Zn(II) Adsorption Study onto Soils of Sarcheshmeh Copper Mine

Haniyeh Jalayeri[1*], Mansour Ziaii[1], and Mohammad Mehdi Salarirad[2]

[1]Department of Mining Engineering, Petroleum and Geophysics, Shahrood University of Technology, Shahrood, Iran

[2]Department of Mining Engineering and Metallurgy, Amirkabir University of Technology, Tehran, Iran

Abstract

Soils around mining sites play a significant role in the transport and control of heavy metals in the environment. Therefore, understanding the adsorption properties of soil is essential in solving pollution problems. The objective of this paper was to study Zn(II) adsorption onto Sarcheshmeh copper mine soils. The adsorption isotherms of Zn(II) were studied. The Langmuir isotherm indicated an excellent fit for the experimental data in comparison with other isotherms. The capacity of Zn(II) adsorption was assessed by distribution coefficient for samples (SA and SE), such that, the SA sample showed high K_d values. Also, the amounts of Zn(II) adsorbed onto the soil decreased with increase in the initial concentration. The results of this study show that soils around mine can play an effective role in decreasing Zn(II) contamination.

Keywords: *adsorption, distribution coefficient, isotherm, soil.*

1. Introduction

Mining activities led to the production of a large volume of acid mine drainage (AMD). AMD involves heavy metals that are highly toxic and may have harmful effects on the environment [1]. The AMD at Sarcheshmeh copper mine (SCM), Iran, contains high zinc concentrations [2]. Although zinc is essential to human life and health, but it can be potentially toxic in high values [3, 4]. Drinking water containing more than 1.0 mg/L of Zn(II) may cause hemochromatosis and gastrointestinal catarrh diseases due to their accumulation in people's liver and kidney [5].

In recent years, increased contents of heavy metals in environments, especially around mines, have caused considerable concern relative to their impact on water contamination.

One of the key elements in nature is soil because of close contact with wastewater. Soil can play an important role in decreasing and immobilizing heavy metals. The capacity of soils to adsorb heavy metals from aqueous solution is considerable and significantly mitigates environmental issues. Adsorption is the main process for attenuating 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 [6, 7]. The adsorption ability of soils depends on soil properties such as pH and the presence of adsorption sites in various soil components such as carbonates, organic matter, clay minerals, and Fe and Al (hydr) oxides [8, 9]. The mechanisms of heavy metals adsorbed onto mine soils have not been fully understood because mine soils have specific characteristics. Therefore, the mechanism of Zn(II) adsorbed onto mine soil was studied by the batch experiments. The experimental results will provide meaningful information about the mechanisms of Zn(II), as well as prevention and control of Zn(II) adsorbed onto mine soil.

The design of an adsorption system can be achieved by finding an appropriate isotherm model because of the representation of an equilibrium state of the adsorption system [10, 11]. Adsorption isotherms describe the adsorption data in batch experiments. The capability of soil adsorption can be obtained by analysis of isotherms.

Sarcheshmeh copper deposit is one of the largest copper mines in the world. In fact, this area involves an important mining site with industrial activities which lead to environmental contamination by heavy metals. The towns surrounding the mining district were affected by contamination. Recently, some researches have been conducted on the AMD and its detrimental environmental effects and also about environmental geochemistry of heavy metals in soils around the Sarcheshmeh porphyry copper mine and AMD treatment [2, 12, 13]. This study has been conducted on Zn(II) adsorption by soil at SCM and the adsorption capability of *in-situ* soil was evaluated. Soils involve various fractions which are strongly capable of absorbing heavy metals and can be used as low cost adsorbent. This study is very essential to this mining site, in order to estimate the efficiency of soil for heavy metals attenuation.

In this study, the adsorption equilibrium of Zn(II) onto SCM soil by different adsorption isotherm models were investigated. To examine the relationship between sorbed and Zn(II) concentrations in aqueous solution at equilibrium, two different parameter sorption isotherm models were used for fitting the equilibrium data. Also, Zn(II) adsorption capability onto SCM soil was evaluated in this mining site.

