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Evaluation of soils for attenuation and retention of Zn(II) ions from aqueous solution

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ABSTRACT

To decrease environmental hazards of mining activities, it is significant to find eco-friendly and efficient methods of using contaminated soils. One way to reduce environmental risks of mining is to use contaminated soil as an adsorbent in environmental decontamination. This study describes the efficiency of contaminated soil as efficient adsorbent for attenuation of Zn(II) ions from aqueous solution. Soil phases play a significant role in controlling heavy metal mobility in soils. Therefore, the understanding of sorption mechanisms in soil is essential in resolving pollution problems. The ability of two different contaminated soil samples from Sarcheshmeh copper mine to retain Zn(II) ions was evaluated. The objectives of this study were to: (1) investigate isotherm and kinetic models and the dominant sorption mechanism; (2) determine Zn retention in contaminated soil; (3) evaluate the influence of various contaminated soil fractions on Zn sorption by batch method and bioavailability of Zn(II) ions and (4) use scanning electron microscopy and fourier transform infrared spectroscopy to monitor sorption process. The results indicated that chemical process and ion exchange were dominant in sorption process. Retention of Zn(II) ions in contaminated soil decreases with reduction of pH during the time. Moreover, carbonate fraction had significant role in Zn attenuation in contaminated soil. Dispersion of Zn(II) on surface of contaminated soil particles increases after sorption in comparison with that for before sorption.

Keywords: Soil; Sorption mechanism; Retention; Bioavailability; Zn(II) ions

1. Introduction

Increasing content of heavy metals in industries and mining has caused considerable concern regarding their impact on water contamination. There is a large amount of wastewaters containing zinc in mining and industries such as galvanization, fertilizers and pesticides, pigment, polymer stabilizers, etc. [1–3]. Zinc is indispensable for human, animal and plant life, but it can be potentially toxic in high values [4,5]. According to World Health Organization (WHO), the permissible limit of Zn(II) in drinking water reported is 4 mg/L [6].

Sorption is one of the most effective processes for heavy metals removal, particularly by using natural adsorbents, because of the lower costs, easy handling and their abundance in surrounding environment. The soil was chosen as natural adsorbent because it can be a combination of different phases that can play significant role in decreasing, and immobilization of heavy metals. Moreover, the usage of contaminated soil as natural adsorbents can decrease environmental risks of these soils in mining sites. The natural attenuation capacity of heavy metals in soils is considerable and mitigates environmental issues. The key process for attenuation of heavy metals is sorption, and this is a criterion on how metals are transferred from the liquid phase toward the surface of a solid phase [7,8]. The sorption ability of soils is related to soil properties such as pH and the presence of sorption sites in

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various soil phases such as clay minerals, carbonates, organic matter, and Fe and Al (hydr)oxides [9–12].

The analysis of isotherms can help us to investigate the capability of soil sorption. However, this information from sorption isotherms is not enough because the interactions between heavy metals and soil are not clear and the actual portion of metals in various components of soil cannot be easily identified [13]. Thus, sequential extraction is a procedure that can be used along with sorption isotherms to better understand the interaction between heavy metals and soil components. Sequential extraction procedures are broadly applied to investigate heavy metals contribution in different soil components [14–16]. This technique obtains metals sorbed in various soil fractions during sorption process and is essential to clarify bioavailability of heavy metal from soil. The distribution coefficient (K_d) indicates distribution of metals between soil and solution at equilibrium. K_d is a useful parameter in investigation for the sorption and retention capability of different soils [17,18].

One of the largest copper mines in the world is Sarcheshmeh copper deposit. In fact, this area is home of various industrial activities and mining sites that has caused serious environmental issues due to heavy metals [19]. A high concentration of Zn has been observed in the wastewater effluent from this mining site. Therefore, this study is fully concentrated on Zn sorption by soil at Sarcheshmeh copper mine. These kinds of studies are extremely essential in mining and industrial sites to estimate efficiency of soil for heavy metals attenuation and bioavailability. Previous studies provide insufficient information regarding Zn sorption process by soil. Thus, this study is intended to provide a better understanding of the interactions between the metals and various components of soil by applying the sequential extraction procedure. In addition, relatively few studies have dealt with sorption reactions involving Zn ions and different phases of soils from mining site, and also no researches have been looking into Zn retention and investigation of Zn bioavailability in the soils of this area.

In this study, the sorption process of Zn(II) ions onto soil using different sorption isotherm and kinetic models was investigated. The capability of contaminated soils in the retention of Zn ions was studied with time for various pH values. In addition, the effect of various components of soils was investigated. Sorption process was evaluated by scanning electron microscopy (SEM) and wavelength-dispersive X-ray (WDX) analysis. The functional groups present in the soil that might have any contribution in the sorption process were identified by fourier transform infrared spectroscopy (FTIR).

2. Materials and methods

2.1. Soil characterization and analysis

The two soil samples were collected from Sarcheshmeh copper mine, 160 km southwest of Kerman (Fig. 1). These soil samples were packed and transported to the laboratory. All samples were air-dried and sieved through 2 mm mesh and were homogenized before soil characterization and sorption studies. All sorption experiments were repeated two times. For determination of particle size distribution, organic matter was oxidized with hydrogen peroxide, and then the fractions larger than 50 μm were separated by sieving and smaller fractions by the international procedure [20]. Soil pH was measured in a 1:1 (w/v) soil/water mixture [21]. The method of Hendershot and Duquette was used to determine the cation-exchange capacity (CEC) [22]. This method measures the effective CEC by determining calcium, magnesium, potassium and aluminium concentrations in a mixture prepared by the reaction of 2 g of soil with a 1 M NH_4Cl solution. Oxide contents were determined by the dithionite-citrate method [23]. Samples were shaken with a solution of sodium hydrosulfite and sodium citrate, and Fe, Al and Mn contents of the extract were determined by inductively coupled plasma optical emission spectrometry (ICP-OES). Carbonate content was determined by volumetric calcimeter according to Allison and Moodie [24]. The procedure of Walkley and Black [25] was used to determine the organic carbon content in soil. Specific surface area (SSA) was identified using the BET method by nitrogen

Fig. 1. Sarcheshmeh area, mine pit, Sarcheshmeh copper industries and showing soil sampling locations.

