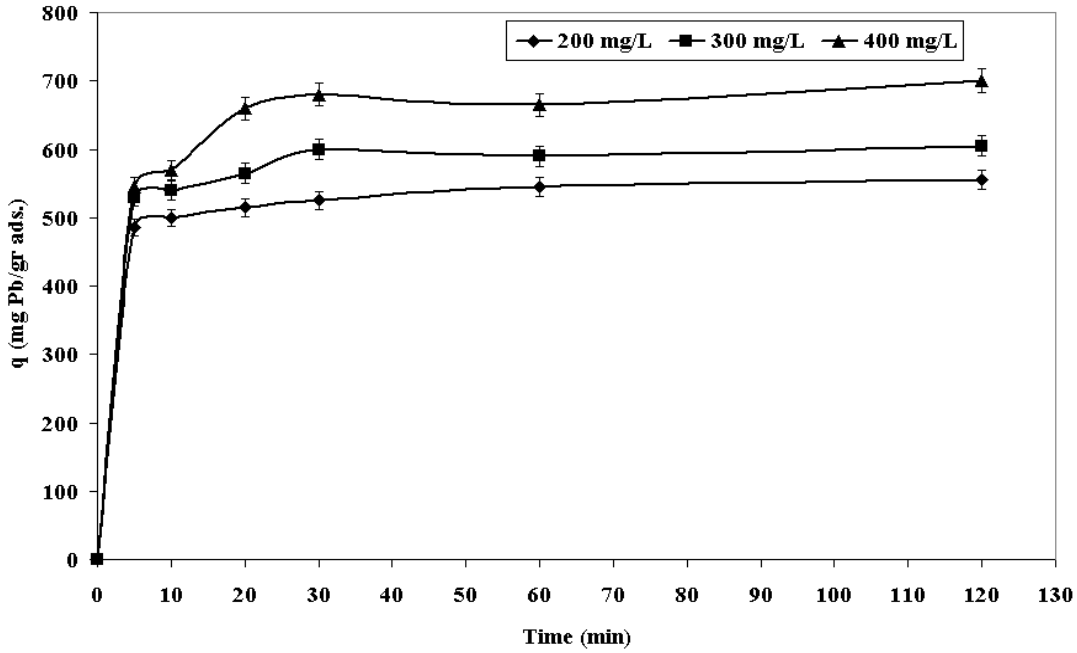

Figure 5. Effect of initial concentration on removal of Pb (II) by nano hydroxyapatite (pH 5.5, adsorbent dosage=0.2 gr/L, 300 rpm agitating rate).

700 (35% removal) to 627.5 mg/g (62.75% removal) with the increasing nano-HAp concentration from 0.2 to 0.4 g/L. This is because at the higher dosage of sorbent due to increased surface area, more adsorption sites are available causing higher removal of Pb (II). A higher initial concentration provides an important driving force to overcome all mass transfer resistances of the pollutant between the aqueous and solid phases, thus increases the uptake (Aksu et al., 2005). Uptake of the Pb (II) also increased with increasing the initial metal concentration tending to saturation at higher metal concentrations. As shown in Figure 5, when the initial Pb (II) concentration increased from 200 to 400 mg/L, the uptake capacity of nano HAp increased from 555 to 700 mg/g.

Effect of temperature

To study the effect of temperature on the uptake of Pb (II) ions by nano-HAp, we selected the following temperatures: 20, 50 and 70°C. Figure 6 illustrates the relationship between temperature and the amount of Pb (II) ions adsorbed onto nano-HAp at equilibrium time (120 min). As seen in Figure 6, the adsorption of Pb (II) on nano-HAp increased from 700 (35% removal) to 1050 mg/g (52.5% removal) when temperature was increased from 20 to 70°C at an initial concentration of 400 mg/L. The increase in the equilibrium sorption of Pb (II) with temperature indicates that Pb (II) ions removal by adsorption on nano-HAp favors a high temperature. This may be a result of increase in the mobility of the Pb (II) ion with temperature. An increasing number of molecules may also acquire sufficient energy to undergo an interaction with active sites at the surface. Furthermore, increasing temperature may produce a swelling effect within the internal structure of the nano-HAp enabling large metal ions to penetrate further (Do˘gan et al., 2003).