2. Materials And Methods

2.1. Soil samples and analysis

Soil samples were collected from the area surrounding the Sarchemeh copper mine, 160 km South West (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 and 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. The samples were analyzed for organic carbon (OC) content [14], pH [15], cation exchange capacities (CEC) [16], oxides contents [17], $CaCO_3$ content [18], and particle size distribution [19]. 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 Figure 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, clinochlore and muscovite.

Table 1. Characteristics of soils

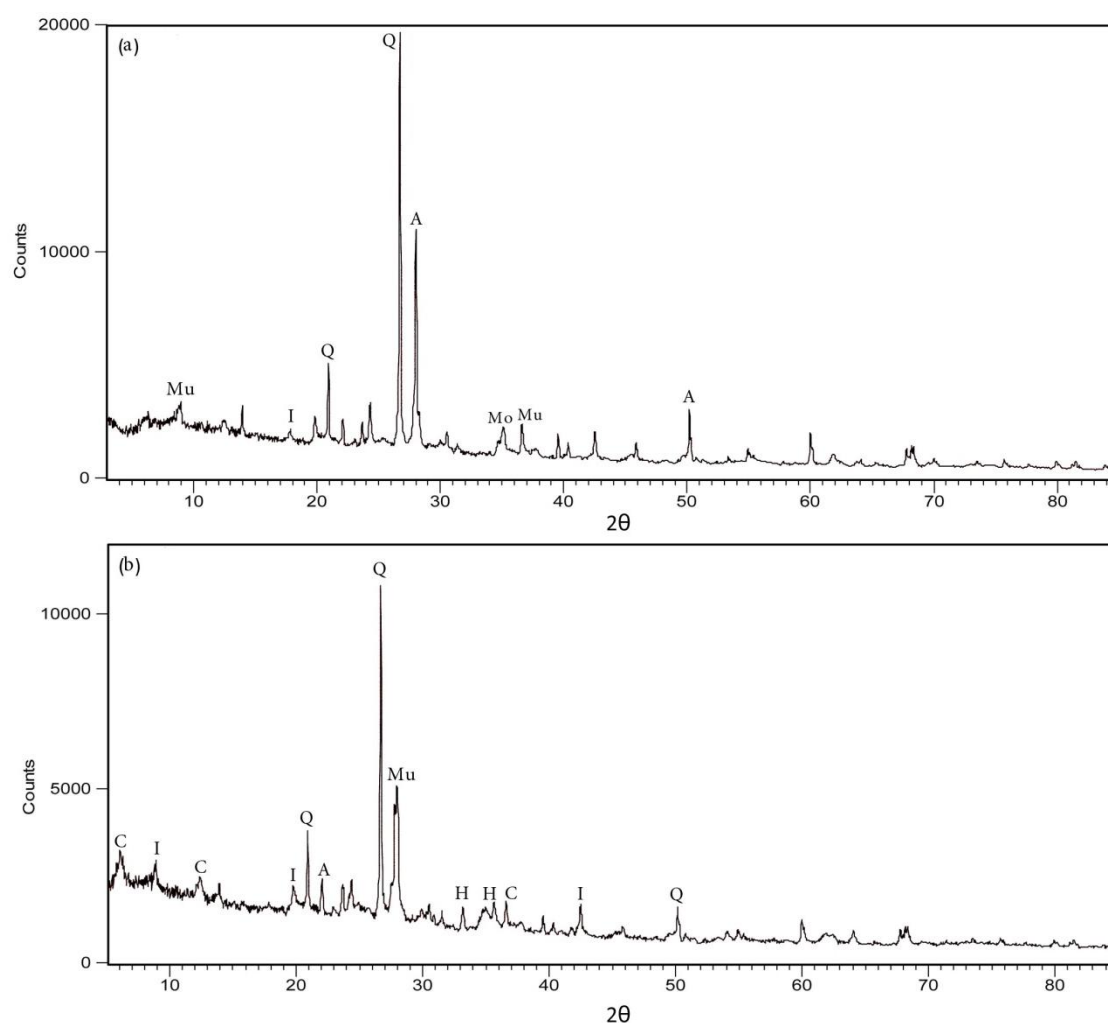| Soil	SA	SE
OC %	0.33	0.29
pH	8.03	7.04
CEC meq/100g	4.21	6.38
Fe2O3%	1.7	2.8
MnO%	0.11	0.12
Al2O3%	4.5	4.4
CaCO3 %	0.5	0.26
Clay %	16	18
Silt %	38	26
Sand %	46	56

