

Kinetics and equilibrium studies for the removal of heavy metals in both single and binary systems using hydroxyapatite

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Abstract Removal of heavy metals is very important with respect to environmental considerations. This study investigated the sorption of copper (Cu) and zinc (Zn) in single and binary aqueous systems onto laboratory prepared hydroxyapatite (HA) surfaces. Batch experiments were carried out using synthetic HA at 30 °C. Parameters that influence the adsorption such as contact time, adsorbent dosage and pH of solution were investigated. The maximum adsorption was found at contact time of 12 and 9 h, HA dosage of 0.4 and 0.7 g/l and pH of 6 and 8 for Cu and Zn, respectively, in single system. Adsorption kinetics data were analyzed using the pseudofirst-, pseudosecond-order and intraparticle diffusion models. The results indicated that the adsorption kinetic data were best described by pseudosecond-order model. Langmuir and Freundlich isotherm models were applied to analyze adsorption data, and Langmuir isotherm was found to be applicable to this

adsorption system, in terms of relatively high regression values. The removal capacity of HA was found to be 125 mg of Cu/g, 30.3 mg of Zn/g in single system and 50 mg of Cu/g, 15.16 mg of Zn/g in binary system. The results indicated that the HA used in this work proved to be effective material for removing Cu and Zn from aqueous solutions.

Keywords Hydroxyapatite · Adsorption · Isotherm · Kinetics

Introduction

The heavy metals are of great concern because of their extreme toxicity even at low concentration and the tendency to accumulate in the food chain (Mohan and Singh 2002). The removal of toxic heavy metals from industrial wastewaters is one of the most important issues of environmental remediation. Heavy metals such as Pb, Cd, Cu, Zn, Hg, Cr, and Ni are the main contaminants of surface water, groundwater, and soils. The main sources of these elements are metal plating industries, abandoned disposal sites, and mining industries (Mulligan et al. 2001). Heavy metal contamination of waters and soils is particularly dangerous to the living organisms. Heavy metals are major pollutants in marine, ground, industrial and even treated wastewaters (Valdman et al. 2001). The presence of toxic heavy metals in water has several problems with animals, plants and human being (Ozer and Pirinççi 2006).

Cu and Zn are among the most toxic metals affecting the environment. The primary sources of Cu in industrial wastewater are metal-process pickling baths and plating baths. Cu may also be present in wastewater from a variety of chemical manufacturing processes employing Cu salts

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or a Cu catalyst (Eckenfelder 2000). Many studies have shown that these metals are toxic even at very low concentrations. However, these metals have many applications in the industry. For example, Cu is known as an excellent conductor of electricity, widely used in the electrical industry in all gauges of wires for circuitry. Cu is also utilized in analytical reagents, in paints for ship keels and in electroplating. Cu acts as an irritant to the skin causing itching and dermatitis, and may cause keratinization of the hands and soles of the feet (Sitting 1981). Zn is often found in effluents discharged from industries involved in acid mine drainage, galvanizing plants, natural ores and municipal wastewater treatment plants and is not biodegradable and travels through the food chain via bioaccumulation (King et al. 2008). Therefore, a systematic study of the removal of Cu and Zn from wastewater is of considerable significance from an environmental point of view.

Many researchers have conducted studies on various methods for the removal of heavy metals from waters and wastewaters. Conventional physicochemical methods such as electrochemical treatment, ion-exchange, precipitation, reverse osmosis, evaporation and oxidation/reduction for heavy metal removal from waste streams are expensive, not eco-friendly and inefficient for metal removal from dilute solutions containing from 1 to 100 mg/l of dissolved metal (Montazer-Rahmati et al. 2011). Efficient and environmental friendly technologies are, therefore, need to be developed to reduce heavy metal contents in wastewaters to acceptable levels at inexpensive costs (Saeed and Iqbal 2003). One alternate effective process is the adsorption which relies on the utilization of solid adsorbents with no chemical degradation. It is attractive due to its merits of effectiveness, efficiency and free sludge (Chu and Chen 2002). Among the various adsorbents, adsorption onto activated carbon (granular or powdered) is widely used; there is still a need to develop low cost and easily available adsorbents for the removal of heavy metal ions from the aqueous environment (Chauhan and Sankararamkrishnan 2011). Hence in recent years, research has been focused on the use of various low cost adsorbents including calcined phosphate (Aklil et al. 2004), activated hazelnut shell ash (Bayrak et al. 2006), orange peel (Feng et al. 2011), black gram husk (Saeed and Iqbal 2003), Coir pith (Ramesh et al. 2011a, 2011b), plants (Benhima et al. 2008; Chiban et al. 2009, 2011a, b, c, 2012), etc.

The present study focuses on the removal of Cu and Zn from aqueous solutions by hydroxyapatite (HA) $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]$. HA is a unique inorganic compound because of its high removal capacity for divalent heavy metal ions, and synthetic HA has been used to remove heavy metals such as Pb (Suzuki et al. 1984; Hashimoto and Sato 2007; Mavropoulos et al. 2002; Shashkova et al. 1999), Zn (Corami et al. 2007), Cd (Lusvardi et al. 2002),

Cr (Shashkova et al. 1999), Fe (Shashkova et al. 1999), Oxovanadium (Vega et al. 2009) and Cu (Corami et al. 2007, 2008) from aqueous solutions.

