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## KINETICS AND ISOTHERM MODELLING OF Zn(II) IONS ADSORPTION ONTO MINE SOILS

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**Abstract:** The soils consist of various components that can play a significant role in control of heavy metals in the environment. Therefore, understanding of adsorption properties of soil is essential in solving pollution problems around mine sites. The goal of this paper is to study Zn(II) ions adsorption onto copper mine soil. Soils were examined via X-ray diffraction and scanning electron microscopy. The influence of various parameters such as effect of pH, adsorbent dose, and initial concentration of Zn(II) ions on adsorption was evaluated by batch method. The adsorption isotherms of Zn(II) ions such as Langmuir, Freundlich, and Temkin were studied. The Langmuir isotherm indicated an excellent fit for the experimental data in comparison with other isotherms that shown monolayer adsorption onto a homogenous surface. A number of kinetic models were tested to fit the kinetic data. The results show that soils can be more effective in decreasing heavy metals contamination specially Zn(II) ions from solution phase.

**Keywords:** copper mine soil, Zn(II), adsorption kinetic, adsorption isotherms

### Introduction

Mining produces large volume of acid mine drainage (AMD). The AMD contains heavy metals that are highly toxic which may have harmful effects on the environment (Macias et al., 2012). The AMD at Sarcheshmeh copper mine (SCM), Iran, contains high zinc values (Khorasanipour et al., 2011). Although zinc is essential to human life and health, but it can be potentially toxic in high concentrations (Acar and Eren, 2006). Drinking water containing more than 1.0 mg/dm<sup>3</sup> of Zn(II) ions may cause hemochromatosis and gastrointestinal catarrh diseases due to their accumulation in people's liver and kidney (Li et al., 2010). In recent years, increased contents of heavy metals in environments especially around the mines have caused considerable concern relative to their impact on water contamination.

Soil can play important role in decreasing and immobilization of heavy metals. The capacity of soils to adsorb heavy metals from aqueous solution is considerable and significantly mitigates environmental issues. Adsorption is a main process for attenuation of potentially toxic metals from wastewaters and also it is studied for the understanding of how metals are transferred from a liquid phase to the surface of a solid phase (Bradl, 2004; Vidala et al., 2009). The adsorption ability of soils depends on soil properties such as pH and the presence of adsorption sites in various soil components as carbonates, organic matter, clay minerals, and Fe and Al (hydro) oxides (Kinniburgh et al., 1999).

Distribution of metals between soil and solution at equilibrium can be indicated by distribution coefficient ( $K_d$ ). Mobility and retention of heavy metals in soil can be related to their  $K_d$ .  $K_d$  is a valuable parameter for investigation the adsorption capability of different soils (Gomes et al., 2001).

The design of an adsorption system can be achieved by finding an appropriate isotherm model because of representing the equilibrium state of an adsorption system (Foo and Hameed, 2010). Adsorption isotherms describe the adsorption data in batch experiments. The capability of soil adsorption can be obtained by analysis of isotherms. Also, the study of adsorption kinetics is highly significant to the design of an adsorption system because it provides valuable information in the reaction pathway, rate of adsorption and its mechanism (Dabrowski, 2001).

The Sarcheshmeh copper deposit is one of the largest copper mine in the world. In fact, this area involves an important mining site with industrial activities which lead to environmental contamination by heavy metals. So this study was conducted on heavy metals adsorption by soil at SCM and the adsorption capability of *in-situ* soil. Soils involve various fractions which are strongly capable to adsorb heavy metals and can be used as low cost adsorbent. This study is very essential in this mining site in order to estimate efficiency of soil for heavy metals attenuation.

In this study, the adsorption process of Zn(II) ions onto the SCM soil using different adsorption isotherm and kinetic models were investigated. Also, the effect of three adsorption parameters such as solution pH, initial concentration and dose of adsorbent was investigated. Maximum adsorption capability of the SCM soil for Zn(II) ions was evaluated in this mining site. Pseudo-first order and pseudo-second order equations have been employed for modelling the kinetics of Zn(II) ions sorption.

