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Kinetics and equilibrium of cadmium removal from aqueous solutions by sorption onto synthesized hydroxyapatite

N. Barka[a,*], K. Ouzaouit[b], M. Abdennouri[c], M. El Makhfouk[c], S. Qourzal[d], A. Assabbane[d], Y. Ait-Ichou[d], A. Nounah[e]

[a]*Equipe de Recherche Gestion de l'Eau et Développement Durable (GEDD), Faculté Polydisciplinaire de Khouribga, Université Hassan 1er, Hay Ezzaitouna, BP. 145, Khouribga, Morocco*
Tel. +212 661 66 66 22; Fax: +212 523 49 03 54; email: barkanoureddine@yahoo.fr
[b]*Laboratoire d'électrochimie, Centre de recherche REMINEX, Site de Hajar, BP. 469 Marrakech, Morocco*
[c]*Equipe de Recherche Analyse Contrôle et Environnement (ERACE), Ecole Supérieure de Technologie de Safi, BP. 89, Route Dar Si Aissa, Safi, Morocco*
[d]*Equipe de Matériaux, Photocatalyse et Environnement, Faculté des Sciences d'Agadir, BP. 8106 Hay Dakhla, Agadir, Morocco*
[e]*Laboratoire des Sciences de l'Environnement, Ecole Supérieure de Technologie de Salé, BP. 227 Salé-Médina, Morocco*

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ABSTRACT

Calcium hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, Hap) was synthesized by a simple and rapid co-precipitation method. The samples were characterized by X-ray diffraction analysis, FT-IR spectral analysis, and transmission electron microscopy coupled energy-dispersive X-ray analysis (transmission electron microscope-energy dispersive X-ray spectrometer). The synthesized Hap was used as an adsorbent for the cadmium ion removal from aqueous solutions in batch mode. The influence of contact time and initial concentration of metal ion was studied and discussed. The equilibrium uptake increases with an increase in the initial cadmium concentration in solution. Adsorption kinetic data were properly fitted with the pseudo-second-order kinetic model. The experimental isotherm data were analyzed using Langmuir, Freundlich, Toth, and Tempkin isotherm equations. The best fit was obtained by the Toth model with high correlation coefficients ($r^2 > 0.99$). The Langmuir model also yielded a good fit to experimental data (r^2 around 0.98–0.99) with a maximum monolayer adsorption capacity of 240.74 mg/g.

Keywords: Cadmium; Adsorption; Hydroxyapatite; Kinetics; Isotherm

1. Introduction

Heavy metals and their compounds are widely used in industrial applications such as metallurgy, battery, paper, and paint manufacture [1]. The presence of heavy metals in the ecosystem involves environmental problems because they are non-degradable and are, therefore, continued to accumulate in water bodies [2,3]. Numerous metals, such as cadmium, mercury, lead, chromium, copper, manganese, etc., are known to be significantly toxic. The presence of toxic heavy metals in water has caused several health problems with animals, plants, and human beings [4]. Among toxic heavy metals, cadmium is one of the most dangerous metals for human health [5]. Cadmium is highly used as corrosion-resistant

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*Corresponding author.

and protective coating for iron, steel, and copper. The industrial uses of cadmium are increasing in plastics, paint pigments, electroplating, batteries, mining, and alloy industries [6]. Cadmium is a highly toxic element and considered as a carcinogen. It can enter the human body by eating food, drinking water, breathing, or smoking. Most of the cadmium that enters the body goes to the kidney and liver and can remain there for many years and can cause serious damage to the kidney and bones [7].

One of the most important challenges for scientists is to develop efficient methods to control environmental pollution. Various methods including precipitation, ion exchange, and adsorption have been frequently practiced for the removal of heavy metals from water [8–13]. Among these methods, sorption is a simple and attractive method for heavy metal removal from aqueous effluents due to its high efficiency and easy handling. Economical feasibility of such processes can be gained by the application of low-cost adsorbents.

Calcium hydroxyapatite (Hap), $Ca_{10}(PO_4)_6(OH)_2$, is an important inorganic material in biology and chemistry [14–16], their availability structure, ion-exchange property, adsorption affinity, and their characteristic to establish bonds with organic molecules of different sizes have conferred to this material to attract more attention during the last two decades. The interaction between macromolecules and hydroxyapatite has received special attention because of the physicochemical properties of this material, which is similar to bone mineral, as well as its biocompatibility, osteoconduction, and bioresorption properties [17,18]. Hydroxyapatite is widely used for chromatographic purposes [19,20] and is suitable for a number of biomedical applications, e.g. artificial bone and roofs of teeth as well as serving as a carrier for drug delivery [21–23]. In addition, this material can be efficient matrixes of water purification. As of now, many studies have reported the use of hydroxyapatite in the removal of rare earths, heavy metals, and organic matters [24–35]. However, these efforts have not produced materials that meet all the demands of sorption activity.

The aim of the present study was to synthesize Hap by simple and rapid co-precipitation between calcium nitrate ($Ca(NO_3)_2$) and di-ammonium hydrogen phosphate ($(NH_4)_2HPO_4H_2O$) at room temperature and its use in cadmium removal from aqueous solutions. The effects, such as equilibrium time and initial metal concentration, were investigated. Kinetic and equilibrium parameters were determined to understand the adsorption mechanism.