Materials and methods

Preparation and characterization of HA nanoparticles

The HA synthesized in the laboratory was used as adsorbent for this study. Analytical grade calcium hydroxide $[\text{Ca}(\text{OH})_2]$, E. Merck, Germany], and di-ammonium hydrogen phosphate [DAP, $(\text{NH}_4)_2\text{HPO}_4$, E. Merck, Germany], were used for the preparation of HA nanoparticles. The amount of the reactants was calculated based on the Ca/P molar ratio ($10/6 = 1.67$). The 0.3-M DAP solution was added to the 0.3-M calcium hydroxide aqueous suspension in 5 min under high-speed stirring conditions. This solution with a pH of 11 (Orion 3 star, Thermo electron, USA) was immediately subjected to the microwave irradiation for about 30 min in a domestic microwave oven (Samsung India, 2.45 GHz, 850 W power). The mixing, crystallization of the HA and its aging occurs under the microwave irradiation in a shorter period. The product obtained after filtration was oven-dried at 70 °C for overnight and the cake obtained after drying was powdered with agate mortar and pestle.

The X-ray diffraction is carried out for the HA powder particles using a Rigaku Ultima III X-ray diffractometer with Cu $K_{\alpha 1}$ radiation ($\lambda = 1.54056 \text{ \AA}$) over the 2θ range of 20–60°, using a step size of 0.02° and step time of 4 s. The functional groups present in the synthesized HA were ascertained by Fourier transform infrared spectroscopy (FTIR, Perkin Elmer, Spectrum One, USA) over the region 400–4,000 cm^{-1} in pellet form for the powder samples of 1 mg mixed with spectroscopic grade KBr (Merck) of 200 mg. Spectra were recorded at 4 cm^{-1} resolution, averaging 80 scans. The size and morphological features of synthesized HA powders were analyzed by transmission electron microscope (TEM, Philips, CM12 STEM, Netherlands). For TEM analysis, the powder sample was ultrasonically dispersed in ethanol to form dilute suspensions, and then few drops were deposited on the carbon-coated Cu grids.

Preparation of stock solutions

Metal salts of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ for Cu and ZnCl_2 for Zn were used to prepare metal ion solutions. The stock solutions (1,000 mg/l) were prepared by dissolving appropriate amounts of metal salts in doubly distilled water. The working solutions (each 10 mg/l) were prepared by diluting the stock solutions to appropriate volumes.

Sorption experiments

Batch kinetic study was conducted with the known dosage of adsorbent (0.006 g of HA) for the 100 ml of metal ion (10 mg/l) solution. The samples were shaken at an agitation rate of 250 rpm. The samples were taken out at 1, 3, 6, 9, 12, 24, 36 and 48 h. The sorbent solution mixtures were then centrifuged for 5 min and the supernatant was analyzed for the metal ion concentration using Thermo Scientific S-series model flame atomic absorption spectrometer. The sorption studies were carried out by shaking a series of bottles containing different amounts of HA dosage (0.002–0.3 g) in 100 ml of metal ions solution prepared in the laboratory. The samples were stirred at room temperature at 250 rpm for equilibrium time. The effect of solution pH on Cu and Zn removal was studied over a pH range of 2–10 which was adjusted with 0.1 N HNO₃ or 0.1 N NaOH at the beginning of the experiment and not controlled during the experiment. Optimized dose of HA powder was added into metal solution and shaken at 250 rpm, for equilibrium time. The amount of each metal ion adsorbed onto the HA was calculated by the difference between the content of the metal ion in the influent solution and that of the effluent solution, corrected with the blank, and it is expressed in percentage. After the removal of heavy metals was completed, the HA samples were separated by filtering and dried at 120 °C in an oven. FTIR analyses were carried out on the dried samples to find out modifications in the functional groups after adsorption process.

Results and discussion

Characterization of HA nanoparticles

In order to characterize HA, XRD, FTIR and TEM analysis were carried out on synthesized HA. A typical XRD pattern of the HA sample is shown Fig. 1. X-ray diffraction (XRD) analysis confirmed the mineralogical identity and the crystallinity of HA. The XRD peaks were markedly broader, which suggested that HA particles were nano-sized and correspond to the hexagonal HA crystal (JCPDS 9-432). The peak broadening of the XRD reflection was used to estimate the crystallite size in a direction perpendicular to the crystallographic plane based on Scherer's formula as given Eq. 1 (Gupta et al. 2006).

$$\text{Crystal size} = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

Where λ is the wave length of X rays, β is full width at half height of peak in radians and θ is the angle of

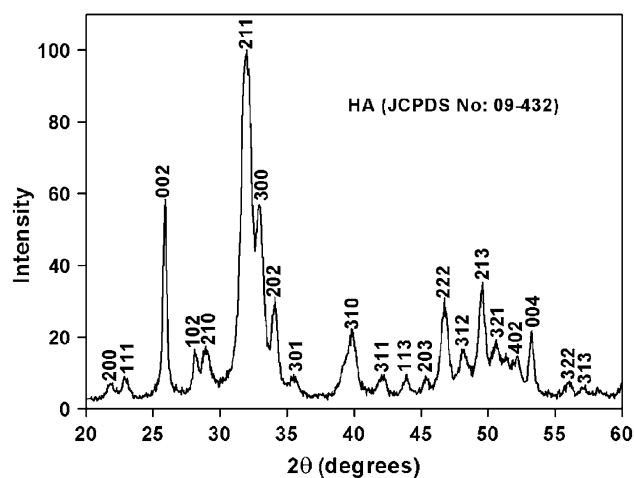


Fig. 1 X-ray diffraction pattern of HA adsorbent in as-synthesized condition

diffraction. The diffraction peak at 25.9° was considered for calculation of the crystal size; since it is sharper and isolated from others. This peak assigns to (0 0 2) Miller's plane family and shows the crystal growth along *c* axis of the HA crystalline structure. The estimated crystallite size was 28 nm for the HA sample.

