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ORIGINAL PAPER

Waste calcite sludge as an adsorbent for the removal of cadmium, copper, lead, and zinc from aqueous solutions

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Abstract Sludge residues, an industrial waste material for the removal of cadmium (Cd^{2+}), copper (Cu^{2+}), lead (Pb^{2+}), and zinc (Zn^{2+}) from aqueous solutions were investigated using batch method. Batch mode experiments were carried out as a function of solution pH, adsorbent dosage, initial concentration, and contact time. The results indicated that the adsorbent showed good sorption potential and maximum metal removal was observed at pH ≥ 3. Within 120 min of operation, about 63.7, 95.2, 99.9, and 88.2% of Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} ions were removed from the solutions, respectively. Sorption curves were well fitted to the Langmuir and Freundlich models. The adsorption capacities for Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} ions at optimum conditions were 121.2, 1067.8, 566.4, and 534.2 mg g^{-1}, respectively. The kinetics of Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} adsorption from aqueous solutions was analyzed by fitting the experimental data to pseudo-first- and pseudo-second-order kinetic models. However, the pseudo-first-order kinetics model provided much better R^2 values and the rate constant was found to be 0.001 min^{-1} for Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} ions. The results revealed that sludge residues can adsorb considerable amount of Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} ions and it could be an economical method for the removal of these ions from aqueous systems.

Keywords Sludge residues · Adsorbent · Cadmium · Copper · Lead · Zinc

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Introduction

The heavy metal pollution produced in industrial wastewaters is a great environmental problem and has been increasing during the last few years. Because of heavy metal ions toxicity, the presence of any of these metals in excessive quantities will interfere with many beneficial uses of the water. Then, the need for a process to remove heavy metals has become a major challenge in recycling water systems (Cardenas et al. 2001). Current methods for the removal of heavy metals generally require the use of chemical reagents for precipitation of these metals from their solutions (Hamidi et al. 2008). Other methods include ion exchange, membrane filtration, adsorption, and biosorption (Kurniawan et al. 2006). In recent years, the removal of toxic heavy metal ions from sewage, industrial, and mining waste effluents has been widely studied and adsorption was known very effective for the treatment of wastewater containing low concentration of heavy metals (Chen et al. 2008).

The development of new products which are abundant in nature, low in cost, and have minimal environmental impact for restoration or remediation of natural resources is an important area of Material Sciences. In general, use of industrial and metallurgical wastes and by-products, biological wastes, natural substances, and minerals have been studied as adsorbents for the wastewater treatment (Pollard et al. 1992; Babel and Kurniawan 2003). Several natural substances or metallurgical wastes were used as adsorbents for heavy metals uptake from water and wastewater including kaolin (Arias et al. 2002), kaolinite (Suraj et al. 1998; Yavuz et al. 2003), perlite (Mathialagan and Viraraghavan 2002), montmorillonite and goethite (Collins et al. 1999; Wu et al. 2003), bentonite (Naseem and Ve Tahir 2001), iron oxides (Beukes et al. 2000; Liu and Huang

2003), dolomite (Brady et al. 1999), amorphous hydrous manganese dioxide (Kanungo et al. 2004), siderite (Erdem and Zverdi 2005), siderite/limestone (Wang and Reardon 2001), activated alumina (Singh and Pant 2004), bauxite (Altundogan and Tumen 2001; Erdem et al. 2004), fly ash (Panday et al. 1984; Bayat 2002), sand, silica and alumina (Yabe and Oliveira 2003), steel converter slag (Ortiz et al. 2001), blast furnace slag (Johansson 1999).

Also, the uptake of heavy metals by calcite ($CaCO_3$) has been studied in considerable detail, because the ubiquity of calcite in the (sub)surface environment combined with its reactive nature makes this mineral a potentially important sink for contaminants in numerous environmental settings (Elzinga et al. 2006). Calcite and hydroxyl-apatite [$Ca_5(PO_4)_3OH$] fulfill both characteristics, and have the potential to retain heavy metals from industrial effluents (Go'mez del Rio et al. 2004). It is used in the primary processes of effluent treatment to adjust pH, in order to optimize the precipitation of metallic oxides and hydroxides. It is also used, with iron and aluminum oxides, as a sorbent. The interaction of cadmium (Cd^{2+}), zinc (Zn^{2+}), and cobalt (Co^{2+}) with calcite has been previously described in the literature (Zachara et al. 1991). Hydroxyl-apatite has shown a certain ability to retain lead (Pb^{2+}), copper (Cu^{2+}), Cd^{2+}, Zn^{2+}, uranium (U), arsenic (As), antimony (Sb), and vanadium (V) (Leyva et al. 2001; Wang et al. 2001; Fuller et al. 2002).

Several studies have shown that all of these uptake mechanisms may be operative in the sequestration of divalent heavy metals by calcite, depending on reaction variables such as metal type and concentration, calcite saturation state, reaction time, and pH (Sturchio et al. 1997; Temmam et al. 2000; Elzinga and Reeder 2002; Godelitsas et al. 2004; Rouff et al. 2005, 2006).

In order to reduce the environmental risks arising from heavy metal pollution of the application of sewage sludge, fertilizers, and industrial activities in the state of Hamedan, western Iran, it is necessary to develop some low-cost remediation methods which do not destroy the soil structure and fertility, and are suitable for application on top soils.

The sorbent used in this study was the sludge obtained from the power plant in Hamedan, and because of its abundance and free cost of it we have used it as a material for evaluation of the heavy metal retention capacity. X-ray diffraction (XRD) analysis confirmed that the material was calcite with Mg impurity.