## Material and methods

### Soil samples and their analysis

The soil samples were collected from the Sarcheshmeh copper mine surrounding area, 160 km SW of Kerman. Previous researches in this area showed that there is a level of heavy metal pollution in the soil. Two sample sites were selected and five samples, approximately 6 kg in each site, were collected from the surface layer (0–20 cm). Soil samples (SA, SE) were packed and transported to the laboratory. All

samples were air-dried and sieved through 2 mm mesh and were homogenized prior to soil characterization and adsorption studies. For determination of particle size distribution, organic matter was oxidized with hydrogen peroxide, after which fractions larger than 50  $\mu\text{m}$  were separated by sieving and smaller fractions by the international procedure (Day, 1965). Soil pH was measured in a 1:1 (w/v) soil/water mixture (Guitian and Carballas, 1976). The method of Hendershot and Duquette (1986) was used to determine the cation exchange capacity. This method measures the effective Cation Exchange Capacity (CEC) by determining calcium, magnesium, potassium and aluminium concentrations in a mixture obtained by the reaction of 2 g of soil with a 1 M  $\text{NH}_4\text{Cl}$  solution. Oxides contents were determined by the dithionite-citrate method (Sherdrick and McKeague, 1975). Samples were shaken with a solution of sodium hydrosulphite and sodium citrate, and the Fe, Al and Mn contents of the extract were determined by ICP-OES.  $\text{CaCO}_3$  was determined by volumetric calcimeter according to Allison and Moodie (1965). The determination of soil organic carbon is based on the Walkley-Black method (Walkley and Black, 1934). Oxidisable matter in the soil is oxidized by 1 N  $\text{K}_2\text{Cr}_2\text{O}_7$  solution. The reaction is assisted by the heat generated when two volumes of  $\text{H}_2\text{SO}_4$  are mixed with one volume of the dichromate. The remaining dichromate is titrated with ferrous sulphate. The titer is inversely related to the amount of C present in the soil sample. The specific surface area (SSA) and pore size distribution of adsorbents were determined from adsorption-desorption isotherm of  $\text{N}_2$  at 77 K. A Quantachrom NOVA 1000 surface area analyzer was used to determine this parameter by applying the 3-point BET (Brunauer–Emmet–Teller adsorption isotherm) (Vernersson et al., 2002). Metal concentrations in the soil were determined by ICP-OES. The soil characteristics are summarized in Table 1. The mineralogy of the clay minerals in SA and SE is illustrated by the X-ray diffraction (XRD) in Fig. 1. The most important minerals of SA soil that are identified by XRD are quartz, albite, muscovite, montmorillonite and illite. The major peaks of SE are related to quartz, hematite, albite, illite, clinocllore and muscovite. In order to observe the surface morphology of the soil samples, scanning electron microscopic (SEM) analysis was employed in this study (Fig. 2).

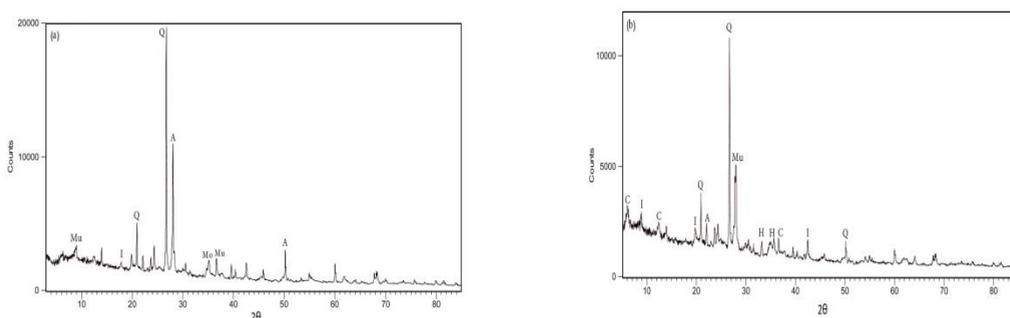


Fig. 1. X-ray diffraction patterns of (a) SA sample and (b) SE sample. Q: quartz, A: albite, C: clinocllore, H: hematite, I: illite, Mo: montmorillonite, and Mu: muscovite