The TEM morphology of HA samples in as-synthesized condition is shown in Fig. 2. The HA particles are found to be of nano-sized with needle-like morphology, with width ranging from 15–20 nm and length around 50–60 nm, the size comparable to that of bone apatite. The infrared spectra of HA before adsorption in the 4,000–400 cm⁻¹ region is shown in Fig. 3. Hydroxyl stretch is observed at 3,560 cm⁻¹ (Manjubala et al. 2011) in the spectra of HA powder. Peaks in the region of 1,650–1,300 cm⁻¹ are due to ν_3 vibrational mode carbonate ion (Rehman and Bonfield 1997). These carbonate bands in the region of 1,650–1,300 cm⁻¹ are assigned to surface carbonate ions, rather than to carbonate ions in the lattice of phosphate ions (Rehman and Bonfield 1997). Hydroxyapatite has three sites for ν_3 vibrational mode centered at 1,608, 1,422 and 1,360 cm⁻¹. Phosphate ν_4 band is present in the region of 660 and 520 cm⁻¹ and is a well-defined and sharp band, observed in the HA. A single intense ν_3 band is present at 1,056 cm⁻¹ (Rehman and Bonfield 1997). The FTIR spectrum of HA after interaction with Cu, Zn and Binary (Cu–Zn) metals are also shown in Fig. 3. FTIR spectra of the solid residues after adsorption are comparable to those of the original HA, suggesting no other phases formed during the heavy metal sorption. Compared with the FTIR spectra before and after adsorption of Cu and Zn in single and binary system, there were clear band shifts and % transmittance increase for HA (Table 1). The changes mainly occur in the OH⁻ and CO₃²⁻ groups of HA that had bound heavy metals.

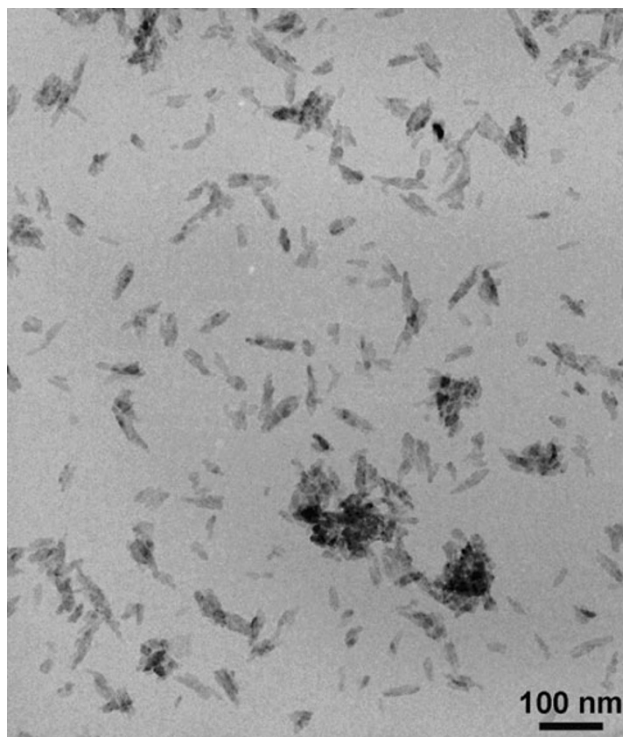


Fig. 2 TEM bright field image of HA

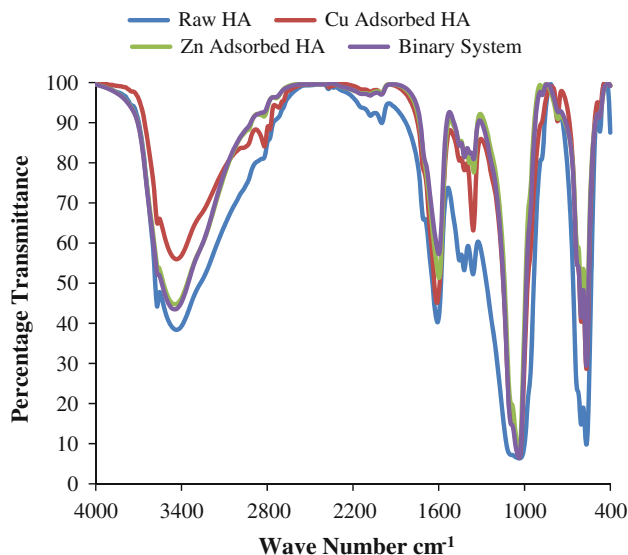


Fig. 3 FTIR spectra for removal of Cu and Zn by HA

Effect of contact time

Metal ion uptake capacities were determined as a function of time to determine an optimum contact time for the adsorption of heavy metal ions on HA. The variation of percentage of adsorbed metal ions with respect to time is shown in Fig. 4. It can be concluded that the removal of metal ions or the adsorption is increasing with increase in

the contact time. Initially, the adsorption was low but increases with time quickly. It also shows that the percent removal of Cu and Zn are 50 and 20 % in 3 h, which increased up to 70 and 22 % in 12 and 9 h, respectively. The less removal of Zn at equilibrium, indicating that more HA was needed to remove Zn ions. In the binary system, 41 % of Cu and 16 % of Zn were removed from the aqueous solution with equilibrium time of 12 and 9 h, respectively. The less removal efficiency in binary system compared to the single metal system at equilibrium time is due to competitive sorption of heavy metals by HA. The equilibrium time for Cu and Zn removal reported by various researchers was compared with present study (Table 2). It was found that the contact time for HA is comparable.

