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Adsorption of copper and zinc from aqueous solutions by using natural clay

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Abstract

In this study, removal of copper (Cu^{2+}) and zinc (Zn^{2+}) from aqueous solutions is investigated using Cankırı bentonite, a natural clay. During the removal process, batch technique is used, and the effects of pH, clay amount, heavy metal concentration and agitation time on adsorption efficiency are studied. Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherms are applied in order to determine the efficiency of natural clay used as an adsorbent. Results show that all isotherms are linear. It is determined that adsorption of Cu^{2+} and Zn^{2+} is well-fitted by the second order reaction kinetic. In addition, calculated and experimental heavy metal amounts adsorbed by the unit clay mass are too close to each other. It is concluded that natural clay can be used as an effective adsorbent for removing Cu^{2+} and Zn^{2+} from aqueous solutions.

Keywords: Natural clay; Copper; Zinc; Freundlich isotherm; Langmuir isotherm; D–R isotherm; Reaction kinetic

1. Introduction

Industrial wastewaters generated from industrialization activities may contain various toxic heavy metals. The heavy metals, apart from being hazardous for living organisms when exceed the specific limits, have accumulating characteristics in nature as they cannot be biodegraded.

Main industries containing heavy metals in discharged waters are mining, metal coating and battery production [1]. [Cu^{2+}] and [Zn^{2+}] are among the most common heavy metals in these wastewaters. While the accumulation of Cu^{2+} in human body causes brain, skin, pancreas and heart diseases, Zn^{2+} being in the list of priority pollutants proposed by Environmental Protection Agency (EPA) gives rise to serious poisoning cases. The main symptoms of zinc poisoning are dehydration, electrolyte imbalance, stomachache, nausea, dizziness and incoordination in muscles [2].

The heavy metals, having hazardous effects on health, can be treated from wastewater by using various physicochemical methods [3]. Adsorption, ion exchange, chemical settling and reverse osmosis are the most frequently preferred methods. Among them, adsorption receives considerable interest with the high efficiency in heavy metal removal. Although there are many adsorbents used in adsorption methods, active carbon is the most common one used in wastewater treatment all over the world [4]. However, its high cost causes restrictions in use [5]. For this reason, many studies have been carried out in order to find out effective and low cost adsorbents. Different adsorbents are used in copper and zinc removal such as chitosan [6], eutrophic and oligotrofic marsh peat [7] and agricultural wastes like wheat shell [8] and cacao shell [9]. Natural clay is evaluated as an appropriate adsorbent due its low cost and high removal efficiency. Their sorption capabilities come from their high surface area and exchange capacities. The negative charge on the structure of clay minerals gives the capability to attract metal ions [5].

Montmorillonite and kaolinite were used for removal of lead and cadmium [10]. It was determined that adsorption capacity of lead and cadmium is greater on montmorillonite (Pb: 0.68, Cd: 0.72 mg/g) than on kaolinite (Pb:0.12, Cd:0.32 mg/g). In another study, removal efficiency of 52.91 mg/g was obtained for zinc removal using bentonite, another type of clay [11].

The adsorption of Cd^{2+} and Zn^{2+} ions on montmorillonite was also evaluated [12]. Since the ionic potential of zinc is higher than cadmium, its hold is stronger on montmorillonite than cadmium.

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Nomenclature

C_e	equilibrium concentration of solution
C_o	initial heavy metal concentration
C_1	integration constant of pseudo-first-order reaction kinetic
C_2	integration constant of pseudo-second order reaction kinetic
E	main energy of adsorption
k	equilibrium constant of Langmuir isotherm
k_1	rate constant of pseudo-first-order adsorption kinetic
k_2	rate constant of pseudo-second-order adsorption kinetic
K_f	Freundlich isotherm constant
K'	adsorption energy constant
m	clay mass
n	adsorption intensity
R	gas constant
r^2	correlation coefficients
t	time
T'	temperature
V	solution volume
V_m	monolayer capacity for Langmuir isotherm
V'_m	D–R adsorption capacity
q_e	amount of adsorbed heavy metal per unit clay mass
$q_{e,\text{experimental}}$	experimental value for amount of adsorbed heavy metal per unit clay mass
$q_{e,\text{calculated}}$	calculated value for amount of adsorbed heavy metal per unit clay mass
q_t	amount of heavy metal adsorbed at time t
ε	Polanyi potential

Chantawong et al., studied adsorption of lead on clay consisting mainly kaolin and illite [13]. In the study, it is confirmed that the adsorption efficiency increases with increase in pH. Nevertheless, presence of co-ions such as Cd^{2+}, Cr^{6+}, Cu^{2+}, Ni^{2+} and Zn^{2+} reduces the lead uptake from aqueous solutions due to the fact that the co-ions bind strongly with organic matter present in clay to form a complex.

