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ORIGINAL ARTICLE

Adsorptive removal of Pb(II) from aqueous solution using nano-sized hydroxyapatite

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Abstract This study investigated the sorption of Pb(II) in aqueous solution onto hydroxyapatite (HA) surfaces. Batch experiments were carried out using synthetic HA. The effect of contact time, HA dosage, and initial pH on removal efficiency were also investigated. The adsorption equilibrium and kinetics of Pb(II) on this adsorbent were then examined at 25 °C. Kinetic data were analyzed by pseudo first, second, and intra-particle diffusion models. The sorption data were then correlated with the Langmuir, Freundlich, Halsey, and Harkins–Jura adsorption isotherm models. The optimum dose of HA for Pb(II) removal is found to be 0.12 g/l with the removal efficiency of 97.3 % at an equilibrium contact time of 1 h. It is found that the adsorption kinetics of the Pb(II) on HA follow the pseudo second-order reaction. All the isotherms fitted well for experimental data. Capacity of HA is found as 357.14 mg Pb(II)/g of HA. The Pb(II) immobilization mechanism was studied. The results indicated that HA can be used as an effective adsorbent for removal of Pb(II) from aqueous solution.

Keywords Hydroxyapatite · Adsorption · Isotherm · Kinetics · Lead removal

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Introduction

Heavy metals are generally recognized to be a threat toward humans and ecosystems because of their high-potential toxicity. They could not be biologically decomposed into harmless materials and, to matters worse, were accumulated in the organisms (Adewunmi et al. 1996). In particular, Pb(II) has been classified as a serious hazardous heavy metal with high priority in the context of environmental risk (Volesky 2001). This metal is extremely toxic and can damage the kidney, liver, brain, nervous, and reproductive systems; among other adverse effects to humans (Godwin 2001). Drinking water containing Pb(II) ions for a long term, even if in a very low concentration, cause a wide range of spectrum health problems, such as renal failure, coma, nausea, cancer, convulsions and subtle effects on metabolism and intelligence (Rashed 2001; Li et al. 2005). It can cause mental retardation and semi-permanent brain damage in young children (Mohammad and Najar 1997). Pb(II) has the ability to replace calcium in the bone to form sites for long-term release (King et al. 2007).

At present, Pb(II) pollution is considered a worldwide problem because this metal is commonly detected in several industrial wastewaters (Davydova 2005). Examples of these wastewaters are those produced by processes, such as mining, smelting, printing, metal plating, explosive

manufacture, and dying. In this context, local legislations have established rigorous standards for Pb(II) concentrations in industrial effluents. Therefore, special attention has been given to develop proper methods for removal of Pb(II) from water (De la Rosa et al. 2008).

Among the various water-treatment techniques described, adsorption is generally preferred for the removal of heavy metal ions due to its high efficiency, easy handling, availability of different adsorbents, and cost effectiveness (Beauvais and Alexandratos 1998). The most widely studied adsorbent is activated carbon, while the application of other adsorbent materials for metal-ion removal is now receiving considerable attention (Corami et al. 2007).

The present study focuses on the removal Pb(II) from aqueous solution by hydroxyapatite (HA) [$Ca_{10}(PO_4)_6(OH)_2$]. HA is a major inorganic constituent of bone and teeth, which belongs to the family of apatite's (Elayaraja et al. 2012). It is one such material with excellent biocompatibility, osteointegrity, and osseous inductivity (Gopi et al. 2012). HA is the most commonly used ceramics in dentistry and bone-repair applications since they show a very good performance due to its similarity with the inorganic component of the bone (Vila et al. 2012). In addition, HA has been used as an adsorbent for removing heavy metals (Ramesh et al. 2012; Corami et al. 2007; Lee et al. 2005), fluoride (Sairam Sundaram et al. 2008), nicotinic acid (Dancu et al. 2011) and phenol (Lin et al. 2009). The study includes an evaluation of the effects of various operational parameters, such as contact time, dose of HA, and pH on the Pb(II) adsorption process. The adsorption kinetic models and equilibrium isotherm models related with the process were also investigated.