On the other hand, traditionally liming of soils has been used to increase the soil pH, thereby reducing the mobility of metals; therefore, calcite is suitable material to remove heavy metals from industrial wastewaters and for the immobilisation of metals in polluted soils.

The aim of this article is to investigate the effects of pH, contact time, and initial metal concentration on the Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} removal from aqueous solution by power plant sludge (waste calcite sludge).

Materials and methods

Standard solutions

All chemicals were of the analytical grade purchased from Merck Company (Darmstadt, Germany). Stock solutions of Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} (1.000 g l^{-1}) were prepared by dissolving appropriated amounts of $CdCl_2{\cdot}H_2O$, $CuCl_2{\cdot}2H_2O$, $PbCl_2$, and $ZnCl_2$ in dionized water.

Pretreatment of the adsorbent

Sludge was collected from power plant in Hamedan, western Iran. Waste calcite sludge was selected because it is low-cost sorbent. Adsorbent was dried and then ground into appropriate particle sizes by sieving with $\neq$10 mesh (2 mm). The pH of waste calcite sludge was measured in distilled water (1:5 ratios). Other waste calcite sludge properties were reported in Table 1.

Apparatus

A Varian model 220 atomic absorption spectrometer was used for determination of concentration of metal ion. The following conditions were used: wavelength: Cd, Cu, Pb, and Zn 228, 324, 217, and 213 nm; slit widths: 0.5, 0.2, 1, and 1 nm; and lamp currents: 4, 4, 5, and 5 mA, respectively. The flow rates of air and acetylene were set as recommended by the manufacturer. A Jenway model 3510 pH-meter with a combined glass electrode was used for pH measurements. The XRD, Seifert 300 diffractometer with CuKα as the radiation source and Ni as the filter in the range $2\theta = 10°–70°$ was used for phase identification and crystallinity of the adsorbent. The scanning electron

Table 1 Characterization of waste calcite sludge

Absorbent	pH[a]	EC[a]	Solution ions[a] (meq l^{-1})									
			Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	HCO_3^-	CO_3^{2-}	PO_4^{3-}	NO_3^-	SO_4^{2-}
Waste calcite sludge	9.39	0.98	3.08	0.02	0.21	8.29	4	0.66	1.80	0.019	0.65	2.29

[a] Measured in 5:1 liquid, solid solution

microscopy (SEM) measurement was carried out using SEM, Camscan mv2300.

Adsorption isotherms

The adsorption isotherms of the Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} on the waste calcite sludge were determined on the basis of batch analysis. Waste calcite sludge was allowed to equilibrate with solutions of cations with known initial concentrations. The concentrations after the equilibration period were measured.

The amount of each cation adsorbed by sorbent was calculated with the equation:

$$S = \frac{(C_i - C)V}{W} \tag{1}$$

where S is the quantity of cation adsorbed (mg kg^{-1}), C_i is the initial concentration of the cation in solution (mg l^{-1}), C is the equilibrium concentration of the cation in solution (mg l^{-1}), V is the solution volume (l), and W is the weight of air-dried sorbent (kg). The corresponding sorption isotherms for Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} were quantitatively described by parameters through fitting the experimental data to the data to the Langmuir and Freundlich equations using the nonlinear procedure with Sigmaplot statistical software package version 10.0:

$$S = \frac{QbC}{(1 + bC)} \tag{2}$$

where b (l mg^{-1}) is a coefficient which reflects the relative sorption and desorption at equilibrium and is thus the bonding energy coefficient, and Q (mg kg^{-1}) is the maximum sorption.

$$S = K_F C^{\frac{1}{n}} \tag{3}$$

where K_F (l kg^{-1}) is the Freundlich distribution coefficient and n is an empirical constant. The goodness-of-fit for all equations was estimated by the coefficient of determination.

The computer program Visual MINTEQ version version 2.30 (Allison et al. 1991) was used to predict the saturation indices (SI) and heavy metal speciation in the equilibrium solution concentration in the sorption experiments. The model inputs consisted of the measured concentrations of Ca^{2+}, Cd^{2+}, Cl^{-}, CO_3^{2-}, Cu^{2+}, HCO_3^{-}, K^{+}, Mg^{2+}, Na^{+}, Ni^{2+}, NO_3^{-}, Pb^{2+}, PO_4^{3-}, SO_4^{2-}, as well as the EC and pH.

Batch experiment

All working solutions of varying concentrations were obtained by successive dilution (AR grade). Residual Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} concentration in the filtrate was determined by atomic absorption spectrophotometer. The batch mode operation was used to study the removal of Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} from synthetic wastewater. Adsorption experiments were carried out using 50 ml of metal ions solution of desired concentration (50 mg l^{-1}). Adsorption experiments covered a wide range of metal concentrations (100–5,000 mg l^{-1}), equilibration times (10, 20, 30, 40, 50, 60, 90, 120, 160, 200, 240, 260, and 300 min), and pH (2–12 for Cd^{2+} and Zn^{2+}, 2–8 for Cu^{2+} and Pb^{2+}, due to solubility constrains), using an orbital shaker at 150 rpm for 120 min in two replicates. Residual Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} concentration in the supernatant was determined as stated above. Blank samples were run under similar conditions of temperature, without adsorbent in all cases to correct for any adsorption on the internal surface of flasks. The percent metal ions removal (R, %) was calculated for each run by following expression:

$$R = \frac{C_i - C}{C_i} \times 100 \tag{4}$$

where C_i and C were the initial and equilibrium concentration of metal ions in the solution, respectively. The adsorption capacity of an adsorbent which is obtained from the mass balance on the sorbate in a system with solution volume is often used to acquire the experimental adsorption isotherms. Under the experimental conditions, the adsorption capacities of all the adsorbents for each concentration of metal ions at equilibrium were calculated using the following equation:

$$q_e = \frac{C_i - C}{M \times V} \tag{5}$$

where V is the volume of solution (l) and M is the mass of adsorbent (in g) used.