Table 1. Characteristics of soil

Soil	SA	SE
OC %	0.33	0.29
pH	8.03	7.04
CEC (m <sub>eq</sub> /100g)	4.21	6.38
Fe <sub>2</sub> O <sub>3</sub> %	1.7	2.8
MnO %	0.11	0.12
Al <sub>2</sub> O <sub>3</sub> %	4.5	4.4
CaCO <sub>3</sub> %	0.5	0.26
Clay %	16	18
Silt %	38	26
Sand %	46	56
SSA (m <sup>2</sup> /g)	17.06	20.3
Total pore volume (cm <sup>3</sup> /g)	0.001	0.0016

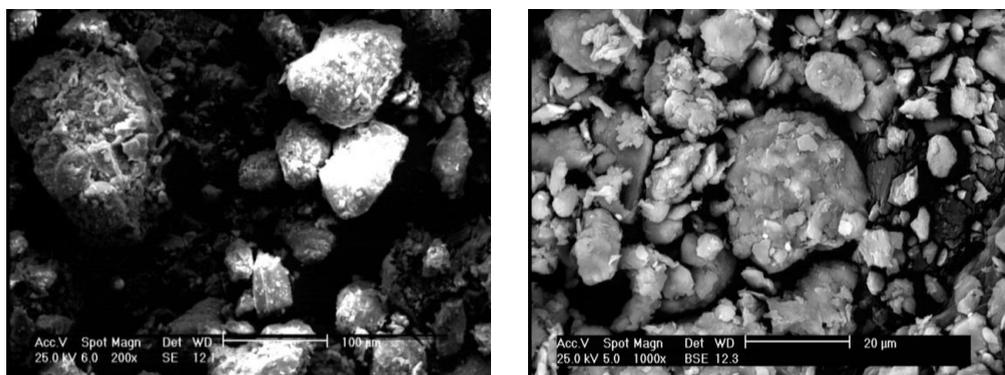


Fig. 2. Scanning electron micrograph of soil samples

### Effect of adsorption parameters

The effect of pH on the adsorption of Zn(II) ions over a pH range of 3–5 was investigated and from 2 to 10 g/dm<sup>3</sup> of adsorbent in 500 cm<sup>3</sup> of solution. The adsorption percentage of Zn(II) ions was determined from Eq.1.

$$\text{Ads\%} = \frac{(C_0 - C_f)}{C_0} \cdot 100 \quad (1)$$

In Eq.1  $C_f$  is the final Zn(II) ions concentration in mg/dm<sup>3</sup>.

### Adsorption equilibrium

Batch adsorption experiments were carried out for fractions smaller than 2 mm. The initial Zn(II) ions concentration of experimental solutions were: 10; 20; 30; 60 and 80 mg/dm<sup>3</sup>. 500 cm<sup>3</sup> of experimental solutions were placed in 25 cm<sup>3</sup> glass bottles containing initial Zn(II) ions concentration 10, 20, 30, 60, and 80 mg/dm<sup>3</sup> and also pH 4 were adjusted. Then, 5 g soil samples were added to 500 cm<sup>3</sup> of aqueous Zn(II) ions solutions. The bottles were rolled at a constant rotation of 100 rpm for 24 h in order to reach the equilibrium. Sampling was performed at various determined time intervals. The Zn(II) ions concentration was analyzed using atomic absorption spectrophotometer (AAS). The concentration of Zn(II) ions retained on the soil was calculated according to Eq. 2.

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (2)$$

where  $C_0$  and  $C_e$  are the initial and equilibrium concentrations of metals in solution (mg/dm<sup>3</sup>), respectively,  $V$  and  $W$  represent volume of the solution (L) and mass of the sorbent (g), respectively.

