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Adsorption of Zn(II) onto Turkish soil: equilibrium, kinetic and thermodynamic studies

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ABSTRACT

Study on the adsorption of Zn(II) onto soil is important since it relates to the bioavailability, potential toxicity of this metal and improving remediation strategies. In the present study, sorption of Zn onto soil was investigated in batch reactors with a maximum contact time of 180 min. Adsorption tests of Zn(II) were carried out using a solution concentration of 1.22 mM at initial pH = 5 and soil dosage of 1:20. The Langmuir and Freundlich models were applied to describe equilibrium isotherms. Sorption isotherms were well described by the Freundlich equation and Dubinin–Radushkevich (D–R) isotherm model was also applied to the equilibrium data. The mean free energy of adsorption (10.33 kJ mol^{-1}) indicated that the adsorption of Zn(II) onto soil may have been carried out via chemical ion-exchange mechanism. Kinetics of sorption was characterized using Lagergren-first-order, pseudo-second-order and intraparticle diffusion models. The sorption kinetics was well described by pseudo-second-order model within the reaction times in this study. Thermodynamic parameters, free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) of adsorption were also calculated.

Keywords: Soil; Zinc; Adsorption; Isotherm model; Thermodynamics; Kinetics

1. Introduction

The contamination of soils, groundwater and surface water by heavy metals is currently a significant concern throughout the world because these compounds are detrimental to both human life and environment [1–3]. Mining and industrial activities, fertilizers, sewage sludge, and urban waste materials can result in significant input of heavy metals. This can lead to either substantial accumulation, and leaching, potentially polluting surface or subsurface water bodies, or both [4–7].

As metals in the contaminated sites are not degraded, they must be either immobilized or removed [8]. Recently attempts have been made to develop effective and economical methods for remediation of soils polluted with heavy metals. However, these require a better understanding of the mechanisms by which the metals are retained/released in soils [9].

Metal behavior is dependent on a variety of factors including metal speciation, complexation, precipitation, and sorption–desorption reactions. The most important chemical reaction that affects heavy metal availability is sorption onto soil solid phases. The knowledge of this process is important to predict the bioavailability of metals and transport mechanism through soil column into groundwater or surface water [10–13]. Many studies have focused on the sorption of these metals on different soil materials and under different experimental conditions [14–17]. It is reported in the literature that the soil composition, particularly the amount and type of clay minerals and the solution chemistry of soil aqueous phase (i.e., pH, ionic strength, organic and inorganic ligands) have considerable effect on sorption of heavy metals by soils. Heavy metals, such as lead and zinc form surface complexes on layer silicates and oxide minerals in soil through inner- and outer-sphere complexes on silanol, aluminol, iron and manganese hydroxides. Clay minerals and organic matter bind metals both through ion exchange and surface complexation. Finally, various precipitation and coprecipitation reactions may occur, mostly at high equilibruim metal concentrations and at high pH [11].

Several studies have been carried out to examine sorption isotherms for heavy metals by soils and individual soil components [18,19]. Because of the heterogeneity of soils, adsorption isotherms are typically different for different soils and elements. Bingham et al. found that Zn^{2+} can be held in amounts exceeding cation exchange capacity (CEC) of soils because it can be retained as zinc hydroxide [16]. Zinc adsorption has been generally described by the Langmuir and Freundlich adsorption isotherms in various soils. However, there is little or no report on the adsorption reaction of Zn by soil from Eskişehir, Turkey.

The objective of the present work was to assess the sorption of Zn(II) in a soil sample from the Eskişehir region (Turkey). For this purpose, a series of batch test results have been presented and the effects of soil dosage, solution pH, contact time and temperature on the sorption of Zn(II) onto soil were investigated. Well-known isotherm models were applied to the equilibrium data. Kinetic and thermodynamic parameters were also calculated to describe the adsorption mechanism.

2. Materials and methods

2.1. Soil characterization

Soil was obtained from Eskişehir Esentepe region and was ground and sieved to 0.140–0.425 mm size. Soil pH was measured with glass electrode using a 1:2.5 suspension of soil to water ratio. Soil organic matter content was determined by the modified Walkley and Black method [20]. The CEC of soil was determined using 1 M NaOAC at pH 8.2 as a saturating solution and Na^+ was replaced NH_4^+ using 1 M NaOAC at pH 7. Sodium ions were measured by flame photometer [20].

