

Equilibrium, kinetic and thermodynamic studies of adsorption of Pb(II) from aqueous solution onto Turkish kaolinite clay

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Abstract

The adsorption of Pb(II) onto Turkish (Bandırma region) kaolinite clay was examined in aqueous solution with respect to the pH, adsorbent dosage, contact time, and temperature. The linear Langmuir and Freundlich models were applied to describe equilibrium isotherms and both models fitted well. The monolayer adsorption capacity was found as 31.75 mg/g at pH 5 and 20 °C. Dubinin–Radushkevich (D–R) isotherm model was also applied to the equilibrium data. The mean free energy of adsorption (13.78 kJ/mol) indicated that the adsorption of Pb(II) onto kaolinite clay may be carried out via chemical ion-exchange mechanism. Thermodynamic parameters, free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) of adsorption were also calculated. These parameters showed that the adsorption of Pb(II) onto kaolinite clay was feasible, spontaneous and exothermic process in nature. Furthermore, the Lagergren-first-order, pseudo-second-order and the intraparticle diffusion models were used to describe the kinetic data. The experimental data fitted well the pseudo-second-order kinetics.

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1. Introduction

Heavy metals are non-degradable in the environment and can be harmful to a variety of living species. For that reason, the removal of these metals from waters and wastewaters is important in terms of protection of public health and environment [1–3]. Many industrial activities such as metal plating, fertilizer industry, mining operations, and dying in textile industries introduce heavy metals to environment via their waste effluents [4–6]. Therefore, the heavy metal levels in wastewater, drinking water, and water used for agriculture should be reduced to the maximum permissible concentration. Several methods have been applied over the years on the elimination of these metal ions present in industrial wastewaters and soils. The usual methods for removal of heavy metal ions from aqueous solutions can be ordered as chemical precipitation, ion-exchange, solvent extraction, phytoextraction, ultrafiltration, reverse osmo-

sis, electro dialysis, and adsorption [7,8]. Adsorption is one of the important procedure for the removal of the heavy metals from the environment. The main properties of the adsorbents are strong affinity and high loading capacity for the removal of heavy metals. Natural adsorbents have generally these properties. Ion-exchange and adsorption mechanisms of clay minerals have been used to remove different heavy metals from aqueous solution [9–12].

Lead (Pb) is one of the major environmental pollutants because of its presence in automobile fuel and subsequent emission into the atmosphere in the exhaust gases [13,14]. Moreover, it penetrates to the water environment through effluents from lead smelters, battery manufacturers, paper and pulp industries, and ammunition industries [15,16]. The adsorption of Pb(II) from aqueous solution have been investigated by using various adsorbents [17–22]. However, the use of kaolinite clay as cheap adsorbent for the adsorption metal ion from aqueous solution is worthwhile.

Kaolinite clay is a 1:1 clay mineral including a tight inter-layer structure with the ideal formula of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ [23,24]. The sorption properties of this clay are solely determined by the nature of its surface and edges. Kaolinite clay possesses a

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variable charge that can be related to the reactions between ionizable surface groups located at the edges and the ions present in aqueous solution [9,23]. It has been used as adsorbent material for the adsorption process of various heavy metals [25–28].

The objective of the present work is to study the adsorption characteristics of the Pb(II) ion from aqueous solution using Turkish (Bandırma region) kaolinite clay. 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. Materials

Kaolinite clay (Bandırma Region) was supplied from Eczacıbaşı natural mineral industry. The clay sample was sieved form 200 mesh and dried in an oven at 105 °C for 24 h and maintained in a desiccator until used [27,29,30].

All chemicals used in this work, were of analytical reagent grade and were used without further purification. Double deionised water (Milli-Q Millipore 18.2 MΩ/cm conductivity) was used for all dilutions.

2.2. Equipments

A pH meter (Sartorius pp-15 Model glass-electrode) was prepared for measuring pH values in the aqueous phase. A Perkin Elmer Analyst 700 flame atomic absorption spectrometer with deuterium background corrector was used. All measurements were carried out in an air/acetylene flame. A 10 cm long slot-burner head, a lamp and an air/acetylene flame were used. The operating parameters for working elements were set as recommended by the manufacturer.