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

2.2. Batch equilibrium experiments

Batch adsorption experiments were carried out in fractions smaller than 2 mm. The initial Zn(II) concentration of experimental solutions were 10, 20, 30, 60 and 80 mg/L. In this study, 500 mL of experimental solutions were placed in 2.5 L glass bottles containing initial Zn(II) concentrations of 10, 20, 30, 60, and 80 mg/L, as well as a pH of 4 were adjusted. Then, 5 g soil samples were added to 500 mL of aqueous Zn(II) 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) concentration was analyzed using atomic absorption spectrophotometer (AAS). The concentration of Zn(II) retained on the soil was calculated according to Equation 1).

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

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

Distribution of metals between soil and solution at equilibrium can be indicated by distribution coefficient (Kd). Mobility and retention of heavy metals in soil can be related to their Kd. Kd is a valuable parameter for investigating the adsorption capability of different soils [20, 21]. For each soil, adsorption capacities for Zn(II) 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 [22], using the following expression:

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

2.3. Change of pH in adsorption

Soil samples weighing 5 g were placed in 2.5 L glass bottles containing 500 mL of 80 mg/L Zn(II) solution and the pH was adjusted to 4. The bottles were rolled at a constant speed of 100 rpm and the pH of the solution was measured at various times.

2.4. Error function

The average relative error (ARE) was calculated between the experimental and calculated data [23]. ARE was calculated by:

$$ARE = \frac{100}{N} \sum_{i=1}^{N} \left| \frac{q_e^{\text{exp}} - q_e^{\text{cal}}}{q_e^{\text{exp}}} \right|_i \quad (3)$$

where q_e^{exp} and q_e^{cal} are experimental and calculated adsorbate concentrations at the 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.

3. Results And Discussion

3.1. Adsorption results

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 was described for monolayer adsorption onto a homogenous surface containing a finite number of identical sites [24]. The model assumes uniform energies of adsorption onto the surface [25]. The Freundlich isotherm was used to illustrate multilayer adsorption onto a heterogeneous surface with a non-uniform distribution of energies of adsorption over the surface [26]. Values and Freundlich constants were related to the capacity and intensity of adsorption, respectively. The lower fractional value of between 0 and 1 indicates that weak

adsorptive forces are effective on the surface. The Temkin model assumes that the heat of adsorption of all molecules in the layer would decrease linearly with coverage [27].

Langmuir isotherm model can be linearized into at least five different types as shown in Table 2. The relative parameters of five different linearized forms of Langmuir isotherm were obtained from plots between [Ce/qe vs. Ce], [1/qe vs. 1/Ce], [qe vs. 1/Ce], [qe/Ce vs. qe], and [1/Ce vs. 1/qe]. Also, the relative parameters of Freundlich and Temkin were obtained from plots between [ln(qe) vs. ln(Ce)] and [qe vs. ln(Ce)], respectively. Linear expression of these isotherm equations and the way to obtain the isotherm parameters are given in Table 2.