The chemical composition of the soil sample was first identified by X-ray diffraction (XRD) (Table 1). Qualitative X-ray diffraction analysis was performed on the soil using a Rigaku Rint 2200 model powder diffractometer with the $K\alpha$ radiation of Cu. Scans were conducted at a rate of 2θ min^{-1}. Chemical analysis of the soil sample was performed using X-ray fluorescence spectroscopy technique (XRF, Rigaku ZSX Primus model) (Table 1). The soil was ground and then sieved to a particle size of less than 65 μm for XRD and XRF measurements. For XRF measurements, the soil was prepared by fluxing of powder samples with $Li_2B_4O_7$.

Table 1
Physico-chemical properties of the soil and chemical composition of the soil identified by XRD

Soil property		Component	Amount
SiO_2 (%)	47.7	Smectite	Moderate
Al_2O_3 (%)	14.8	Serpentine	Moderate
Fe_2O_3 (%)	12.8	Amphibole	Moderate
CaO (%)	11.9	Quartz	Little
MgO (%)	6.7	Feldspar	Moderate
K_2O (%)	0.7	Feldspar	Moderate
Na_2O (%)	2.0	Calsite	Trace
TiO_2 (%)	3.2	Dolomitic	Trace
MnO (%)	0.2	–	–
pH	8	–	–
OM (%)	0.63	–	–
CEC (cmol kg^{-1})	15.48	–	–
Clay (%)	30	–	–

Result of XRF indicates the presence of silica and alümina, iron and calcium oxides as major constituents along with traces of magnesium, potassium, sodium, titanium and mangan oxides in the form of impurites.

Soil was moderately basic (pH 8). The CEC of the soil was 15.48 cmol kg^{-1}.

2.2. Experimental procedures

A Zn(II) stock solution of 1 g L^{-1} was obtained by dissolving $Zn(NO_3)_2 \cdot 6H_2O$ in distilled water. 10 ml portions of 1.2 mM of metal ion solutions were added to 0.5 g of soil samples. The pH values of the suspensions were adjusted as 5.0 using either 0.1 M NaOH or 0.1 M HNO_3. Control experiments were performed with the same metal ion solutions without added the soils at each pH value. The centrifuge tubes were agitated at 150 rpm for 180 min in a shaker at 25°C. After equilibrium, the concentrations of metals in the aqueous phase were analyzed by a Perkin-Elmer atomic absorption spectrophotometer. Sorbed Zn(II) concentration by the soil was calculated from the difference between initial Zn(II) concentration in solution and Zn(II) concentration remained in the supernatant after sorption. Zn(II) sorption to tube surfaces was not determined.

The effects of soil dosage, pH, initial Zn(II) ion concentration and temperature on Zn(II) removal were studied, respectively. Then, the kinetic study was completed.

3. Results and discussion

3.1. Effect of soil dosage

To determine the effect of soil dosage on the adsorption efficiency of Zn(II) ions, soil dosage was varied between 0.3 and 1.5 g. Soil dosage is an important parameter because it determines the metal-retention capacity of soil at a given initial metal concentration. As shown in Fig. 1, the adsorption efficiency of the Zn(II) increased with increasing soil dosage from 0.3 to 0.5 g, and the adsorption efficiency was almost constant at soil dosages higher than 0.5 g. With increasing soil dosage, more surface area is available for adsorption due to increase in active sites on the soil and thus making easier retention of metal ions onto the sorption sites [21]. Jain [22] showed that percent sorption of Zn(II) on bed sediments increased with increasing of adsorbent dosage. A similar trend was reported by Du and Hayashi [14] for the adsorption of cadmium on Ariake clay.

On the other hand, the adsorbed Zn(II) ion quantity q per unit weight of soil decreased by increasing the soil quantity. This may be attributed to the tendency for soil aggregates to form at higher soil dosage, resulting in a decrease in active adsorption area.