Bentonite, consisting of clay, silt and sand, was also used in zinc removal [11]. The sorption process usually follows the Langmuir isotherm. In another study, it was reported that adsorption capacities of 20 mg of Pb^{2+}/g were achieved by bentonite at pH 3.4 [14].

Besides providing high removal efficiency in heavy metal removal from waste streams, clay is an appropriate adsorbent with its low cost. Among the main factors of choosing adsorbent in wastewater treatment, the cost and the availability come after the efficiency. Clay is a natural substance widely available and abundant in Turkey. In this study, Cankırı bentonite was used for removing copper and zinc from aqueous solutions. The effects of pH, clay amount, metal concentration and contact time on adsorption efficiency were analyzed, and the optimum values were determined from the experimental studies. In order to determine the reaction of heavy metals with Cankırı bentonite, experimental results were applied to Langmuir, Freundlich and Dubinin–Radushkevich adsorption isotherms and isotherm constants were obtained. Adsorption kinetics were applied in order to determine adsorption mechanism and adsorption characteristic constants. With this purpose, first and second order reaction kinetics were calculated.

2. Materials and methods

2.1. Instrumentation

Copper and zinc analyses were carried out using a HACH DR 2000 model spectrophotometer. Bicinnchoninate Method (Method No. 8506) and Zinc Zincan Metod (Method No. 8009) were followed for copper and zinc analyses, respectively. NUVE model shaker was used in all adsorption experiments and pH adjustments were performed in TESTO model pH-meter.

2.2. Chemicals

Copper(II) nitrate trihydrate ($CuN_2O_6 \cdot 3H_2O$) and zinc sulphate heptahydrate ($ZnSO_4 \cdot 7H_2O$) were used in adsorption experiments. pH adjustments were carried on using 0.1N hydrochloric acid (HCl) and 0.1N sodium hydroxide (NaOH). The chemicals used in copper and zinc analyses were supplied from SESA Electronic Industry and Trade Corporation.

2.3. Adsorbent

Cankırı bentonite was used as the adsorbent. The chemical composition of Cankırı bentonite is provided in Table 1. The structure of the clay is given as $(Si_{7.156}\ Al_{0.844})\ O_{20}\ (Al_{1.356}\ 9Fe_{0.460}Mg_{0.4265}Ti_{0.0609})\ [Ca_{0.4806}\ K_{0.2975}\ Na_{0.379}](OH)_4$.

2.4. General procedure

Adsorption of copper and zinc with clay was carried out in a batch reactor. 1000 mg/L of copper stock solution was prepared by dissolving 3.8 g of $Cu(NO_3)_2 \cdot 3H_2O$ in 1 L distilled water, and 1000 mg/L of zinc stock solution was prepared by dissolving 4.397 g of $ZnSO_4 \cdot 7H_2O$ in 1 L distilled water. Standard copper and zinc solutions ranging between 20 and 160 mg/L were prepared by diluting the stock solutions. The volume of the

Table 1
Chemical composition of Cankırı bentonite (%)

Compound	Amount (%)
SiO_2	63.55
Al_2O_3	16.55
Fe_2O_3	5.45
CaO	1.74
MgO	2.53
Na_2O	2.00
K_2O	0.89
TiO_2	0.72

samples was determined to be 100 mL. pH adjustments were carried out using 0.1N HCl and 0.1N NaOH. 200 rpm stirring rate and 23 °C temperature were applied in the shaker. Samples with clay content in the range of 0.1–0.9 g were taken from the shaker at regular contact time intervals and the clay was separated by filtering. The concentration of copper and zinc remained in the solution was analyzed by spectrophotometer. In the study, the effects of several factors such as pH, concentration of solution, clay mass and contact time on copper and zinc removal efficiency were examined.

2.5. *Adsorption models*

Equilibrium isotherms for copper and zinc were obtained by performing batch adsorption studies. Solutions of 100 mg/L concentration were adjusted to optimum pH values and clay amounts ranging between 0.1 and 0.9 g were added to solutions.