Kinetic model

The pseudo-first- and pseudo-second-order kinetic models were used to describe the sorption kinetic data of Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} measured on sorbent (Alyüz and Veli 2009):

The linear form of the models is shown below

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{6}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{7}$$

where q_e and q_t are the amounts of metal ions adsorbed onto the adsorbents (mg g^{-1}) at equilibrium and at time t, respectively. k_1 is the rate constant of first-order (min^{-1}), and k_2 is the rate constant of second-order sorption (g mg^{-1} min^{-1}). By plotting $\ln(q_e - q_t)$ and t/q_t versus t, the first-order constant k_1, the second-order constant k_2, and the equilibrium capacity q_e can be obtained from the slope and intercept, respectively.

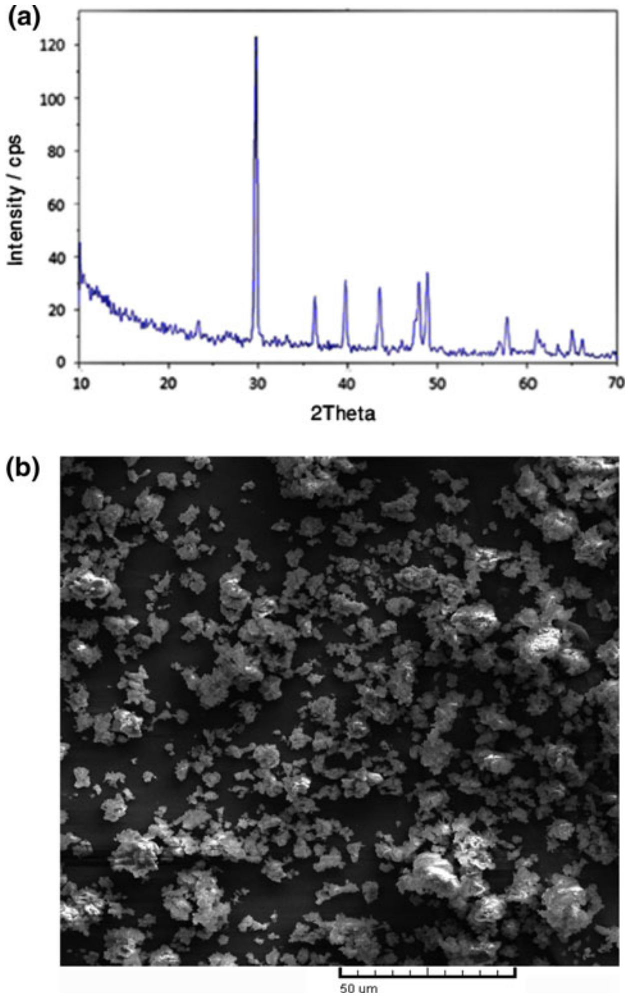

Fig. 1 X-ray diffraction pattern (**a**) and Scanning Electron Microscopy (SEM) (**b**) of waste calcite sludge

Results and discussion

XRD and SEM

X-ray diffraction patterns and SEM obtained for orientated sample indicated that the sample was mainly containing calcite with Mg impurity (Fig. 1).

The sorption isotherm of Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} on sorbent

The relationships between sorbed Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} and equilibrium Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} concentration for the sorbent are shown in Fig. 2. Cadmium, Cu^{2+}, Pb^{2+}, and Zn^{2+} sorption and equilibrium solution Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} concentration increased with increasing amounts of Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} added. The adsorption rate was high for small concentrations of added Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} and the percentage of Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} adsorbed decreased with the increasing levels of added Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+}. At a low rate of added (100 mg l^{-1}) Cd^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+}, the amounts of Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} adsorbed were 1199 mg Cd^{2+} kg^{-1} (99%), 21112 mg Cu^{2+} kg^{-1} (84.5%), 22000 mg Pb^{2+} kg^{-1} (88%) and 24577 mg Zn^{2+} kg^{-1} (98%). At the high rate of added (5000 mg l^{-1}) Cd^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+}, however, the amounts of Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} adsorbed were 127,500 mg Cd^{2+} kg^{-1} (10.2%), 975,000 mg Cu^{2+} kg^{-1} (78%), 575,000 mg Pb^{2+} kg^{-1} (46%), and 500,000 mg Zn^{2+} kg^{-1} (40%). This shows that a greater proportion of the added Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} were sorbed at low Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} concentrations.

Many researchers tested the sorption capacity of the calcite samples, and the obtained results can be compared. For example, it has been observed that divalent metals smaller than Ca^{2+} (Fe^{2+}, Mg^{2+}, Mn^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}) are incorporated into the calcite far more easily than larger cations (Ba^{2+}, Sr^{2+}, Pb^{2+}) (Ettler et al. 2006). The precipitation of calcite is responsible for heavy element removal from landfill leachate-polluted waters through incorporation into the calcite structure or adsorption on its surface (Ettler et al. 2006). However, at low initial metal concentrations ($<10^{-5}$ M), metal retention is controlled rather by adsorption on the calcite surface (Zachara et al. 1991).

Other result indicates that more than 90% of heavy metals could be removed from the solution with a limestone quantity of above 45 g in 100 ml heavy metals solution (Hamidi et al. 2008). A study on metals adsorption by calcite concluded that heavy metals are retained on calcite according to the following sequence: Cr^{3+}, Zn^{2+}, and Cd^{2+} (Sanchez and Ayuso 2002). Precipitation will cause huge retention of Cr^{3+} and Zn^{2+} on this mineral. Calcite beds can effectively retain Cr^{3+} and Zn^{2+} from real wastewaters of electroplating processes: (a) $CdCO_3$ was the compound which precipitates on calcite surface after Cd^{2+} adsorption via exchange; (b) Zn^{2+} retention on calcite occurs by precipitation of hydrozincite, $Zn_5(OH)_6(CO_3)_2$ on its surface.