Adsorption isotherms

Analysis of the equilibrium data is important to develop an equation which accurately represents the results and which could be used for design purposes (Aksu, 2002). Several isotherm equations have been used for the equilibrium modeling of adsorption systems.

The sorption data have been subjected to different sorption isotherms, namely, Langmuir, Freundlich and Dubinin–Kaganer–Radushkevich (DKR). The equilibrium data for metal cations over the concentration range from 100 to 400 mg/L at 20°C have been correlated with the Langmuir isotherm (Langmuir, 1918):

$$\frac{C_e}{q_e} = \frac{1}{Q_0 K} + \frac{C_e}{Q_0} \quad (4)$$

Where C_e is the equilibrium concentration of metal in solution (mg/L), q_e is the amount absorbed at equilibrium onto nano-HAp (mg/g), Q_0 and K are Langmuir constants

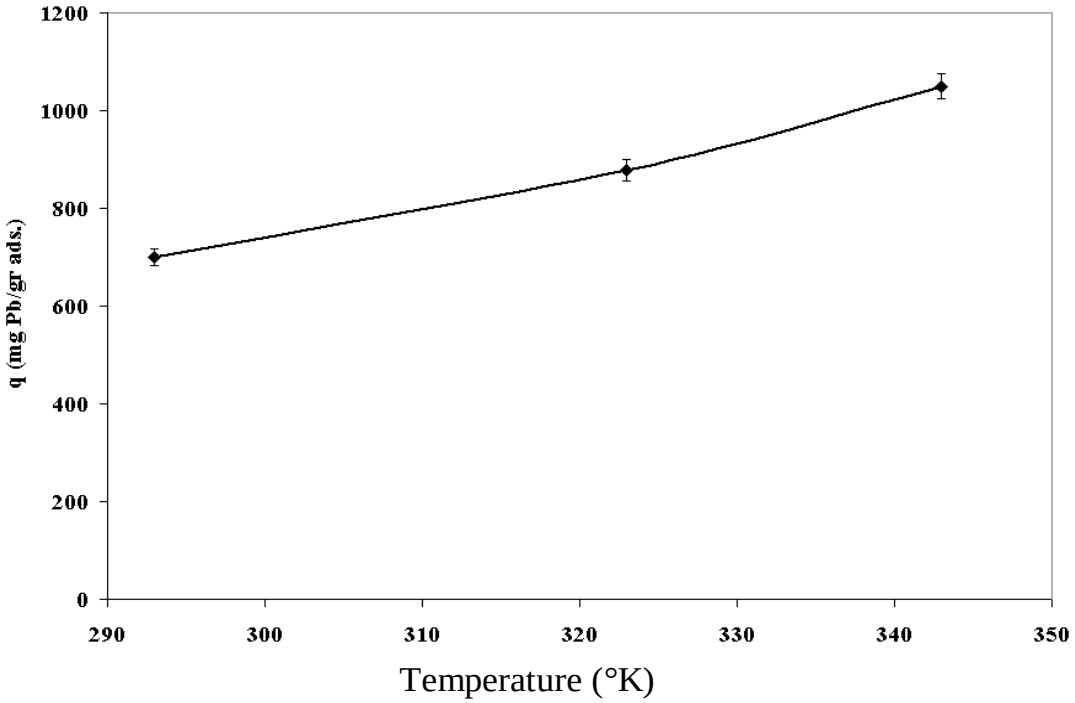

Figure 6. The uptake capacity of Pb (II) ions at different temperature (pH 5.5, initial metal concentration = 400 mg/L, adsorbent dosage=0.2 gr/L, 300 rpm agitating rate).

related to sorption capacity and sorption energy, respectively. Maximum sorption capacity (Q_0) represents monolayer coverage of sorbent with sorbate and K represents enthalpy of sorption and should vary with temperature. A linear plot is obtained when C_e/q_e is plotted against C_e over the entire concentration range of metal ions investigated.

