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1st Nano Update

Comparative of the removal of Pb^{2+}, Cd^{2+} and Ni^{2+} by nano crystallite hydroxyapatite from aqueous solutions: Adsorption isotherm study

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Abstract Release of heavy metal onto the water and soil as a result of agricultural and industrial activities may pose a serious threat to the environment. In this study, the adsorption behavior of nano hydroxyapatite with respect to Pb^{2+}, Cd^{2+} and Ni^{2+} has been studied in order to consider its application to purity metal finishing wastewater. The batch method has been employed, using metal concentrations in solution ranging from 100 to 400 mg/L. The uptake capacity and distribution coefficients (K_d) were determined for the adsorption system as a function of sorbate concentration. The Langmuir, Freundlich, and Dubinin–Kaganer–Radushkevich (DKR) isotherms applied for sorption studies showed that the amount of metal sorbed on nano hydroxyapatite. It was found that the adsorption phenomena depend on charge density and hydrated ion diameter. According to the equilibrium studies, the

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selectivity sequence can be given as $Pb^{2+} > Cd^{2+} > Ni^{2+}$. These results show that nano hydroxyapatite holds great potential to remove cationic heavy metal species from industrial wastewater.

1. 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 (Malkoc, 2006). Numerous processes exist for removing dissolved heavy metals, including ion exchange, precipitation, phytoextraction, ultrafiltration, reverse osmosis, and electrodialysis (Applegate, 1984; Sengupta and Clifford, 1986; Erdem et al., 2004). The use of alternative low-cost materials as potential sorbents for the removal of heavy metals has been emphasized recently.

Calcium hydroxyapatite (HAp), $Ca_{10}(PO_4)_6(OH)_2$, has also been 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 and Sharrock, 2002; Takeuchi and Arai, 1990). Calcium hydroxyapatite (Ca-HAp) is a principal component of 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 Ca-HAP 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. 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 (Krestou et al., 2004). HAp has been utilized in the 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 (Chen et al., 1997; Czerniczyniec et al., 2003; Vega et al., 1999; Reichert and Binner, 1996; Leyva et al., 2001; Fuller et al., 2002; McGrellis et al., 2001). They have reported the sorption is taking 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 the removal of Pb^{2+}, Cd^{2+} and Ni^{2+} cations from aqueous solutions. The Langmuir, Freundlich and D–K–R models were used to fit the equilibrium isotherm.

2. Material and methods

2.1. Preparation of nano crystallite 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 via solution-precipitation method (Mobasherpour et al., 2007) using $Ca(NO_3)_2{\cdot}4H_2O$ (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 $Ca(NO_3)_2{\cdot}4H_2O$ was vigorously stirred at constant temperature 25 °C. A solution of $(NH_4)_2HPO_4$ was slowly added dropwise to the $Ca(NO_3)_2{\cdot}4H_2O$ solution. In all experiments the pH of $Ca(NO_3)_2{\cdot}4H_2O$ solution was kept 11 using ammonia solution. The precipitin HAp was removed from the solution by the centrifuge method at a rotation speed of 3000 rpm. The resulting powder was dried at 100 °C. The particles synthesized were characterized by the following methods. Transmission electron microscopy (TEM) was used to characterize the HAp particles. For this purpose, particles were deposited onto Cu grids, which support a "holey" carbon film. The particles were deposited onto the support grids 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 crystal phase was identified by powder X-ray diffraction (XRD) using Siemens (30 kV and 25 mA) X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5404$ Å) and XPERT software.

2.2. Reagents

Inorganic chemicals were supplied by Merck analytical-grade reagents and deionized water was used. The metal ions studied were Pb^{2+}, Cd^{2+} and Ni^{2+}. We prepared a synthetic stock solution of cadmium and nickel using their sulfate salts, $3CdSO_4{\cdot}8H_2O$ (Merck Art No. 2026) and $NiSO_4{\cdot}7H_2O$ (Merck Art No. 6725), respectively, in deionized water. The stock solution of lead was prepared using $Pb(NO_3)_2$ (Merck Art No. 7397) salts.