3.2. Effect of pH

To determine the effect of pH on the adsorption efficiency of Zn(II) ions, pH was varied between 3.0 and 7.0. The adsorption efficiency of Zn(II) ions on the soil increased as the pH of Zn(II) ion solutions were increased (Fig. 2). Several reasons may be attributed to the increased adsorption of Zn(II) ions by the soil relative to adsorbate solution pH. A large number of active sites of the soil surface may become positively charged at very low pH, thus increasing the competition between H^+ and the metal ions for available adsorption sites. However, as pH increases, this competition decreases as these surface active sites become more negatively charged, which enhances the adsorption of the positively charged metal ions through electrostatic force of attraction [23].

3.3. Sorption equilibrium of Zn(II) ions onto soil

Langmuir and Freundlich isotherm models were applied to establish the relationship between the amount of Zn(II) ion adsorbed to the soil and the unadsorbed Zn(II) ion concentration in the solution at equilibrium.

The Langmuir adsorption isotherm model assumes that adsorption takes place at specific homogeneous sites within the adsorbent [24] and the Langmuir isotherm is commonly presented as [25,26]:

$$q_e = \frac{q_m K C_e}{1 + K C_e} \tag{1}$$

q_e is the amount of solutes sorbed per unit weight of sorbent at equilibrium concentration, C_e is the solute equilibrium concentration in solution, q_m is the maximum amount of sorbed material required to give a complete monolayer on the surface, and K is a measurement of relative sorption affinity and it is a constant related to the energy of sorption. A large value of the Langmuir constant, K, implies strong bonding.

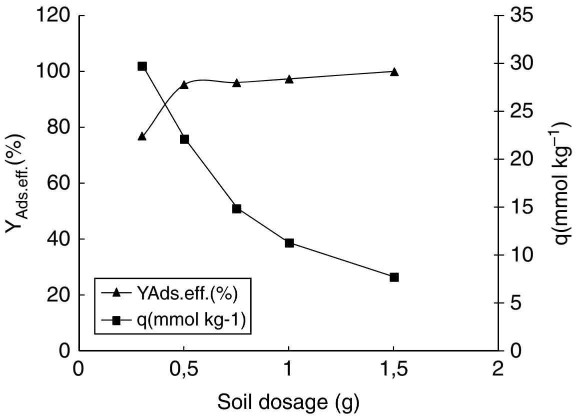

Fig. 1. The effect of soil dosage on Zn(II) sorption efficiencies by soil (C_i, 1.20 mM ; temperature, 25°C; pH, 5; stirring rate, 150 rpm).

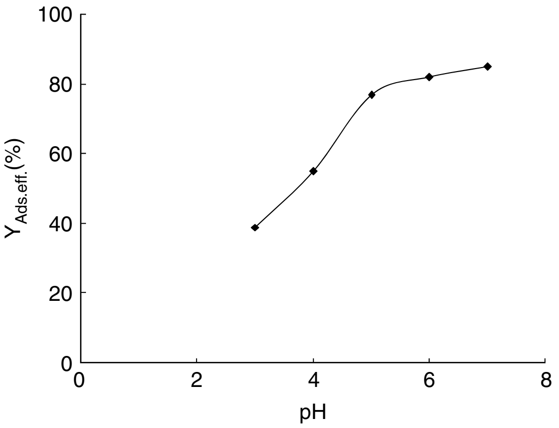

Fig. 2. The effect of pH on Zn(II) sorption efficiencies by soil (C_i, 1.20 mM; temperature, 25°C; amount of soil, 0.3 g; stirring rate, 150 rpm).

Freundlich isotherm is an empirical equation describing adsorption onto a heterogeneous surface [27]:

$$q_e = K_F C_e^{1/n} \tag{2}$$

In this expression, K_F and n are the Freundlich constants related to the adsorption capacity and adsorption intensity of the sorbent, respectively.

To determine the sorption isotherms, initial Zn(II) ion concentrations were varied between 0.70 and 3.77 mmol l^{-1}. At an initial Zn(II) ion concentration of 0.70 mmol l^{-1}, 100% of the Zn(II) was bound to the soil. The sorption efficiencies of Zn(II) decreased slightly with increasing initial Zn(II) concentration. The obtained adsorption efficiency was 90% even at high initial Zn(II) concentration of 3.77 mmol l^{-1} (Fig. 3).