For each soil, adsorption capacities for Zn(II) ions were compared using the estimated distribution coefficients ( $K_d$ ). Adsorption data were collected and then  $K_d$  for the metals in each soil at equilibrium were calculated (Covelo et al., 2004a) using the following expression (Eq. 3):

$$K_d = \frac{\text{concentration of metal sorbed (mg / dm}^3\text{)}}{\text{concentration of metal in solution (mg / dm}^3\text{)}} \quad (3)$$

### Kinetic studies

Batch kinetic experiments were performed under similar conditions mentioned above for equilibrium experiments. A sample of 5 g of soil was added to 500 cm<sup>3</sup> aqueous solutions of Zn(II) ions in 25 cm<sup>3</sup> glass bottles at ambient temperature. Initial Zn(II) ions concentrations were 30 mg/dm<sup>3</sup> and 70 mg/dm<sup>3</sup> and pH = 4 was adjusted. The system was rotated at 100 rpm in a bottle roll apparatus. Samples were drawn at regular time intervals and the Zn(II) ions concentration was analyzed using an atomic absorption spectrophotometer (AAS). The amount of Zn(II) ions adsorbed by soil at time  $t$ ,  $q_t$  (mg/g), was calculated by Eq. 4.

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (4)$$

where  $C_t$  is Zn(II) ions concentration at time  $t$ , (mg/dm<sup>3</sup>).

## Error function

Average relative error (ARE) has been calculated between experimental and calculated data (Kapoor and Yang, 1989). The ARE was calculated by means of Eq. 5.

$$ARE = \frac{100}{N} \sum_{i=1}^N \left| \frac{q_e^{\text{exp}} - q_e^{\text{cal}}}{q_e^{\text{exp}}} \right|_i \quad (5)$$

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

## Results and discussion

### Effect of pH

The pH is the important factor that influences the adsorption of Zn(II) ions. There was dependence on Zn(II) ions adsorption in relation to the pH. When the pH value is low, Zn(II) ions faced competition with abundance of  $H^+$  for available permanent charged sites, so the adsorption of Zn(II) ions onto soil is limited. While at high pH value, this competition decrease, and thus, more Zn(II) ions is adsorbed onto SA and SE. Adsorption percentage of Zn(II) ions onto SA and SE was shown in Fig. 3.

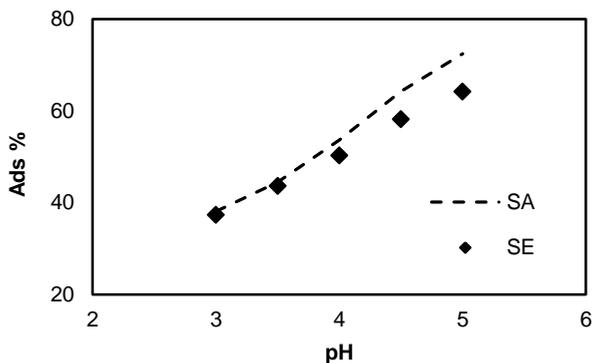


Fig. 3. Effect of pH on adsorption percentage of Zn(II) ions onto SA and SE. Soil mass 5 g, solution volume 500 cm<sup>3</sup>, stirring speed 100 rpm, contact time 24 h

### Effect of adsorbent dose

Adsorbent dose is an important parameter in adsorption studies because it determines the capacity of adsorbent for a given initial concentration of metal ion solution. The effect of soil dose on the percent adsorption of Zn(II) ions is shown in Fig. 4. It is observed that increasing of soil increased the adsorption percentage of Zn(II) ions up to 53 for SA and 50 for SE. Adsorption percentage increased with increasing the soil

dose because increasing soil dose provides greater surface area or more adsorption sites.

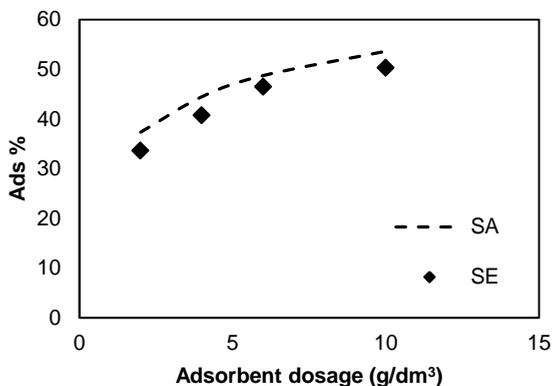


Fig. 4. Effect of soil dose on the adsorption percentage of Zn(II) ions onto SA and SE. pH 4, solution volume 500 cm<sup>3</sup>, stirring speed 100 rpm, contact time 24 h