2.3. Batch adsorption procedure

Adsorption experiments were carried out at desired pH value (pH 5), contact time (30 min) and adsorbent dosage (0.1 g) and the temperature (20 °C). Different initial concentration of Pb(II) solutions was prepared by proper dilution from stock 1000 mg/L Pb(II) standard. Sodium phosphate buffer (0.1 mol/L) was prepared by adding an appropriate amount of phosphoric acid to sodium dihydrogen phosphate solution to result in a solution of pH 2. Ammonium acetate buffers (0.1 mol/L) were prepared by adding an appropriate amount of acetic acid to ammonium acetate solutions to result in solutions of pH 4–6. Ammonium chloride buffer solutions (0.1 mol/L) were prepared by adding an appropriate amount of ammonia to ammonium chloride solutions to result in solutions of pH 8–9.

Necessary amount of adsorbent material was then added and contents in the flask were shaken for the desired contact time in a thermostatic reciprocating shaker at 110 rpm. The experiments were repeated at 20, 30, 40, and 50 °C. The time required for reaching the equilibrium condition estimated by drawing samples at regular intervals of time till equilibrium was reached. The contents of the flask were filtered through filter paper and

the filtrate was analyzed for metal concentration by using flame AAS.

The percent adsorption of metal ion was calculated as follows:

$$\text{Adsorption (\%)} = \frac{(C_i - C_f)}{C_i} \times 100 \quad (1)$$

where C_i and C_f are the initial and final metal concentrations, respectively. Adsorption experiments for the effect of pH were conducted by using a solution having 10 mg/L of Pb(II) concentration with an adsorbent dosage of 0.1 g. Throughout the study, the contact time was varied from 5 to 120 min, the pH of the solution from 2 to 9, the initial metal concentration from 10 to 400 mg/L and the amount of adsorbent from 0.01 to 0.5 g.

2.4. Adsorption isotherm models

Three important isotherm models were selected in this study, which are namely the Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherm models.

Langmuir and Freundlich isotherm models were applied to establish the relationship between the amount of Pb(II) adsorbed onto kaolinite clay and its equilibrium concentration in aqueous solution. Langmuir adsorption isotherm [31] is applied to equilibrium adsorption assuming monolayer adsorption onto a surface with a finite number of identical sites and is represented in linear form

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad (2)$$

where C_e is equilibrium concentration of the metal (mg/L) and q_e is the amount of the metal adsorbed (mg) by per unit of the adsorbent (g). q_m and K_L are Langmuir constant relating adsorption capacity (mg/g) and the energy of adsorption (L/g), respectively. These constants are evaluated from slope and intercept of the linear plots of C_e/q_e versus C_e , respectively.

Based on the further analysis of Langmuir equation, the dimensionless parameter of the equilibrium or adsorption intensity (R_L) can be expressed by

$$R_L = \frac{1}{1 + K_L C_0} \quad (3)$$

where C_0 (mg/L) is the initial amount of adsorbate. The R_L parameter is considered as more reliable indicator of the adsorption. There are four probabilities for the R_L value: (i) for favorable adsorption, $0 < R_L < 1$, (ii) for unfavorable adsorption, $R_L > 1$, (iii) for linear adsorption, $R_L = 1$, and (iv) for irreversible adsorption, $R_L = 0$ [9,20].

The adsorption data obtained were then fitted to the Freundlich adsorption isotherm [32], which is the earliest relationship known describing the adsorption equilibrium and is expressed in linear form by the following equation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

where K_F (mg/g) and n are Freundlich constants incorporating all factors affecting the adsorption process such as of adsorption

capacity and intensity of adsorption. These constants are determined from the intercept and slope of linear plot of $\log q_e$ versus $\log C_e$, respectively.