The linearized Langmuir adsorption isotherms of Pb (II) ions are given in Figure 7 a. An adsorption isotherm is characterized by certain constants that express the surface properties and affinity of the sorbent and can also be used to find the sorption capacity of sorbent.

The Freundlich sorption isotherm, one of the most widely used mathematical descriptions, usually fits the experimental data over a wide range of concentrations. This isotherm gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies. The Freundlich adsorption isotherms were also applied to the removal of Pb (II) on nano-HAp (Figure 7 b).

$$Lnq_e = Lnk_f + \frac{1}{n} Lnc_e \quad (5)$$

where q_e is the amount of metal ion sorbed at equilibrium per gram of adsorbent (mg/g), C_e the equilibrium concentration of metal ion in the solution (mg/L), k_f, n the Freundlich model constants (Malkoc et al., 2003; Kadirvelu et al., 2001). Freundlich parameters, k_f and n, were determined by plotting $\ln q_e$ versus $\ln C_e$. The numerical value of $1/n < 1$ indicates that adsorption capacity is only slightly suppressed at lower equilibrium concentrations. This isotherm does not predict any saturation of the sorbent by the sorbate; thus infinite surface coverage is predicted mathematically, indicating multilayer adsorption on the surface (Hasany et al., 2002).

The Dubinin–Kaganer–Radushkevich (DKR) equation has been used to describe the sorption of metal ions on clays. The DKR equation has the form,

$$\text{Ln } C_{ads} = \text{Ln } X_m - \beta\varepsilon^2 \quad (6)$$

Where C_{ads} is the number of metal ions adsorbed per unit weight of adsorbent (mol/g), X_m (mol/g) is the maximum sorption capacity, β (mol^2/J^2) is the activity coefficient related to mean sorption energy and ε is the Polanyi potential, which is equal to

$$\varepsilon = RT\, ln(1 + 1/Ce) \quad (7)$$

Where R is the gas constant (kJ/mol.K) and T is the temperature (K). The saturation limit X_m may represent the total specific micropore volume of the sorbent. The sorption potential is independent of the temperature but varies according to the nature of sorbent and sorbate (Khan et al., 1995). The slope of the plot of $\ln C_{ads}$ versus ε gives β (mol^2/J^2) and the intercept yields the sorption capacity, X_m (mol/g). The sorption space in the vicinity of