2. Materials and methods

2.1. Preparation and characterization of Hap

All reagents used in the preparation and the adsorption studies were of analytical grade. Hap was synthesized by the co-precipitation method. A calcium nitrate solution $Ca(NO_3)_2{\cdot}4H_2O$ (Scharlau, Spain) was immediately poured at room temperature into a di-ammonium hydrogen phosphate $(NH_4)_2HPO_4$ (Riedel-de Haën, Germany) and the pH of the solution was adjusted to 7 by ammoniac solution. After low agitation for 2 h, the suspension was filtered on a large Buchner funnel, washed with distilled water, dried at 70°C for 48 h, and sieved in particle sizes lower than 63 μm. A specimen was characterized by X-ray diffraction (XRD) using a XPERT-PRO diffractometer system, Infrared spectroscopy IR using VERTEX 70 spectrophotometer, and transmission electron microscope-energy dispersive X-ray spectrometer (TEM-EDX) using a ZALUZEC Model.

2.2. Adsorption experiments

A stock solution of Cd^{2+} was prepared by dissolving an appropriate amount of $Cd(NO_3)_2 \cdot 4H_2O$ in distilled water, and the concentrations used were obtained by dilution of the stock solution. Adsorption experiments were conducted in 250 mL conical flasks at constant agitation and at room temperature (25°C). The experiments were carried out by varying the contact time from 5 to 180 min and the initial concentration from 50 to 500 mg/L. After each adsorption procedure was completed, the sample was centrifuged at 3,000 rpm for 10 min to separate the solid phase from the liquid phase. The supernatants were analyzed for residual Cd^{2+} concentrations by an atomic absorption spectrophotometer type GBC 904.

The adsorbed quantity was determined by using the following equation.

$$q = \frac{(C_0 - C)}{R} \quad (1)$$

where q (mg/g) is the quantity of cadmium adsorbed per unit mass of adsorbent, C_0 (mg/L) is the initial metal concentration, C (mg/L) is the metal concentration after adsorption, and R (g/L) is the mass of adsorbent per liter of aqueous solution.

3. Results and discussion

3.1. Characterization of adsorbent

Fig. 1 shows XRD patterns of synthesized adsorbent before and after the reaction with Cd^{2+}. The

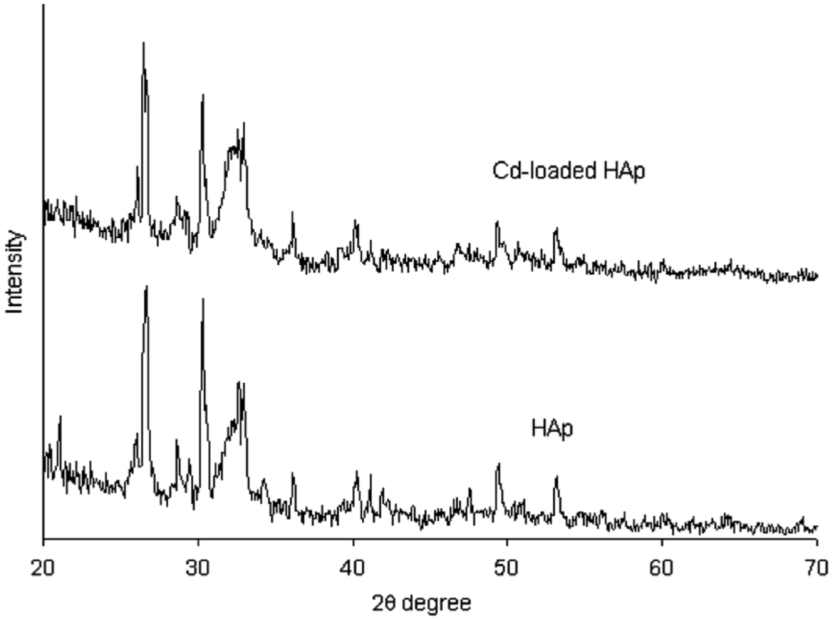

Fig. 1. XRD patterns of unloaded and Cd^{2+}-loaded Hap.

figure shows reflections characteristic of hydroxyapatite. The samples yielded broad and overlapping reflections, indicating its low crystallinity. The unit cell dimensions *a* and *c* obtained from the XRD pattern of the Hap particles before the reaction were 0.943 and 0.689 nm, respectively. These dimensions slightly decreased after the reaction to 0.941 and 0.686 nm, respectively. This result may be due to the substitution of Ca^{2+} by Cd^{2+} in the Hap crystal lattice. The intensity of XRD pattern of Cd-loaded Hap was apparently lower than that of original Hap, which indicates that the degree of crystallinity decreases after cadmium adsorption.

The IR spectra are dominated by bands characteristic of hydroxyapatite (Fig. 2). The bands located at 3,564 cm^{-1} and at 624 cm^{-1} arise from stretching and librational vibration modes, respectively, of OH^- ions. The two bands at 1,080 and 1,030 cm^{-1} arise from ν_3 PO_4. The 960 cm^{-1} band arises from ν_1 PO_4. The bands at 600 and 565 cm^{-1} arise from ν_4 PO_4, and 470 cm^{-1} arises from ν_2 PO_4. The spectra also display bands of CO_3^{2-} and HPO_4^{2-} impurity ions at 1,394 and 894 cm^{-1}, respectively.