2.3. Batch sorption study

All sorption experiments were carried without imposing any pre equilibration processes during the performance of any experiments. Batch adsorption experiments were conducted using 0.1 g, 0.25 g and 2 g of adsorbent with 500 ml of solutions containing Pb^{2+}, Cd^{2+} and Ni^{2+} ions of desired concentrations, respectively, at constant temperature (20 ± 1 °C) in 1000 ml glass bottles. The bottles were stirred for 120 min. The agitator stirring speed was 300 rpm. After 120 min, the sorbents were separated from the solution by centrifuge and filtration through the filter paper (Whatman grade 6).

The initial pH of the solution was adjusted to the value between 5 and 6 by adding NH_3 and HCl. The exact concentrations of metal ions were determined by AAS (GBC 932 Plus atomic absorption spectrophotometer). All experiments were carried out twice.

The mass balance of heavy metal ion is given by:

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

where m, q, V, C_0, and C are the mass of nano-HAp (g), amount of heavy metal ion removed by unit of weight of HAp (Uptake capacity: mg metal/g HAp),volume of heavy metal solution (L), initial metal concentration of solution (mg metal/L), After 120 min C and q will reach equilibrium value Ce and qe.

The distribution ratio (K_d) were calculated using the equations:

$$K_\mathrm{d} = \frac{\text{amount of metal in adsorbent}}{\text{amount of metal in solution}} \times \frac{V}{m} \tag{2}$$

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

3. Results and discussion

3.1. Characteristics of adsorbent

TEM micrograph of the HAp powders after drying at 100 °C is shown in Fig. 1(a). The microstructure of the HAp crystalline after drying was almost needle shape, with a size in the range of 20–30 nm. The crystal structure analysis of HAp particles was performed, using X-ray diffraction, and the obtained diffractograms are represented in Fig. 1(b). The reflection patterns matched the ICDD standards (JCPDS) for HAp phase.