Materials and methods

Adsorbent characterization

The laboratory prepared hydroxyapatite (Ramesh et al. 2012) was characterized by using the X-ray diffraction (XRD), transmission electron microscope (TEM) and Fourier Transform Infrared (FTIR) analyzer.

The point of zero charge (PZC) was determined using the solid addition method (Oladoja and Aliu 2009) viz: a series of 100 mL conical flasks, 45 mL of 0.1 M KNO_3 solution was transferred. The pH_0 values of the solution were roughly adjusted from 3.5 to 8.1 by adding either 0.1 N HNO_3 or NaOH. The total volume of the solution in each flask was made exactly to 50 mL by adding the KNO_3 solution. The pH_0 of the solutions were then accurately noted. HA (1 g) was added to each flask and securely capped, immediately. The suspension was then manually agitated. The pH values of the supernatant liquid were noted. The difference between the initial and final pH (pH_f) values ($\Delta pH = pH_0 - pH_f$) was plotted against the pH_0. The point of intersection of the resulting curve at which pH_0 gave the PZC.

Sorption experiments

Metal salt of $Pb(NO_3)_2$ was used to prepare metal ion (Pb(II)) solution. The stock solution (1,000 mg/L) was prepared by dissolving appropriate amounts of metal salt in double distilled water. The working solution (10 mg/L) was prepared by diluting the stock solution to appropriate volume.

Kinetic study was conducted with the known dosage of HA (0.006 g) for the 100 mL of metal ion solution. The samples were shaken at an agitation rate of 250 rpm. The samples were taken out at different time intervals. The sorbent solution mixtures were then centrifuged for 5 min and the supernatant was analyzed for the Pb(II) concentration. After the removal of Pb(II), the HA samples were separated by filtering and dried at 120 °C in an oven.

The batch sorption studies were carried out by shaking a series of bottles containing different amounts of HA dosage between 0.002 and 0.2 g in 100 mL of metal ions solution prepared in the laboratory. The samples were stirred at room temperature at 250 rpm for 1 h (equilibrium time), and their content was then centrifuged for 5 min and the supernatant liquid was analyzed for Pb(II) concentration. Initial and equilibrium metal ion concentration in the aqueous solution was determined by using a Thermo Scientific S-series model flame atomic absorption spectrometer.

The effect of the pH of the initial solution on the adsorption process was analyzed by adjusting the pH the aqueous solution between 2 and 10 with 0.5 N HCl or 0.5 N NaOH. An Orion EA 940 expandable ion analyzer was used to adjust a desired pH value.

Results and discussion

Characterization of HA

XRD and TEM images of nano-sized HA have been given in our previous work (Ramesh et al. 2012). The estimated crystallite size was 28 nm for the HA sample. The HA particles are found to be of nano-sized with needle-like morphology, with width ranging from 15 to 20 nm and length around 50–60 nm, the size comparable to that of bone apatite (Ramesh et al. 2012). Figure 1 shows the infrared spectra of HA before and after Pb(II) adsorption in the 4,000–400 cm^{-1} region. The various bands of HA is given in Table 1. The pH of PZC of the HA is shown in Fig. 2. The PZC of HA was found to be 6.86. It was

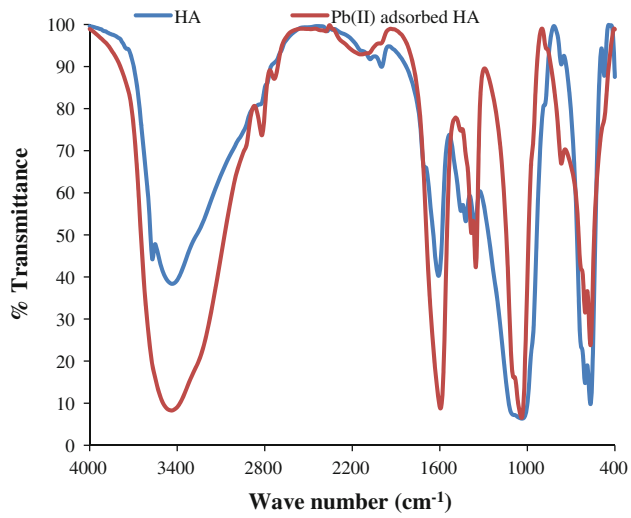

Fig. 1 FTIR spectra for Hydroxyapatite before and after Pb(II) adsorption

observed that at pH <6.86, the surface of the HA is predominated by positive charges while at pH >6.86, the surface is predominated by negative charges.