The Langmuir and Freundlich sorption isotherms obtained at pH 5 for Zn(II) ions are shown in Fig. 4. The coefficients of multiple determination (R^2) between the experimental values and the predicted values using the models were found as 0.9686 and 0.9889 for Langmuir and Freundlich isotherm models, respectively. The R^2 values for both the Langmuir and Freundlich isotherm models were above 0.95, suggesting that both models closely fit the experimental results. However, the R^2 values indicate that the Freundlich isotherm fit the experimental data better than the Langmuir isotherm.

As the value of Freundlich sorption constant, n (1.78), was found to be higher than one, this value indicates the favourable sorption. n is a constant representing the mutual interaction of sorbed species. Experimental values of n are usually greater than unity and this means that the forces between the sorbed molecules are repulsive. In addition, the closer the n value of the Freundlich sorption equation is the zero, the more heterogeneous is the system [8]. Freundlich adsorption capacity, KF, was found to be 39.06 mmol^{-n} l^{n}.

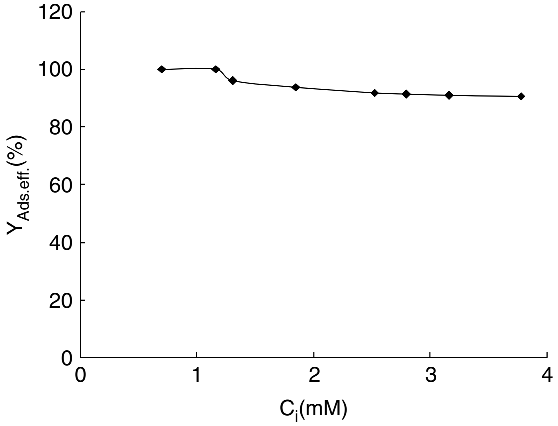

Fig. 3. The effect of initial Zn(II) concentration on Zn(II) sorption efficiencies by soil (pH, 5.0; temperature, 25°C; amount of soil, 0.5 g; stirring rate, 150 rpm).

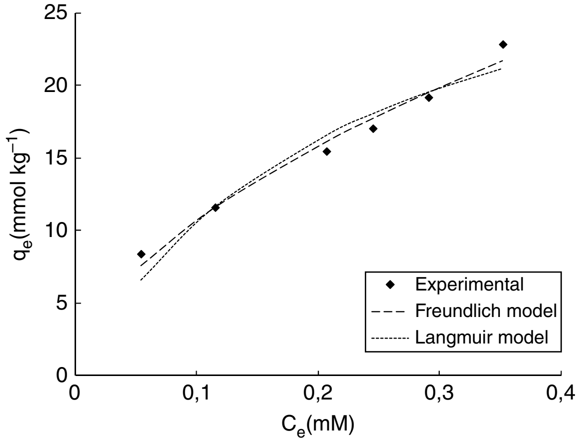

Fig. 4. Comparison of the Langmuir and Freundlich sorption isotherms for Zn(II) sorption onto soil at 25°C.

The Langmuir adsorption maxima, q_m, was found as 34.97 mmol kg^{-1}. The Langmuir equilibrium constant, K, had value of 4.368 L mmol^{-1}. Table 2 presents a comparison of the sorption capacities of the different soils [3,28]. It can be seen from the table that studied soil shows the comparable sorption capacity with respect to the other soils, revealing that it has high sorption capacity. The most important parameters controlling heavy metal adsorption and their distribution between soil and water are soil type, metal speciation, metal concentration, soil pH, solid: solution mass ratio, and contact time. In general, greater metal retention and lower solubility occurs at high soil pH. Also, the soil type and composition plays an important role for heavy metal retention. Soil organic matter exhibits a large number and variety of functional groups and high CEC values, which results in enhanced heavy metal retention ability mostly by surface complexation, ion exchange, and surface precipitation [29]. The higher CEC indicates a higher negative charge of the clay fraction and, hence, a higher heavy metal sorption capacity [23,30].