(N_2) as the sorbate by Quantachrome NOVA 1000 [26]. The soil characteristics are summarized in Table 1. The concentrations of metals in soils were analyzed by ICP-OES that heavy metal contamination in these soils was observed (Table 2). Mineralogical properties of the clay minerals in S1 and S2 were investigated using the X-ray diffraction (XRD) and are shown in Fig. 2. The most important minerals of S1 soil that are recognized by XRD are quartz, muscovite, montmorillonite, albite and illite. The major peaks of S2 are related to quartz, hematite, albite, illite, clinochlore and muscovite.

2.2. Sorption studies

The relation between the amounts of adsorbate removed from solution at equilibrium by unit of adsorbent mass at constant temperature is explained by the equilibrium isotherm. The Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D–R) isotherms were investigated in the current study. The Langmuir isotherm is applied to illustrate monolayer sorption onto a homogenous surface containing a limited number of identical sites [27–29]. This model assumes uniform energies of sorption onto the surface of adsorbent [30]. The Freundlich isotherm expresses multilayer sorption onto a heterogeneous surface with an irregular distribution of energies of sorption over the surface [31]. Values K_F and $1/n$ are Freundlich constants that are related to capacity and intensity of sorption, respectively. The Temkin model assumes that heat of sorption of all molecules in the layer decreases linearly with coverage [32]. D–R isotherm is commonly used to express sorption mechanism with a Gaussian energy distribution onto a heterogeneous surface [33]. D (mol²/kJ²) is a constant associated with sorption energy, and E (kJ/mol) is sorption energy. If $E > 8$ kJ/mol, physical sorption dominates; chemical sorption or ion exchange is most significant if the sorption energy is between 8 and 16 kJ/mol; and for $E > 16$ kJ/mol, particle diffusion reaction is dominant. This model is applied to distinguish the physical and chemical sorption of metal ions with sorption. Linear expression of these isotherm equations and the way to obtain the isotherm parameters are listed in Table 3.

Table 1
Characteristics of soils

Soil	S1	S2
OC, %	0.33	0.29
pH	8.03	7.04
CEC, meq/100 g	4.21	6.38
Fe_2O_3, %	1.7	2.8
MnO, %	0.11	0.12
Al_2O_3, %	4.5	4.4
$CaCO_3$, %	0.5	0.26
Clay, %	16	18
Silt, %	38	26
Sand, %	46	56
SSA, m²/g	17.06	20.30

Table 2
Metal concentrations in the soils

	S1	S2
As, ppm	97.3	107.8
Ba, ppm	638	575
Ca, ppm	9,373	14,656
Cd, ppm	0.9	2.3
Ce, ppm	53	41
Co, ppm	15	30
Cr, ppm	32	45
Cu, ppm	270	1,325
Fe, ppm	34,613	57,781
K, ppm	24,435	23,782
Mg, ppm	7,151	12,164
Mn, ppm	1,107	1,271
Mo, ppm	6.5	23.4
Na, ppm	23,354	20,129
Ni, ppm	26	60
P, ppm	810	1,163
Pb, ppm	71	77
S, ppm	612	1,272
Zn, ppm	144	178

500 mL of experimental solutions were placed in 2.5 L glass bottles containing initial Zn(II) ions concentration 10, 20, 30, 60 and 80 mg/L, and the pH was adjusted, as well. Then, 5 g soil samples were added to 500 mL aqueous solution of Zn(II) ions. The bottles were placed on the bottle roll at a constant rotation of 100 rpm for 24 h to reach the equilibrium. Samples were taken at various pre-determined time

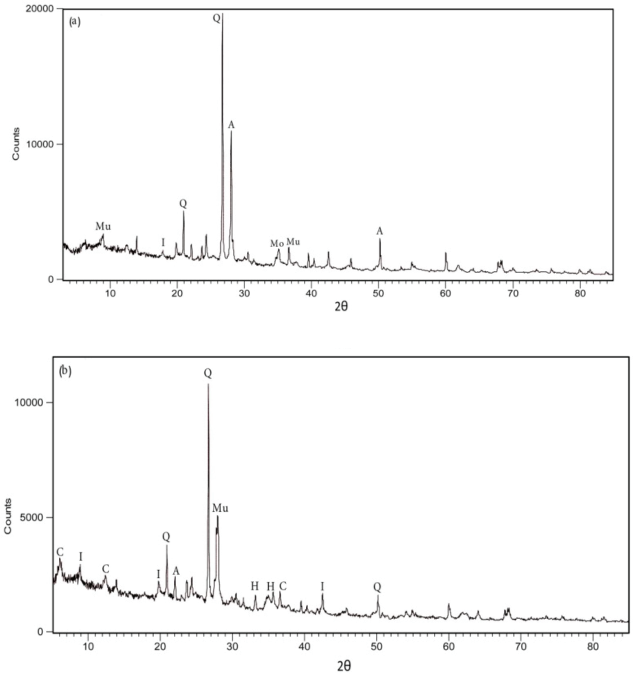

Fig. 2. X-ray diffraction patterns of (a) S1 sample and (b) S2 sample: Q: quartz, A: albite, C: clinochlore, H: hematite, I: illite, Mo: montmorillonite, and Mu: muscovite.

Table 3
Isotherms and their linearized expressions

Isotherms	Equations	Linear expression	Plot	Parameters	Ref.
Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	$C_e / q_e = (1/K_L q_m) + (C_e / q_m)$	C_e / q_e vs. C_e	$q_m =$ (slope)$^{-1}$, K_L = slope/intercept	[34,35]
Freundlich	$q_e = K_F C_e^{1/n}$	$\ln q_e = \ln K_F + (1/n) \ln C_e$	$\ln q_e$ vs. $\ln C_e$	$K_F = \exp(\text{intercept})$, $n = (\text{slope})^{-1}$	[36,37]
Temkin	$q_e = q_m \ln(K_T C_e)$	$q_e = q_m \ln K_T + q_m \ln C_e$	q_e vs. $\ln C_e$	$K_F = \exp(\text{intercept/slope})$, q_m = slope	[38]
Dubinin–Radushkevich	$q_e = q_m \exp(-D\varepsilon^2)$ $\varepsilon = RT \ln(1 + C_e^{-1})$	$\ln q_e = \ln q_m - D\varepsilon^2$	$\ln q_e$ vs. ε^2	$q_m = \exp(\text{intercept})$ $D = -$slope	

Note: R – gas constant (8.314 J/mol K), T – the absolute temperature (K), C_e – adsorbate equilibrium concentration (mg/L) and q_m – the maximum capacity of adsorption (mg/g).

intervals. The concentration of Zn(II) ions was analyzed by atomic absorption spectrophotometer (AAS). The concentration of Zn(II) ions retained on the soil is considered according to Eq. (1):

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

where C_0 and C_e are the initial and equilibrium concentrations (mg/L) of ions in solution, respectively. V and W represent volume of the solution (L) and mass of the sorbent (g), respectively.