Various workers have also reported that $CaCO_3$ may be the dominant sorbent for a variety of metals in carbonate aquifers (Davis et al. 1987; Fuller and Davis 1987; Zachara et al. 1991). Also, powder sorption experiments have shown that divalent Co^{2+}, Cd^{2+}, Zn^{2+}, and Ni^{2+} cations are strongly sorbed by the $CaCO_3$ surface (McBride 1980; Davis et al. 1987; Zachara et al. 1991). On the other hand, Pb^{2+} adsorbs onto calcite and that the Pb^{2+} ions move into Ca^{2+} sites, despite the large ionic radius of Pb^{2+} relative to Ca^{2+} (Sturchio et al. 1997). Furthermore, heavy metals were reported to be sorbed on the surface of calcite (Lorens 1981), and sorption is defined as a surface process

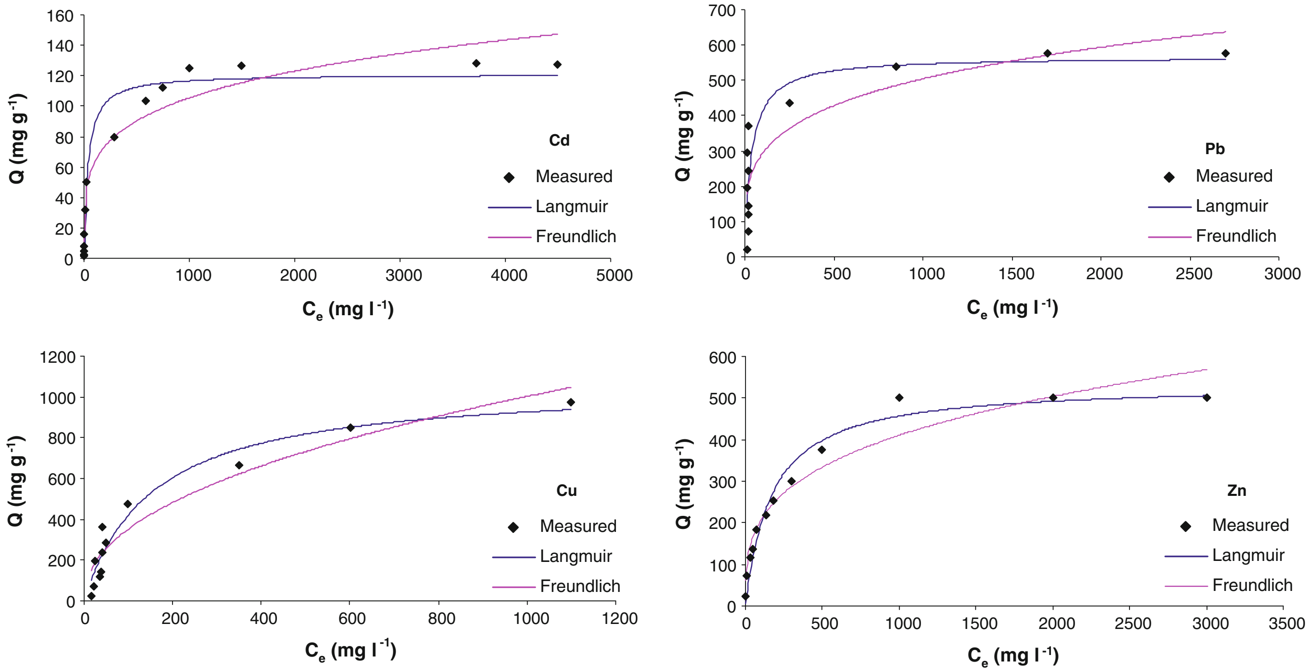

Fig. 2 Adsorption isotherm of Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} and fitted models

irrespective of mechanism, adsorption or precipitation (Sposito 1984). Both mechanisms involve characteristic reactions of some metals with $CaCO_3$ surfaces, with adsorption occurring at low concentration of metals solution, and precipitation dominating at high concentrations (Sposito 1984; McBride 1980). As the XRD analysis showed that the adsorbent material used in this study was calcite, these mechanisms are expected to occur.

In order to investigate the sorption isotherm, two equilibrium models were analyzed: Langmuir and Freundlich isotherm equations. Correlation coefficients (R^2) and standard error along with sorption constants for the fitted models are presented in Table 2.

Cadmium, Cu^{2+}, Pb^{2+}, and Zn^{2+} sorption on sludge followed good trend in two models with high correlation coefficient ($R^2 > 0.97$). The higher correlation coefficient indicates that there is a strong positive relationship for the data, and that all experimental sorption data are well fitted to the Langmuir model. Consequently, it can be concluded that these ions adsorbed by the sludge are adsorbed either in a monolayer or as a one-directional process (Jang et al. 2005).

The Freundlich model was also well fitted to the experimental data (Table 2). The Freundlich distribution coefficient (K_F) and constant (n) may be taken as measures of the extent of adsorption and the energy of adsorption, respectively. The K_F for Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} is 22.6, 43.5, 99, and 52.8 l kg^{-1}, respectively (Table 2).

Cadmium, Cu^{2+}, Pb^{2+}, and Zn^{2+} sorption capacity of sorbent is considered to affect the partitioning of Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} between solution and the sorbent. Maximum sorption of Cu^{2+} (Q), and bonding energy constant (b) of Cd^{2+} and Pb^{2+} obtained from the Langmuir equation, was higher than others.