Effect of mass of adsorbent on heavy metal removal

The effect of adsorbent dosage on heavy metal removal was analyzed by varying the dosage of HA and the results are shown in Fig. 5. It was found that the removal efficiency increases with the increase in HA dose. But the saturation of the adsorbent sites by the adsorption of the metal ions at the dosage levels of 0.4 and 0.7 g/l with the removal efficiency of 99 and 98 % for Cu and Zn, respectively. In the binary system, the same percentage removal has been achieved with very high amount of HA (0.9 g/l for Cu and 3 g/l for Zn).

Effect of pH

The uptake of Cu and Zn was examined over a pH range from 2.0 to 10. The variation of the equilibrium uptake of Cu and Zn with the solution pH is shown in Fig. 6. It was observed from Fig. 6 that the amount of Cu and Zn removal by adsorption increased with an increase of pH up to about pH 6.0 for Cu and pH 8 for Zn, respectively. Then the removal efficiency remains constant over the pH range of 6–10 for Cu and 8–10 for Zn. However, Cu uptake was consistently higher than Zn uptake over the whole range of pH from 2.0 to 6. It is also noted that, for pH 2, the metal uptake for Cu increased at a much greater rate than that of Zn. However, at the solution pH greater than 4.0, the uptakes of both Cu and Zn increased at a similar rate. The behavior observed at pH 2 denotes a strong competition effect between the Zn and the H_3O^+ ion for the active sites of the adsorbent. As a result, the Zn does not become adsorbed (G'omez-Tamayo et al. 2008).

Adsorption kinetics

It is known that adsorption process could be controlled with different kinds of mechanisms, such as mass transfer,

Table 1 FTIR absorption band and corresponding functional groups

Observed peak (cm ⁻¹)	% Transmittance (Cu loaded)	% Transmittance (Zn loaded)	% Transmittance (Cu and Zn loaded)	Peak range (cm ⁻¹)	Functional group
3560	Increasing	Increasing	Increasing	3200–3600	–OH stretching vibration
1608	Increasing	Increasing	Increasing	1300–1650	CO ₃ ²⁻
1360	Increasing	Increasing	Increasing	1300–1650	CO ₃ ²⁻
1422	Increasing	Increasing	Increasing	1300–1650	CO ₃ ²⁻
1056	No change	No change	No change	900–1300	PO ₄ ³⁻
612	Increasing	Increasing	Increasing	520–660	PO ₄ ³⁻
566	Increasing	Increasing	Increasing	520–660	PO ₄ ³⁻

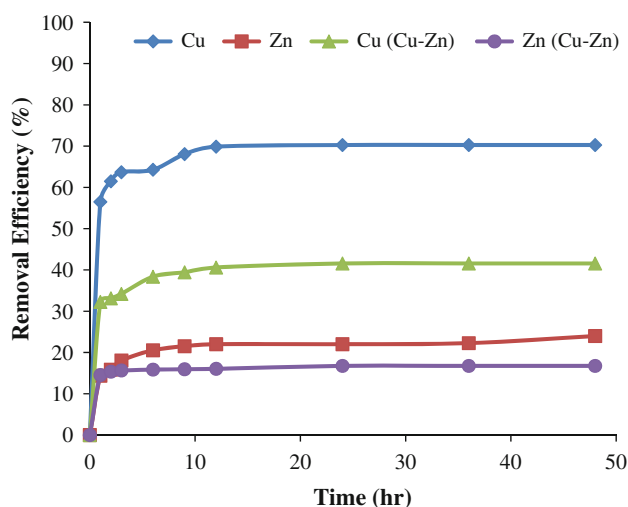


Fig. 4 Effect of contact time on removal of Cu and Zn

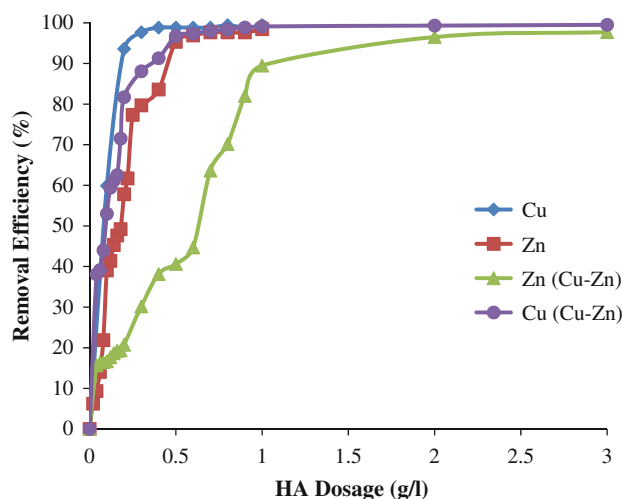


Fig. 5 Effect of dosage on removal of Cu and Zn

Table 2 Comparison of contact time for Cu and Zn removal by various adsorbents

Adsorbent	Equilibrium time (min)		Reference
	Cu	Zn	
Ash	120	90	Al-Madhoun et al. (2005)
Oil shale	1,440	1,440	Al-Asheh and Banat (2001)
Fungal pellets of <i>Aspergillus niger</i> 405	300	300	Filipovic-Kovacevic et al. (2000)
HA	–	1,440	Go’mez del Rí’o et al. (2004)
HA	1,440	1,440	Corami et al. (2007)
Cork powder	–	100	Kanawade and Gaikwad (2011)
Peanut hulls	120	60	Oliveira et al. (2010)
Microwave incinerated rice husk ash	720	1,080	Kutty et al. (2011)
HA	720	540	Present study

diffusion control, chemical reactions and particle diffusion. In order to clarify the adsorption process, several adsorption models were applied to evaluate the experimental data. For this purpose, Lagergren’s pseudofirst-order kinetic model and pseudosecond-order kinetic model were considered and fitted with the experimental data. The pseudofirst-order equation is generally expressed as (Lagregren 1898),

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t, \tag{2}$$

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 pseudofirst-order adsorption (1/min).