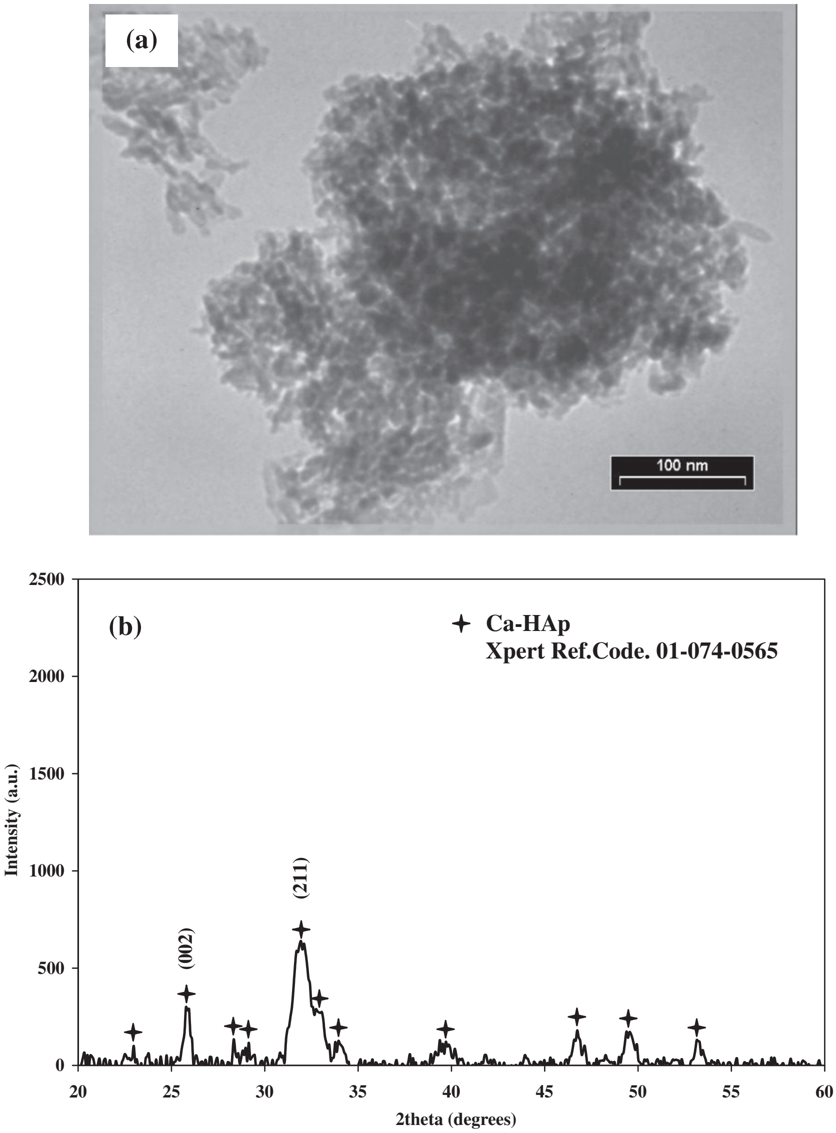

Figure 1 TEM micrograph (a) and XRD pattern (b) of the calcium nanocrystalline hydroxyapatite after drying at 100 °C.

The patterns only showed the peaks' characteristic of HAp with no obvious evidences on the presence of other additional phases. The broad peaks around (2 1 1) and (0 0 2) planes indicated that the crystallites were very tiny in nature with much atomic oscillations. The analysis of the HAp sample has confirmed a low-crystalline product, with the specific surface area 94.9 m^2/g.

3.2. *Adsorption of metals on nano crystalline hydroxyapatite*

The adsorption of Pb^{2+}, Cd^{2+} and Ni^{2+} onto nano crystalline hydroxyapatite as a function of their concentrations was studied at 20 °C by varying the metal concentration from 100 to 400 mg/L while keeping all other parameters constant. The results are shown in Figs. 2 and 3. Amount of heavy metal ion removed (q) for Pb^{2+}, Cd^{2+} and Ni^{2+} increases with increasing metal concentration in aqueous solutions.

As shown in Fig. 2, when the initial metal cations concentration increased from 100 to 400 mg/L, the uptake capacity of nano HAp increased from 430 to 700 mg/g, 134 to 142 mg/g and 20 to 36.25 mg/g for Pb^{2+}, Cd^{2+} and Ni^{2+}, respectively. A higher initial concentration provided an important driving force to overcome all mass transfer resistances of the pollutant between the aqueous and solid phases thus increased the uptake (Aksu and Tezer, 2005).

Fig. 3 illustrates K_d as a function of metal ions concentration. The K_d values increase with the decreasing concentration of metal ions. In other words, the K_d values increase as dilution of metal ions in solution proceeds. These results indicate that energetically less favorable sites become involved with increasing metal concentration in the aqueous solution.

3.3. *Adsorption isotherms models*

Analysis of the equilibrium data is important to develop an equation which accurately represents the results and can be used for the design purposes (Aksu, 2002). Several isotherm

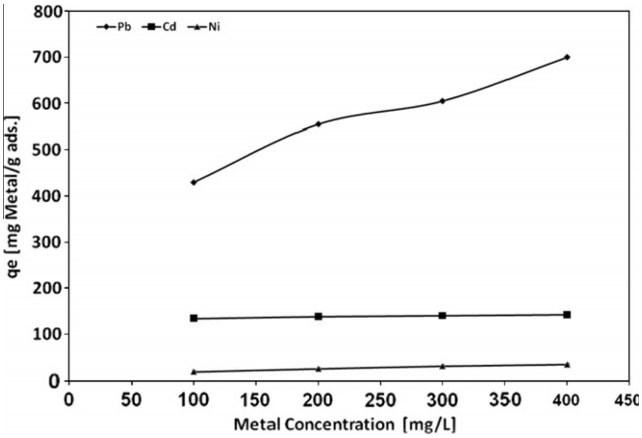

Figure 2 Uptake capacity of metal ions by nano hydroxyapatite sample as a function of initial concentration: V = 500 ml, pH 5–6, time = 120 min.