Fig. 3 displays the TEM micrographs of the Hap particles after the reaction with Cd^{2+}. The products are fine rod-like particles. The particles turn into agglomerates less than 3 μm diameter composed of small primary particles. EDX analysis performed during TEM observations is presented in Fig. 4. The obtained peaks were identified as relative to Ca, P, O, Cd, C, and Cu. C and Cu peaks are provided from the grid. Ca, P, O, and Cd represent Cd-loaded Hap sample. This result indicates that the cadmium is effectively adsorbed on the surface of the hydroxyapatite.

3.2. Adsorption kinetics

Fig. 5 shows the plot of adsorbed amounts of Cd^{2+} vs. contact time. The result revealed that a removal takes place in two different steps: the first step was found to be rapid (first 60 min), the second one exhibits a subsequent removal until equilibrium is reached, which is slow and a quantitatively insignificant step. The equilibrium time was 180 min. In order to characterize the kinetics involved in the adsorption process, pseudo-first-order, pseudo-second-order, and intraparticle diffusion models were proposed and the kinetic data were analyzed.

The first-order rate expression of Lagergren based on solid capacity is generally expressed as follows [36]:

$$q = q_e(1 - e^{-k_1 t}) \tag{2}$$

where q_e and q (both in mg/g) are, respectively, the amounts of cadmium adsorbed at equilibrium and at any time "t", and k_1 (1/min) is the rate constant of adsorption.

The pseudo-second-order model proposed by Ho and McKay [37] was used to explain the sorption kinetics. This model is based on the assumption that the adsorption follows second-order chemisorption. The pseudo-second-order model can be expressed as:

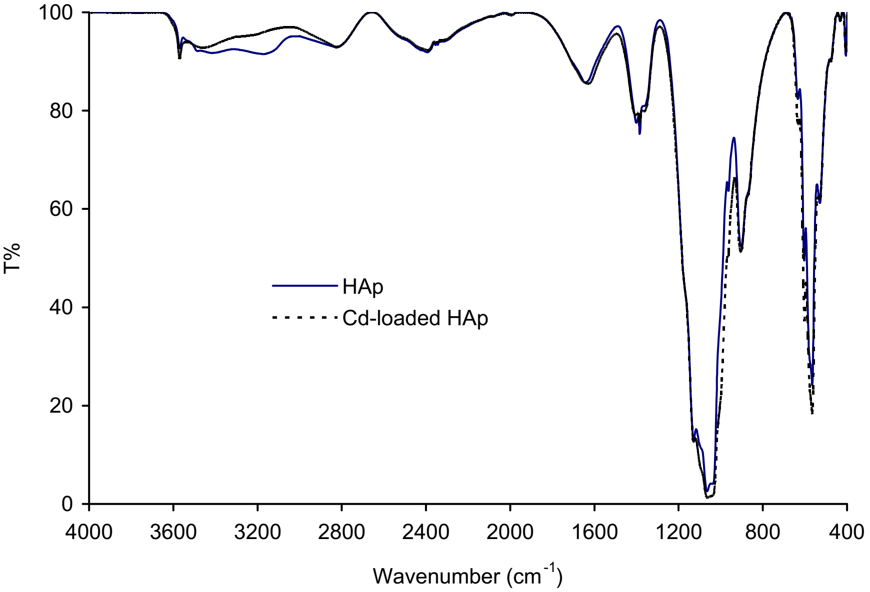

Fig. 2. FT-IR spectra of unloaded and Cd^{2+}-loaded Hap.

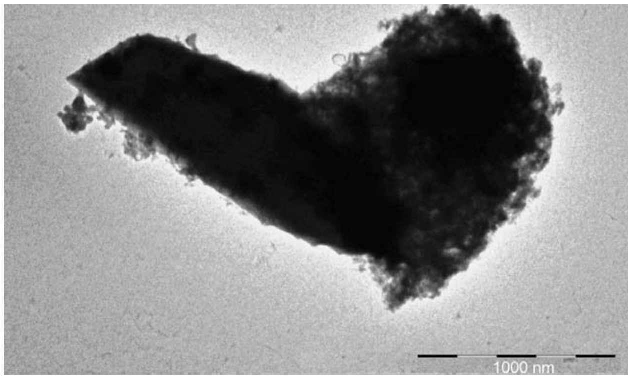

Fig. 3. TEM pictures of Cd^{2+}-loaded Hap.

$$q = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{3}$$

where k_2 (g/mgmin) is the rate constant of pseudo-second-order adsorption.

For the interpretation of experimental kinetic data, from a mechanistic viewpoint, prediction of the rate-limiting step is an important consideration. The adsorbate transport from the solution phase to the surface of the adsorbent particles occurs in several steps. The overall adsorption process may be controlled either by one or more steps, e.g. film or external diffusion, pore diffusion, surface diffusion, and adsorption on the pore surface, or a combination of more than one step. The possibility of intra-particle diffusion was explored by using the intra-particle diffusion model [38]:

$$q = k_{id} t^{0.5} + I \tag{4}$$

where k_{id} is the intra-particle diffusion rate constant ($mg/g\,min^{1/2}$) and I (mg/g) is a constant.