### Effect of initial Zn(II) concentration

The adsorption of Zn(II) ions onto SA and SE was studied at different initial concentrations of Zn(II) ions ranging from 10 mg/dm<sup>3</sup> to 80 mg/dm<sup>3</sup>. Data on the adsorption of Zn(II) ions are shown in Fig. 5. The adsorption percentage of Zn(II) ions was decreased with increasing in initial concentration from 10 mg/dm<sup>3</sup> to 80 mg/dm<sup>3</sup>. This shows that active adsorption sites were decreased.

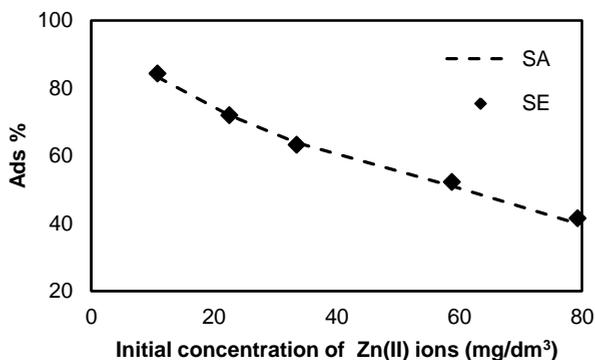


Fig. 5. Effect of Zn(II) ions concentration on the adsorption percentage of Zn(II) ions onto SA and SE. pH 4, soil mass 5 g, solution volume 500 cm<sup>3</sup>, stirring speed 100 rpm, contact time 24 h

### Adsorption isotherm

An equilibrium isotherm expresses the relation between the amounts of adsorbate removed from solution at equilibrium by unit of adsorbent mass at constant

temperature. The Langmuir, Freundlich, and Temkin isotherms were applied in this study. The Langmuir isotherm is described for monolayer adsorption onto a homogenous surface containing a finite number of identical sites (El Nemr, 2009). The model assumes uniform energies of adsorption onto the surface (Sreejalekshmi et al., 2009). The Freundlich isotherm is used to illustrate multilayer adsorption onto a heterogeneous surface with a non-uniform distribution of energies of adsorption over the surface (Adamson and Gast, 1997). Values  $K_f$  and  $1/n$  are Freundlich constants related to capacity and intensity of adsorption, respectively. The lower fractional value of  $1/n$  between 0 and 1 indicates that weak adsorptive forces are effective on the surface (Foo and Hameed, 2010). The Temkin model assumes that heat of adsorption of all molecules in the layer would decrease linearly with coverage (Aharoni and Ungarish, 1977). Linear expression of these isotherm equations and the way to obtain the isotherm parameters are given in Table 2.

Table 2. Isotherms and their linearized expressions

Isotherms	Langmuir	Freundlich	Temkin
Equations	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	$q_e = K_F C_e^{1/n}$	$q_e = q_m \ln(K_T C_e)$
Linear expression	$C_e/q_e = (1/K_L q_m) + (C_e/q_m)$	$\ln q_e = \ln K_F + (1/n) \ln C_e$	$q_e = q_m \ln K_T + q_m \ln C_e$
Plot	$C_e/q_e$ vs. $C_e$	$\ln q_e$ vs. $\ln C_e$	$q_e$ vs. $\ln C_e$
Parameters	$q_m = (\text{slope})^{-1}$ , $K_L = \text{slope}/\text{intercept}$	$K_F = \exp(\text{intercept})$ , $n = (\text{slope})^{-1}$	$K_T = \exp(\text{intercept}/\text{slope})$ , $q_m = \text{slope}$
Reference	Langmuir, 1916	Freundlich, 1906	Temkin and Pyzhev, 1940

The isotherms are useful for providing information on the adsorption potential of an adsorbent. The experimental data were compared to the Langmuir, Freundlich, and Temkin equilibrium equations. The applicability of each isotherm to describe the adsorption process was identified by the correlation coefficients ( $R^2$  values). The values of parameters and correlation coefficients, and ARE were listed in Table 3. In this case, adsorption process was judged by high correlation coefficients values beside lower ARE. So Langmuir-type isotherm model of the SA and SE samples was fitted better than the other isotherm models because of high correlation coefficient and low ARE. The correlation coefficients for linearized form of Freundlich and Temkin isotherms were high but ARE values were low therefore these isotherms cannot be good models for describing of experimental data. The adsorption isotherm models were fitted to the experimental data for SA sample in the order of: Langmuir > Freundlich > Temkin isotherms. In SE sample, the isotherm models were fitted to the data as follows: Langmuir > Temkin > Freundlich isotherms.