Effect of contact time

The time-dependent behavior of Pb(II) adsorption was measured by varying the contact time between adsorbate and adsorbent in the range of 5–120 min. The percentage adsorption of Pb(II) with different contact time is shown in Fig. 3. From Fig. 3, it can be observed that the rate of removal of Pb(II) ions was higher at the initial stage, due to the availability of more active sites on the surface of HA and became slower at the later stages of contact time, due to the decreased or lesser number of active sites (Kannan and Karrupasamy 1998). It is apparent from Fig. 3 that until 1 h, the percentage removal of Pb(II) from aqueous solution increases rapidly and reaches up to 89 %. A further increase in contact time has a negligible effect on the percentage removal. Therefore, a 1 h shaking time was considered as equilibrium time for maximum adsorption. The decrease in rate of removal of Pb(II) with time may also be due to aggregation of Pb(II) around the HA particles. This aggregation may hinder the migration of adsorbate, as the adsorption sites become filled up, and also resistance to diffusion of Pb(II) molecules in the adsorbents increases (Mittal et al. 2010). The equilibrium time for Pb(II) removal using various adsorbents reported by various researchers was compared with present study (Table 2). From Table 2, it was found that the contact time for Pb(II) removal using HA is comparable to other adsorbents.

Effect of mass of adsorbent on Pb(II) removal

The effect of HA dosage on Pb(II) removal was analyzed by varying the dosage of HA and the result is shown in Fig. 4. It was observed that the removal efficiency increases with the increase in HA dosage. This reveals that the instantaneous and equilibrium sorption capacities of Pb(II) are functions of the HA dosage. The percentage removal of Pb(II) from aqueous solution by HA increases rapidly up to 67.5 % for a dose of 0.01 g/L. This is mainly due to increase in sportive surface area and availability of more adsorption sites. After that the removal efficiency increases slowly up to a value of 97.3 %. A further increase in HA dose has a negligible effect on the percentage removal. The decrease in the amount sorbed per unit mass with increasing sorbent dosage is due to the split in the flux or the concentration gradient between solute concentration in solution and the solute in the surface of the adsorbent (Vadivelan and Kumar 2005).

Effect of pH

The pH is a significant factor for determining the form of the metallic species in aqueous media. It influences the adsorption process of metal ions, as it determines the magnitude and sign of the charge on ions (Gupta et al. 2011). The effect of solution pH on the sorption of Pb(II) ions from the aqueous solution using HA was investigated in the pH range of 2–10 with the initial Pb(II) concentration of 10 mg/L. The result is shown in Fig. 5. It was found that the adsorption capacity of HA increases with increase in pH in acidic medium. But in alkaline conditions, the removal efficiency remains constant. This is because at low pH (<6), positively charged Pb(II) species are dominant and adsorption on HA takes place in faster rate. But in case of high pH values (pH = 7–11), there are several lead species with different charges like $Pb(OH)^+$ and $Pb(OH)_2$ and thus the removal of lead is possibly accomplished by simultaneous precipitation of $Pb(OH)_2$ and sorption of $Pb(OH)^+$ (Gupta et al. 2011).