If the Weber–Morris plot of q vs. $t^{0.5}$ satisfies the linear relationship with the experimental data, then the sorption process is found to be controlled by intra-particle diffusion only. However, if the data exhibit multi-linear plots, then two or more steps influence the sorption process.

Fig. 6 shows the pore-diffusion plot of cadmium adsorption onto hydroxyapatite. The plots are multi-linear, having at least three linear segments. The first, sharper portion is attributed to the diffusion of adsorbate through the solution to the external surface of adsorbent or boundary layer diffusion of solute molecules. The second, linear portion is the gradual equilibrium stage with intra-particle diffusion dominating. The third portion is attributed to the final equilibrium stage for which the intra-particle diffusion starts to slow down due to the extremely low adsorbate concentration left in the solution [39]. A decrease in the slope (which is equal to k_{id}) of each segment was observed. This decrease for macro-to mesopore diffusion is a normal consequence of the relative free path for diffusion that is available in each pore size. As the pore size decreases, the path available for diffusion becomes smaller, which leads to a decrease in the rate of diffusion.

Parameters of the pseudo-first-order, pseudo-second-order, and intra-particle diffusion models were estimated with the aid of the nonlinear regression. The obtained data and the correlation coefficients, r^2,

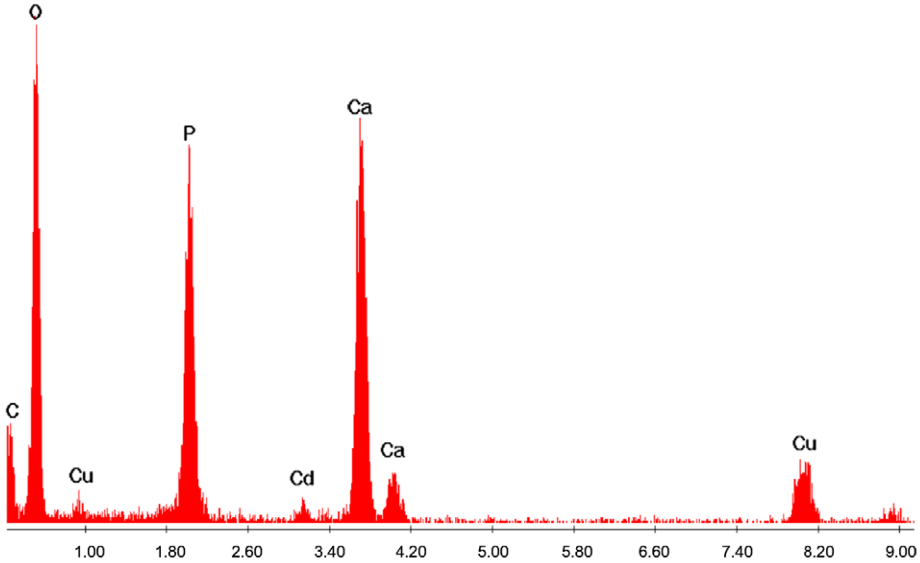

Fig. 4. EDX analyses of Cd^{2+}-loaded Hap.

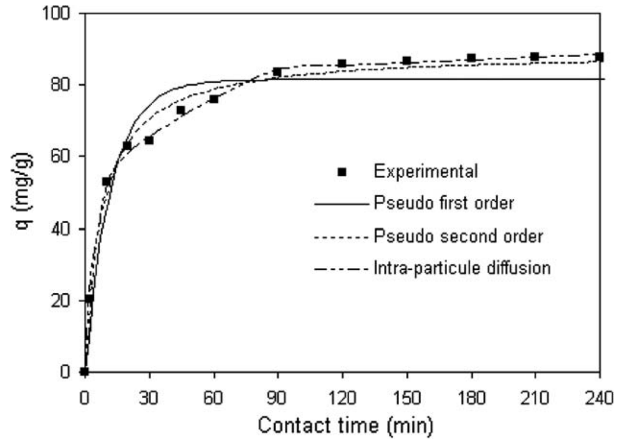

Fig. 5. Effect of contact time on the adsorption of Cd^{2+} by hydroxyapatite: $C_0 = 200$ mg/L, $R = 1$ g/L, temperature = 25° C, pH = 5.5.

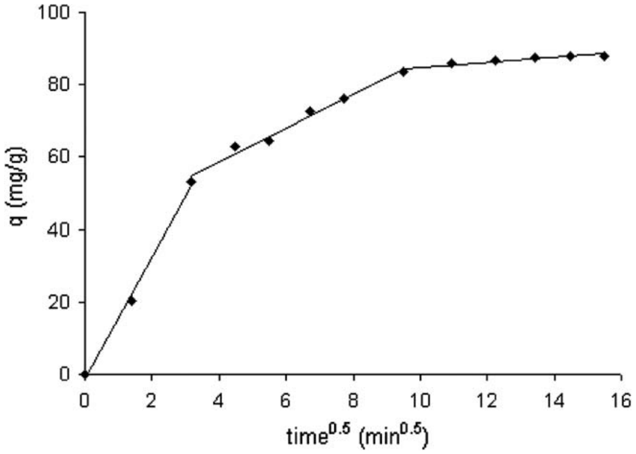

Fig. 6. Intraparticle diffusion plots for the adsorption of Cd^{2+} by hydroxyapatite.

are given in Table 1. The table shows that the correlation coefficient for the pseudo-second-order kinetic model is close to unity than those of the other models. From these results, it was concluded that the pseudo-second-order model was better than the Lagergren first-order and the intra-particle diffusion models for the systems investigated in this work. Since ion adsorption follows pseudo-second-order kinetics, this suggested that boundary layer resistance was not the rate-limiting step [40]. The rate of cadmium adsorption may be controlled largely by a chemisorption process, in conjunction with the chemical characteristics of the hydroxyapatite and cadmium ions.