The adsorbed heavy metal amount (q_e) per unit absorbent mass was calculated as follows:

$$q_e = \frac{(C_o - C_e)V}{m} \tag{1}$$

where C_o is the initial heavy metal concentration, C_e is the concentration of heavy metal at equilibrium (mg/L), m is the clay mass (mg) and V is the solution volume (L).

Calculations were made by using these data and adsorption curves were obtained.

2.6. *Kinetic studies*

Kinetic studies for copper and zinc were performed by using different concentrations (20,100,160 mg/L). Optimum conditions were used during these experiments. pH was adjusted to 7, 8 and clay mass was 0.4 and 0.5 g for copper and zinc. The method followed during experimental study is given in Section 2.4.

3. Results and discussion

3.1. *Effect of pH*

In order to investigate the effect of pH on copper and zinc adsorption with Cankırı bentonite, metal solutions of 100 mL in volume and 100 mg/L in concentration were used at pH ranging from 2 to 10. In the experiments, clay content was kept constant (0.5 g) and agitation time was determined to be 2 h at 200 rpm. The results are shown in Fig. 1.

The highest removal efficiency in the copper and zinc adsorption with natural clay was obtained at pH > 6. At lower pH values, the adsorption efficiency was decreased. The effect of pH changes due to the adsorbent type, its behavior in the solution and the type of ions adsorbed [15]. In this study, the optimum pH values for the copper and zinc removal were determined as 7 and 8, respectively.

The main mechanisms influencing the adsorption characteristics of bentonites can be explained by dissolution, ion exchange/adsorption, and precipitation [16]. Exchangeable cations present in the bentonite structure are exchanged for Cu^{2+} and Zn^{2+} cations in the aqueous solutions. In high pH level hydroxyl complexes of copper and zinc form such as $Cu_2(OH)_2^{2+}$, $Cu_3(OH)_4^{2+}$, $CuOH^+$, Cu_2OH^{3+}, $Cu(OH)_2$ and $ZnOH^+$, $Zn(OH)_2$. Optimum removal efficiency for zinc is achieved at pH > 7 levels. At higher pHs zinc hydroxyl species may participate in the adsorption and precipitate onto bentonite structure. As a result zinc hydroxyls are less than copper in aqueous media [17].

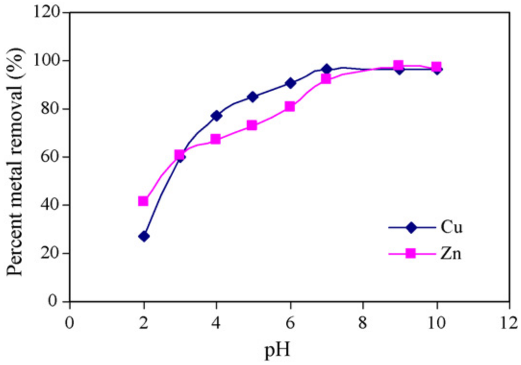

Fig. 1. Effect of pH on the removal of Cu^{2+} and Zn^{2+} by Cankırı bentonite. Initial metal concentrations 100 mg/L, clay dosage 0.5 g/100 mL, contact time 2 h.

Optimum pH values were used in the further experiments analyzing the effects of other factors such as the amount of clay, the metal concentration and the agitation time.

3.2. *Effect of clay dosage*

In experimental studies carried on in order to determine the optimum clay dosage, solutions with an initial metal concentration of 100 mg/L were used at optimum pH values. During the contact time of 2 h, the amount of clay added to the solutions varied between 0.1 and 0.9 g. The results are shown in Fig. 2.

In the copper and zinc removal, it is seen that the adsorption efficiency increases as the clay amount increases. The increase in the efficiency can be explained by the increasing surface area where the adsorption takes place. As seen in Fig. 2, optimum clay dosages that can be used in copper and zinc removal are 0.4 and

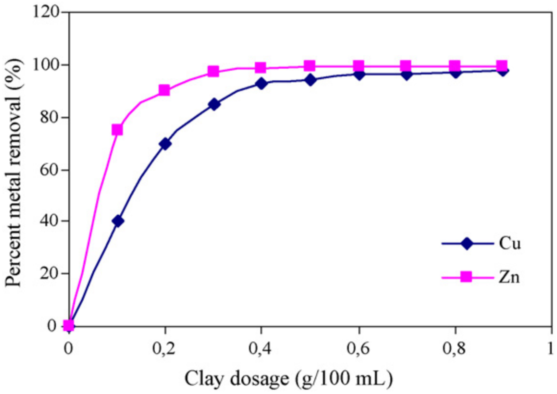

Fig. 2. Effect of clay dosage on the removal of Cu^{2+} and Zn^{2+} by Cankırı bentonite. Initial metal concentrations 100 mg/L, pH 7 and 8, contact time 2 h.