The adsorption data was also modeled by D–R isotherm to determinate the adsorption type (physical or chemical). The linear form of this model [33] is expressed by

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (5)$$

where q_e is the amount of the metal adsorbed onto per unit dosage of the adsorbent (mol/L); q_m , the monolayer adsorption capacity (mol/g); β , the activity coefficient related to mean sorption energy (mol²/J²) and ε is the Polanyi potential ($\varepsilon = RT \ln(1 + 1/C_e)$). The mean sorption energy E (kJ/mol), can be calculated using the following equation [13,33,34]

$$E = \frac{1}{\sqrt{-2\beta}} \quad (6)$$

2.5. Adsorption kinetic models

In an attempt to present the kinetic equation representing adsorption of Pb(II) onto kaolinite clay, three kinds of kinetic models were used to test the experimental data. These are Lagergren-first-order equation, second-order equation, and intraparticle diffusion model.

2.5.1. Lagergren-first-order equation

Lagergren-first-order equation is the most popular kinetics equation. The form is

$$dq/dt = k_1 (q_e - q_t) \quad (7)$$

After definite integration by applying the conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, Eq. (7) becomes the following [35–37]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (8)$$

where q_t (mg/g) is the amount of adsorption time t (min); k_1 , the rate constant of the equation (min⁻¹) and q_e is the amount of adsorption equilibrium (mg/g). The adsorption rate constant k_1 , can be determined experimentally by plotting of $\ln(q_e - q_t)$ versus t .

2.5.2. Pseudo-second-order equation

The second-order equation is in the following form:

$$dq/dt = k_2(q_e - q_t)^2 \quad (9)$$

After definite integration by applying the conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, Eq. (9) becomes the following [38,39]:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (10)$$

where k_2 (g/mg min) is the rate constant of the second-order equation; q_t (mg/g), the amount of adsorption time t (min) and q_e is the amount of adsorption equilibrium (mg/g).

2.5.3. Intraparticle diffusion model

An intraparticle mass transfer diffusion model proposed by Weber and Morris [40] was used in this research. In the model,

the fractional approach to the equilibrium changes according to a function of $(Dt/r^2)^{0.5}$, where D is the diffusion coefficient within the solid adsorbent and r is the particle radius.

The intraparticle diffusion rate equation can be written as follows [40,41]:

$$q_t = k_{id} t^{1/2} + C \quad (11)$$

where q_t (mg/L) is the amount of adsorption time t (min) and k_{id} (mg/g/min) is the rate constant of intraparticle diffusion.

2.6. Thermodynamic of adsorption

Thermodynamic parameters can be determined using the equilibrium constant, $K(q_e/C_e)$ which depends on temperature. The change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) associated to the adsorption process were calculated by using following equations [9,13,14].

$$\Delta G^\circ = -RT \ln K \quad (12)$$

where R is the universal gas constant (8.314 J/mol K) and T is temperature (K).

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (13)$$

According to Eq. (13), ΔH° and ΔS° parameters can be calculated from the slope and intercept of the plot of $\ln K$ versus $1/T$ yields, respectively.

3. Results and discussion

3.1. Characterization of adsorbent

The mineralogical composition of the dried kaolinite clay was determined by X-ray powder diffractometry (RIGAKU D-MAX 2200 model). It is composed of 48.0% SiO₂; 36.6% Al₂O₃; 2.0% K₂O; 0.3% MgO; 0.92% Fe₂O₃; 0.07% CaO; 0.1% Na₂O; 0.05% TiO₂. Mineralogical data show that the kaolinite mineral contents in the studied samples are 83.0% kaolinite clay; 13.0% mica; 2% feldspar; and 2% other minerals. The ignition loss of the clay at 1273 K was also found to be 12.0% (w/w). The X-ray diffraction spectrograph of the kaolinite clay was also shown in Fig. 1. The specific surface area of the kaolinite clay was found

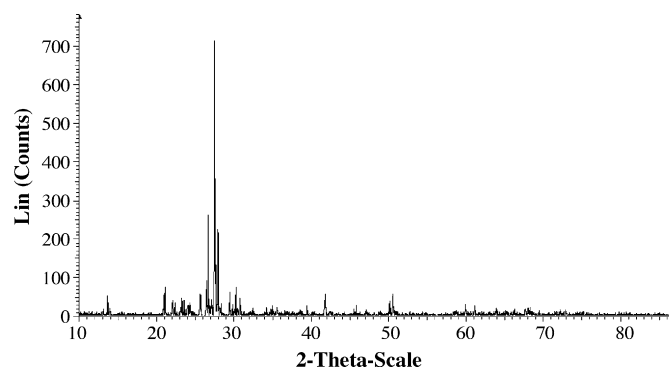


Fig. 1. XRD pattern of the kaolinite clay.