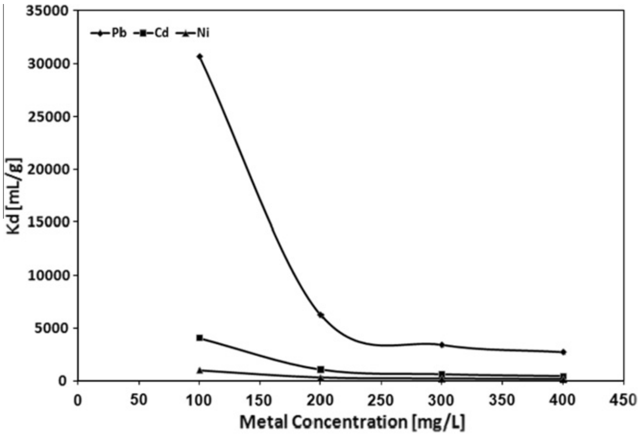

Figure 3 Variation of metal ions on nano hydroxyapatite as a function of initial concentration: V = 500 ml, pH 5–6, time = 120 min.

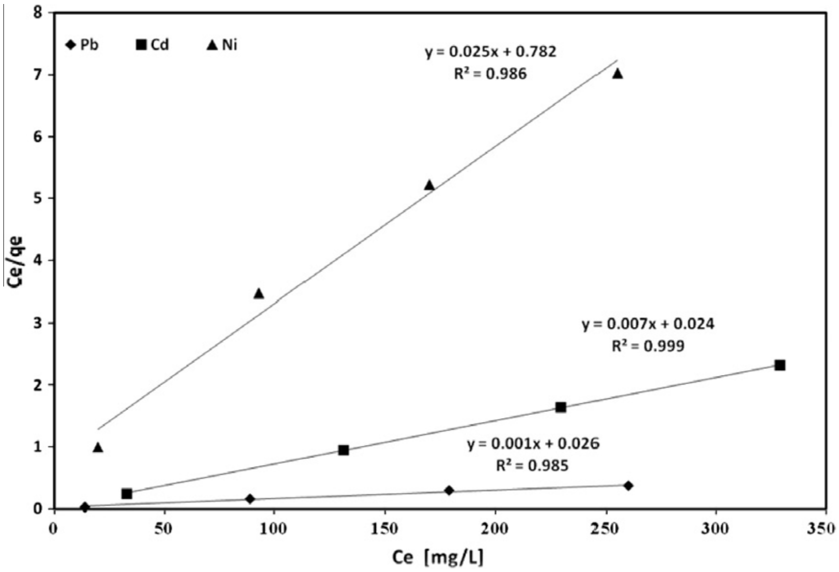

Figure 4 Langmuir plots for metal ions adsorption onto nano hydroxyapatite.

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). An adsorption isotherm is characterized by certain constants which values express the surface properties and affinity of the sorbent and can also be used to find the sorption capacity of sorbent.

The equilibrium data for metal ions over the concentration range from 100 to 400 mg/L at 20 °C have been correlated with the Langmuir isotherm (Langmuir, 1918):

$$\frac{C_e}{q_e} = \frac{1}{Q_0 K} + \frac{C_e}{Q_0} \tag{3}$$

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 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 was obtained when C_e/q_e was plotted against C_e over the entire concentration range of metal ions investigated.