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

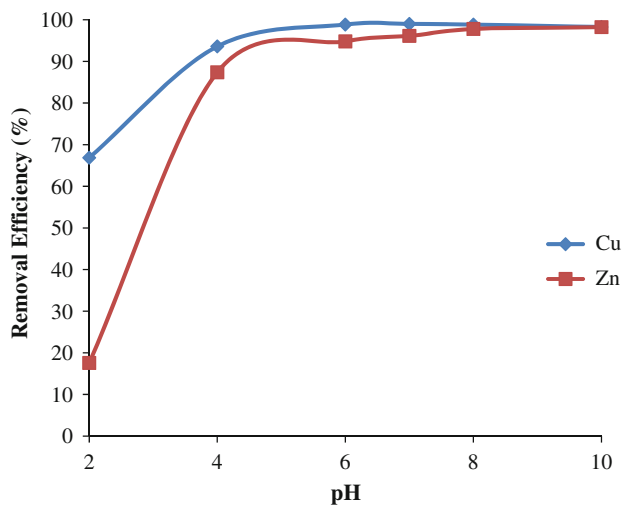


Fig. 6 Effect of pH on removal of Cu and Zn

$$\left(\frac{t}{q_t}\right) = \frac{l}{k_2 q_e^2} + \frac{l}{q_e}(t), \quad (3)$$

where k_2 is the rate constant of pseudosecond-order adsorption (g/mg/min).

Figures 7 and 8 show the plot of the first-order, and second-order models for adsorption of heavy metals by the HA, respectively. Experimental and theoretically calculated adsorption capacities at equilibrium (q_e) values 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 are not good when compared to the second-order model. These results suggest that the adsorption of Cu and Zn metal ions on HA is not pertaining to first-order reaction. It is evident from the results of second-order model that the correlation coefficients for Cu and Zn are very high and the experimental and theoretical q_e values are in good match. These results suggest that the adsorption of the Cu and Zn ions in single and binary system on HA follows the second-order type kinetic reaction.

Rate limiting step in adsorption can be found out from intra particle diffusion model. The Weber and Morris (1963) intraparticle diffusion model is expressed as

$$q_t = k_{id}t^{1/2} + C, \quad (4)$$

where C is the intercept and k_{id} is the intraparticle diffusion rate constant ($\text{mg/g min}^{0.5}$), which can be evaluated from the slope of the linear plot of q_t versus $t^{1/2}$. Intra particle diffusion model for Cu and Zn removal by HA in single and binary system is shown in Fig. 9. Figure 9 shows that the adsorption of Cu and Zn onto HA is multi-step process. It is having two regions. The first region is the instantaneous adsorption or external surface adsorption and the second region is the gradual adsorption stage where intraparticle diffusion is the rate limiting (Hammed 2009).

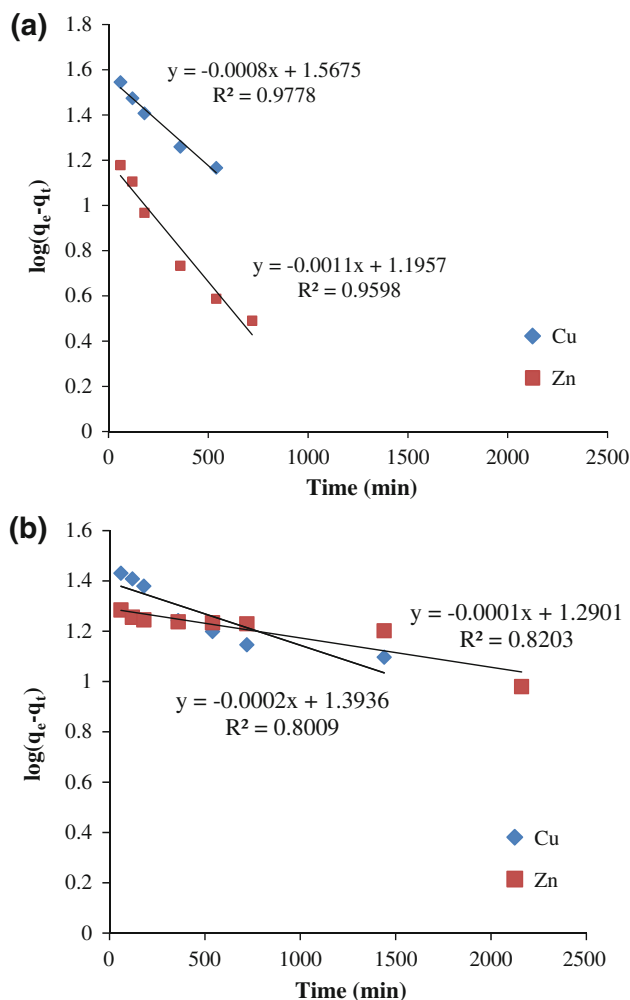


Fig. 7 Pseudofirst-order model plot for sorption of Cu and Zn by HA (a) single (b) binary system

Adsorption isotherms

The equilibrium relationships between adsorbent and adsorbate are best explained by sorption isotherms (Mittal et al. 2010). The experimental values are fitted with Freundlich and Langmuir isotherm equations. The applicability of the isotherm equations was compared by judging the correlation coefficients, R^2 . The Langmuir isotherm is developed by assuming that a fixed number of adsorption sites are available, and that the adsorption is reversible. The Langmuir isotherm may be used when the adsorbent surface is homogeneous. The Langmuir isotherm is expressed as (Langmuir 1915)

$$\frac{1}{X/M} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} b C_e}, \quad (5)$$

where b is the constant that increases with increasing molecular size (mg/l), q_{\max} is the amount adsorbed to form a complete monolayer on the surface (mg/g).