For each soil sample, sorption capacities of Zn(II) ions were compared by using the estimated distribution coefficients (K_d). Sorption data were collected, and then K_d for the Zn(II) ions in each soil sample at equilibrium was calculated [39] using the following expression:

$$K_d = \frac{\text{concentration of metal sorbed (mg/L)}}{\text{concentration of metal in solution (mg/L)}} \tag{2}$$

5 g of soil obtained in sorption stage was dried and used for retention experiments in various pH. Retention experiments were carried out in 500 mL of distilled water with pH 2, 3 and 4 in 2.5 L glass bottles during the time.

2.3. Kinetic studies

Batch kinetic experiments were conducted under similar conditions as in previous section for equilibrium experiments. 5 g of soil samples was added to 500 mL aqueous solutions of Zn(II) ions in 2.5 L glass bottles at ambient temperature. Initial Zn(II) ions concentration was 30 mg/L, and pH 4 was adjusted. The system was rolled at 100 rpm by bottle roll apparatus. Samples were taken at regular time intervals, and the Zn(II) ions concentration was analyzed using AAS. The amount of Zn(II) ions adsorbed by soil at time t, q_t (mg/g), was calculated by:

$$q_t = \frac{(C_0 - C_t)V}{W} \tag{3}$$

where C_0 and C_t (mg/L) are initial concentration and concentration at time t of Zn(II) ions, respectively.

2.4. Validity of isotherm and kinetic models

Average relative error (ARE) is applied to validate sorption isotherms and kinetic models. ARE was calculated between experimental and calculated data as follows [40]:

$$\text{ARE} = \frac{100}{N} \sum_{i=1}^{N} \left| \frac{q_e^{\text{exp}} - q_e^{\text{cal}}}{q_e^{\text{exp}}} \right|_i \tag{4}$$

where q_e^{exp} and q_i^{cal} are experimental and calculated adsorbate concentration at equilibrium, respectively, and N is the number of experiments. Commonly, lower ARE besides high R^2 values can be a good criterion for indicating the best-fit model.

2.5. Sequential extraction

To determine mechanisms of sorption in soils, metals were added to a soil sample in sorption process. Sequential extraction was performed to evaluate the speciation of metals in soils before and after sorption. Sequential extraction of soil samples is based on the protocol of Tessier et al. [14,41]. The five soil components studied were exchangeable, carbonate, iron and manganese oxides, organic matter and residual phases.

After sorption process, the soil samples were filtered and were dried at the ambient temperature and homogenized afterward. The cone and quartering method was applied to choose 2 g of each soil sample, and then each sample elected was placed in a 50-mL polypropylene centrifuge tube. After reaction with the appropriate reagent in each step, the mixture was centrifuged to separate the supernatant and the residue. The supernatant was analyzed by AAS, whereas the residue was washed with deionized water and dried prior to the next step.

3. Results and discussion

3.1. Characterization of the soils

3.1.1. SEM characterization

The morphology of soil samples was obtained through SEM. WDX studies were carried out to evaluate the count of Zn(II) onto soil surface. Figs. 3(a) and (c) represent the surface morphology of S1 sample before and after sorption process, respectively. The distribution map and relative contribution of Zn(II) over the scanned area can be detected before sorption (Fig. 3(b)). It can be recognized that the S1 sample has a negligible Zn(II) content before sorption. The significant amounts of Zn(II) ions are observed over the scanned area after sorption in Fig. 3(d). The surface morphology of S2 sample is depicted before and after sorption in Figs. 4(a) and (c). The Zn(II) on surface of S2 sample is highly distributed after sorption compared with before sorption as it is shown in Figs. 4(b) and (d).

3.1.2. FTIR analysis

The FTIR analysis was conducted to study the functional groups on the surface of soils. Figs. 5(a) and (b) shows the FTIR spectra obtained for an S1 sample before and after Zn sorption. In Fig. 5(a), the bands at 3,695, 3,623 and 3,427 cm^{-1} are attributed to OH stretching vibration of the Si–OH groups and H–OH vibration of the water molecules sorbed on soils. Two bands at 2,922 and 2,840 cm^{-1} are corresponded to the C–H stretch of aliphatic structures. The band at 1,629 cm^{-1} is probably related to the C=O stretching vibration of carbonyl groups. The spectrum of S1 sample shows band at 1,027 cm^{-1} attributed to the Si–O stretching vibrations. The band at 903 cm^{-1} is pertained to an Al–O–H bending vibration. The peak at wavelength <800 cm^{-1} might be related to inorganic materials such as minerals. The bands at 536 and 470 cm^{-1} are associated with Si–O–Al and Si–O–Si bending vibrations, respectively. Changes in intensity and shift in position of the peaks are detected in Fig. 5(b) after Zn(II) sorption on S1 sample. The OH peak was shifted from 3,695 to 3,706 cm^{-1} and from 3,427 to 3,433 cm^{-1} when Zn(II) was adsorbed. The bands at 2,922 and 2,840 cm^{-1} were moved to 2,933 and 2,850 cm^{-1}, and their intensity decreased after sorption process. The C=O stretching peak also was changed from 1,629 to 1,635 cm^{-1}. The band at 903 cm^{-1} was reduced significantly after Zn(II) sorption. The Si–O–Al and Si–O–Si absorption peak was declined. The shifting and changes in intensify of peaks indicate that the involvement of these functional groups in the Zn(II) sorption process onto S1 sample. The FTIR spectra obtained for an S2 sample before and after Zn sorption are shown in Figs. 6(a) and (b). The bands of clay minerals can be represented by the SiO–H stretches at 3,693, 3,620 and 3,432 cm^{-1} (kaolin) and the Si–O–Si stretch at 1,029 cm^{-1}. There are two