The Langmuir model parameters and the statistical fits of the sorption data to this equation are given in Fig. 4 and Table 1. The Langmuir model effectively described the sorption data with all R^2 values > 0.985. According to the Q_0 parameter, sorption on nano hydroxyapatite is produced following the sequence $Pb^{2+} > Cd^{2+} > Ni^{2+}$. The preference of sorption exhibited by the nano hydroxyapatite for Pb over Cd and Ni may be attributed to Pb's smaller hydrated radius ($Pb^{2+} = 0.401$ nm, $Cd^{2+} = 0.426$ nm, $Ni^{2+} = 0.404$ nm) and hydration energy ($Pb^{2+} = -1481$ kJ/mol, $Cd^{2+} = -1807$ kJ/mol, $Ni^{2+} = -2106$ kJ/mol).

The groups present on the nano hydroxyapatite are OH^- and PO_4^{3-} group, which are hard Lewis bases. Pb^{2+} is a borderline hard Lewis acid while Cd^{2+} and Ni^{2+} is a soft Lewis acid. This could be one of the reasons for greater affinity of Pb as compared to Cd and Ni. The other reason for affinity could be the higher electronegativity of Pb than Cd and Ni for electrostatic and inner sphere surface complexation reactions.

According to LeGerose and LeGerose (1984), cations with ionic radii smaller than Ca^{2+} (0.099 nm) have less of a chance to be incorporated into a hydroxyapatite structure compared with cations with larger ionic radii. Therefore, precipitation of Ni^{2+} (0.072 nm) with Ca^{2+} would be less likely compared with the precipitation of larger cations Pb^{2+} (0.118 nm) and Cd^{2+} (0.097 nm).

Table 1 Characteristic parameters and determination coefficient of the experimental data according to the Langmuir equation.

Metal	Q_0 (mg/g)	K (L/g)	R^2
Pb^{2+}	1000.000	0.038	0.985
Cd^{2+}	142.857	0.292	0.999
Ni^{2+}	40.000	0.032	0.986

Table 2 Freundlich adsorption equations and constants (k_f and n) for metal cations on nano hydroxyapatite.

Metal	k_f (mg/g)	n	R^2
Pb^{2+}	282.308	6.493	0.964
Cd^{2+}	122.854	41.667	0.986
Ni^{2+}	9.806	4.329	0.984

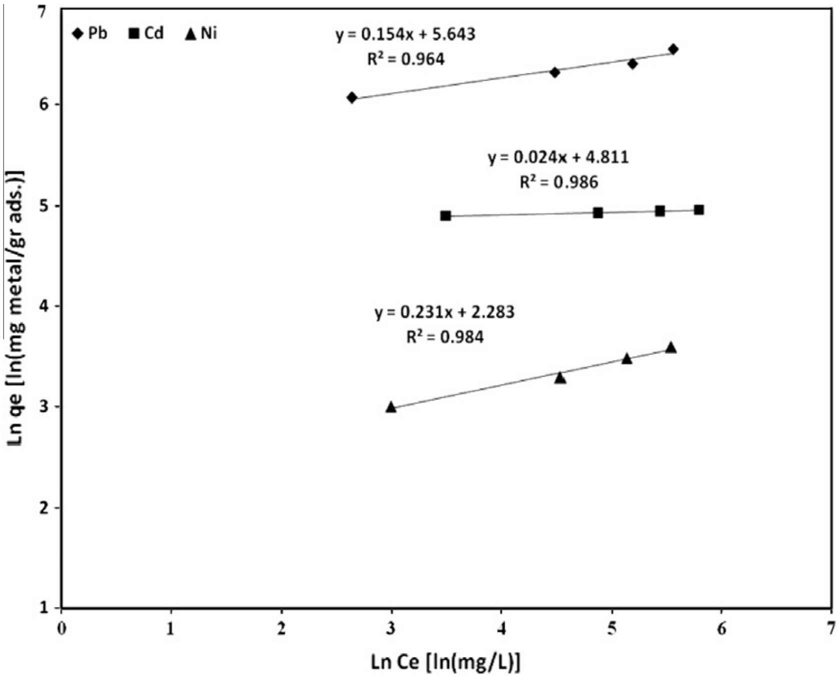

Figure 5 Freundlich plots for metal ions adsorption onto nano hydroxyapatite.