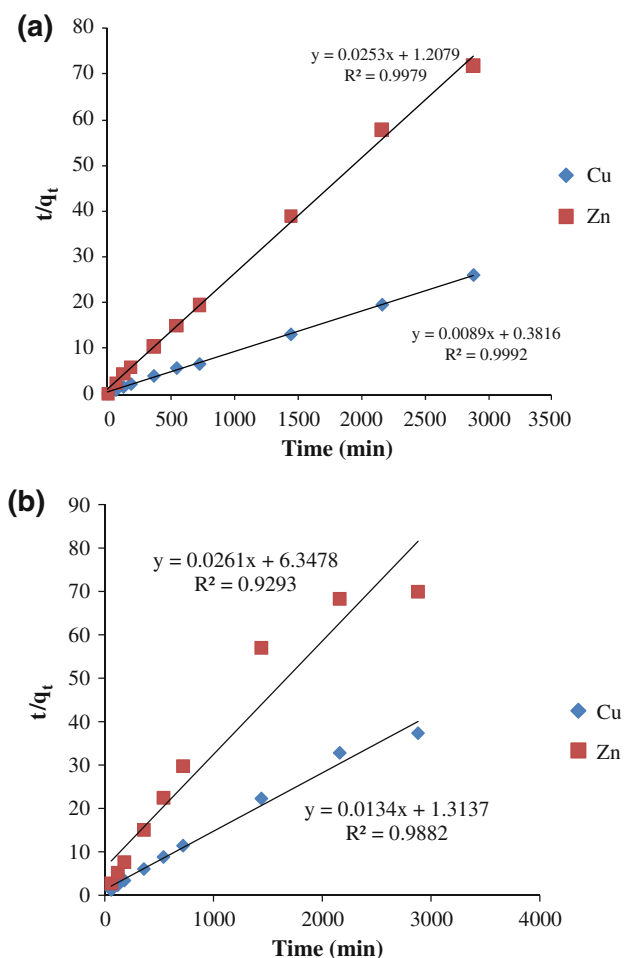


Fig. 8 Pseudo-second-order model plot for sorption of Cu and Zn by HA (a) single (b) binary system

The Freundlich isotherm is a result of the assumption that the adsorption occurs on a heterogeneous surface and non-uniform distribution of the heat of adsorption over the adsorbent surface takes place (Mittal et al. 2010). The Freundlich isotherm is expressed as (Freundlich 1906)

$$\log q_e = \log k + \frac{1}{n} \log C_e \tag{6}$$

Where q_e is the equilibrium adsorption uptake of heavy metal ions, in mg/g, C_e is the equilibrium concentration of heavy metal ions, in mg/l, and k and n are the Freundlich

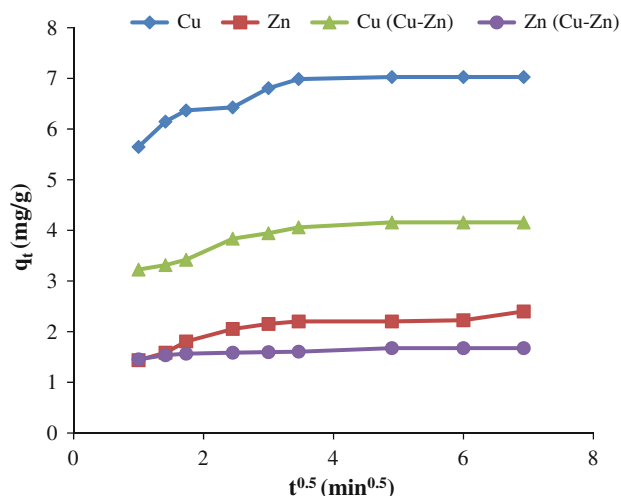


Fig. 9 Intraparticle diffusion model plots for the adsorption of Cu and Zn onto HA

constants which are related to adsorption capacity and intensity, respectively.

The Langmuir and Freundlich isotherm plots are shown in Figs. 10 and 11, respectively. The isotherm constants were evaluated and are reported in Table 4. It was observed that the R^2 of Langmuir model is higher than the Freundlich's (except Cu in single system), which means that the adsorption belongs to the monolayer adsorption (Chen and Chen 2011). The Freundlich constant n value lying in the range of 1–10 for single and binary system confirms the favorable conditions for adsorption (Shokoohi et al. 2009). The adsorption capacity of HA is 125 mg of Cu/g, and 30.3 mg of Zn/g.

In the Cu–Zn system, competitive sorption between the aqueous heavy metals affected retention of metals by HA. Zn sorption (13.16 mg of Zn/g) was lower than that of Cu (50 mg of Cu/g). The same trend has been observed in single metal system. Preferential sorption is the adsorption rate limiting parameter in binary system. Preferential sorption depends on effective ionic radius. For Zn and Cu have effective ionic radius of 74 and 71 Å, respectively (Shannon 1976). Since both metals have almost same effective ionic radius, the removal from aqueous solution should be equal for both metals. In the present study, the removal of Cu and Zn are 99 and 98 %, respectively. This

Table 3 Adsorption kinetic model rate constants of Cu and Zn removal by HA

System	Heavy metals	Pseudo 1st-order co-efficients			Pseudo 2nd-order coefficients			q_e exp (mg/g)
		q_e (mg/g)	k_1 (1/min)	R^2	q_e (mg/g)	k_2 (g/mg/min)	R^2	
Single	Cu	37	0.0018	0.97	113	0.012	0.99	110
	Zn	15.69	0.0025	0.95	41	0.0004	0.99	40
Binary	Cu	25	0.0004	0.80	75	0.00012	0.98	78
	Zn	20	0.0002	0.82	39	0.00014	0.92	42