Table 2 Parameters of adsorption models used to describe adsorption of Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} in waste calcite sludge

Models	Cd^{2+}	Cu^{2+}	Pb^{2+}	Zn^{2+}
Freundlich				
K_F (l g^{-1})	22.6	43.5	99.0	52.8
N	4.50	2.20	4.20	3.40
R^2	0.96	0.96	0.88	0.96
SE	0.11	1.43	0.47	0.63
Langmuir				
Q (mg g^{-1})	121.2	1067.8	566.4	534.2
b (l mg^{-1})	0.02	0.0059	0.02	0.0065
R^2	0.98	0.97	0.90	0.97
SE	0.20	0.75	0.50	0.32

Effect of pH

The pH of the aqueous solution is an important monitoring parameter in the process of adsorption and thus the effect of pH has been studied by varying the same in the range of 2–12 for Cd^{2+} and Zn^{2+}, and in the range of 2–8 for Pb^{2+} and Cu^{2+} (Fig. 3). Such study helps in designing the appropriate pH of the effluent/wastewater for achieving maximum efficiency in the removal of metal ions by an

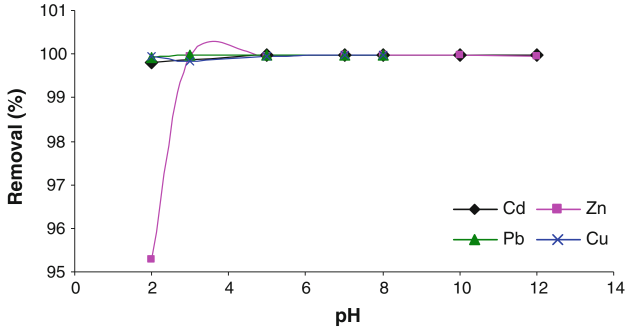

Fig. 3 Effect of pH on the adsorption of Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} onto waste calcite sludge as adsorbent

adsorbent. The optimum pH value for adsorption of Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} by the selected adsorbents was found to be pH ≥ 3. For waste calcite sludge percentage removal efficiency was observed to be 99.8, 99.8, 99.9, and 99.9% for Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} adsorption, respectively, at optimum pH values.

The pH of the aqueous solution was clearly an important parameter that controlled the adsorption process (Argun et al. 2007).

Waste calcite sludge is alkaline in nature, the pH of 50 ml water + 10 g sludge was 9.39 (Table 1). Because of alkalinity of adsorbent, equilibrium pH tend to be alkaline (in our experiment it was observed that initial acidic pH reached to pH higher than 8.5). Then as we expected, removal efficiency of metal ions in these equilibrium solutions were higher than the other reports. Solubility of Cd^{2+}, Pb^{2+}, and Zn^{2+} is reduced as the pH becomes more alkaline (Gupta and Torres 1998).

Speciation of heavy metal ions

The speciation of total Cd, Cu, Pb, and Zn in different forms is necessary for the understanding of Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} exchange mechanisms by sorbent and their potential removed from aqueous solutions. The speciation-solubility geochemical Visual MINTEQ version 2.30 (Allison et al. 1991) model was used to determine the equilibrium concentrations of metal species in the solution as a function of pH, and for calculation the degree of saturation with respect to the mineral phases. In addition to the measurement of Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+}, pH of the solutions was also measured. The distribution of the Cd, Cu, Pb, and Zn chemical species in the aqueous solutions is presented in Fig. 4. In this Figure, the curves are made up of species concentration corresponding to various pH ranges.

Cd: the dissolution/precipitation modeling result showed that Cd^{2+} was the main form of Cd in the solution at acid, neutral, and basic condition Cadmium was not oversaturated with respect to any minerals in this simulation in acid and neutral conditions, but in basic condition the solution