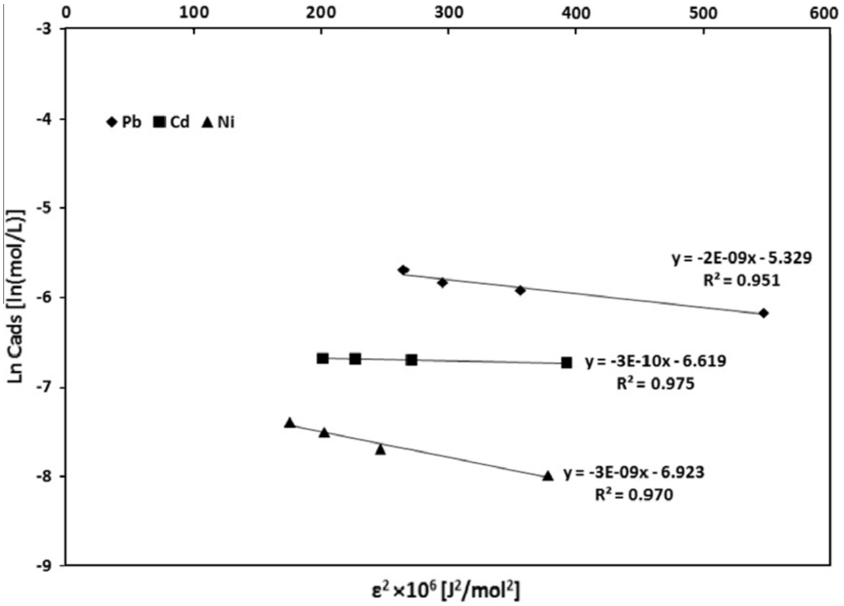

Figure 6 DRK plots of metal ions on nano hydroxyapatite at constant temperature.

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 gave 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^{2+}, Cd^{2+} and Ni^{2+} on nano-HAp (Fig. 5).

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \qquad (4)$$

where q_e is the amount of metal ion sorbed at equilibrium per gram of adsorbent (mg/g), C_e is the equilibrium concentration of metal ion in the solution (mg/L), and k_f and n are the Freundlich model constants (Malkoc and Nuhoğlu, 2003; Kadirvelu et al., 2001). Freundlich parameters, k_f and n, were determined by plotting $\ln q_e$ versus $\ln C_e$. The constant k_f and n were calculated for each cation (Table 2). 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) has been used to describe the sorption of metal ions on clays. The DKR equation has the form:

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

Table 3 Parameter obtained in the DKR equation.

DKR	Pb^{2+}	Cd^{2+}	Ni^{2+}
X_M (mg/g)	1003.726	150.028	57.812
β (mol^2/J^2)	-2×10^{-9}	-3×10^{-10}	-3×10^{-9}
Sorption energy (E, kJ/mol)	15.811	40.825	12.909
Correlation coefficient, R^2	0.951	0.975	0.970

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

Table 4 Adsorption capacities of various adsorbents.

Adsorbents	q_m (mg/g)	Reference
Pb^{2+} adsorbents		
Chitin, natural	264	Yadanaparthi et al. (2009)
Clinoptilolite	166	Yadanaparthi et al. (2009)
Coconut	4.38	Yadanaparthi et al. (2009)
Red soil	21.7	Yadanaparthi et al. (2009)
Sepiolite, natural	185.2	Yadanaparthi et al. (2009)
Zeolites, amasya	34.48	Yadanaparthi et al. (2009)
Phosphate activated	175.44	Yadanaparthi et al. (2009)
Phosphate, natural	131.75	Yadanaparthi et al. (2009)
Nano hydroxyapatite	1000.00	Present work
Cd^{2+} adsorbents		
Tea-industry waste	11.29	Cay et al. (2004)
Olive cake	10.56	Doyurum and Celik (2006)
Black gram husk	39.99	Saeed et al. (2005)
Kraft lignin	137.14	Mohan et al. (2006)
Activated carbon derived from bagasse	27.47–49.07	Mohan and Singh (2002)
Activated carbon (Filtrasorb 400)	307.50	Kapoor et al. (1999)
Carbon aerogel	400.80	Meena et al. (2005)
Nano hydroxy apatite	142.86	Present work
Ni^{+} adsorbents		
Alternanthera philoxeroides biomass	9.73	Wang and Qin (2006)
Waste of tea factory	18.42	Padilha et al. (2005)
PAC	31.08	Rao et al. (2002)
Calcium-alginate	10.5	Huang et al. (1996)
Cone biomass of *Thuja orientalis*	12.42	Malkoc (2006)
Nano hydroxyapatite	40.00	Present work