3.3. Adsorption isotherm

The equilibrium sorption capacity of the hydroxyapatite for cadmium ions increased with a rise in initial concentration, as shown in Fig. 7. Cadmium removal is highly concentration dependent. The increase in adsorption capacity with concentration is probably due to a high driving force for mass transfer. In fact, high concentration in solution implicates high metal ions fixed at the surface of the adsorbent. Several theories of adsorption equilibrium were applied for the analysis of equilibrium sorption data obtained.

Table 1
Kinetic constants for Cd^{2+} adsorption onto hydroxyapatite

Pseudo-first-order model	
k_1(1/min)	0.0818
q_e (mg/g)	81.49
r^2	0.95
Pseudo-second-order model	
k_2 (g/mgmin)	0.0014
q_e (mg/g)	89.33
r^2	0.99
Intra-particle diffusion model	
$k_{id}{}^1$ (mg/g min$^{0.5}$)	16,85
r^2	0,99
$k_{id}{}^2$ (mg/g min$^{0.5}$)	4,68
r^2	0980
$k_{id}{}^3$ (mg/g min$^{0.5}$)	0704
r^2	0,86

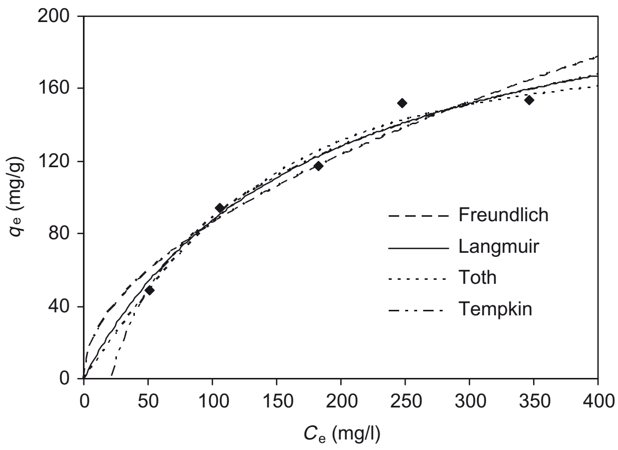

Fig. 7. Effect of Cd^{2+}concentration on its adsorption by hydroxyapatite: $R = 1$ g/L, contact time = 120 min, temperature = 25°C, pH = 5.5.

3.3.1. Langmuir adsorption model

The Langmuir adsorption model [41] is established based on the following hypotheses: (1) uniformly energetic adsorption sites, (2) monolayer coverage, and (3) no lateral interaction between adsorbed molecules. Graphically, a plateau characterizes the Langmuir isotherm. A basic assumption is that sorption takes place at specific homogeneous sites within the adsorbent. Once a cadmium ion occupies a site, no further adsorption can take place at that site. A mathematical expression of the Langmuir isotherm is:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{5}$$

where q_e (mg/g) is the adsorbed amount at equilibrium, C_e is the equilibrium concentration of the metal ion (mg/L), K_L is Langmuir equilibrium constant, and q_m is the maximum adsorption capacity (mg/g).

3.3.2. Freundlich model

The Freundlich isotherm endorses the heterogeneity of the surface and assumes that the adsorption occurs at sites with different energy of adsorption. The energy of adsorption varies as a function of surface coverage [42]. This equation is also applicable to multilayer adsorption and is expressed by the following equation:

$$q_e = K_F C_e^{1/n} \tag{6}$$

where K_F is the Freundlich constant and n is the heterogeneity factor. The K_F value is related to the adsorption capacity, while $1/n$ value is related to the adsorption intensity.

3.3.3. Toth model

Toth has modified the Langmuir equation to reduce the error between experimental data and predicted values of equilibrium adsorption data. He assumes a quasi-Gaussian energy distribution. Most sites have an adsorption energy lower than the peak or maximum adsorption energy. The application of his equation is best suited to multilayer adsorption similar to BET isotherm which is a special type of Langmuir isotherm and has very restrictive validity [43]. The Toth correlation is given as [44]:

$$q_e = \frac{q_m C_e}{(1/K_T + C_e^t)^{1/t}} \tag{7}$$

where q_e is the adsorbed amount at equilibrium (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L), q_m is the Toth maximum adsorption capacity (mg/g), K_T is the Toth equilibrium constant, and t is the Toth model exponent. The Toth model is reduced to the Langmuir model when the exponent t is equal to unity.