Table 2
Absolute experimental capacities for copper and zinc

Amount of clay (g)	$q_{\mathrm{e,experimental}}$ (mg/g)	
	Cu^{2+}	Zn^{2+}
0.1	40	75
0.2	35	45
0.3	28.33	32.36
0.4	23.25	24.55
0.5	18.8	19.8
0.6	15.94	16.5
0.7	13.78	14.17
0.8	12.10	12.40
0.9	10.83	11.02

0.5 g/100 mL, respectively. Absolute experimental capacities for copper and zinc are given in Table 2. Further experiments were carried on by using these selected values.

3.3. Effect of metal concentration

Optimum concentrations were determined after experimental studies done under various metal concentrations ranging between 20 and 160 mg/L. The adsorption efficiency increased to a certain level, and remained stable as the concentration increased. Following the saturation on the surface where the adsorption takes place, no more metal ions can be adsorbed. The optimum metal concentration was determined as 100 mg/L. The results obtained from the experimental studies are shown in Fig. 3.

3.4. Effect of agitation time

The agitation time was also evaluated as one of the most important factors affecting the adsorption efficiency. By using the previously determined optimum values of pH, clay mass and metal concentration, the effect of time on removal efficiency was analyzed. At the study carried out in a batch system, samples were taken at different time periods varying between 3 and 150 min, and the remaining concentrations were analyzed by the spectrophotometer.

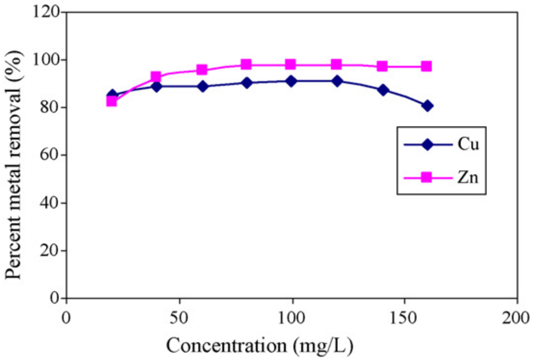

Fig. 3. Effect of metal concentration on the removal of Cu^{2+} and Zn^{2+} by Cankırı bentonite. Clay dosage 0.4 g/100 mL and 0.5 g/100 mL, pH 7 and 8, contact time 2 h.

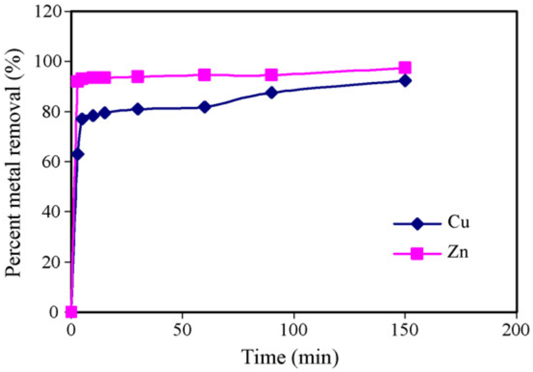

Fig. 4. Effect of contact time on the removal of Cu^{2+} and Zn^{2+} by Cankırı bentonite. Initial metal concentration 100 mg/L, clay dosage 0.4 g/100 mL and 0.5 g/100 mL, pH 7 and 8.

The optimum time for copper and zinc removal were determined at 10 and 5 min, respectively (Fig. 4). As a result of the experimental studies, it is seen that high efficiency for copper and zinc adsorption can be obtained at short time periods.

3.5. Adsorption isotherms

3.5.1. Langmuir isotherm

Langmuir isotherm models the single coating layer on adsorption surface. This model supposes that the adsorption takes place at a specific adsorption surface. The attraction between molecules decreases as getting further from the adsorption surface [18]. Langmuir isotherm can be defined according to the following formulas:

$$q_e = \frac{V_m k C_e}{1 + kC_e} \quad (2)$$

where q_e is the amount of adsorbed heavy metal per unit clay mass (mg/g), V_m is the monolayer capacity, k is the equilibrium constant and C_e is the equilibrium concentration of the solution (mg/L).

Eq. (2) can be written in the following linear form:

$$\frac{C_e}{q_e} = \frac{1}{kV_m} + \frac{C_e}{V_m} \quad (3)$$

The results obtained from the empirical studies were applied to Langmuir isotherm. The dependence of C_e/q_e from C_e was obtained by using empirical results (Fig. 5a).