Adsorption kinetics

The kinetic studies of a sorption process are paramount because the data obtained from such studies are necessary to understand the variables that influence the sorption of solutes. The results can also be used to determine the equilibrium time and the rate of adsorption can be used to develop predictive models for column experiments (Oladoja et al. 2008a). For this purpose, Lagergren's pseudo first-order kinetic model, pseudo second-order

Table 1 FTIR spectra of HA before and after Pb(II) adsorption

Observed peak (cm^{-1})	% transmittance (Pb(II) loaded)	Peak range (cm^{-1})	Functional group	References
3,464	Decreasing	3,200–3,600	–OH stretching vibration	Manjubala et al. (2001)
1,608	Decreasing	1,300–1,650	CO_3^{2-}	Rehman and Bonfield (1997)
1,360	Decreasing	1,300–1,650	CO_3^{2-}	Rehman and Bonfield (1997)
1,314	Increasing	1,300–1,650	CO_3^{2-}	Rehman and Bonfield (1997)
1,479	Increasing	1,300–1,650	CO_3^{2-}	Rehman and Bonfield (1997)
1,056	No change	900–1,300	PO_4^{3-}	Rehman and Bonfield (1997)
571	Increasing	520–660	PO_4^{3-}	Rehman and Bonfield (1997)

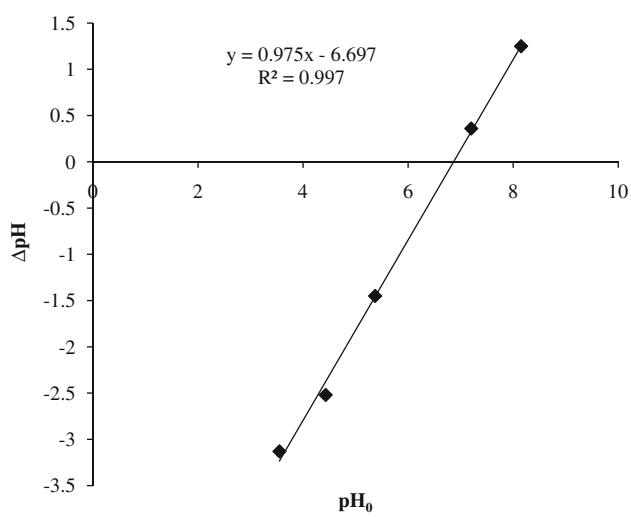

Fig. 2 PZC for HA

kinetic model, and intra-particle diffusion model were considered and fitted with the experimental data.

The pseudo first-order equation is generally expressed as (Lagergren 1898),

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \quad (1)$$

where q_e and q_t are the adsorption capacity at equilibrium and at time t, respectively (mg/g), k_1 is the rate constant of pseudo first-order adsorption (1/min). The values of log ($q_e - q_t$) were linearly correlated with t. The plot of log ($q_e - q_t$) versus t should give a linear relationship from which k_1 and q_e can be determined from the slope and intercept of the plot, respectively.

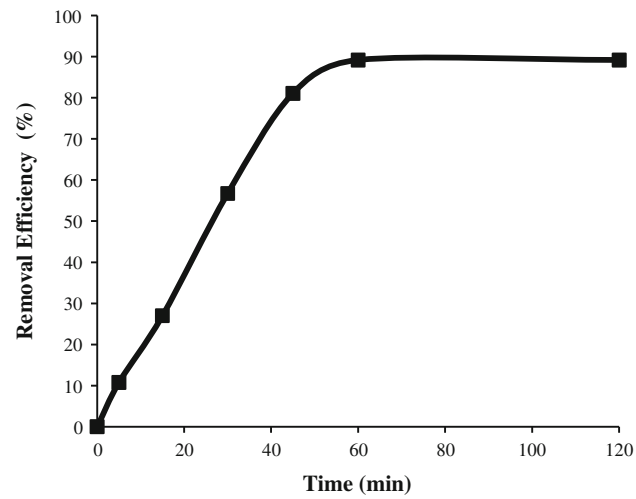

Fig. 3 Effect of contact time on removal of Pb(II)

Table 2 Comparison of contact time for Pb(II) removal

No.	Adsorbent	Equilibrium time	References
1	Activated alumina-supported iron oxide	4, 8, 12 and 36 h, corresponding to Pb(II) initial concentrations of 0.1, 0.2, 0.4 and 0.8 mM, respectively.	Huang et al. (2007)
2	Rice husk, maize cobs and sawdust	90 min	Abdel-Ghani et al. (2007)
3	*Syzygium cumini* L.	10 min	King et al. (2007)
4	Bamboo dust carbon	45 min	Kannan and Veemaraj (2009)
5	Commercial activated carbon	35 min	Kannan and Veemaraj (2009)
9	Calcite	10 min	Yavuz et al. (2007)
7	HA	60 min	Present study