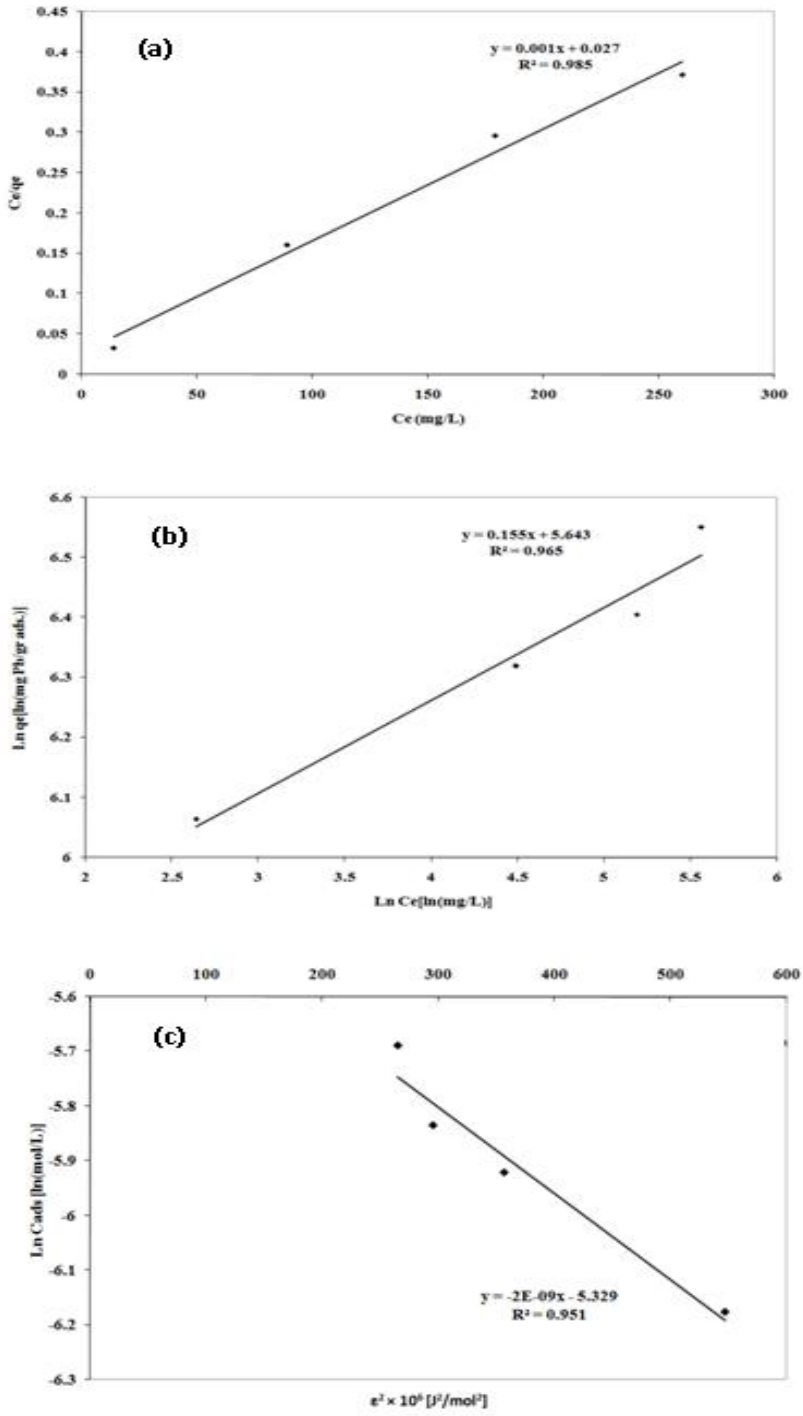

Figure 7. Linear fits of experimental data obtained using Langmuir (a), Freundlich (b) and DKR (c) sorption isotherms for the adsorption of Pb (II) onto nano Hydroxyapatite.

a solid surface is characterized by a series of equipotential surfaces having the same sorption potential. This sorption potential is independent of the temperature but varies according to the nature of sorbent and sorbate. The sorption energy can also be worked out using the following relationship:

$$E = 1/\sqrt{-2\beta}\,. \quad (8)$$

The plot of Ln C_{ads} against ε^2 for metal ion sorption on nano-HAp is shown in Figure 7c. The Langmuir, Freundlich and DKR adsorption constants from the

Table 1. Langmuir, Freundlish and DKR constants for adsorption of Pb (II) onto nano Hydroxyapatite.

Langmuir adsorption isotherms constants		
Q_0 (mg/g)	K (L/mg) 0.052	R^2
714.286		0.985
Freundlich adsorption isotherms constants		
k_f (mg/g)	n	R^2
282.421	6.464	0.965
DKR adsorption isotherms constants		
X_m (mg/g)	β (mol^2/J^2)	R^2
1003.525	-2×10^{-9}	0.951

isotherms and their correlation coefficients are also presented in Table 1.

The correlation factors R (0.985, 0.965 and 0.951 for Langmuir, Freundlich and DKR model, respectively) confirm good agreement between both theoretical models and our experimental results. The maximum sorption capacity, Q_0, calculated from Langmuir equation is 714.286 mg/g, while Langmuir constant K is 0.052 L/mg. The values obtained for Pb (II) from the Freundlich model showed a maximum adsorption capacity (K_f) of 282.421 mg/g with an affinity value (n) equal to 6.464. The values of sorption constants, derived from DKR model are: 1003.525 mg/g (4.848 mmol/g) for X_m, -2×10^{-9} mol^2/J^2 for β and 15.811 kJ/mol for E.