The linear form of Langmuir equation for copper and zinc adsorption on clay is given by the following expressions:

$$\frac{C_e}{q_e} = 0.1732 + 0.0223C_e \quad r^2 = 0.99 \quad Cu^{2+} \quad (4)$$

$$\frac{C_e}{q_e} = 0.045 + 0.0124C_e \quad r^2 = 0.93 \quad Zn^{2+} \quad (5)$$

3.5.2. Freundlich isotherm

Freundlich isotherm is used for modeling the adsorption on heterogeneous surfaces. This isotherm can be explained by the

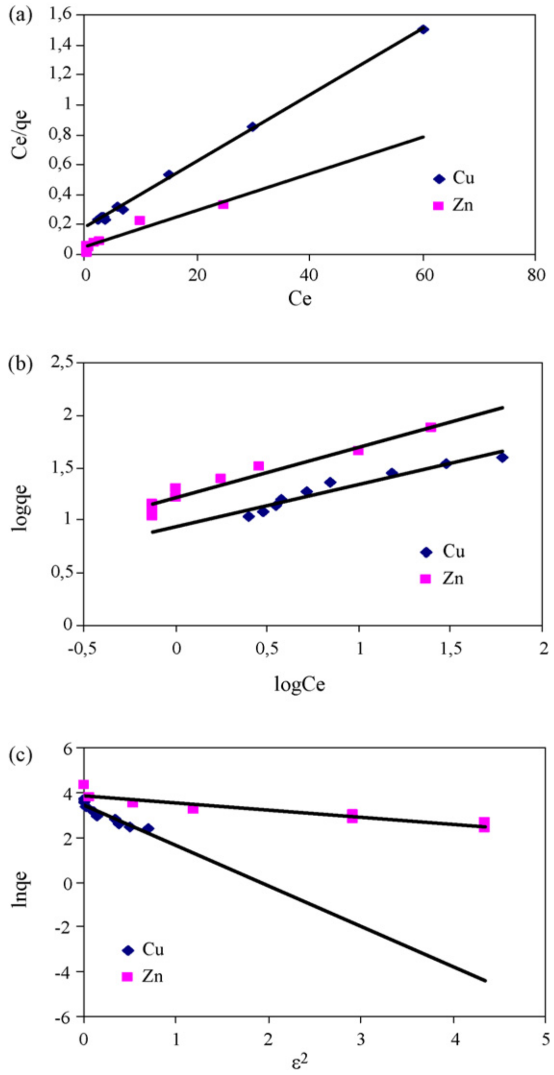

Fig. 5. Langmuir (a), Freundlich (b), and D–R (c) adsorption models for interactions of Cu^{2+} and Zn^{2+} on Cankırı bentonite.

following equation:

$$q_e = K_f {C_e}^{1/n} \tag{6}$$

where K_f is the Freundlich constant (mg/g) and $1/n$ is the adsorption intensity:

The linear form of the Eq. (6) can be written as:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{7}$$

Fig. 5b shows the dependence of $\log q_e$ from $\log C_e$.

It is seen that the Freundlich isotherm curves are linear both in copper and zinc adsorption. The Freundlich constant K_f and adsorption intensity $1/n$ for copper and zinc are calculated from the slopes of these curves (Table 3).

The linear form of the Freundlich isotherm is given with the following formulas for both heavy metals:

$$q_e = 8.71 C_e^{0.406} \quad r^2 = 0.95 \quad Cu^{2+} \tag{8}$$

$$q_e = 16.22 {C_e}^{0.487} \quad r^2 = 0.93 \quad Zn^{2+} \tag{9}$$

3.5.3. Dubinin–Radushkevich (D–R) isotherm

Langmuir and Freundlich isotherms are insufficient to explain the physical and chemical characteristics of adsorption. D–R isotherm is commonly used to describe the sorption isotherms of single solute systems. In previous studies, D–R isotherm was used to express the adsorption processes of bentonite. [19]. The D–R isotherm, apart from being analogue of Langmuir isotherm, is more general than Langmuir isotherm as it rejects the homogeneous surface or constant adsorption potential [20].

The D–R isotherm is expressed as:

$$\ln q_e = \ln V'_m - K' \varepsilon^2 \tag{10}$$

where q_e is the heavy metal amount (mg/g) that is removed per unit clay mass, V'_m is the D–R adsorption capacity (mg/g), K' is the constant related with adsorption energy ($mol^2 k/J^2$), and ε is the Polanyi potential.