3.3.4. Tempkin model

Temkin and Pyzhev considered the effects of some indirect adsorbate/adsorbate interactions on adsorption isotherms and suggested that because of these interactions, the heat of adsorption of all the

Table 2
Adsorption isotherm constants for the adsorption of Cd^{2+} onto hydroxyapatite

Langmuir			Freundlich			Toth				Tempkin		
q_m	K_L	r^2	K_F	n	r^2	q_m	K_T	t	r^2	A	b	r^2
240.74	0.0057	0.988	7.636	1.905	0.974	178.01	0.00006	1.879	0.991	0.047	43.367	0.973

molecules in the layer would decrease linearly with coverage. The Tempkin isotherm has been used in the following form [45]:

$$q_e = \frac{RT}{b}\ln(AC_e) \quad (8)$$

where q_e is the adsorbed amount at equilibrium (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L), and A and b are Tempkin parameters. The constant b is related to the heat of adsorption.

3.3.5. Analysis of adsorption isotherms

The amounts of adsorbed quantities of cadmium ions at the equilibrium (q_e) vs. equilibrium ions concentration are drawn in Fig. 7. The experimental adsorption isotherms obtained were compared with the adsorption isotherm models and the constants appearing in each equation of those models were determined by nonlinear regression analysis. The results of these analyses are tabulated in Table 2. The correlation coefficients (r^2) are also shown in this table. The table indicates that the best fit was obtained by the Toth model with high correlation coefficients ($r^2 > 0.99$). The Langmuir model also yielded a good fit to experimental data (r^2 around 0.98–0.99) with a high maximum monolayer adsorption capacity of 240.74 mg/g for cadmium.

The obtained adsorption capacity of synthesized hydroxyapatite was compared to previously reported works on adsorption capacities of cadmium (II) ions by different adsorbents as summarized in Table 3. The table shows that, except some activated carbons and D152 exchange resin, the experimental data of the present study were found to be higher than those of many corresponding adsorbents. Although a direct comparison of co-precipitated Hap with the other adsorbent materials is difficult, the synthesized hydroxyapatite in this study shows high affinity for cadmium compared to nano hydroxyapatite synthesized by Mobasherpour et al. [33]. This result is due to the differences in experimental conditions.

Table 3
Comparison of adsorption monolayer capacities of hydroxyapatite with those of various adsorbents

Sorbent material	q_m ($mg\,g^{-1}$)	References
Phosphogypsum	131.58	[46]
Aluminium oxide	89.28	[47]
Tourmaline	66.67	[48]
Bentonite	61.35	[49]
Magnetic clay composite	63.29	[49]
Acid-modified clinoptilolite	7.41	[50]
Manganese nodule residue	19.8	[51]
Melon peel	81.97	[52]
Municipal wastewater biosolids	42.72	[53]
Carboxymethylcellulose	28.7	[54]
Scolymus hispanicus L.	54.05	[11]
D152 resin	378	[55]
Activated carbon prepared from coconut coirpith	93.40	[56]
Activated carbon (Filtrasorb 400)	307.50	[57]
Carbon aerogel	400.80	[58]
Nano hydroxyapatite	142.86	[33]
Co-precipitated hydroxyapatite	240.74	Present work

4. Conclusions

In this study, synthesized hydroxyapatite was used for the removal of cadmium ions from aqueous solutions. The obtained results show that hydroxyapatite has a high affinity for Cd^{2+} ions. The adsorption was rapid and kinetic data were better described by the pseudo-second-order model.

The equilibrium uptake was increased with increasing the initial concentration of metal ions in solution. The adsorption isotherm could be well fitted by the Toth and Langmuir equations. Finally, calcium hydroxyapatite can be used as an effective adsorbent for the treatment of wastewater containing cadmium.

References

[1] A. Ozverdi, M. Erdem, Cu^{2+}, Cd^{2+} and Pb^{2+} adsorption from aqueous solution by pyrite and synthetic iron sulphide, J. Hazard. Mater. 137 (2006) 626–632.

[2] I. Christl, R. Kretzschmar, Comparative sorption of copper and lead at the oxide water interface: Implications for surface site density, Geochim. Cosmochim. Acta 63 (1999) 2929–2938.

[3] E.H. Larbi, A. Laghzizil, A. Saoiabi, P. Barboux, M. Meyer, S. Brandes, R. Guilard, Some factors affecting the removal of lead (II) ions from aqueous solution by porous calcium hydroxyapatite, Adsorpt. Sci. Technol. 24 (2006) 507–516.

[4] A. Özer, H.B. Pirinççi, The adsorption of Cd(II) ions on sulphuric acid-treated wheat bran, J. Hazard. Mater. 137 (2006) 849–855.

[5] S. Mandjiny, K.A. Matis, A.I. Zouboulis, M. Fedoroff, J. Jeanjean, J.C. Rouchaud, N. Toulhoat, V. Potocek, C. Loos-Neskovic, P. Maireles-Torres, D. Jones, Calcium hydroxyapatites: Evaluation of sorption properties for cadmium ions in aqueous solution, J. Mater. Sci. 33 (1998) 5433–5439.

[6] S. Al-Asheh, Z. Duvnjak, Sorption of cadmium and other heavy metals by pine bark, J. Hazard. Mater. 56 (1997) 35–51.

[7] U.S. Department of Health and Human Services, Toxicological Profile for Cadmium, Agency for Toxic Substances and Disease Registry (Editor), 1999.