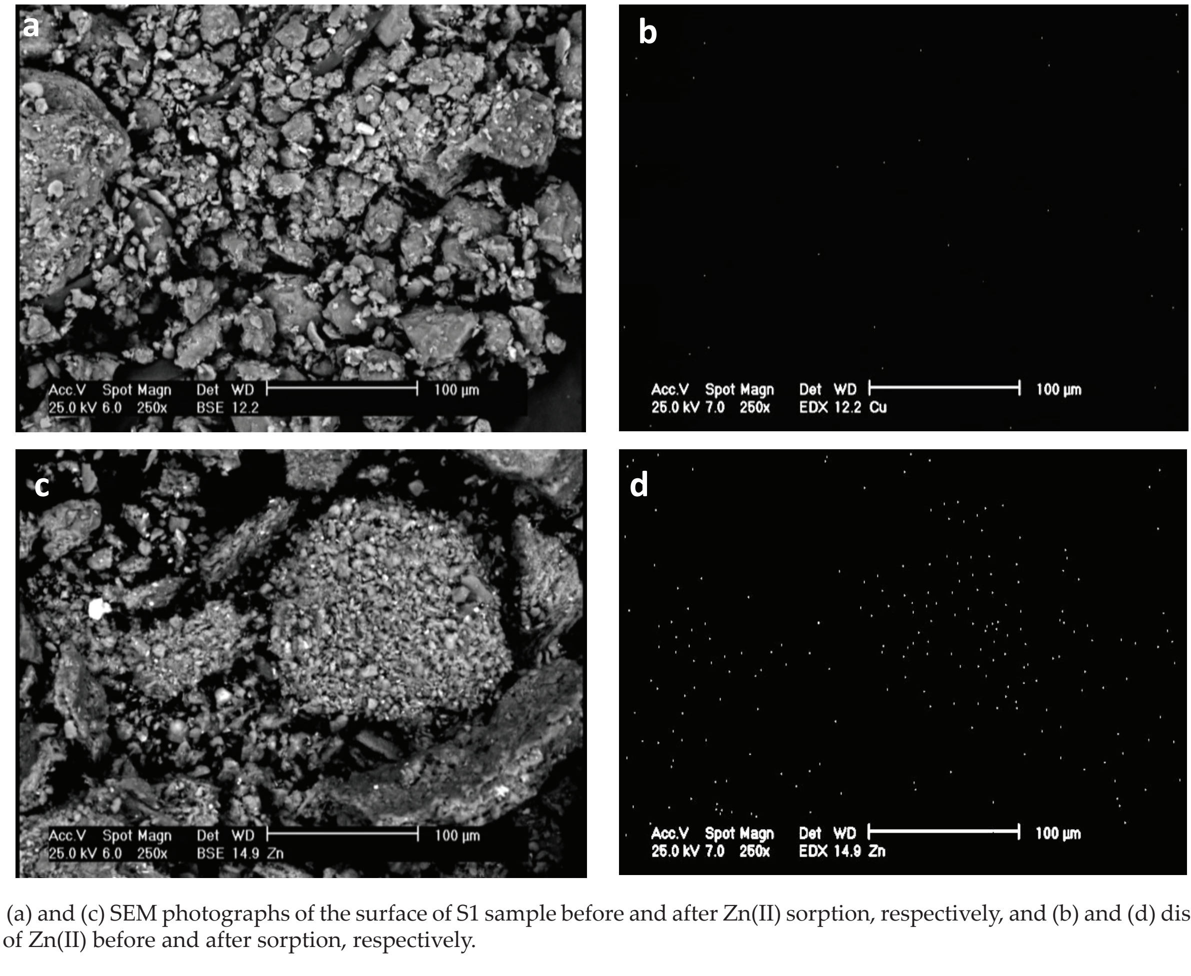

Fig. 3. (a) and (c) SEM photographs of the surface of S1 sample before and after Zn(II) sorption, respectively, and (b) and (d) dispersion maps of Zn(II) before and after sorption, respectively.