According to the Eq. (10), the Polanyi potential (ε) can be given as:

$$\varepsilon = RT' \ln\left(1 + \frac{1}{C_e}\right) \tag{11}$$

where R is the gas constant ($kJ\,K^{-1}\,mol^{-1}$) and T' is the temperature (K).

The main energy of adsorption (E) is calculated by using the following formula:

$$E = (-2K')^{-0,5} \tag{12}$$

where E gives information about the physical and chemical features of adsorption.

The D–R isotherm is applied to the data obtained from the empirical studies. A plot of $\ln q_e$ against ε^2 is given in Fig. 5c.

As it is seen in Fig. 5c, the D–R plot yields a straight line. In the D–R isotherm, adsorption capacities (V'_m), adsorption energy constants (K') and the main adsorption energies (E) are calculated for copper and zinc removal.

All of the isotherm model parameters for the adsorption of copper and zinc are provided in Table 3. As seen from Table 3 in

Table 3
Langmuir, Freundlich and D–R isotherm parameters

Langmuir isotherm constants				Freundlich isotherm constants			D–R isotherm constants			
Metals	V_m (mg/g)	k	r^2	K_f	n	r^2	K' ($mol^2\,k/J^2$)	V'_m (mg/g)	E (kJ/mol)	r^2
Cu^{2+}	44.84	0.12	0.99	8.71	2.46	0.95	−1.7976	2997.73	0.5273	0.88
Zn^{2+}	80.64	0.27	0.93	16.22	2.05	0.93	−0.3199	7266.07	1.2503	0.88

Langmuir isotherm calculated adsorption capacities for copper and zinc are 44.84 and 80.64 mg/g, respectively. In Langmuir isotherm adsorption intensities are found to be 2.46 and 2.05 for copper and zinc metals. By using D–R isotherm, adsorption energies for copper and zinc are calculated as 0.523 and 1.2503 (kJ/mol).

3.6. *Kinetics of adsorption*

Adsorption kinetics are used in order to explain the adsorption mechanism and adsorption characteristics.

3.6.1. *Pseudo-first-order reaction kinetic*

The adsorption rate constant proposed by Lagergreen [21] and Ho [22] using first order reaction kinetic is shown below:

$$\frac{\mathrm{d}q_\mathrm{t}}{\mathrm{d}t} = k_1(q_\mathrm{e} - q_\mathrm{t}) \qquad (13)$$

where k_1 is the adsorption rate constant for the first order adsorption, q_t is the amount of heavy metal adsorbed at time t (mg/g) and q_e is the amount of heavy metal adsorbed at saturation (mg/g).

The integration of the Eq. (13) gives the following expression:

$$\ln(q_\mathrm{e} - q_\mathrm{t}) = -k_1 t + C_1 \qquad (14)$$

where C_1 is the integration constant for first order reaction kinetic.

If it is supposed that $q = 0$ at $t = 0$, then:

$$\ln(q_\mathrm{e} - q_\mathrm{t}) = \ln q_\mathrm{e} - k_1 t \qquad (15)$$

3.6.2. *Pseudo-second-order reaction kinetic*

Adsorption data was also evaluated according to the Pseudo-second-order reaction kinetic proposed by Ho and McKay [23]:

$$\frac{\mathrm{d}q_\mathrm{t}}{\mathrm{d}t} = k_2(q_\mathrm{e} - q_\mathrm{t})^2 \qquad (16)$$

where k_2 is the second order reaction constant. If Eq. (16) is integrated, the following expression is obtained:

$$\frac{1}{q_\mathrm{e} - q_\mathrm{t}} = k_2 t + C_2 \qquad (17)$$

In Eq. (17), C_2 is the integration constant of the second order reaction kinetic. With an algorithmic arrangement, the following statement is formed:

$$\frac{t}{q_\mathrm{t}} = \frac{1}{k_2 {q_\mathrm{e}}^2} + \frac{t}{q_\mathrm{e}} \qquad (18)$$

In the study, the initial copper and zinc concentrations were determined as 20, 100, 160 mg/L. The dependences of these concentrations against time are shown in Fig. 6a and b.

In order to calculate the adsorption rate constants of copper and zinc, the first order reaction kinetic was applied. For both metals, it is seen that the curves in the plots of $\ln(q_\mathrm{e} - q_\mathrm{t})$ against time, are linear. First order reaction kinetics for copper and zinc adsorption onto clay are shown in Fig. 7a and b. Rate constants (k_1) were calculated from the slopes of the curves (Table 4).