Clays are known for their ability to effectively remove heavy metals by specific adsorption and cation exchange as well as metal oxyhydroxides. Clay minerals have different adsorption capacities for metal ions depending on the conditions at which the adsorption reactions were carried out [23]. The sorption capacities of clay minerals are reported to decrease in the order of smectites > chlorites > illites > kaolins. Because soil used in this study contains smectite as clay mineral it has high metal sorption capacity [3,8]. Smectite, which is a clay, is a promising material for a large number of applications. This is due to its specific properties that is cation exchange and

Table 2
Maximum adsorption capacities of different soils for Zn(II) sorption

	q_m (mmol kg^{-1})	CEC (cmol kg^{-1})	OM (%)	pH	Kaolinite (%)	Smectite (%)	Feldspars (%)	Quartz (%)	Granite (%)	Amphibolite (%)
Studied soil	34.97	15.48	0.63	8.00	–	Moderate	Moderate	Little	–	Moderate
Soil 1 [3]	11.69	61.53	0.21	8.28	16.07	75.00	–	1.79	–	–
Soil 2 [3]	10.48	73.10	0.30	8.10	25.42	66.10	–	1.49	–	–
Soil 3 [3]	6.11	30.04	0.24	8.23	4.55	–	–	3.85	–	–
Soil 4 [3]	10.25	62.78	0.46	7.79	58.86	28.42	–	5.22	–	–
Soil 5 [3]	5.63	26.91	0.72	7.42	15.22	23.91	10.87	2.17	–	–
Soil 6 [3]	8.33	50.40	0.75	7.42	33.03	47.71	1.83	0.92	–	–
Soil 7 [28]	8.64	4.40	3.00	4.4	–	–	–	–	100	–
Soil 8 [28]	11.5	4.10	3.20	5.2	–	–	–	–	–	100

surface complexation on amphoteric edge sites used to describe the uptake of aqueous metal species [31].

The sorption data were also modeled by Dubinin–Radushkevich (D–R) isotherm to determine the adsorption type (physical or chemical). The linear form of this model is expressed by:

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \tag{3}$$

where q_e is the amount of the metal adsorbed onto per unit dosage of the soil (mol g^{-1}), q_m the monolayer capacity (mol g^{-1}), C_e is the equilibrium concentration (mol l^{-1}), and β is the activity coefficient related to mean sorption energy (mol^2 J^{-2}). ε is the Polanyi potential described as:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{4}$$

The mean sorption energy, E (kJ mol^{-1}), can be calculated by Eq. (5):

$$E = \frac{1}{\sqrt{-2\beta}} \tag{5}$$

The value of mean sorption energy, E, gives information about chemical and physical sorption. As seen in Fig. 5, the slope of ln q_e versus ε^2 gives β constant (slope gradient) and the q_m value (y-axis intercept). The β constant and the q_m value were found to be 9.37×10^{-9} mol^2 J^{-2} and 129 mmol kg^{-1}, respectively. The mean free energy of adsorption, E, gives information about adsorption mechanism whether it was chemical ion-exchange or physical adsorption. If E value is between 8 and 16 kJ mol^{-1}, the adsorption process is chemical ion-exchange, and if $E < 8$ kJ mol^{-1}, the adsorption is physical in nature. From Eq. (5) the value of E was calculated as 10.33 kJ mol^{-1} indicating that the adsorption may be carried out via chemical ion-exchange mechanism [22].

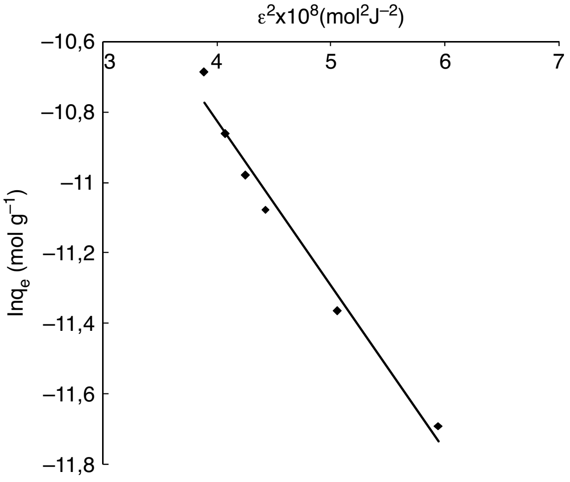

Fig. 5. Dubinin–Radushkevich (D–R) plot for the adsorption of Zn(II) ions onto soil at 25°C.