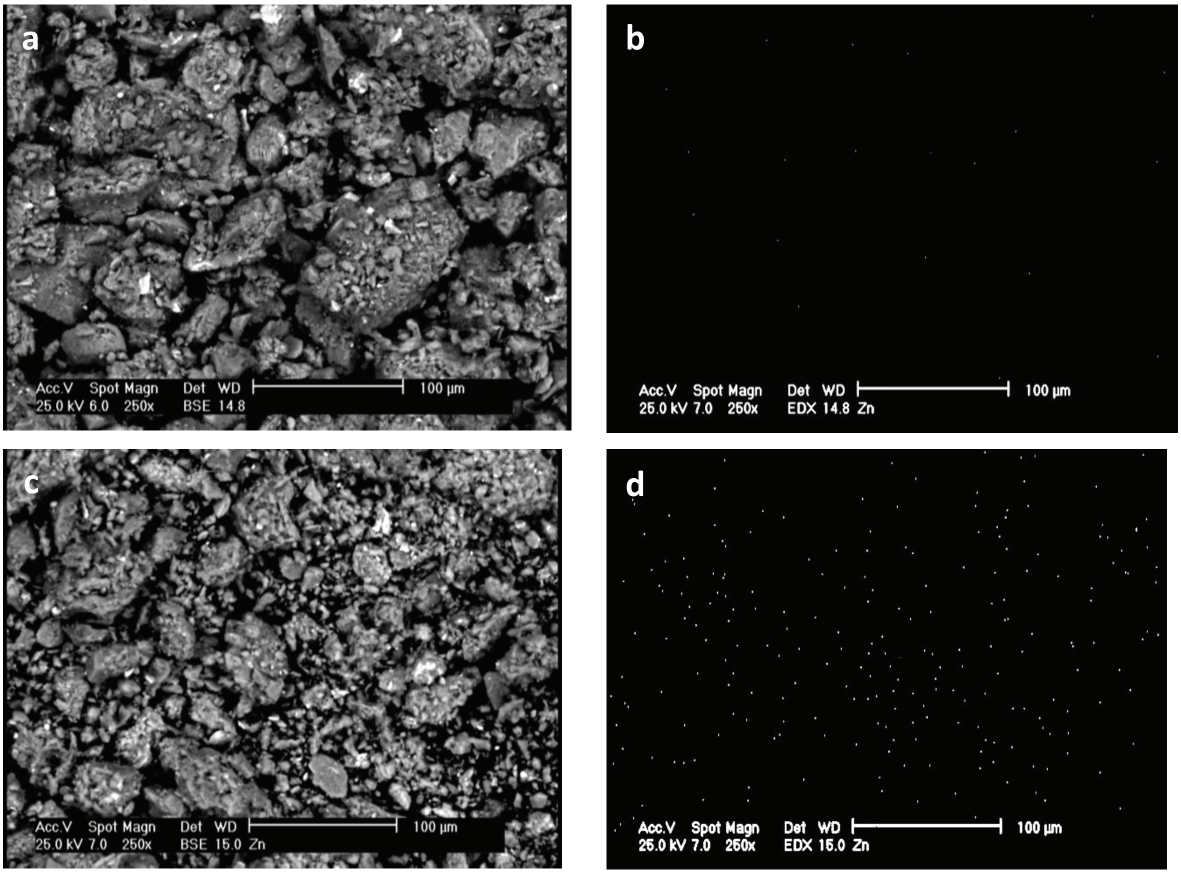

Fig. 4. (a) and (c) SEM photographs of the surface of S2 sample before and after Zn(II) sorption, respectively, and (b) and (d) distribution maps of Zn(II) before and after sorption, respectively.

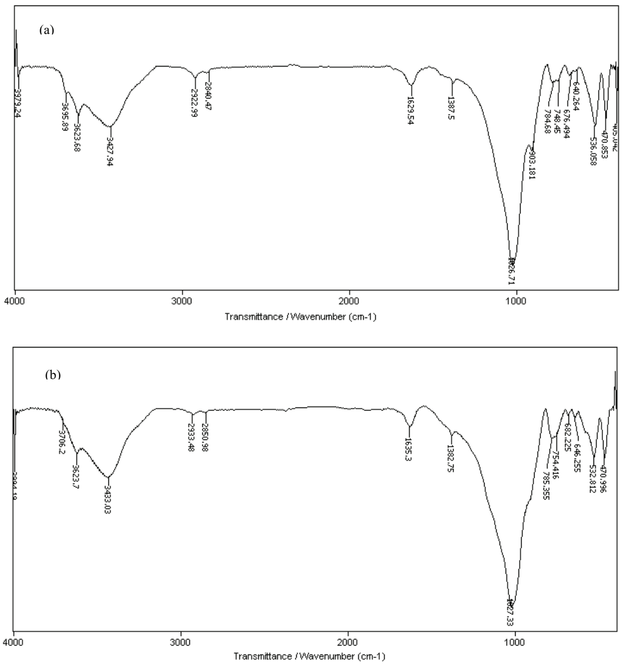

Fig. 5. FTIR spectra of S1 sample (a) before and (b) after Zn sorption.

bands at ~2,900 cm^{-1}, attributed to the C–H stretch of aliphatic structures. The majority of bands were moved relative to first position in S2 sample after sorption process. The changes in FTIR spectra after sorption confirm the complexation of Zn(II) with functional groups present in this soil sample.

3.2. Sorption study

The applicability of each isotherm to explain the sorption process was identified by the correlation coefficients (R^2 values). The values of parameters and correlation coefficients, and ARE were given in Table 4. In this case, sorption process was judged by high correlation coefficients values along with lower ARE. Langmuir isotherm model of the S1 and S2 soil samples were fitted better than the other isotherm models because of high correlation coefficient and low ARE. The maximum sorption capacities of soil determined from the Langmuir isotherms that it was 3.83 mg/g as shown in Table 4. Similar studies were investigated on various soil that the maximum sorption capacities were calculated. The maximum Zn sorption capacity in recent studies determined from 1.29 to 4.36 mmol/kg and 7.52 to 16.92 mmol/kg [42,43]. The results of maximum sorption capacities (23.7 mmol/kg) in comparison with recent studies showed that soil samples enjoy appropriate efficiency in sorption process. The correlation coefficients for linearized form of Freundlich and Temkin isotherms were high but ARE values were high, as well, and therefore, these isotherms cannot be good models for describing experimental data.

D–R isotherm shows high correlation coefficient and low ARE as shown in Table 4. This can be expressed that D–R model of the S1 and S2 samples was fitted well with experimental data. According to calculated sorption energy, chemical process and ion exchange were dominant in sorption process.

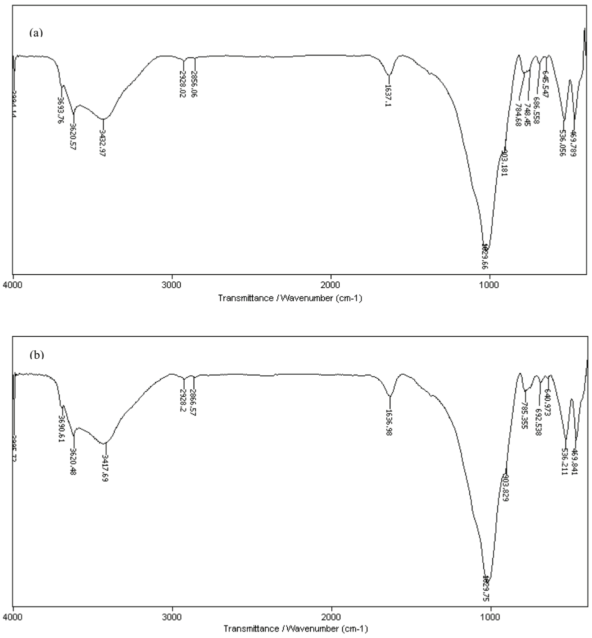

Fig. 6. FTIR spectra of S2 sample (a) before and (b) after Zn sorption.

Mobility of metals in soil can be evaluated by estimation of K_d values [44]. High values of K_d show that the ions tend to sorb onto the soil and low values indicate that an important proportion remains soluble. K_d was calculated at varying initial Zn(II) ions concentrations and is depicted in Fig. 7. The range of Zn(II) ions K_d values was 0.7–5 and 0.7–5.3, for S1 and S2 samples, respectively. S2 sample showed higher K_d values compared with S1 samples, and this indicates that S2 has higher potential for Zn(II) ions sorption than S1. With the increase of initial Zn(II) ions concentration from 10 to 80 mg/L, K_d values decreased for both S1 and S2. As a result, K_d was extremely dependent on the initial metal concentration. In addition, this proves that the sorption capacity of soil decreases in high concentrations of Zn(II) ions.