The second-order Lagergren equation was given by (Ho and McKay 1999). It is expressed as:

$$\left(\frac{t}{q_t}\right) = \frac{l}{k_2 q_e^2} + \frac{l}{q_e}(t) \quad (2)$$

where k_2 is the rate constant of pseudo second-order adsorption (g/mg/min). The plot of (t/q_t) and t should give a linear relationship from which q_e and k_2 can be determined from the slope and intercept of the plot, respectively.

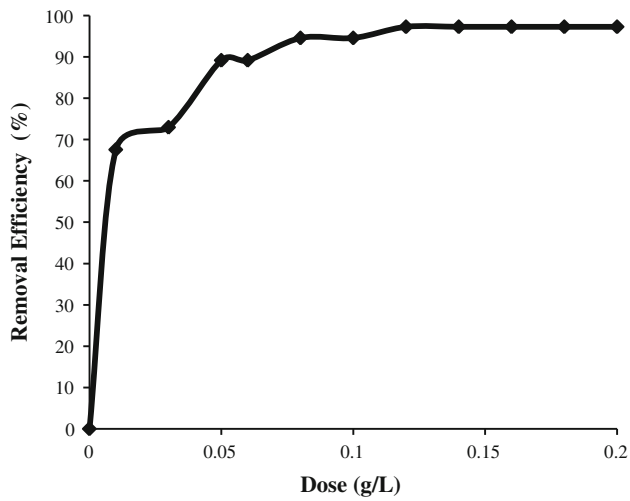

Fig. 4 Effect of dosage on removal of Pb(II)

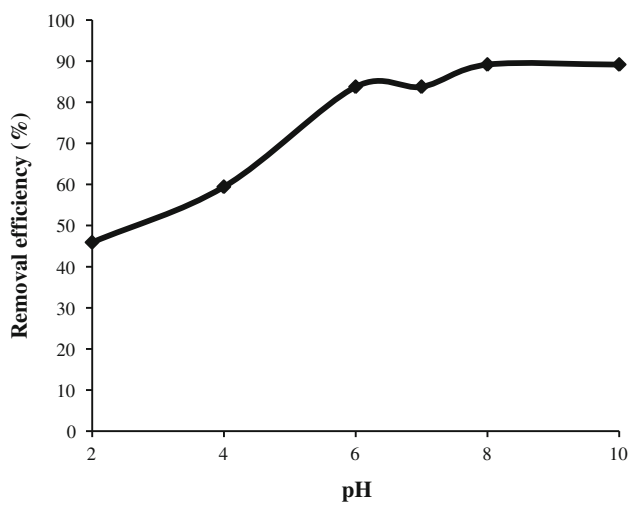

Fig. 5 Effect of pH on removal of Pb(II)