The Zn(II) ions adsorption isotherms are similar to L-curves (Fig. 6a and b). In the L-shaped isotherm, the ratio between the concentration of Zn(II) ions remaining in solution and adsorbed on adsorbent decreases when Zn(II) ions concentration increases. Also, the soil does not show clearly a limited sorption capacity (Limousin et al., 2007). This trend can be due to decrease in vacant adsorption sites resulted from covering by adsorbate (Covelo et al., 2004b). It can be implied that the soil particles have higher affinity to adsorb metals ions at low concentration and show a reducing tendency as the concentration of adsorbed metals reaches the maximum adsorption capacity of the soil (Sparks, 2003).

Table 3. Isotherms parameters, correlation coefficients value and ARE

Soils	SA	SE	SA	SE	SA	SE
Isotherms	R <sup>2</sup>		ARE (%)		Parameters	
Langmuir	0.99	0.99	7.45	8.48	q <sub>m</sub> = 3.83; K <sub>L</sub> = 0.13	q <sub>m</sub> = 3.83; K <sub>L</sub> = 0.13
Freundlich	0.98	0.98	150.70	137.10	K <sub>F</sub> = 1.35; n = 2.43	K <sub>F</sub> = 1.31; n = 2.49
Temkin	0.98	0.97	161.30	50.01	q <sub>m</sub> = 1.73; K <sub>T</sub> = 1.25	q <sub>m</sub> = 0.50; K <sub>T</sub> = 0.75

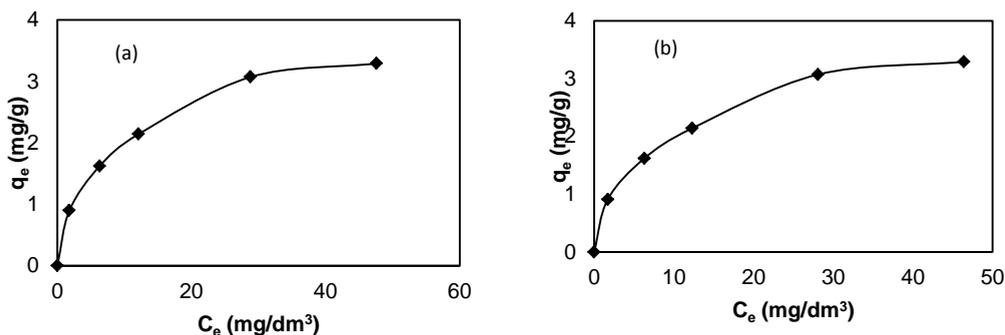


Fig. 6. Zn(II) ions adsorption isotherms: (a) for SA and (b) for SE sample

Distribution coefficients ( $K_d$ ) represent the affinity of the metal retention in soil versus solution. In fact, the mobility and fate of metals can be estimated by  $K_d$  values in soil (Reddy and Dunn, 1986). High values of  $K_d$  indicates that the metal tends to retain in the solid phase through adsorption reactions and low values indicate that an important proportion remains soluble. The value of  $K_d$  was calculated at varying initial Zn(II) ions concentrations in Fig. 7. Range of Zn(II) ions:  $K_d$  values were 0.7–5 and 0.7–5.3 for SA and SE samples, respectively. SE samples showed higher  $K_d$  values against SA samples which this indicates SE has higher potential for Zn(II) ions adsorption than SA. The  $K_d$  was extremely dependent on the initial metal concentration so that with increase of initial Zn(II) ions concentration from 10 mg/dm<sup>3</sup> to 80 mg/dm<sup>3</sup>,  $K_d$  values decreased for both SA and SE. This proves that the

adsorption capacity of soil decreases in high Zn(II) ions concentrations. SE shows a higher CEC and clay contents than SA and hence an increased adsorption capacity can be due to the presence of adsorption sites on clay mineral.