The values indicate that the adsorption pattern for Pb (II) on nano-HAp followed third the DKR isotherm (R^2 > 0.951), the Freundlich isotherm (R^2 > 0.965) and the Langmuir isotherm (R^2 > 0.985) at all experimental situations. It is clear that the Langmuir isotherm has best fitted for the sorption of Pb (II) on nano-HAp. When the system is in a state of equilibrium, the distribution of Pb (II) between the nano HAp and the Pb (II) solution is of fundamental importance in determining the maximum sorption capacity of nano HAp for the Lead ion from the isotherm. The E values are 15.811 kJ for Pb (II) on the nano HAp. It is the orders of an ion-exchange mechanism, in which the sorption energy lies within 8 to 16 kJ/mol (Helferrich, 1962; Rieman et al., 1970). Generally, HAp selectivity towards divalent metal cations is a result of the ion-exchange process with Ca^{2+} ions (MonteilRivera et al., 2002). Ionic radius of Lead (1.19A°) slightly differ from that of Ca^{2+} (0.99A°), and it can substitute Ca^{2+} in the HAp crystal lattice. Figure 8 presents the XRD patterns of Pb^{2+}-loaded sample.

No structural changes of nano HAp were detected by the powder X-ray diffraction analysis of the solid residue with maximum amount of uptake capacity of Pb (II), obtained after interaction 0.2 g/L of nano HAp with 400 mg/L Pb (II) solution, at pH 5.5, at 300 rpm with 120 min of contact time. The sample was indexed in the hexagonal system with space group $P6_3/m$ and Calcium Lead Hydroxide Phosphate ICSD name (Ref.Code.01-084-0814 in XPERT software). The unit cell parameters of the starting nano Ca-HAp (Figure 2) were a = b = 0.9424 nm and c = 0.6879 nm, while values of a = b = 0.9880 nm and c = 0.7417 nm were calculated for the Pb-exchanged sample. These shifts are indicative to the increase in unit cell dimensions which is due to the replacement of Ca^{2+} by Pb (II) (ionic radius 1.19 Å), which is larger than Ca^{2+} (ionic radius 0.99 Å), into the crystal lattice of apatite molecules. These data strongly support the ion-exchange mechanism for Pb (II) sorption by nano HAp. The reaction mechanism corresponds to equimolar exchange of lead and calcium yielding $Ca_{10-x}Pb_x(PO_4)_6(OH)_2$, where *x* can vary from 0 to 10 depending on the reaction time and experimental conditions. Our results of synthesized nano-HAp agreed with those described elsewhere that the proposed mechanism for lead removal by HAp comprises two steps: firstly, rapid surface complexation of the lead on the ≡POH sites of the HAp which causes the decrease of the pH (from pH = 5.5 to pH = 4.5 for initial metal concentration = 400 mg/L, dosage = 0.2 g/L, 300 rpm agitating rate) and secondly, partial dissolution of calcium followed by the precipitation of an apatite with formula: $Pb_xCa_{10-x}(PO_4)_6(OH)_2$ (Baillez et al., 2007).

In which lead ions are first adsorbed on the nano HAp surface and substitution with Ca occurs as described by the following equation:

$$Ca_{10}(PO_4)_6(OH)_2+xPb^{2+}\rightarrow Ca_{10-x}Pb_x(PO_4)_6(OH)_2+xCa^{2+} \quad (9)$$

Determination of thermodynamic parameters

Thermodynamic parameters such as free energy change ($\Delta G°$), enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) can be estimated using equilibrium constants changing with temperature. The free energy change of the sorption reaction is given by the following equation.