3.4. Effect of temperature and thermodynamics of adsorption

An adsorption efficiency of 100% was obtained when 0.5 g soil was used at all temperatures. Thus, to investigate the effect of temperature on the adsorption of Zn(II) onto soil, 0.3 g soil dosage was used and the distribution coefficient, K_d (L g^{-1}), was calculated at the temperatures of 298, 308, 318 and 328 K by using Eq. (6) [32]:

$$K_d = \frac{q_e}{C_e} \tag{6}$$

Adsorption efficiencies and the K_d values calculated for the adsorption of Zn(II) on the soil are given in Table 3. As seen from the results, the K_d value and adsorption efficiency increased with increasing temperature (from 298 to 328 K) revealing that the adsorption of Zn(II) onto soil to be endothermic.

The thermodynamic parameters, the change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) for the adsorption of Zn(II) to soil are calculated using the following equations (Table 3):

$$\Delta G^\circ = -RT \ln K_d \tag{7}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{8}$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{9}$$

The values of ΔH° and ΔS° were determined from the slope and the intercept of the linear plot of lnK_d versus $1/T$ [33]. The ΔH° parameter obtained from the ln$K$ versus $1/T$ plot (Fig. 6) had a value of 56.54 kJ mol^{-1} and the ΔS° parameter was found to be 170.95 J mol^{-1} K^{-1}.

Table 3
Thermodynamic parameters calculated for the adsorption of Zn(II) ions onto soil at various temperatures

T(K)	K_d (L g^{-1})	$Y_{\text{Ads.eff.}}$ (%)	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})
298	0.106	76.19	5.59	–	–
308	0.208	86.21	3.88	–	–
–	–	–	–	56.54	170.95
318	0.459	93.23	2.17	–	–
328	0.833	96.15	0.46	–	–

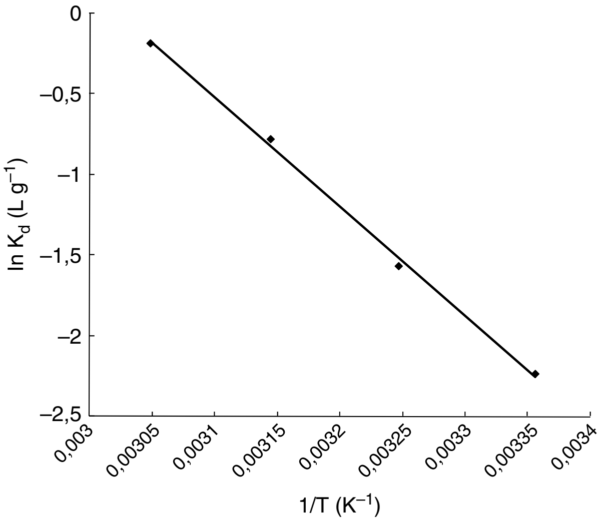

Fig. 6. Plot of ln K_d versus $1/T$ for the estimating of thermodynamic parameters for the adsorption of Zn(II) ions onto soil (pH, 5.0; amount of soil, 0.3 g; stirring rate, 150 rpm).

The enthalpy of the adsorption $\Delta H°$ is a measure of the energy barrier that must be overcome by reacting molecules. The positive value of the enthalpy suggests that the adsorption of Zn(II) onto soil are endothermic in nature meaning that increasing temperature will favour the adsorption Zn(II) onto soil [23] and the large $\Delta H°$ value indicates that there are strong interactions between the metal ions and the functional group (Si–O–) on the surface of soil [24,34].

From Eq. (7), Gibbs free energy change of adsorption ($\Delta G°$) was calculated using ln K values at different temperatures. It was found as +5.59, +3.88, +2.17, and +0.46 kJ mol^{-1} for the adsorption of Zn(II) onto soil at 298, 308, 318, and 328 K, respectively. $\Delta G°$ values obtained was positive which suggests that the adsorption of Zn(II) onto soil require some small amount of energy for adsorption. This is further supported by the positive $\Delta H°$ value obtained for the adsorption of Zn(II) onto soil. This may not suggest that the adsorption of Zn(II) onto soil is non spontaneous, rather it could indicate that soil may show better performance in the adsorption of Zn(II) in the higher temperature. This indicates the presence of an energy barrier in the adsorption process. In addition, the adsorption occured was chemical because $\Delta G°$ values were higher than –20.0 kJ mol^{-1}. This result was in well agreement with that obtained from the D–R isotherm [23,32].