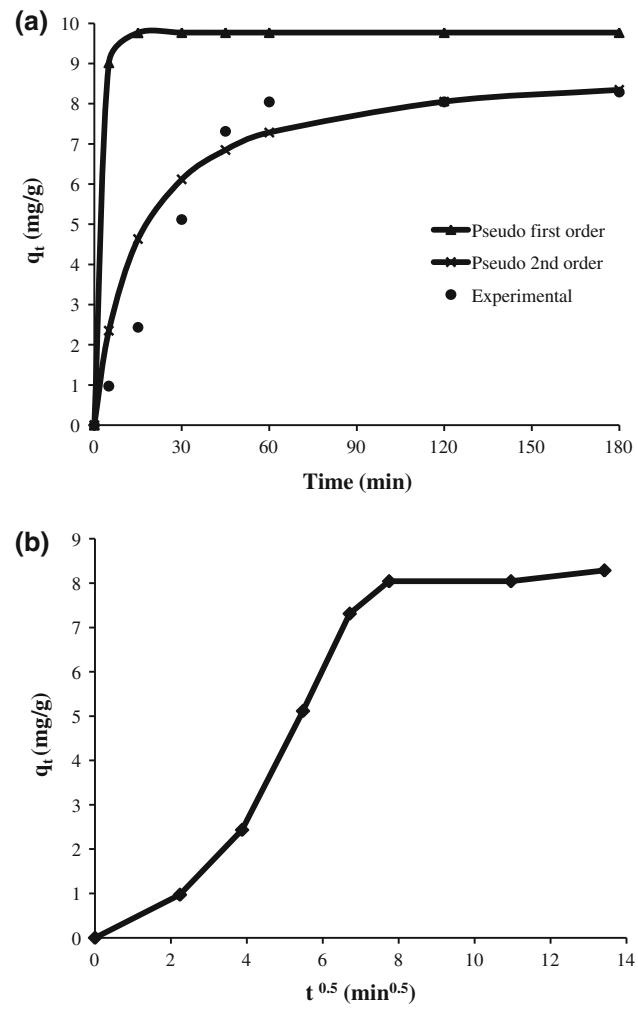

Fig. 6 Kinetic models for removal of Pb(II) by HA **a**, first-order and second-order model **b** intraparticle diffusion model

Though there is a high possibility for pore diffusion to be the rate limiting step in a batch process, the adsorption rate parameter, which controls the batch process for most of the contact time, is the intraparticle diffusion (Weber and Morris 1963; Allen et al. 1989). The most widely applied intraparticle diffusion equation for sorption system is given by Weber and Morris (1963) as follows:

$$q_t = k_i t^{0.5} + c \quad (3)$$

where k_i is the intraparticle rate constant (mg/g mm$^{0.5}$).

Figure 6 shows the plot of the kinetic model for adsorption of Pb(II) on HA. Experimental and theoretically calculated adsorption capacities (q_e) at equilibrium and coefficients related to kinetic plots are listed in Table 3. It can be seen from Table 3 that the linear correlation coefficients for first-order and second-order model are good and based on the comparison between experimental and theoretically calculated q_e values, it was found that the pseudo second-order model fitted better than pseudo first-order model for removal of Pb(II) by HA.

Intraparticle diffusion plot (Fig. 6) shows multi-linearity between $t^{0.5}$ and q_t for the removal of Pb(II) by HA. It was also found that the intra-particle diffusion of Pb(II) within HA occurred in two stages. The first straight portion is attributed to the macro-pore diffusion and the second linear portion to micro-pore diffusion (Allen et al. 1989).

Adsorption isotherms

Equilibrium isotherm is described by a sorption isotherm, characterized by certain constants whose values express the surface properties and affinity of the sorbent sorption equilibrium is established when the concentration of sorbate in the bulk solution is in dynamic balance with that at the sorbent interface (Oladoja et al. 2008b). The adsorption isotherm study is carried out on well-known isotherms,

Table 3 Adsorption kinetic model rate constants for Pb(II) removal

q_e (Exp) (mg/g)	Pseudo first-order			Pseudo second-order		
	q_e (cal) (mg/g)	k_1 (min^{-1})	R^2	q_e (cal) (mg/g)	k_2 (g/mg/min)	R^2
7.07	9.77	0.0513	0.9898	9.01	7.86×10^{-3}	0.991

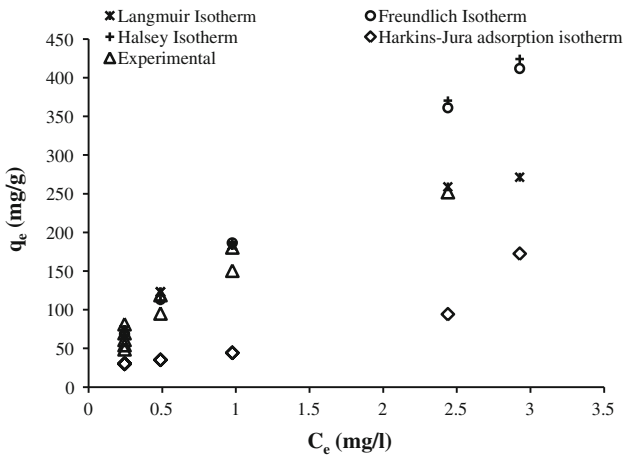

Fig. 7 Isotherm plots for sorption of Pb(II) by HA

such as Langmuir, Freundlich, Halsey, and Harkins–Jura adsorption isotherm models. The linear form of Langmuir isotherm is expressed as (Langmuir 1915):