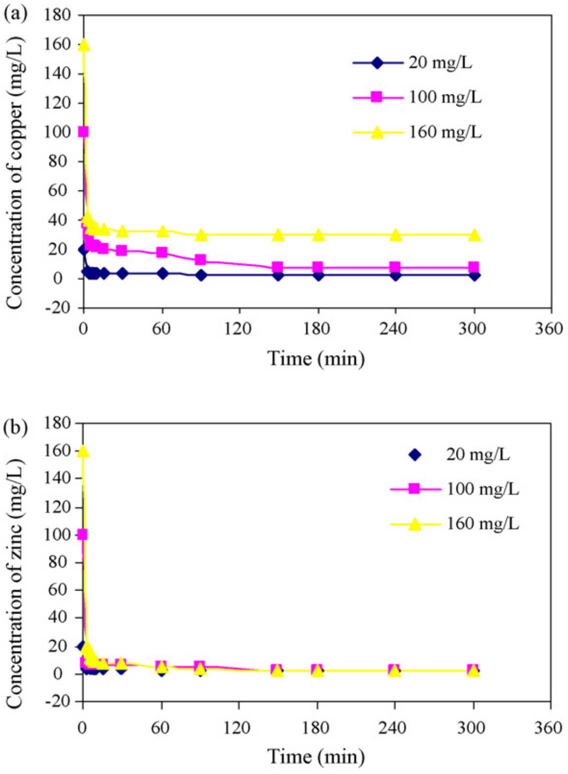

Fig. 6. Kinetics of adsorption of copper (a) and zinc (b) on natural clay.

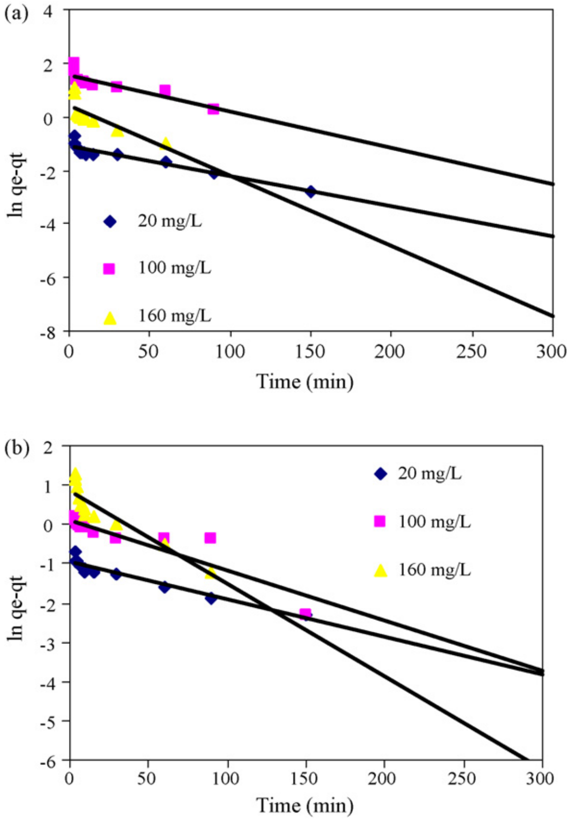

Fig. 7. Pseudo-first order reaction kinetics for the adsorption of copper (a) and zinc (b) on natural clay.

Table 4
Comparison of adsorption rate constants, experimental and calculated q_e values for the pseudo-first and -second order reaction kinetics of removal of copper and zinc by natural clay

Heavy metals	Initial metal concentration (mg/L)	$q_{e,experimental}$(mg/g)	Pseudo-first order			Pseudo- second order		
			k_1 (1/min)	$q_{e,calculated}$ (mg/g)	r^2	k_2 (g/mg min)	$q_{e,calculated}$ (mg/g)	r^2
Cu^{2+}	20	4.37	1.13×10^{-2}	0.3340	0.9012	1.11×10^{-2}	4.37	0.9999
	100	23.12	1.36×10^{-2}	4.6223	0.7506	1.9×10^{-3}	23.31	0.9996
	160	32.37	2.63×10^{-2}	1.5089	0.6189	9.6×10^{-6}	32.36	1.000
Zn^{2+}	20	3.6	0.94×10^{-2}	0.3773	0.9211	2.98×10^{-2}	3.60	0.9998
	100	19.6	1.28×10^{-2}	1.1160	0.8162	9.8×10^{-5}	19.60	0.9999
	160	31.6	2.36×10^{-2}	2.2983	0.8411	1.9×10^{-5}	31.64	1.000

Pseudo-second-order kinetic was also applied for the experimental data of each metal.