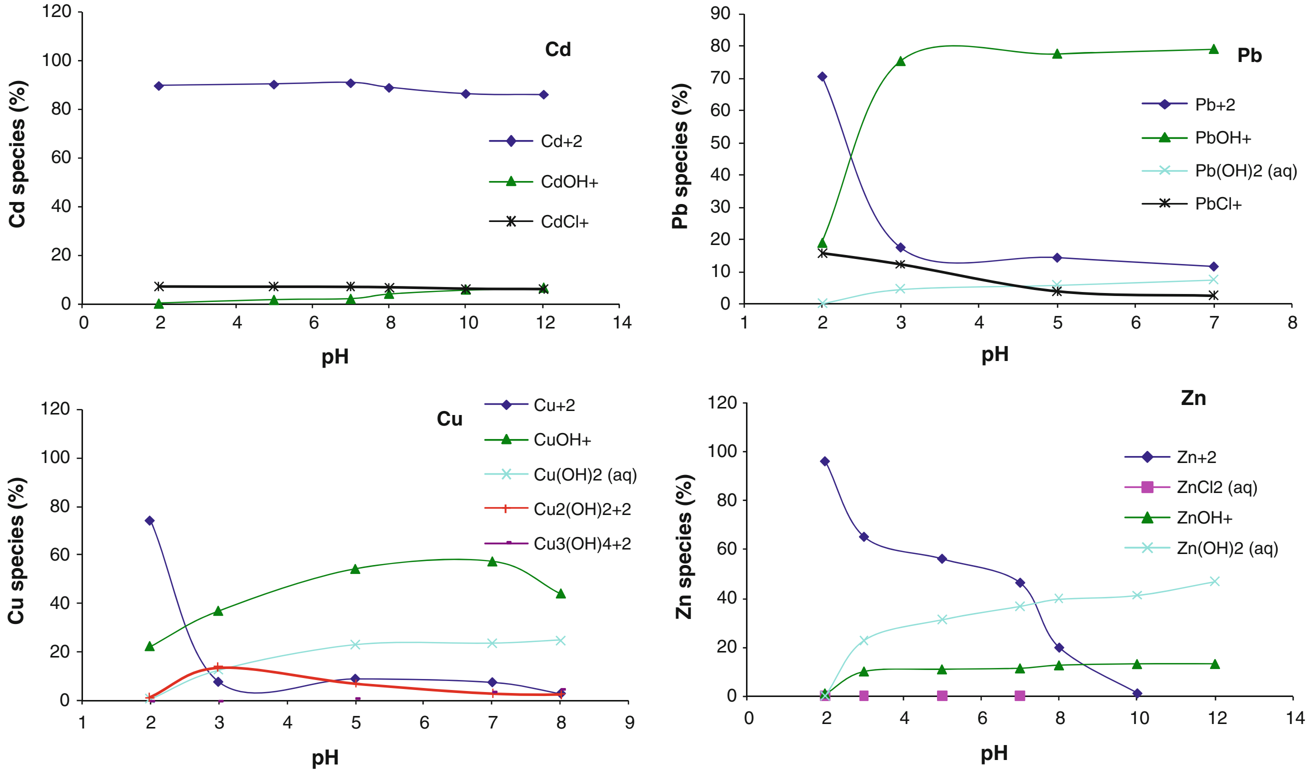

Fig. 4 The effect of pH on Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} species (species frequency greater than 1%) in aqueous solution

was oversaturated with respect of hydroxyapatite. Against of our results, Zhang et al. (2008b) showed that Cd precipitated mainly as the form of $Cd(OH)_2$ at high alkaline pH.

Cu: According to the speciation diagram for pH, the predominant species at pH 2, was Cu^{2+}, and between 5 and 8, was $CuOH^{+}$. In the pH range 3–5, the precipitation/dissolution modeling results indicated that Cu precipitated mainly as hydroxyapatite and tenorite (c). These results are similar to simulation indicates that at pH values between 6 and 7, Cu precipitates as copper hydroxide (Komnitsas et al. 2004). These results were supported by other researchers that observed CuO as precipitated mineral in pH rang of 5–7 (Zhang et al. 2008a).

Pb: the results of simulation indicate that, Pb^{+2} was the predominant form of Pb in strong acid condition (pH 2) and hydroxide species such as $PbOH^{+}$ was the main form of Pb in acid and natural condition (pH 3–7). Under strong alkaline conditions, Pb combined with OH^{-} and the species of $Pb(OH)_3^{-}$ was formed (Pierrard et al. 2002, Zhang et al. 2008a). Lead was oversaturated with respect to $Pb(OH)_2$ in pH ranges of 7–9 and this mineral was precipitated in this situation with saturation index, +1.505. Therefore, Pb existed mainly as $Pb(OH)_2$ at basic condition (pH 8–13), meanwhile, $Pb(OH)_2$ can be dissolved and the concentration of Pb^{2+} increased at pH 14 (Zhang et al. 2008b). Furthermore, Pierrard et al. (2002) reported the low Pb solubility in pH range of 8–9 due to the major formation of $Pb(OH)_2$.

Zn: the results of simulation are in concordance with the experiment analysis without considering surface complexation in model. So, it can be concluded that behavior of Zn is determined by dissolution/precipitation mechanism. Zinc element existed in the solution predominantly (>50%) as the forms of Zn^{2+} on acid condition (pH 2–5); and it existed in the solution mainly as the forms of $Zn(OH)_2(aq)$, at basic condition (pH 8–12); the percentage of $Zn(OH)_2$ decreased after pH 10, and it may be due to ZnO precipitation ($SI = +0.026$) in high alkaline pH. Previous studies indicate that Zn may precipitate as hydroxide at neutral pH values (Blowes and Jambor 1990) or as ZnO in pH range between 6 and 14 (Van Herck et al. 2000). Other results indicate that Zn precipitate mainly as $ZnCO_3$ in the pH ranges 5–8 and as ZnO for pH values above 8 (Zhang et al. 2008a).

The removal efficiencies for Cu^{2+}, Zn^{2+}, and Cd^{2+} can also be specified depending on the range of $pH_{initial}$ values (Kwon et al. 2010). An increase in removal of heavy metals in the higher pH ranges seems to be due to precipitation as hydroxides (Kwon et al. 2010).

The pH may affect the ionization degree of the sorbate and the surface property of the sorbent (Lin and Yang 2002). Chemically, the solution pH influences metal speciation. For instance, heavy metal ions may form complexes with inorganic ligands such as OH^{-}.

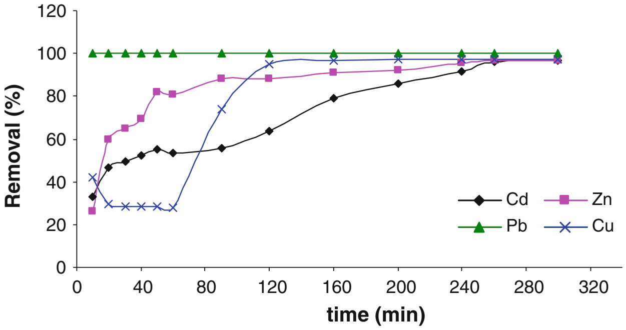

Fig. 5 Effect of contact time on the adsorption of Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} onto waste calcite sludge as adsorbent

The extent of the complex formation varies with pH, the ionic composition, and the particular metal concerned. The exact speciation of a metal has a significant impact on the removal efficiency of the adsorbent (Ouki and Kavannagh 1997). The selectivity of metal ion by calcite is also influenced by the character of the metal complex that predominates at a particular solution pH.