$$\frac{1}{X/M} = \frac{1}{q_{max}} + \frac{1}{q_{max} b} \frac{1}{C_e} \quad (4)$$

where b is the constant that increases with increasing molecular size, q_{max} is the amount adsorbed to form a complete monolayer on the surface (mg/g), X is weight of substance adsorbed (mg), M is weight of adsorbent (g), and C_e is the concentration remaining in solution (mg/L).

The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L, which is a dimensionless constant referred to as separation factor or equilibrium parameter (Weber and Chakkravorti 1974):

$$R_L = \frac{1}{1 + bC_0} \quad (5)$$

The value of R_L indicates the type of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

The Freundlich isotherm is expressed as (Freundlich 1906).

$$\log q_e = \log K + \frac{1}{n} \times \log C \quad (6)$$

where K and n are the constants depending on temperature.

The Harkin–Jura (Harkins and Jura 1944) adsorption isotherm can be expressed as:

Table 4 Isotherm parameters for sorption of Pb(II) by HA

Isotherm model	Parameters	Value	R^2
Langmuir	b	1.079	0.84
	q_{max} (mg/g)	357.14	
	R_L	0.085	
Freundlich	n	1.343	0.83
	K (mg/g)	189.89	
Halsey	n_H	1.343	0.83
	k (mg/g)	1,149.32	
Harkins– Jura	A	10,000	0.88
	B	0.5	

$$\frac{1}{q_e^2} = \frac{B}{A} - \frac{\log C_e}{A} \quad (7)$$

where B and A are the isotherm constants. The isotherm equation accounts for multilayer adsorption and can be explained by the existence of a heterogeneous pore distribution (Venckatesh et al. 2010). The plot between log C_e and $1/q_e^2$ gives a straight line with slope of $1/A$ and intercept of B/A.

The Halsey (1948) adsorption isotherm can be given as:

$$\ln C_e = \frac{\ln k}{n_H} - \frac{\ln C_e}{n_H} \quad (8)$$

where n_H and k are Halsey isotherm constants. This equation is suitable for multilayer adsorption and the fitting of the experimental data to this equation attest to the heteroporous nature of the adsorbent. The Halsey isotherm parameters are obtained from the plot of ln (q_e) versus ln (C_e).

An isotherm plot for sorption of Pb(II) by HA is shown in Fig. 7. The intercept and slope of each straight line were used to obtain the isotherm constants and given in Table 4. The value of 'n' indicates that the Freundlich isotherm is favorable for removal of Pb(II) by HA. The value of R_L also indicates that Langmuir isotherm is favorable. From Fig. 7, it can be concluded that Langmuir isotherm is the best fit among other isotherms. The adsorption capacity of HA was 357.14 mg Pb(II)/g of HA. The adsorption capacity of HA for Pb(II) is compared with other adsorbents (Table 5). The value of Pb(II) uptake by HA found in this work is significantly higher than that of other adsorbents. From the Table 5, it can be seen that HA is an efficient biosorbent for the uptake of Pb(II) from aqueous solution.

Mechanism

Three types of reactions may control Pb(II) immobilization by HA: surface adsorption, cation substitution or