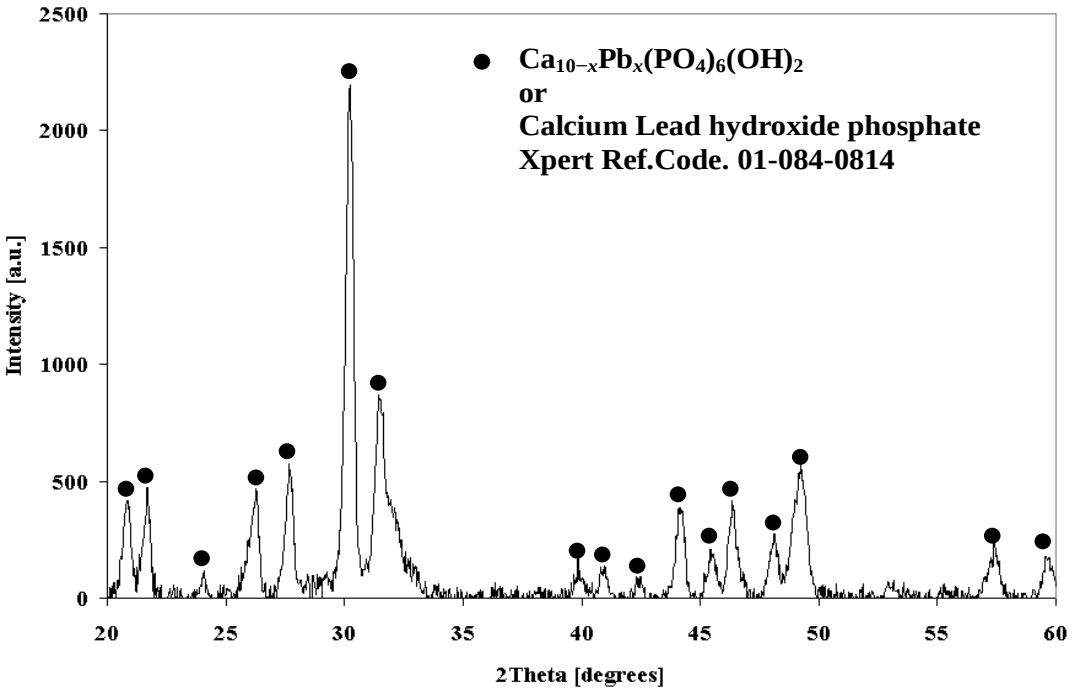

Figure 8. XRD pattern of the solid residue with maximum amount of uptake capacity of Pb (II).

Table 2. Thermodynamic parameters for the adsorption of Pb (II) onto nano Hydroxyapatite.

T °K	K_d	ΔG^0 (J/mol)	ΔH^0 (J/mol)	ΔS^0 (J/mol.°K)
293	1346.15	-17551.40		
323	1954.77	-20350.20	11901	100.32
343	2763.20	-22597.30		

$$\Delta G^{\circ} = -RT\,Ln\,K_d \quad (10)$$

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

$$\Delta G^{\circ} = \Delta H^{\circ} - T\,\Delta S^{\circ} \quad (11)$$

The distribution ratio (K_d) values increased with temperature, indicating the endothermic nature of adsorption. A plot of Gibbs free energy changes, ΔG° versus temperature, T(K); was found to be linear. The values of ΔH° and ΔS° were determined from the slope and intercept of the plots. The thermodynamic parameters Gibbs free energy change, ΔG°, are shown in Table 2.

The enthalpy change, ΔH° and the entropy change, ΔS°, for the sorption processes are calculated to be 11.90 and 100.32 kJ/mol, respectively. The negative values of ΔG° at various temperatures indicate the spontaneous nature of the adsorption process. The positive value of ΔS° indicates that there is an increase in the randomness in the system solid/solution interface during the adsorption process. In addition, the positive value of ΔH° indicates that the adsorption is endothermic. The positive value of ΔS° reflects the affinity of the nano-HAp for Pb (II) ions and suggests some structural changes in Lead and nano-HAp (Ho, 2003).