Effect of contact time

The experimental runs measuring the effect of contact time on the batch adsorption of initial metal ion concentration of 500 mg l^{-1} Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} using the optimum pH value is shown in Fig. 5. The removal of Cd^{2+}, Cu^{2+}, and Zn^{2+} ions increases with time and attains saturation in about 240, 120, and 120 min, respectively. The removal of Pb^{2+} ion showed no difference in uptake amount onto adsorbent with stirring time, and it shows 100% uptake from initial time of shaking.

Basically, the removal of sorbate is rapid, but it gradually decreases with time until it reaches equilibrium. Figure 5 represents the percent removal of Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} ions versus the contact time for the initial concentration and by using the optimum pH value which was obtained for the four heavy metals. Zinc showed fast rate of sorption during the first 40 min of the sorbate–sorbent contact and the rate of percent removal becomes almost insignificant due to a quick exhaustion of the adsorption sites. The rate of percent metal removal is higher in the beginning due to a larger surface area of the adsorbent being available for the adsorption of the metals. The two-stage sorption mechanism with the first rapid and quantitatively predominant and the second slower and quantitatively insignificant, has been extensively reported in literature (Saeed et al. 2005).

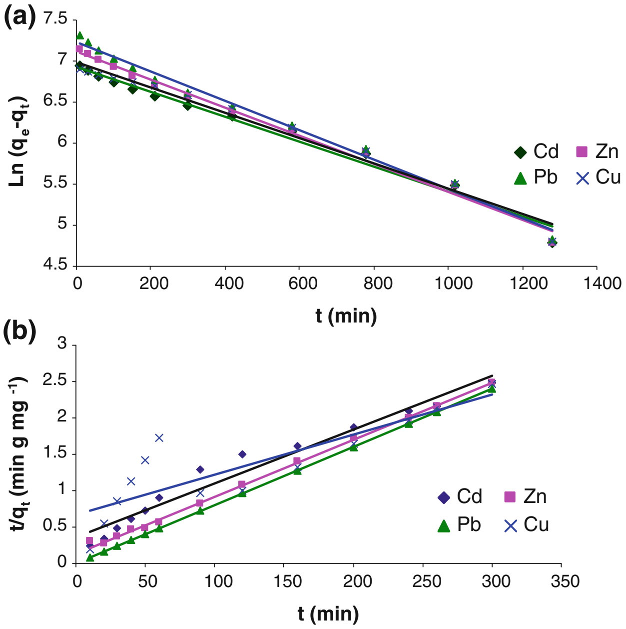

Fig. 6 Pseudo-first-order (**a**) and pseudo-second-order (**b**) sorption kinetics of Cd^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+}

The fit between the pseudo-first- and pseudo-second-order model and experimental data is shown in Fig. 6. The calculated value of q_e (Table 3) from the pseudo-second-order kinetics model was dramatically lower than the experimental value. However, the linearized pseudo-first-order kinetics model (Fig. 6; Table 3), provided much better R^2 values (all values greater than or equal to 0.97) than those for the second-order model, even though the calculated values did not closely approximate the measured experimental values. As a result, the sorption system appears to follow pseudo-first-order reaction kinetics. The pseudo-first-order kinetics rate constants for the adsorption of Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} ions on waste calcite sludge were 0.001 min^{-1}.

Successful presentation of the pseudo-second-order model for heavy metals sorption has been reported by Madhava Rao et al. (2008), Xiao and Howard Huang (2009). A linear fit to the pseudo-second-order model indicates that in the process of adsorption, concentration of all sorbate (Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+}) and sorbent (sludge) are involved in rate determining step (Madhava Rao et al. 2008), which may be considered to be a chemical sorption or chemisorption (Ho and McKay 1998).

A study on metals adsorption by exchange resins concluded that pseudo-second-order reaction kinetic has provided a realistic description for removal of Zn^{2+} with closer experimental and calculated values of q_e. Also, correlation coefficients are higher in pseudo-second-order kinetics than the pseudo-first-order (Alyüz and Veli 2009). The other researchers, was observed that the pseudo-first-order model fitted well for Cu^{2+} and Zn^{2+} ions in the tested sorption with zeolite (Hui et al. 2005). Furthermore, the result of the sorption system with sawdust, indicated that the kinetics data were best modeled by a pseudo-first-order kinetics equation for Cu^{2+}, Ni^{2+}, and Cr^{3+} ions (Argun et al. 2007).

Effect of initial metal ion concentration

The metal uptake mechanism is particularly dependent on the initial heavy metal concentration: at low concentrations, metals are adsorbed by specific sites, while with increasing metal concentrations the specific sites are saturated and the exchange sites are filled (Lehman and Harter 1984). Figure 7 shows the effect of metal concentration on

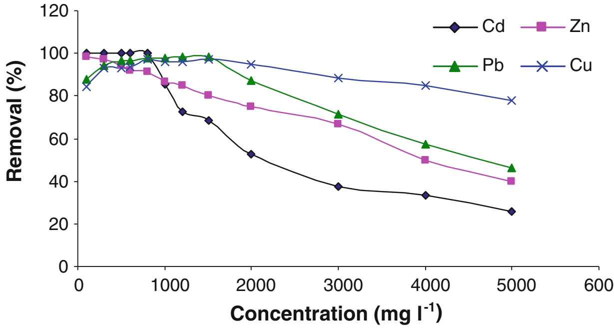

Fig. 7 Effect of initial concentration on the adsorption of Cd^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+} onto waste calcite sludge as adsorbent (the weight of adsorbent: 2.5 g)