The retention of Zn(II) ions by S1 and S2 samples is illustrated in Figs. 8(a) and (b), respectively. The highest retention percentage was observed in pH 4 for both of soil samples. It shows that all of Zn(II) ions remain onto soil surface in this pH. The retention percentage of Zn(II) ions decreased with reduction in pH values. The retention percentages for S1 sample in pH values 2, 3 and 4 were 37%, 81% and 99%, and for S2 sample were 27%, 81% and 99%, respectively. Heavy metals can be easily desorbed on the surface of soil particles with a reduction in pH values when they are in cation-exchange phases [45]. This indicates that the bioavailability of Zn increases in this component of soil. Therefore, the majority of Zn ions desorbed in low pH might be associated with exchangeable fraction.

3.3. Kinetic study

The results demonstrate that the sorption rate is fast for the first 30 min of the process. The sorption kinetics of Zn(II) ions onto soil was examined with pseudo-first-order and

Table 4
Isotherms parameters, correlation coefficients value and ARE

Soils	S1	S2	S1	S2	S1	S2
Isotherms	R^2		ARE%		Parameters	
Langmuir	0.99	0.99	7.45	8.48	$q_m = 3.83$; $K_L = 0.13$	$q_m = 3.83$; $K_L = 0.13$
Freundlich	0.98	0.98	150.70	137.10	$K_F = 1.35$; $n = 2.43$	$K_F = 1.31$; $n = 2.49$
Temkin	0.98	0.97	161.30	50.01	$q_m = 1.73$; $K_T = 1.25$	$q_m = 0.50$; $K_T = 0.75$
Dubinin–Radushkevich	0.98	0.99	4.66	9.95	$q_m = 0.000348839$ $D = 7.00E-09$ $E = 8.45$	$q_m = 0.000171728$ $D = 4.00E-09$ $E = 11.18$

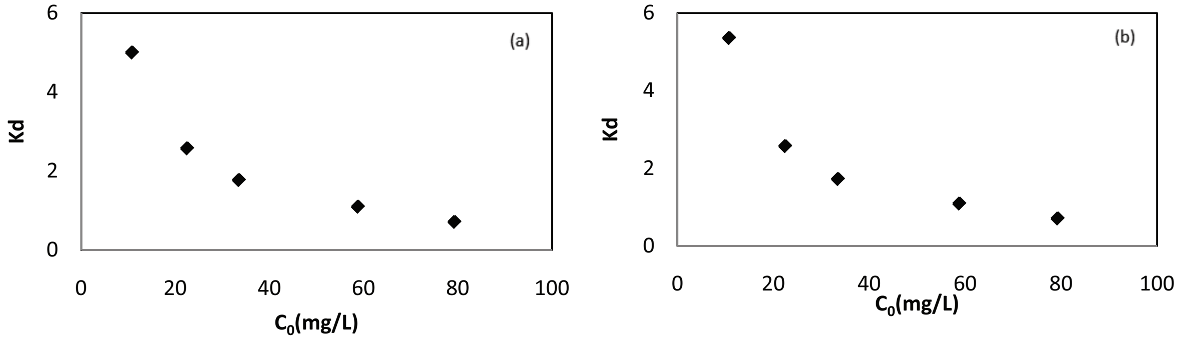

Fig. 7. K_d values vs. initial concentration of Zn(II) ions for (a) S1 and (b) S2 samples.

pseudo-second-order kinetic models. Linear expression of these kinetic equations and the approach to obtain the kinetic parameters are explained in Table 5.

High correlation coefficients and low ARE confirm that pseudo-second-order model obtains a good regression. In S1 sample, the correlation coefficient and ARE for pseudo-second-order equation were 0.99 and 1.31, respectively. Furthermore, the calculated q_e values using this model are matching better with experimental data. It can be concluded that the sorption of Zn(II) ions onto S1 is most appropriately represented by a pseudo-second-order kinetic model. In S2 sample, the correlation coefficient and ARE values of pseudo-second-order equation were 0.99 and 0.83, respectively (Table 6).

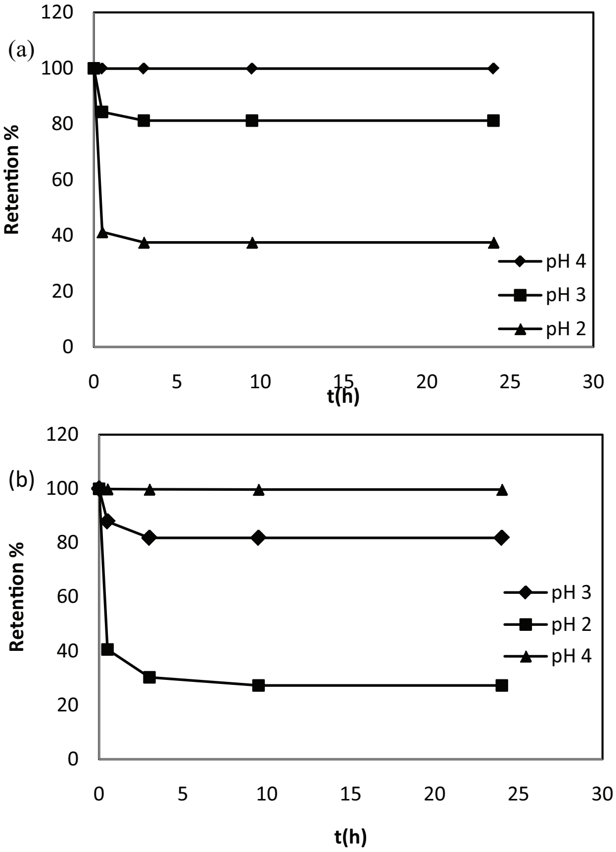

Fig. 8. Zn(II) ions retention in (a) S1 and (b) S2 samples in various pH during the time.