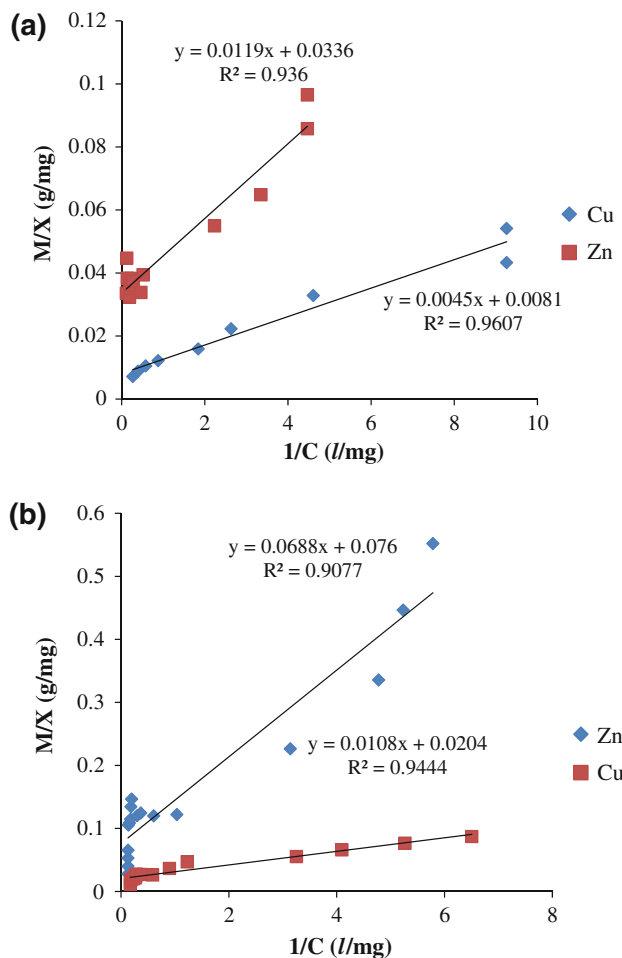


Fig. 10 Langmuir isotherm plot for sorption of Cu and Zn by HA (a) single (b) binary system

satisfies the above condition. But the adsorption capacity of HA is higher for Cu than Zn. Similar results have been reported by Zacaria et al. (2002), Shawabkeh et al. (2004), Issabayeva and Aroua (2011) and Kutty et al. (2011). It was also inferred that the selectivity sequence of HA may be system specific which depended on the properties of the adsorbent and the experimental set-up used (Hui et al. 2005).

The maximum adsorption capacity of various adsorbents for Cu and Zn adsorption in single system together with the present study is given in Table 5. HA is found to have a relatively large adsorption capacity compared to other adsorbents. This indicates that HA can be considered as promising material for removing Cu and Zn from aqueous solution.

Sorption mechanism

Sorption of Zn and Cu undergoes two step processes. Rapid complexation of heavy metals on specific sites of HA

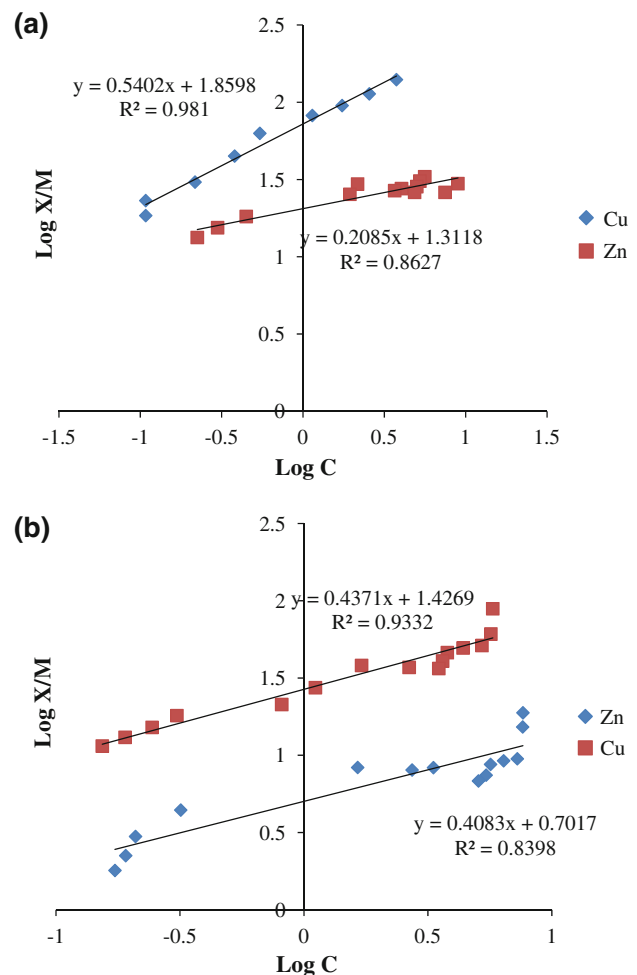


Fig. 11 Freundlich isotherm plot for sorption of Cu and Zn by HA (a) single (b) binary system

surface is the first step. A metal diffusion into the HA structure or to a heavy metal-containing HA formation is the second step in the sorption process (Corami et al. 2007). The sorption mechanisms have been inferred by the values of molar ratios (Q_s) of cations bound by HA to Ca desorbed from HA in single metal system and binary metal system (Corami et al. 2007) as given in Table 6. For the present study all the values of Q_s are less than one for single and binary system. This indicates that dissolution of HA and precipitation of new phosphate phase with lower cation to phosphate molar ratio occurs during sorption process (Corami et al. 2007). The increase in solution Ca increased with increasing metal disappearance was very high for Cu adsorption than that of Zn (Fig. 12). In the present study, Q_s is not equal to 1 indicates that the no possibility of ion exchange of cations between the HA and the solution (Corami et al. 2007). The adsorption energies (E) from Dubinin–Radushkevich isotherm plot (not shown) were 4.08, 3.16, 3.16 and 2.3 kJ mol⁻¹ for Cu, Zn, Cu (Cu–Zn) and Zn (Cu–Zn), respectively. For