The positive entropy change value corresponds to an increase in randomness at the solid–liquid interface and significant changes possibly occur in the internal structure of the soil through the adsorption of Zn(II) on soil [24].

3.5. Effects of contact time and kinetics of adsorption

Sorption of Zn(II) onto soil was measured in the times 2, 5, 15, 30, 45, 60, 90, 120, 150, 180, 240, 300, 420 min to determine the effect of contact time. The adsorption of Zn(II) onto soil abruptly increased up to 15 min (93%). However, the removal increased from 15 to 180 min at a slower rate and the removal was constant after 180 min (98%) (Fig. 7). It can be seen that it took about 15 min for Zn(II) to reach the equilibrium conditions. But, the 180 min of contact time, is need to reach a satisfactory equilibruim. Therefore, for the following batch tests which focused on investigating the influence of initial Zn(II) ion concentration, pH, soil dosage and temperature, contact time was set as 180 min.

In order to find out the mechanism involved in the sorption process, three kinds of kinetic models were used to test the experimental data. These are Lagergren-first-order, pseudo-second-order and intraparticle diffusion models. Among them the Lagergren-first-order rate equation is the most popular kinetic equation. The form is:

$$\frac{dq}{dt} = k_1\left(q_e - q_t\right) \tag{10}$$

After definite integration by applying the conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, Eq. (10) becomes:

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \tag{11}$$

where q_t (mmol kg^{-1}) is the amount of Zn(II) adsorbed in time t (min); k_1 is the rate constant of the equation (min^{-1}) and q_e is the amount of Zn(II) adsorbed

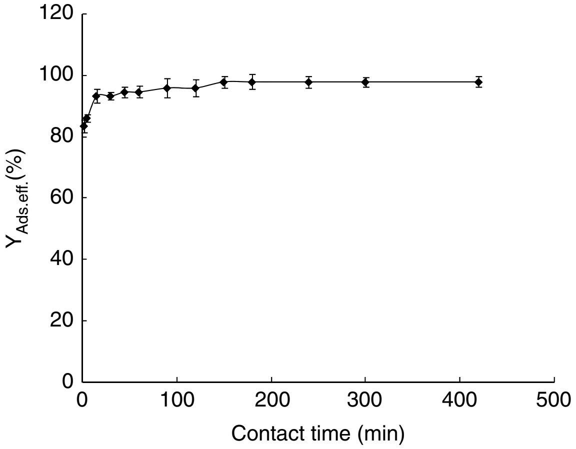

Fig. 7. The effect of contact time for the adsorption of Zn(II) ions onto soil (C_i, 1.2 mM; pH, 5.0; temperature, 25°C; amount of soil, 5 g; stirring rate, 150 rpm).

at equilibrium (mmol kg^{-1}). The adsorption rate constant k_1 can be determined experimentally by plotting ln ($q_e - q_t$) versus t.

Pseudo-second-order equation is in the following form:

$$\frac{dq}{dt} = k_2 \left(q_e - q_t \right)^2 \tag{12}$$

After definite integration by applying the conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, Eq. (12) becomes:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{13}$$

where k_2 (kg mmol^{-1} min^{-1}) is the rate constant of the second-order equation; q_t (mmol kg^{-1}), the amount of Zn(II) adsorbed in time t (min) and q_e is the amount of Zn(II) adsorbed at equilibrium (mmol kg^{-1}), values of k_2 and q_e can be calculated from the plot of t/q_t against t.

The Lagergren- first-order and pseudo-second-order models cannot identify the diffusion mechanism. For this reason, the kinetic results were then subjected to analyze by the intraparticle diffusion model. The intraparticle diffusion equation can be written as follows [25]:

$$q_t = k_{id} t^{1/2} + C \tag{14}$$

where q_t (mmol kg^{-1}), is the amount of Zn(II) adsorbed in time t (min) and k_{id} (mmol kg^{-1} min$^{-1/2}$) is the rate constant of intraparticle diffusion. If the plots of q_t versus $t^{1/2}$ yield straight lines passing through the origin, intraparticle diffusion is likely to control the kinetics of the adsorption process. The slope gives the rate constant k_{id}.