They are useful for providing information on the adsorption potential of 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 are listed in Table 3. In this case, the adsorption process was judged by high correlation coefficient values beside the lower ARE. So, the Langmuir-type (I) isotherm model of the SA and SE samples fitted better than the other isotherm models because of high correlation coefficient and low ARE. The correlation coefficients for the linearized form of the Freundlich and Temkin isotherms were high but the ARE values were low; therefore, these isotherms cannot be good models for describing experimental data. The adsorption isotherm models were fitted to the experimental data for SA sample in the following order: Langmuir type (I)> Langmuir type (V)> Langmuir type (IV)> Langmuir type (II)> Langmuir type (III)> Freundlich> Temkin isotherm. In SE sample, the isotherm models were fitted to the data as follows: Langmuir type (I)> Langmuir type (V)> Langmuir type (IV)> Langmuir type (II)> Langmuir type (III)>Temkin> Freundlich isotherm.

Table 2. Isotherms and their linearized expressions

Isotherms	Equations	Linear expression	Plot	Parameters	Ref.
Langmuir		Type (I) $C_e/q_e = (1/K_L q_m) + (C_e/q_m)$	C_e/q_e vs. C_e	$q_m = (slope)^{-1}$, $K_L = slope/intercept$	[28]
		Type (II) $1/q_e = (1/K_L q_m C_e) + (1/q_m)$	$1/q_e$ vs. $1/C_e$	$q_m = (intercept)^{-1}$, $K_L = intercept/slope$	
	$q_e = \dfrac{q_m K_L C_e}{1 + K_L C_e}$	Type (III) $q_e = q_m - (1/K_L)(q_e/C_e)$	q_e vs. $1/C_e$	$q_m = intercept$, $K_L = -(slope)^{-1}$	
		Type (IV) $q_e/C_e = K_L q_m + K_L q_e$	q_e/C_e vs. q_e	$q_m = -(intercept/slope)$, $K_L = -(slope)$	
		Type (V) $1/C_e = K_L q_m(1/q_e) + K_L$	$1/C_e$ vs. $1/q_e$	$q_m = slope/intercept$, $K_L = -(intercept)$	
Freundlich	$q_e = K_F C_e^{1/n}$	$\ln q_e = \ln K_F + (1/n)\ln C_e$	$\ln q_e$ vs. $\ln C_e$	$K_F = \exp(intercept)$, $n = (slope)^{-1}$	[29]
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. $\ln C_e$	$K_F = \exp(intercept/slope)$, $q_m = slope$	[30]

Table 3. Parameters, correlation coefficients value and ARE

Soils	SA	SE	SA	SE	SA	SE
Isotherms	R^2		ARE%		Parameters	
Langmuir						
Type(I)	0.99	0.99	7.45	8.48	q_m=3.83; K_L=0.13	q_m=3.83; K_L=0.13
Type(II)	0.97	0.97	8.98	9.97	q_m=3.18; K_L=0.21	q_m=3.1; K_L=0.23
Type(III)	0.75	0.74	9.75	10.32	q_m=2.87; K_L=0.25	q_m=2.84; K_L=0.27
Type(IV)	0.89	0.86	8.18	9.25	q_m=3.58; K_L=0.16	q_m=3.53; K_L=0.17
Type(V)	0.97	0.97	8.88	9.89	q_m=3.24; K_L=0.2	q_m=3.17; K_L=0.22
Freundlich	0.98	0.98	150.7	137.1	K_F=1.35; n=2.43	K_F=1.31; n=2.49
Temkin	0.98	0.97	161.3	50.01	q_m=1.73; K_T=1.25	q_m=0.50; K_T=0.75