Table 5 Comparison of Pb(II) adsorption capacities of different adsorbents

No.	Adsorbent	Adsorption capacity (mg/g)	References
1	Activated alumina-supported iron oxide	35.45	Huang et al. (2007)
2	Chicken feathers	8.63	De La Rosa et al. (2008)
3	Kaolinite clay	2.35	Jiang et al. (2010)
4	*Moringa oleifera* Bark	34.6	Reddy et al. (2010)
5	*Trichoderma viride*	49.74	Singh et al. (2010)
6	Powder activated carbon	20.7	Matheickal and Yu (1996)
7	Granulated activated carbon	31.1	Muraleeddharan et al. (1995)
8	Grape stalks	49.7	Martínez et al. (2006)
9	Carbon nanotube sheets	117.64	Tofighy and Mohammadi (2011)
10	Commercial activated carbon, bamboo dust carbon	5.95, 2.15	Kannan and Veemaraj (2009)
11	*Gelidium* algae	64	Wehrheim And Wettern (1994)
12	Crab shell, arca shell	19.83, 18.33	Dahiya et al. (2007)
13	HA	357.14	Present Study
14	HA (50 wt.%)/polyurethane composite foam	150	Jang et al. (2008)
15	Dithiocarbamate-anchored polymer/organosmectite composites	170.7	Say et al. (2006)
16	Activated phosphate	155	Mouflih et al. (2005)

precipitation. The first mechanism is the adsorption of Pb(II) ions on the HA surfaces and following ion exchange reaction between Pb(II) ions adsorbed and Ca^{2+} ions of HA (Suzuki et al. 1984). This ion exchange reaction mechanism is expressed as:

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

Ma et al. (1994) showed that HA dissolution and hydroxypyromorphite (HP) precipitation were the main mechanisms for Pb(II) immobilization by HA in the absence of other metals. These chemical reactions can be described as follows:

$$Ca_{10}(PO_4)_6(OH)_2 + 14H^{2+} \rightarrow 10Ca^{2+} + 6H_2PO_4^- + 2H_2O \text{ (Dissolution)} \quad (10)$$

$$10Pb^{2+} + 6H_2PO_4^- + 2H_2O \rightarrow 14H^{2+} + Pb_{10}(PO_4)_6(OH)_2 \text{ (Percipitation)} \quad (11)$$

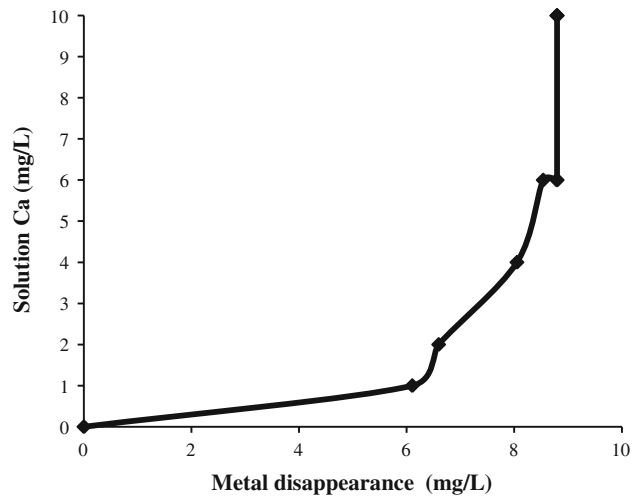

Fig. 8 Metal disappearance for removal of Pb(II) by HA

Information about the sorption mechanisms have been inferred by the values of molar ratios (Q_s) of cations bound by HA to Ca desorbed from HA (Aklil et al. 2004). The Ca desorbed from HA with Pb(II) adsorption is shown in Fig. 8. The values of metal disappearance, solution Ca and molar ratio were found as 8.79 (mg/L), 10 (mg/L) and 0.879, respectively. Since the value of molar ratio is less than 1, dissolution and precipitation are the main mechanisms for Pb(II) adsorption by HA (Corami et al. 2007).

Conclusions

The capability of HA for Pb(II) adsorption was examined using equilibrium and kinetic analysis. The result shows that HA is a powerful adsorbent for removing Pb(II) from aqueous solution. The optimum dose of HA for Pb(II) removal is found to be 0.12 g/L with the removal efficiency of 97.3 %. It is found that the adsorption kinetics of the Pb(II) on HA follow the pseudo second-order reaction. Langmuir isotherm had best fit than Freundlich, Halsey, and Harkins–Jura isotherms for experimental data. The adsorption capacity of HA was found to be 357.14 mg/g.

HA dissolution and hydroxypyromorphite precipitation were the main mechanisms for Pb(II) immobilization by HA.

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