[8] A. Jaiswal, M.C. Chattopadhayaya, Removal of zinc ion from industrial effluents by hydrotalcite-like compound, Desalin. Water. Treat. 12 (2009) 127–132.

[9] S. Mustafa, K.H. Shah, A. Naeem, M. Waseem, M. Tahir, Chromium (III) removal by weak acid exchanger amberlite IRC-50 (Na), J. Hazard. Mater. 160 (2008) 1–5.

[10] S. Tunali, T. Akar, A.S. Ozcan, I. Kiran, A. Ozcan, Equilibrium and kinetics of biosorption of lead (II) from aqueous solutions by cephalosporium aphidicola, Sep. Purif. Technol. 47 (2006) 105–112.

[11] N. Barka, M. Abdennouri, A. Boussaoud, M. El Makhfouk, Biosorption characteristics of Cadmium (II) onto *Scolymus hispanicus L.* as low-cost natural biosorbent, Desalination 258 (2010) 66–71.

[12] M. Allawzi, S. Al-Asheh, Use of Jordanian natural zeolite as sorbent for removal of cadmium from aqueous solutions, Desalin. Water Treat. 22 (2010) 349–354.

[13] L. Mouni, D. Merabet, A. Bouzaza, L. Belkhiri, Removal of Pb^{2+} and Zn^{2+} from the aqueous solutions by activated carbon prepared from Dates stone, Desalin. Water. Treat. 16 (2010) 66–73.

[14] J. Arends, J. Christoffersen, M.R. Christoffersen, H. Eckert, B. O. Fowler, J.C. Heughebaert, G.H. Nancollas, J.P. Yesinowski, S.J. Zawacki, A calcium hydroxyapatite precipitated from an aqueous solution: An international multimethod analysis, J. Crystal. Growth 84 (1987) 515–532.

[15] J.C. Elliott, Structure and Chemistry of the Apatites and Other Calcium Orthophosphates, Elsevier, Amsterdam, 1994.

[16] R.Z. LeGeros, Calcium Phosphates in Oral Biology and Medicine, Karger, Basel, 1991.

[17] R. Marcus, D. Feldman, J. Kelsey, Osteoporosis, Academic Press, San Diego, CA, 1996.

[18] M.R. Urist, B.T. O'Connor, R.G. Burwell, Bone Grafts, Derivates and Substitutes, Butterworth-Heinemann Ltd, Oxford, 1994.

[19] T. Kawasaki, Hydroxyapatite as a liquid chromatographic packing, J. Chromatogr. A 544 (1991) 147–184.

[20] M.J. Gorbunoff, The interaction of proteins with hydroxyapatite. I: Role of protein charge and structure, Anal. Biochem. 136 (1984) 425–432.

[21] H. Aoki, Science and medical applications of hydroxyapatite, Ishiyaku Euro America, Tokyo, 1994.

[22] A. Barroug, M.J. Glimcher, Hydroxyapatite crystals as a local delivery system for cisplatin: Adsorption and release of cisplatin in vitro, J. Orthop. Res. 20 (2002) 274–280.

[23] M.R. Cannon, P.K. Bajpai, Continuous delivery of azidothymidine by hydroxyapatite or tricalcium phosphate ceramics, Biomed. Sci. Instrum. 31 (1995) 159–164.

[24] N. Barka, S. Qourzal, A. Assabbane, A. Nounah, Y. Ait-Ichou, Removal of reactive yellow 84 from aqueous solutions by adsorption onto hydroxyapatite, J. Saudi Chem. Soc. 15 (2011) 263–267.

[25] K. Lin, J. Pan, Y. Chen, R. Cheng, X. Xu, Study the adsorption of phenol from aqueous solution on hydroxyapatite nanopowders, J. Hazard. Mater. 161 (2009) 231–240.

[26] W. Wei, R. Sun, J. Cui, Z. Wei, Removal of nitrobenzene from aqueous solution by adsorption on nanocrystalline hydroxyapatite, Desalination 263 (2010) 89–96.

[27] N. Barka, S. Qourzal, A. Assabbane, A. Nounah, Y. Aît Ichou, Adsorption of disperse blue SBL Dye by synthesized poorly crystalline Hydroxyapatite, J. Environ. Sci. 20 (2008) 1268–1272.

[28] 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.

[29] A. Krestou, A. Xenidis, D. Panias, Mechanism of aqueous uranium (VI) uptake by hydroxyapatite, Miner. Eng. 17 (2004) 373–381.

[30] E.D. Vega, J.C. Pedregosa, G.E. Narda, P.J. Morando, Removal of oxovanadium(IV) from aqueous solutions by using commercial crystalline calcium hydroxyapatite, Water Res. 37 (2003) 1776–1782.

[31] M.F. Elkady, M.M. Mahmoud, H.M. Abd-El-Rahman, Kinetic approach for cadmium sorption using microwave synthesized nano-hydroxyapatite, J. Non-Cryst. Solids 357 (2011) 1118–1129.

[32] Z. Zhang, M. Li, W. Chen, S. Zhu, N. Liu, L. Zhu, Immobilization of lead and cadmium from aqueous solution and contaminated sediment using nano-hydroxyapatite, Environ. Pollut. 158 (2010) 514–519.