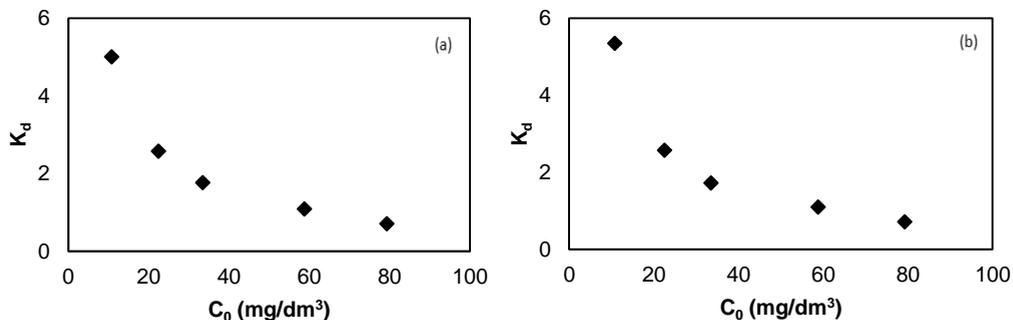


Fig. 7.  $K_d$  values versus initial concentration of Zn(II) ions for SA and SE samples

### Kinetic study

The adsorption kinetics of Zn(II) ions onto soil was examined with pseudo first and second order kinetic models. Linear expression of these kinetic equations and the way to obtain the kinetic parameters are explained in Table 4.

Table 4. Kinetic models and their linearized expressions

Kinetic models	Pseudo-first order	Pseudo-second order
Equations	$q_t = q_e [1 - \exp(-k_{1p}t)]$	$q_t = k_{2p}q_e^2t / (1 + q_e k_{2p}t)$
Linear expression	$\ln(q_e - q_t) = \ln q_e - k_{1p}t$	$t / q_t = 1 / k_{2p}q_e^2 + t / q_e$
Plot	$\ln(q_e - q_t)$ vs. $t$	$t/q_t$ vs. $t$
Parameters	$q_e = \exp(\text{intercept}), k_{1p} = -(\text{slope})$	$q_e = \text{slope}^{-1},$ $k_{2p} = (\text{slope}^2)/\text{intercept}$
Reference	Nandi et al., 2009	Kumar and Sivanesan, 2006

High correlation coefficients and low ARE confirm that pseudo-second order model gives a good regression. In SA soil, the correlation coefficient and ARE for pseudo-second order equation were 0.99 and 1.31%, respectively. Furthermore, the calculated through this model  $q_e$  values are close to the experimental ones. This can be concluded that the sorption of Zn(II) ions onto SA is most appropriately represented by a pseudo-second order kinetic model. In SE soil, the correlation coefficient and ARE for pseudo-second order equation were 0.99 and 0.83%, respectively (see Table 5). Also, the linear plots of  $\ln(q_e - q_t)$  vs.  $t$  and  $t/q_t$  vs.  $t$  were presented in Fig. 8.

Table 5. Kinetic models parameters for the adsorption of Zn(II) ions onto soils

Soils	SA	SE	SA	SE	SA	SE
Kinetic	R <sup>2</sup>		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	$q_e = 2.45$ ; $K_{2p} = 1.86$	$q_e = 2.55$ ; $K_{2p} = 13.76$