mean sorption energy, and ε is the Polanyi potential, which is equal to:

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

where R is the gas constant (8.314 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^2 gives β (mol^2/J^2) and the intercept yields the sorption capacity, X_m (mol/g). The sorption space in the vicinity of 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:

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

It is known that magnitude of apparent adsorption energy E is useful for estimating the type of adsorption and if this value is below 8 kJ/mol the adsorption type can be explained by physical adsorption, between 8 and 16 kJ/mol the adsorption type can be explained by ion exchange, and over 16 kJ/mol the adsorption type can be explained by a stronger chemical adsorption than ion exchange (Lin and Juang, 2002; Wang et al., 2004; Krishna et al., 2000).

The plot of $\ln C_{ads}$ against ε^2 for metal ion sorption on nano hydroxyapatite is shown in Fig. 6. The DKR parameters are calculated from the slope of the line in Fig. 6 and listed in Table 3. As shown in Table 3, the E value are 15.811 for Pb^{2+}, 40.825 for Cd^{2+}, and 12.909 kJ/mol for Ni^{2+} on the nano HAp. The E values are 15.811 and 12.909 kJ for Pb^{2+} and Ni^{2+}, on the nano HAp, respectively. They are the orders of an ion-exchange mechanism, in which the sorption energy lies within 8–16 kJ/mol. on the other hand, the E values is 40.825 kJ for Cd^{2+} cations on the nano HAp. It is the orders of a stronger chemical adsorption than ion exchange. The sorption capacity X_m in the DKR equation is found to be 1003.726 for Pb^{2+}, 150.028 for Cd^{2+}, and 57.812 mg/g for Ni^{2+}.

Results show that, it is clear that the Langmuir isotherm has best fitted for the sorption of heavy metal cations on nano-HAp. When the system is in a state of equilibrium, the distribution of cations between the nano HAp and the cations solution is of fundamental importance in determining the maximum sorption capacity of nano HAp for the metal ion from the isotherm.

The values of the adsorption capacities for the adsorption of Pb^{2+}, Cd^{2+} and Ni^{2+} cations on different adsorbents used in the literature with adsorbent of the present study are summarized in Table 4. Although direct comparison of the nano HAp with other adsorbent materials is difficult, owing to the differences in experimental conditions, it was found that the adsorption capacity of nano HAp was higher than adsorbents presented in Table 4.

4. Conclusions

Sorption performance of nano was studied for the removal of Pb^{2+}, Cd^{2+} and Ni^{2+} from aqueous solutions. The removal capacity of Pb^{2+}, Cd^{2+} and Ni^{2+} increases with an increasing at initial concentration. Isotherm studies indicated that the Langmuir model fitted the experimental data better than Freundlich and D–K–R models. The adsorption equilibrium was described well by the Langmuir isotherm model with maximum adsorption capacity of 1000.000, 142.857 and 40.000 mg/g for Pb^{2+}, Cd^{2+} and $Ni^{2+,}$ respectively, on nano HAp. Finally, affinity to the nano HAp was found to be in the sequence $Pb^{2\pm} \geqslant Cd^{2\pm} \geqslant Ni^{2\pm}$ and the preference of this sorbent for a metal may be explained on the basis of electronegativity of the metal ions and on the basis of their cation/anion state.

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