Zn adsorption isotherms are similar to L-curves (Fig. 2a and b). In the L-shaped isotherm, the ratio between the concentration of Zn remaining in solution and adsorbed on adsorbent decreases when the concentration of Zn increases. Also, the soil does not clearly show a limited sorption capacity [31]. This trend can be due to decrease in vacant adsorption sites as a result of covering by adsorbate. It can be implied that the soil particles have higher affinity to adsorb metal ions at low concentration and show a reducing tendency as the concentration of adsorbed metals reaches the maximum adsorption capacity of the soil [32].
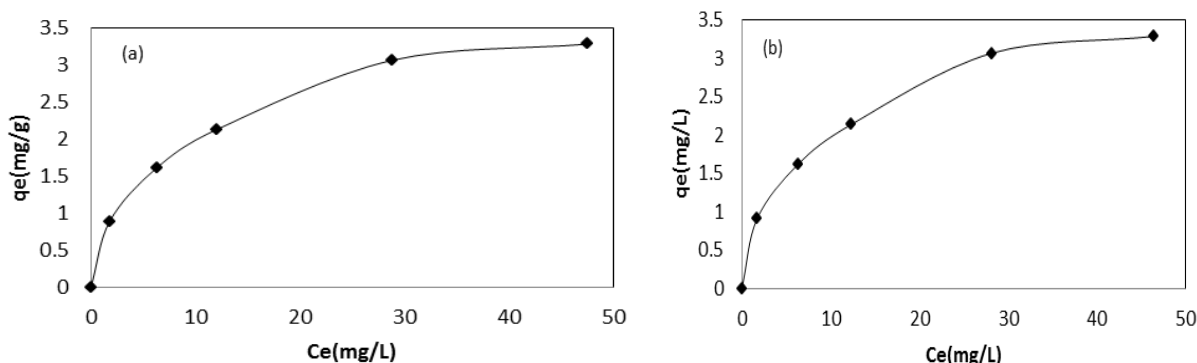
Fig. 2. Zn(II) adsorption isotherms: a) for SA and b) SE sample

Distribution coefficients (Kd) represent the affinity of metal retention in soil versus solution. In fact, the mobility and fate of metals can be estimated by Kd values in soil [33]. High values of Kd indicate that the metal tends to retain in the solid phase through adsorption reactions and low values indicate that an important proportion remains soluble [34]. The value of Kd was calculated at varying initial Zn concentrations in Figure 3. The range of Zn-Kd values were obtained for SA and SE 0.7 to 5 and 0.7 to 5.3, respectively. SE samples showed higher Kd values against SA samples which indicates that SE has higher potential for Zn adsorption than SA. The Kd was extremely dependent on the initial metal concentration, so that with increase of the initial Zn concentration from 10 to 80 mg/L, Kd values decreased for both SA and SE. This proves that the adsorption capacity of soil decreases in high Zn 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.
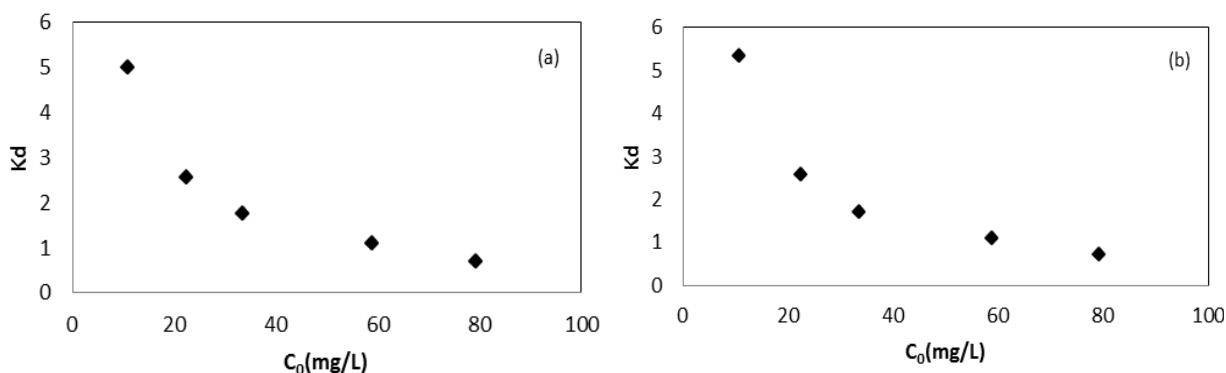