The curves in the plot of t/q_t against t are linear and k_2 rate constants can be calculated from the slope of these curves (Fig. 8 a and b).

The values of $q_{e,calculated}$ are found from the intersection points of the first and second degree reaction kinetic curves. Table 4 presents all of the data.

As the difference between $q_{e,calculated}$ and $q_{e,experimental}$ values is considered, it is seen that the Cu^{2+} and Zn^{2+} removal with natural clay is well described by the second order reaction kinetic. Moreover, all the correlation coefficients of second order reaction kinetic are higher than that of the first order reaction kinetic.

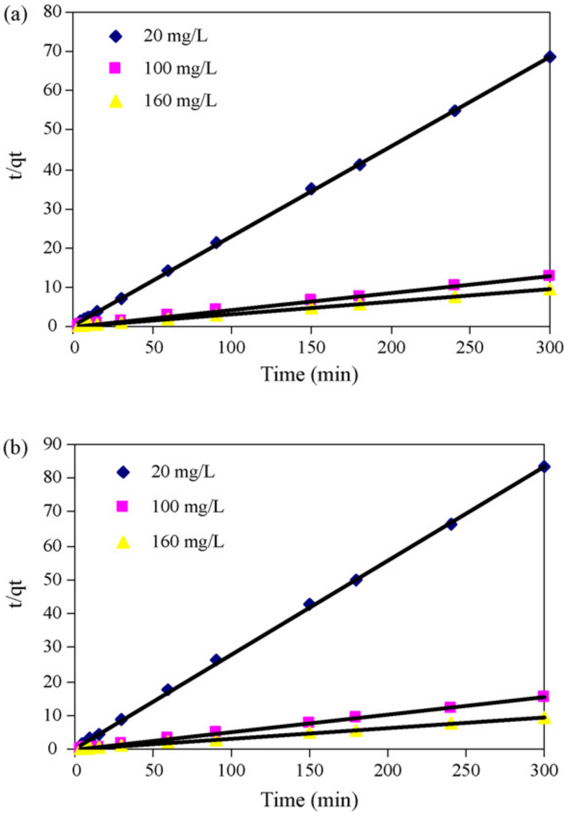

Fig. 8. Pseudo-second order reaction kinetics for the adsorption of copper (a) and zinc (b) on natural clay.

4. Conclusions

In this study, removal of Cu^{2+} and Zn^{2+} is investigated using Cankırı bentonite. pH is a significant factor in adsorption processes since it causes electrostatic changes in the solutions. Hydrogen ions themselves are strongly competing with adsorbates. At the end of experiments carried out at 23 °C and 200 rpm, optimum pH values for Cu^{2+} and Zn^{2+} removals are determined as 7 and 8.

It is also determined that the adsorption is completed in relatively short time periods. Maximum removal efficiencies were succeeded within 10 min for both metals. Optimum contact times are 10 min and 5 min for copper and zinc removal, respectively.

The empirical values are evaluated according to the Langmuir, Freundlich and D–R isotherms that are generally used to describe the adsorption processes. It is stated that all of isotherm models fit very well. By using the Langmuir isotherm, the adsorption capacities for Cu^{2+} and Zn^{2+} are found as 44.84 mg/g and 80.64 mg/g. In the Freundlich isotherm calculated adsorption intensities for copper and zinc are 2.46 and 2.05, respectively. The correlation coefficients for copper and zinc are 0.88. Moreover, in the D–R isotherm, adsorption energies are calculated to state the physical and chemical characteristics of adsorption. The magnitudes of E for copper and zinc adsorption are 0.5273 and 1.2503 kJ/mol, respectively. These low values of adsorption energy show that the adsorption has a physical nature.

Cu^{2+} and Zn^{2+} adsorption from aqueous solutions using Cankırı bentonite is well described with the second order reaction kinetic. In the second order reaction kinetic, $q_{e,calculated}$ and $q_{e,experimental}$ values are quite close to each other whereas in the first order kinetic the difference between these values are greater. Furthermore, the correlation coefficients are higher in the second order reaction kinetic.

As a result of this study, it may be concluded that Cankırı bentonite [24,25] may be used for elimination of heavy metal pollution from wastewater since it is a low-cost, abundant and locally available adsorbent.

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