The calculated values of adsorbed of Zn(II) ions onto S1 and S2 samples with time for different kinetic models are presented in Fig. 9. Based on this figure, the pseudo-second-order kinetic model is fitted with the experimental data for both soil samples, and this indicates that the main sorption mechanism is chemical sorption for Zn(II) sorption onto soils.

3.4. Sequential extraction

Sequential extraction was conducted for identifying the main sorbents of ions in soils [45]. The amount of heavy metals in different fractions of soil can be determined by this method. For S1 sample, 49% of Zn(II) sorbed is associated with carbonate phases. After carbonate, exchangeable fraction was more effective in sorption process (Fig. 10(a)). The percentage fractionation of zinc in S1 before and after sorption (Fig. 11(a)) follows this order: residual > iron and manganese oxides > organic matter > carbonates > exchangeable, and carbonate > exchangeable > iron and manganese oxides > organic matter > residual, respectively. Amounts of Zn(II) sorbed onto carbonate and exchangeable fractions of S1 were 1.39 and 0.93 kg/L, respectively. Results indicate that carbonate phase for Zn(II) sorption in this soil plays a major role in sorption process (Fig. 10(b)). Before sorption process, the percentage of Zn distribution onto the fractions of S2 sample was in the order of: residual > organic matter > iron and manganese oxides > carbonates > exchangeable (Fig. 11(b)). The highest amount of Zn(II) was sorbed onto carbonate phase of S2 sample. In addition, exchangeable phase, iron and

Table 5
Kinetic models and their linearized expressions

Kinetic models	Equations	Linear expression	Plot	Parameters	Ref.
Pseudo-first order	$q_t = q_e[1-\exp(-k_{1p}t)]$	$\ln(q_e - q_t) = \ln q_e - k_{1p}t$	$\ln(q_e - q_t)\,\text{vs}.\,t$	$q_e = \exp(\text{intercept}),\ k_{1p} = -(\text{slope})$	[43]
Pseudo-second order	$q_t = k_{2p}q_e^2t/(1+q_ek_{2p}t)$	$t/q_t = 1/k_{2p}q_e^2 + t/q_e$	$t/q_t\,\text{vs}.\,t$	$q_e = \text{slope}^{-1}$, $k_{2p} = (\text{slope}^2)/\text{intercept}$	[46]

Table 6
Kinetic models parameters for the sorption of Zn(II) ions onto soils

Soils	S1	S2	S1	S2	S1	S2
Kinetic	R^2		ARE%		Parameters	
Pseudo-first order	0.75	0.61	95.89	98.00	$q_e = 0.25$; $k_{1p} = 0.10$	$q_e = 0.07$; $k_{1p} = 0.36$
Pseudo-second order	0.99	0.99	1.31	0.83	$q_e = 2.45$; $k_{2p} = 1.86$	q_e=2.55; $k_{2p} = 13.76$

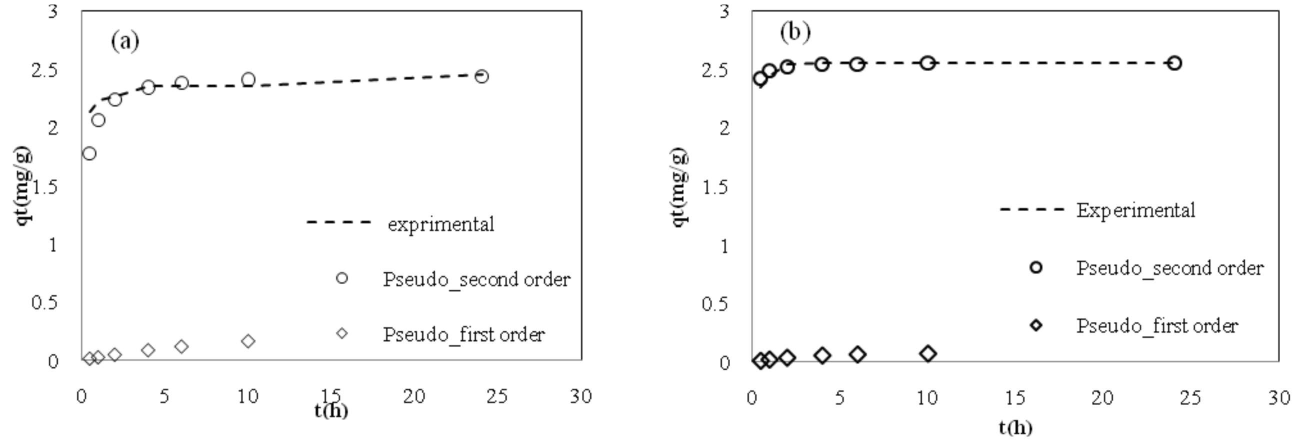

Fig. 9. Sorption kinetic models of Zn(II) ions onto (a) S1 and (b) S2.