Table 4 Isotherm constants of Cu and Zn removal by HA

System	Heavy metals	Langmuir coefficients			Freundlich co-efficients		
		q_{max} (mg/g)	b (1/min)	R^2	k (mg/g)	n	R^2
Single	Cu	125	2	0.96	72.41	1.852	0.981
	Zn	30.3	3	0.936	20.5	4.807	0.862
Binary	Cu	50	2	0.944	26.66	2.288	0.933
	Zn	13.16	1.118	0.907	5.02	2.451	0.839

Table 5 Comparison of maximum Cu and Zn adsorption capacity of various adsorbents

Adsorbent	Capacity (mg/g)		Reference
	Cu	Zn	
Peanut hulls	8	8.96	Zacaria et al. (2002)
Lignin	–	95	Srivastava et al. (1994)
Palm shell activated carbon	21	15	Issabayeva and Aroua (2011)
Biomodified palm shell activated carbon	22	19	Issabayeva and Aroua (2011)
Chitosan-bound Fe ₃ O ₄	21.5	–	Chang and Chen (2005)
Hydrated amorphous TiO ₂	84.79	–	Kanna et al. (2005)
Amberlite 200	88.90	85.60	Zacaria et al. (2002)
Cornstarch	8.57	6.87	Zacaria et al. (2002)
Amberlite IRC-718	127.00	156.96	Zacaria et al. (2002)
Lewatit TP 207	85.09	89.60	Zacaria et al. (2002)
HA	96	76.52	Corami et al. (2007)
HA	125	30.3	Present study

Table 6 Molar ratio values of Cu and Zn removal by HA

System	Metal	Metal disappearance (mg/l)	Solution Ca (mg/l)	Molar ratio (Q_s)
Single	Cu	9.88	12	0.823
	Zn	9.76	14	0.666
Binary	Cu–Zn	19.65	38	0.515

$E < 8 \text{ kJmol}^{-1}$, indicates that physisorption dominates the sorption mechanism (Argun et al. 2007). Therefore, it can be concluded that no ion-exchange between heavy metal adsorbed and Ca released into the solution.

Conclusions

The present study has demonstrated that HA has the adsorption capacity for removal of Cu and Zn from an aqueous solution. The equilibrium time for Cu and Zn removal was found as 12 and 9 h in both systems. The

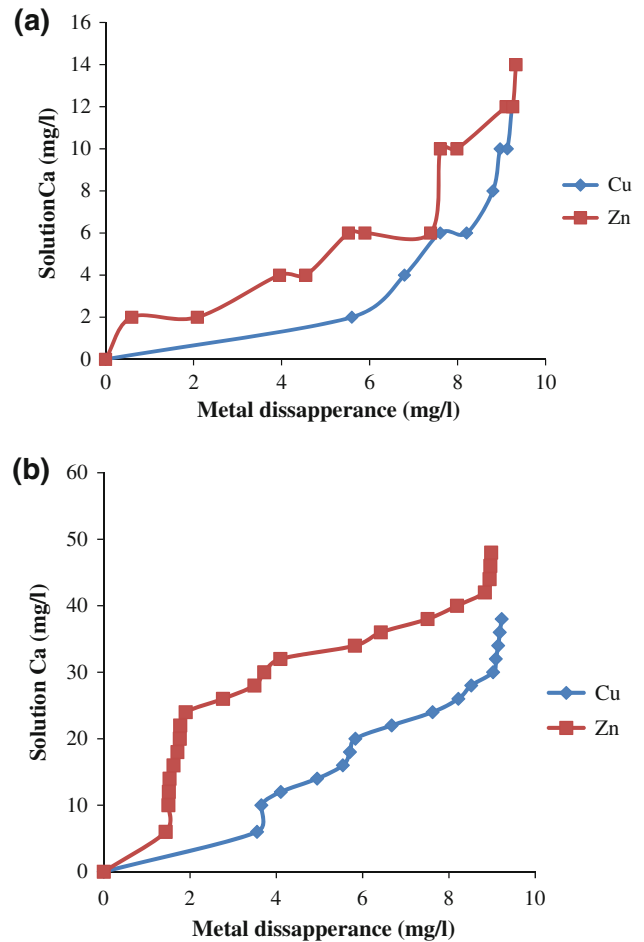


Fig. 12 Metal disappearance for (a) single (b) binary system

optimum dose of HA was found to be 0.4 and 0.7 g/l for Cu and Zn with the removal efficiencies of 99 and 98 %, respectively for single system. Similar efficiency was obtained for HA dosage of 0.9 g/l for Cu and 3 g/l for Zn in binary system. The maximum removal of Cu and Zn were occurred at pH of 6 and 8, respectively. Adsorption of Cu and Zn onto HA followed the pseudosecond-order kinetic model. Langmuir model fitted the experimental data better than Freundlich model, even though adsorption is favorable for Freundlich isotherm. The removal capacity of HA was found to be 125 mg of Cu/g, 30.3 mg of Zn/g in single system and 50 mg of Cu/g, 15.16 mg of Zn/g in binary

system. The results showed that HA is a good adsorbent for the removal of Cu and Zn from aqueous solutions.

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