Conclusions

Nano HAp exhibited high adsorption capacity. The present investigation shows that the nano HAp is an effective adsorbent for the removal or Pb (II) from aqueous solutions. The aqueous Pb concentration (400 mg/L) at 5 min was reduced to 291 mg/L by nano HAp. The adsorption process is a function of the adsorbent dosage, initial Pb (II) concentration, temperature. The efficiency of Pb (II) adsorption increased with an increase

in the adsorbent dosage. Isotherm studies indicate that the Langmuir model fits the experimental data better than Freundlich and DKR model. The adsorption equilibrium was described well by the Langmuir isothermal model with maximum adsorption capacity of 714.286 mg/g of Pb (II) on nano crystallite HAp particles. The results of XRD analysis strongly support the ion-exchange as a main mechanism for Pb (II) removal by nano HAp. The results show that the lead uptake by nano hydroxyapatite proceeds with a rapid surface complexation of the lead on the ≡POH site before the formation of a pyromorphite compound of formula $Ca_{10-x}Pb_x(PO_4)_6(OH)_2$. Thermodynamic calculations showed that the Lead sorption process of nano HAp has endothermic and spontaneous nature. Thermodynamic calculations showed that the lead sorption process of nano crystallite HAp particles had endothermic and spontaneous nature.

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REFERENCES

Aklil A, Mouflih M, Sebti S (2004). "Removal of heavy metal ions from water by using calcined phosphate as a new adsorbent." J. Hazard. Mater., 112: 183-190.

Aksu Z (2002). "Determination of the equilibrium, kinetic and thermodynamic parameters of the batch biosorption of nickel(II) ions onto *Chlorella vulgaris*." Process Biochem., 38: 89-99.

Aksu Z, Tezer S (2005). "Biosorption of reactive dyes on the green alga *Chlorella vulgaris*." Process Biochem., 40: 1347-1361.

Baillez S, Nzihou A, Bernache-Assolant D, Champion, E.,Sharrock P (2007). "Removal of aqueous lead ions by hydroxyapatites: Equilibria and kinetic processes." J. Haz. Mater., A139: 443-446.

Chaturvedi PK, Seth CS, Misra V (2006). "Sorption kinetics and leachability of heavy metal from the contaminated soil amended with immobilizing agent (humus soil and hydroxyapatite)." Chemosphere, 64: 1109-1114.

Chen X, Wright JV, Conca JL, Peurrung LM (1997). "Effects of pH on heavy metal sorption on mineral apatite." Environ. Sci. Technol., 31: 624-631.

Czerniczyniec M, Farias S, Magallanes J, Cicerone D (2003). Arsenic adsorption on biogenic HAP: Solution composition effects. 11th International Conference on Surface and Colloid Science, Foz do Iguazu, Brazil, p. 269.

Do˘gan M, Alkan M (2003). "Adsorption kinetics of methyl violet onto perlite." Chemosphere, 50: 517-528.

Elliott JC (1994). Structure and Chemistry of the Apatites and Other Calcium Orthophosphates. Amsterdam: Elsevier.

Fuller C, Bargar J, Davis J, Piana M (2002). "Mechanisms of uranium interactions with hydroxyapatite: Implications for groundwater remediation." Environ. Sci. Technol., 36: 158-165.

Hasany SM, Saeed MM, Ahmed M, Radioanal J (2002). "Sorption and thermodynamic behavior of zinc(II)-thiocyanate complexes onto polyurethane foam from acidic solutions." Nucl. Chem., 252: 477-484.

Helferrich F (1962). Ion Exchange. New York : McGraw–Hill.

Ho YS (2003). "Removal of copper ions from aqueous solution by tree fern." Water Res., 37: 2323-2330.

Kadirvelu K, Thamaraiselvi K, Namasivayam C (2001). "Adsorption of nickel (II) from aqueous solution onto activated carbon prepared from coirpith." Sep. Purif. Technol., 24: 497-505.

Khan SA, Rehman UR, Khan MA (1995). "Adsorpton of chromium (III), chromium (VI) and silver (I) on bentonite." Waste Manage., 15: 271-282.