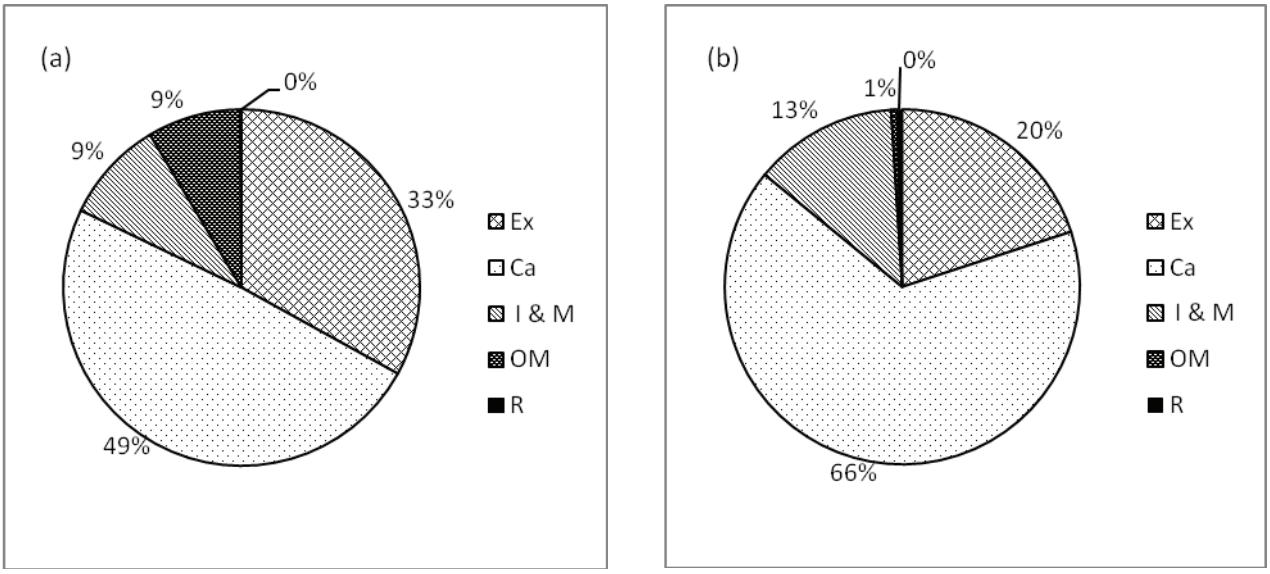

Fig. 10. The percentage of Zn(II) sorption onto fractions: Ex: exchangeable, Ca: carbonate, I&M: iron and manganese oxides, OM: organic matter and R: residual of (a): S1 and (b): S2.

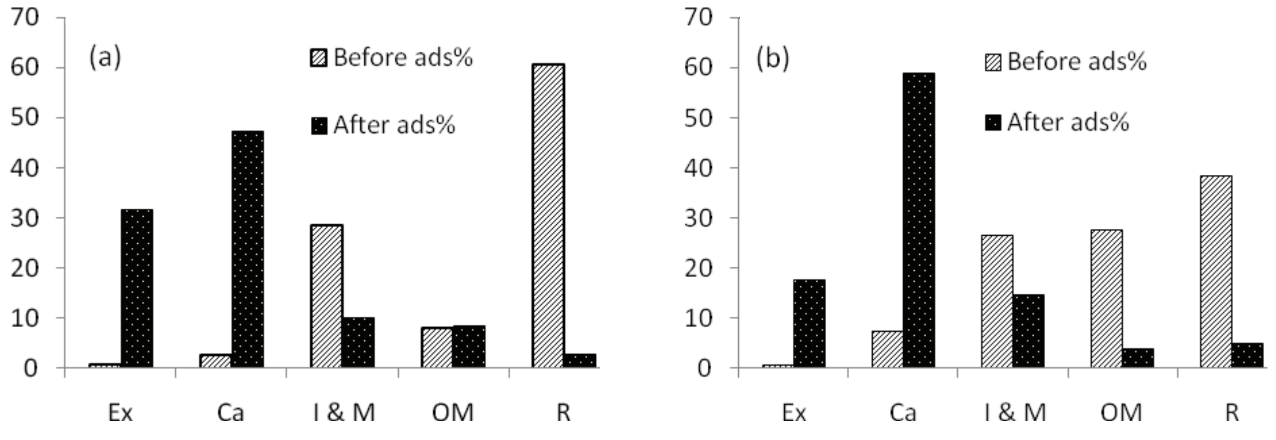

Fig. 11. The percentage of Zn(II) onto fractions: Ex: exchangeable, Ca: carbonate, I&M: iron and manganese oxides, OM: organic matter and R: residual of samples S1 (a) and S2 (b) before and after sorption.

manganese oxides, and organic matter retained zinc, respectively. Results obtained from sequential extraction show that dominant processes are associated with ion exchange and sorption onto carbonate. These findings confirm the results of sorption energy of D–R model. After carbonate, ion-exchange phase is the most effective phase in zinc sorption in both soil samples. Bioavailability of heavy metal in exchangeable phase of soil is high due to the fact that desorption of heavy metal sorbed by ion-exchange mechanisms can easily occur [45]. Small changes in soil environment cause some of Zn(II) ions to be separated from exchangeable phase and lead to triggering the contamination problem. Therefore, in this case, the mobility and bioavailability of Zn ions are high because large amounts of Zn ions were adsorbed by exchangeable phase of soils.

4. Conclusion

This paper introduced contaminated soils from Sarcheshmeh copper mine as efficient adsorbents to remove Zn(II) ions from aqueous solution. Although contaminated soils seem a worthless material, they can be used to overcome a main environmental problem such as heavy metal in acid mine drainage. In this study, these soils were more effective to attenuate Zn(II) ions and retain them in soils.

Sorption tests are useful for a quick evaluation of the risk resulting from metal contamination in soils, especially regarding metal mobility. Sorption isotherms were better described by Langmuir and D–R models in comparison with Freundlich and Temkin models for S1 and S2 samples. According to the results of sorption isotherms, chemical process and ion exchange were dominant in sorption process. The sorption kinetics of Zn(II) ions onto soils confirms that the kinetic data closely follow the pseudo-second-order kinetic. Sequential extraction procedures have provided important information about heavy metal interactions with soil surfaces and partitioning of these species among several soil fractions and some clues about sorption mechanisms. The results of sequential extraction show that large amount of zinc ions were attenuated by carbonate and exchangeable fractions. The retention of Zn(II) ions by exchangeable fraction was lower in comparison with carbonate fraction, and this implies that the bioavailability of Zn(II) in exchangeable phase would be higher. It should be noted that the experimental approaches such as the one studied in this research are highly recommended to be applied to other heavy metal systems in order to evaluate the applicability of the technique as well as to better understand interactions between soils and heavy metal contaminations.

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Symbols

K_L — Langmuir isotherm constant, L/mg
K_F — Freundlich constant, (mg/g) $(L/g)^{1/n}$
$1/n$ — Freundlich exponent
K_T — Temkin isotherm constant, L/mg
D — Dubinin–Radushkevich isotherm constant, mol^2/kJ^2
E — Sorption energy
k_{1p} — Pseudo-first order kinetic model constant, 1/h
k_{2p} — Pseudo-second order kinetic model constant, g/mg h
N — Number of experimental measurements
K_d — Distribution coefficients
ARE — Average relative error
C_e — Equilibrium concentration, mg/L
C_0 — Initial concentration, mg/L
C_t — Concentration at time t, mg/L
q_m — Monolayer sorption capacity, mg/g
q_e — Amount of Zn adsorbed at equilibrium, mg/g
q_t — Amount of Zn adsorbed at time t, mg/g
t — Time, h
V — Volume of the solution, L
W — Mass of the sorbent, g

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