The plots of linear form of the Lagergren-first-order, pseudo-second-order and intraparticle diffusion models for the adsorption of zinc(II) ions were obtained at the temperature of 25°C (not showed). The kinetic parameters for the adsorption of Zn(II) ions onto soil are summarized in Table 4. The zinc adsorption data from the soil were successfully described by Lagergren-first-order and pseudo-second-order kinetic models according to the significant R^2 values presented in Table 4. However, the most excellent fit was found between experimental data and pseudo-second-order kinetic model. The correlation coefficient obtained were very high (0.9999) for the pseudo-second-order model. This result imply that the adsorption fits the pseudo-second-order kinetic model at all time intervals and also the rate-limiting step of this sorption system may be chemical sorption [35]. This result was in well agreement with that obtained from the D–R isotherm.

Whether the process of adsorption is controlled by intraparticle diffusion was tested by plotting q_t versus $t^{1/2}$ as in Eq. (14). The plot was linear with regression coefficient of 0.97 upto 45 min. This value indicates substantial diffusion of Zn(II) ions into the intraparticle of the soil up to 45 min. However, the plot does not pass through the origin. Therefore, although intraparticle diffusion might have considerable influence on the adsorption process, it may not be the controlling factor in determining the kinetics of the process [33].

Table 4
Kinetic parameters for the adsorption of Zn(II) ions onto soil at 25°C

k_1 (min^{-1})	q_e (mmol kg^{-1})	R^2
Lagergren-first-order		
0.0226	1.426	0.9202
k_2 (kg mmol^{-1} min^{-1})	q_e (mmol kg^{-1})	R^2
Pseudo-second-order		
0.1037	11.223	0.9999
k_{id} (mmol kg^{-1} min$^{-1/2}$)	C (mmol kg^{-1})	R^2
Intraparticle diffusion		
0.2518	9.397	0.9741

4. Conclusions

The adsorption process of Zn(II) onto soil is important to predict the bioavailability of metals and transport mechanism through soil column into groundwater or surface water. For this purpose, the sorption characteristics of Zn(II) onto typical urban soil material from Eskişehir region of Turkey were investigated in this study. In order to reach maximum adsorption efficiency, the adsorbent dosage and contact time was selected as 0.5 g and 180 min, respectively, as the optimal operating parameters.

The sorption efficiency of Zn(II) to the soil varied between 100% and 90% with increasing concentrations of Zn(II) ions in the range of 0.7–3.77 mM. It was concluded that smectite is the most important soil constituent exerting the greatest effect on Zn(II) sorption. Smectites appear to be good indicators for predicting heavy metal adsorption. The presence of smectites as dominant clays may ensure a high metal sorption capacity that is an important factor regulating the sorption of heavy metals by soils. This situation may not pose groundwater problems because Zn(II) has strong affinity to soil. Sorption of Zn(II) to the soil was nonlinear, and the soil-Zn(II) isotherms fitted well by the Freundlich model, (n-value > 1, showing favorable sorption). The higher Zn(II) sorption capacity, K_F (39.06 mmol^{-n} l^n), and intensity, n (1.78), were obtained for the soil.

The mean free energy of adsorption E (10.33 kJ mol^{-1}) calculated from examination of D–R isotherm indicated that the adsorption of Zn(II) onto soil may be carried out via chemical ion-exchange mechanism. The positive value of the enthalpy change indicates that the adsorption is endothermic. $\Delta G°$ values obtained was positive which suggests that the adsorption of Zn(II) onto soil require some small amount of energy for adsorption. The positive entropy change value corresponds to an increase in randomness at the solid–liquid interface and significant changes probably occur in the internal structure of the soil through the adsorption of Zn(II) on the soil.

By applying the kinetic models to the experimental data, it was found that the adsorption of Zn(II) onto soil follows the pseudo-second-order rate kinetics.

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