Fig. 3. K_d values versus Zn(II) initial concentration for SA and SE samples

3.2. Changes of pH in adsorption process

The pH of the adsorption systems changed in the adsorption of heavy metals onto the soil, which was related to the adsorption mechanisms. Figure 4 shows that the pH of adsorption changed with adsorption in both soils. The tendency of pH changes occurring in the adsorption systems with time in the adsorption of Zn were similar, and can be divided into two stages: in the first stage, the pH increased rapidly, which indicated that adsorption was dominant in this process; in the second stage, the pH changed gradually and tended to stability. The increase of pH in SA soil during the adsorption process might be due to the amount of $CaCO_3$ relative to the SE soil.
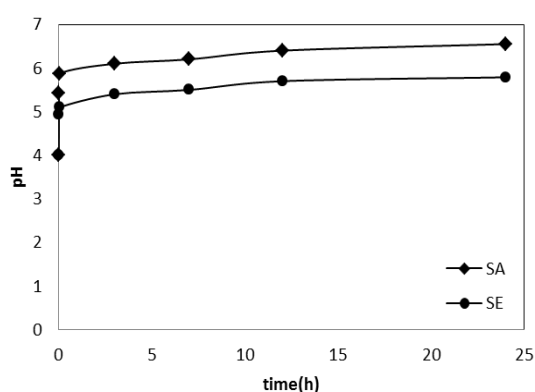
Fig. 4. pH changes in adsorption processes of Zn(II)

4. Mechanism of adsorption

The adsorption amounts of Zn(II) were related to the pH of these soil samples. This indicated that the adsorption of Zn(II) onto mine soils is influenced by soil pH. In addition, Zn(II) adsorption onto soil was influenced by the surface properties of soil. However, increase in soil pH did not only improve the adsorption capacity of the soil for heavy metals, but also, the effects of other physiochemical properties of soil on the adsorption of heavy metals. Zn(II) concentrations of soil after adsorption were analyzed by the Tessier sequential extraction method [35]. The results show that Zn(II) in SA and SE were in the carbonate bound form. This implied that the precipitation reaction was dominant in the adsorption processes and the degree of precipitation was mainly affected by soil pH.

5. Conclusion

The adsorption capacity of these soil samples was investigated by isotherm models. For SA, the Langmuir type (I) isotherm model fitted the equilibrium data better than the other isotherm models, revealing that the adsorption of Zn(II) onto SA was as monolayer adsorption. Also, these results were similar to those obtained for SE. The K_d values of SA were high in comparison to those of SE that show SA sample has higher potential of Zn(II)adsorption than SE.Mainly, there was a precipitation reaction that formed the carbonate bound in the adsorption of Zn onto soil samples resulting from the exchanges between heavy metal ions and calcium ions in soil.The results show that the soils surrounding mines could be effective in decreasing heavy metal contamination in mining sites.

Nomenclature

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)
k	fractional power kinetic model constant(mgg^{-1}h^{-v})
k_0	zero order kinetic model constant (mgg^{-1}h^{-1})
k_1	first order kinetic model constant (1/h)
k_{1p}	pseudo-first order kinetic model constant (1/h)
k_2	second order kinetic model constant (gmg^{-1}h^{-1})
k_{2p}	pseudo-second order kinetic model constant(gmg^{-1}h^{-1})
k_p	intraparticle diffusion kinetic model constant(gmg^{-1}h$^{-0.5}$)
R^2	correlation coefficient
ARE	average relative error
N	number of experimental measurements
C_e	equilibrium concentration (mg/L)
C_0	initial concentration (mg/L)
q_e	amount of Zn(II) adsorbed at equilibrium (mg/g)
q_m	monolayer sorption capacity (mg/g)
T	temperature (K)
V	volume of the solution (L)
W	mass of soil (g)
α	Elovich kinetic model constant (gmg^{-1}h^{-1})
β	Elovich kinetic model constant (g/mg)
N	fractional power kinetic model constant

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