Table 3 Pseudo first and second-order adsorption rate constants for Cd^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+}

Metal	Pseudo-first-order			Pseudo-second-order		
	K_1 (min^{-1})	q_e ($mg\ g^{-1}$)	R^2	K_2 ($g\ mg^{-1}\ min^{-1}$)	q_e ($mg\ g^{-1}$)	R^2
Cd	0.001	1025	0.98	1.55×10^{-4}	135	0.93
Cu	0.001	1080	0.97	4.57×10^{-5}	181	0.72
Pb	0.001	1352	0.98	–*	–	–
Zn	0.001	1227	0.99	4.38×10^{-4}	128	0.96

* The data did not fit

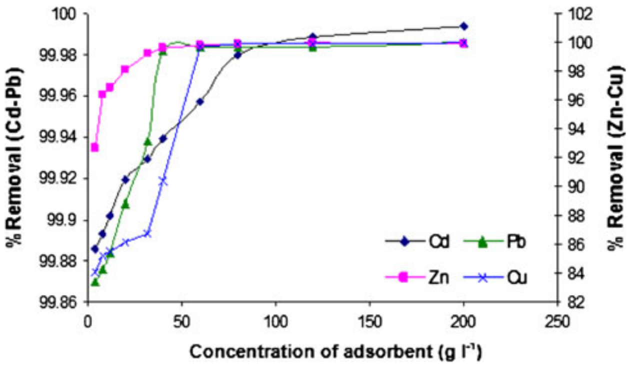

Fig. 8 Effect of adsorbent concentration on the adsorption of Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} onto waste calcite sludge as adsorbent

Table 4 Adsorption capacity of waste calcite sludge at different adsorbent doses

Adsorbent dose (g l^{-1})	Cd^{2+} (mg g^{-1})	Cu^{2+} (mg g^{-1})	Pb^{2+} (mg g^{-1})	Zn^{2+} (mg g^{-1})
4	124.8	105.1	124.8	115.8
8	62.4	53.3	62.4	60.2
12	41.6	35.6	41.6	40.3
20	24.8	21.5	24.9	24.5
32	15.6	13.5	15.6	15.5
40	12.5	11.3	12.5	12.4
60	8.3	8.3	8.3	8.3
80	6.2	6.2	6.3	6.2
120	4.1	4.1	4.1	4.1
200	2.4	2.5	2.5	2.4

the percent removal of Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} ions. It is clear that with increasing initial concentrations, the percent metal removal decreases.

Effect of adsorbent concentrations

One of the parameters that strongly affect the sorption capacity is the concentration of the adsorbents. The removal of Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} was studied by varying the adsorbent dose (0.1, 0.2, 0.3, 0.5, 0.8, 1.0, 1.5, 2.0, 3.0, and 5.0 g 25 ml^{-1}) in Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} ions aqueous system while keeping initial metal concentration (500 mg l^{-1}), and pH (5.5) constant at predetermined contact times. With the fixed metal concentration, it can easily be inferred that the percent removal of metal ions increases with increasing weight of the adsorbents as shown from Fig. 8. This is due to the greater availability of the exchangeable sites or surface area at higher concentration of the adsorbent. This can be explained due to the fact that higher the dose of adsorbent in the solution, greater the availability of exchangeable sites for metal ions and greater the surface area (Garg et al. 2004). But adsorption capacity decreased with increase in adsorbent dosage (Table 4). This may be due to overlapping of adsorption sites as a result of over-crowding of adsorbent particles (Namasivayam and Kumuthu 1998).

Comparison of adsorption capacity for ion metals removal with different adsorbents reported in literature

The adsorption capacities of the adsorbents for the removal of Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} have been compared with those of other adsorbents reported in literature. A list showing the adsorption capacity of different adsorbents for the adsorption of Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} from aqueous solutions is given in Table 5. As it can be seen, the observed adsorption capacity of waste calcite sludge for Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} are comparable with other low-cost adsorbents.

Conclusion

This study shows that sludge residues are an effective adsorbent for the removal of Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} ions from aqueous solutions. The adsorption process is a function of the adsorbent and adsorbate concentrations, pH, and time of

Table 5 Comparison of adsorption capacity of various adsorbents for heavy metals

Metals	Sorbent	Adsorption capacity (mg g^{-1})	Ref.
Zn^{2+}	Calcined phosphate	23.7	Aklil et al. (2004)
Cu^{2+}, Zn^{2+}	Commercial Zeolite 4A	53.4, 31.5	Hui et al. (2005)
Cd^{2+}, Zn^{2+}	Zeolite A	78.6, 152.6	El-Kamash et al. (2005)
Cd^{2+}, Cu^{2+}, Pb^{2+}	Clinoptilolite	4.8, 22.7, 26.8	Sprynskyy et al. (2006)
Cu^{2+}	Activated poplar sawdust	9.2	Acar and Eren, (2006)
Cd^{2+}	Palygorskite, sepiolite, calcite	9.7, 46.1, 2.3	Shirvani et al. (2005)
Cu^{2+}	Spent-activated clay	10.9	Weng et al. (2007)
Ni^{2+}, Zn^{2+}	Ion exchange resins	156.2, 222.2	Alyüz and Veli (2009)
Cd^{2+},Cu^{2+},Pb^{2+},Zn^{2+}	Waste calcite sludge	121.2, 1067.8, 566.4, 534.2	This study

agitation. The effective pH for the Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} removal was 3. Equilibrium was achieved practically in 120 min. The equilibrium sorption data are satisfactorily fitted to the Langmuir and Freundlich models. The results would be useful for the design of wastewater treatment plants for the removal of Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+}.

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