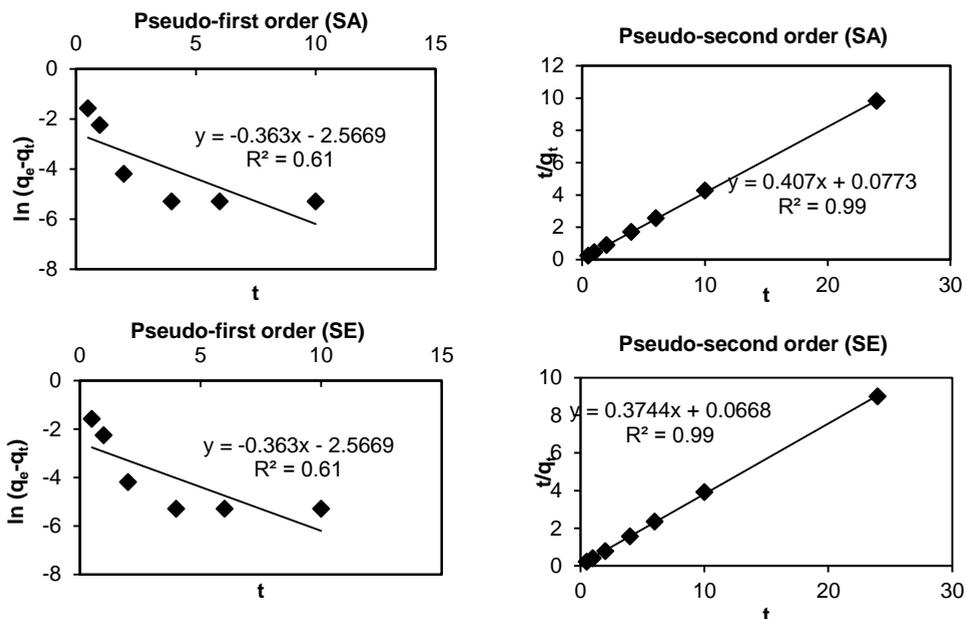
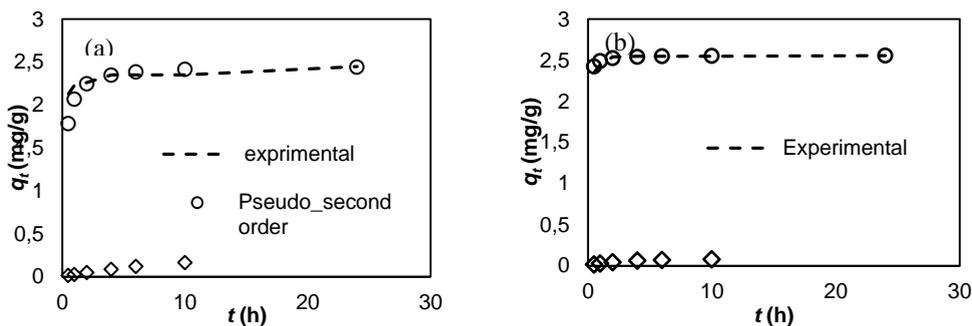


Fig. 8. The linear plots of pseudo-first order and pseudo-second order kinetic

The calculated values of adsorbed amount of Zn(II) ions onto SA and SE soils versus time for kinetic models are represented in Fig. 9. These show that the pseudo-second order kinetic model is match with the experimental data for both soil samples.

Fig. 9. The adsorbed amount of Zn(II) ions as a function of time for adsorption process realized using initial adsorbate concentration of 30 mg/dm<sup>3</sup>.

(a): Zn(II) ions adsorption onto SA, (b): Zn(II) ions adsorption onto SE

## Conclusion

Natural soil around the Sarcheshmeh Copper Mine was used in this paper as an adsorbent for Zn(II) ions removal. Sorption process was affected by experimental parameters such as pH, initial metal ion concentration, and adsorbent dosage. The adsorption percentage increased from pH 3 to pH 5. It was observed that increasing of soil increased the adsorption percentage. Also, the adsorption percentage of Zn(II) ions was decreased with increasing in initial concentration. The Zn(II) ions adsorption isotherms are L-curves. The adsorption capacity of these soil samples was investigated by isotherm models. For SA and SE, the Langmuir isotherm model fitted the equilibrium data better than the other isotherm models, revealing that the adsorption of Zn(II) onto SA and SE was monolayer. The adsorption kinetics of Zn(II) ions onto soils confirms that the kinetic data closely follow the pseudo-second order kinetic. The results show that mine soils can be effective in decreasing Zn(II) ions contamination from acid mine drainage around of mine sites.

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