Krestou A, Xenidis A, Panias D (2004). "Mechanism of aqueous uranium (VI) uptake by a natural zeolitic tuff." Miner. Eng., 16: 1363-1370.

Langmuir I (1918). "The adsorption of gases on plane surfaces of glass, mica and platinum." J. Am. Chem. Soc., 40: 1361-1403.

Laperche V, Traina SJ, Gaddam P, Logan TJ, Ryan JA (1996). "Chemical and mineralogical characterizations of Pb in a contaminated soil: Reactions with synthetic apatite." Environ. Sci. Technol., 30: 3321-3326.

Leyva A, Marrero J, Smichowski P, Cicerone D (2001). "Sorption of antimony onto hydroxyapatite." Environ. Sci. Technol., 35: 3669-3675.

Ma QY, Traina SJ, Logan TJ, Ryan JA (1993). "*In situ* lead immobilization by apatite." Environ. Sci. Technol., 27: 1803-1810.

Ma QY (1994). "Effects of Aqueous Al, Cd, Cu, Fe(II), Ni, and Zn on Pb immobilization by hydroxyapatite." Environ. Sci. Technol., 28: 1219-1228.

Malkoc E, Nuho˘glu Y (2003). "The removal of chromium(VI) from synthetic wastewater by Ulothrix zonata." Fres. Environ. Bull., 12: 376-381.

Mavropoulos E, Rossi AM, Costa AM, Perez CA, Moreira JC, Saldanha M (2002). "Studies on the mechanisms of lead immobilization by hydroxyapatite." Environ. Sci. Technol., 36: 1625-1629.

McGrellis S, Serafini J, Jean J, Pastol J, Fedoroff M (2001). "Influence of the sorption protocol on the uptake of Cd ions in calcium hydroxyapatite." Sep. Purif. Technol., 24: 129-138.

Mobasherpour I, Heshajin MS, Kazemzadeh A, Zakeri M (2007). "Synthesis of nanocrystalline hydroxyapatite by using precipitation method." J. Alloys Comp., 430: 330-333.

MonteilRivera F, Fedoroff M (2002). Sorption of Inorganic Species on Apatites from Aqueous Solutions In: Encyclopedia of Surface and Colloid Science. New York: Marcel Dekker. Inc.

Nzihou A, Sharrock P (2002). "Calcium phosphate stabilization of fly ash with chloride extraction." Waste Manage., 2002: 235-239.

Prasad M, Saxena S (2004). "Sorption mechanism of some divalent metal ions onto low-cost mineral adsorbent." Ind. Eng. Chem. Res., 43: 1512-1522.

Reichert J, Binner J (1996). "An evaluation of hydroxyapatite-based filters for removal of heavy metal ions from aqueous solutions." J. Mater. Sci., 31: 1231-1241.

Rieman W, Walton H (1970). Ion Exchange in Analytical Chemistry. Oxford: Pergamon.

Sahin Y, Ozturk A (2005). "Biosorption of chromium(VI) ions from aqueous solution by the bacterium Bacillus thuringiensis." Process Biochem., 40: 1895-1901.

Takeuchi Y, Arai H (1990). Removal of coexisting Pb2+, Cu2+, Cd2+ ions from water by addition of hydroxyapatite powder. J. Chem. Eng. Jpn., 23: 75-80.

Tanaka H, Futaoka M, Hino R, Kandori K, Ishikawa T (2005). "Structure of synthetic calcium hydroxyapatite particles modified with pyrophosphoric acid" J. Colloid Interface Sci., 283: 609-612.

Vangronsveld J, Colpaert J, Tichelen KV (1995). "Reclamation of a bare industrial area contaminated by non-ferrous metals: physicochemical and biological evaluation of the durability of soil treatment and revegetation." Environ. Pollut., 94: 131-140.

Vega ED, Pedregosa JC, Narda GE (1999). "Interaction of oxovanadium(IV) with crystalline calcium hydroxyapatite: surface mechanism with no structural modification." J. Phys. Chem. Solids, 60: 759-766.