[33] I. Mobasherpour, E. Salahi, M. Pazouki, Removal of divalent cadmium cations by means of synthetic nanocrystallite hydroxyapatite, Desalination 266 (2011) 142–148.

[34] R. Zhu, R. Yu, J. Yao, D. Mao, C. Xing, D. Wang, Removal of Cd^{2+} from aqueous solutions by hydroxyapatite, Catal. Today 139 (2008) 94–99.

[35] G. Lusvardi, G. Malavasi, L. Menabue, M. Saladini, Removal of cadmium ion by means of synthetic hydroxyapatite, Waste Manage. 22 (2002) 853–857.

[36] S. Lagergren, Zur theorie der sogenannten adsorption gelöster stoffe, Kungliga Svenska Vetenskapsakademiens, Handlingar, Band 24 (1898) 1–39.

[37] Y.S. Ho, G. Mckay, The kinetics of sorption of basic dyes from aqueous solution by sphagnum mass peat, Can. J. Chem. Eng. 76 (1998) 822–827.

[38] W.J. Weber, Jr., J.C. Morris, Kinetics of adsorption on carbon from solution, J. Sanit. Eng. Div. ASCE 89 (1963) 31–59.

[39] J. Crank, The Mathematics of Diffusion, Clarendon Press, Oxford, 1965.

[40] Y.S. Ho, G. McKay, Pseudo-second-order model for sorption processes, Process Biochem. 34 (1999) 451–465.

[41] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica, and platinum, J. Am. Chem. Soc. 40 (1918) 1361–1403.

[42] H. Freundlich, Uber die adsorption in losungen, J. Phys. Chem. 57 (1907) 385–470.

[43] A.R. Khan, R. Ataullah, A. Al-Haddad, Equilibrium adsorption studies for some aromatic pollutants from dilute aqueous solutions on activated carbon at different temperatures, J. Colloid Interface Sci. 194 (1997) 154–165.

[44] J. Toth, Calculation of the BET-compatible surface area from any type I isotherms measured above the critical temperature, J. Colloid Interface Sci. 225 (2000) 378–383.

[45] M.J. Tempkin, V. Pyzhev, Kinetics of ammonia synthesis on promoted iron catalysts, Acta Physiochim. URSS 12 (1940) 217–222.

[46] N. Balkaya, H. Cesur, Adsorption of cadmium from aqueous solution by phosphogypsum, Chem. Eng. J. 140 (2008) 247–254.

[47] T.K. Sen, M.V. Sarzali, Removal of cadmium metal ion (Cd^{2+}) from its aqueous solution by aluminium oxide (Al_2O_3): A kinetic and equilibrium study, Chem. Eng. J. 142 (2008) 256–262.

[48] J. Kan, S. Tie-heng, S. Li-na, L. Hai-bo, Adsorption characteristics of copper, lead, zinc and cadmium ions by tourmaline, J. Environ. Sci. 18 (2006) 1221–1225.

[49] Z. Orolınova, A. Mockovciakova, J. Skvarla, Sorption of cadmium (II) from aqueous solution by magnetic clay composite, Desalin. Water Treat. 24 (2010) 284–292.

[50] V.O. Vasylechko, G.V. Gryshchouk, Y.B. Kuzma, V.P. Zakordonskiy, L.O. Vasylechko, L.O. Lebedynets, M.B. Kalytovska, Adsorption of cadmium on acid-modified Transcarpathian clinoptilolite, Micropor. Mesopor. Mater. 60 (2003) 183–196.

[51] A. Agrawal, K.K. Sahu, Kinetic and isotherm studies of cadmium adsorption on manganese nodule residue, J. Hazard. Mater. 137 (2006) 915–924.

[52] O. Hamdaoui, F. Saoudi, M. Chiha, Utilization of an agricultural waste material, melon (*Cucumis melo* L.) peel, as a adsorbent for the removal of cadmium from aqueous phase, Desalin. Water Treat. 21 (2010) 228–237.

[53] R. Fouladi Fard, A.A. Azimi, G.R. Nabi Bidhendi, Batch kinetics and isotherms for biosorption of cadmium onto biosolids, Desalin. Water Treat. 28 (2011) 69–74.

[54] Y. Yalcinkaya, L. Soysal, A. Denizli, M.Y. Arica, S. Bektas, O. Genc, Biosorption of cadmium from aquatic systems by carboxymethylcellulose and immobilized Trametes versicolor, Hydrometallurgy 63 (2002) 31–40.

[55] C.H. Xiong, C.P. Yao, Study on the adsorption of cadmium (II) from aqueous solution by D152 resin, J. Hazard. Mater. 166 (2009) 815–820.

[56] K. Kadirvelu, C. Namasivayam, Activated carbon from coconut coirpith as metal adsorbent: Adsorption of Cd(II) from aqueous solution, Adv. Environ. Res. 7 (2003) 471–478.

[57] A. Kapoor, T. Viraraghavan, D.R. Cullimore, Removal of heavy metals using the fungus Aspergillus niger, Bioresour. Technol. 70 (1999) 95–104.

[58] A.K. Meena, G.K. Mishra, P.K. Rai, C. Rajagopal, P.N. Nagar, Removal of heavy metal ions from aqueous solutions using carbon aerogel as an adsorbent, J. Hazard. Mater. 122 (2005) 161–170.