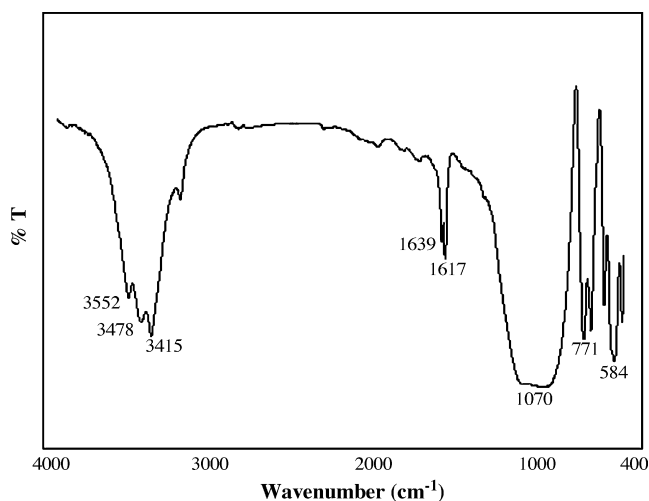


Fig. 2. FT-IR spectrum of the kaolinite clay.

to be 18.4 m²/g by using a surface analyzer (Quantachromosorb) and BET method.

The adsorbent was also characterized by FT-IR spectrophotometer (JASCO-430 model) at room temperature (Fig. 2). The broad bands observed at 3552, 3478 and 3415 cm⁻¹ is due to the O–H stretching vibration of the silanol (Si–OH) groups and HO–H vibration of the water molecules adsorbed on the silica surface. The spectral bands at 1639 and 1617 cm⁻¹ reflect the bending H–OH bond of water molecules retained in the silica matrix. The bands observed at 1070, 771 and 584 cm⁻¹ represent the Si–O–Si groups of the tetrahedral sheet and the deforming and bending modes of the Si–O bond, respectively.

3.2. Effect of adsorbent dosage

Adsorbent dosage is an important parameter because this determines the capacity of an adsorbent for a given initial concentration of the adsorbate at the operating conditions. The influence of adsorbent dosage on the adsorption of Pb(II) is shown in Fig. 3. The adsorption of the metals increased with

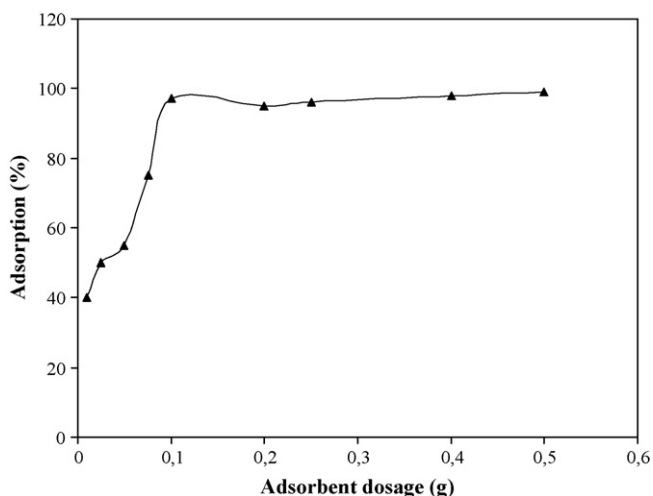


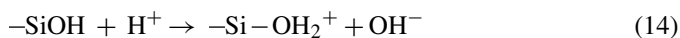
Fig. 3. Effect of adsorbent dosage on the adsorption of Pb(II) onto kaolinite clay. (Metal concentration: 10 mg/L; pH 5; temperature: 20 °C.)

increasing dosage of the clay, and the adsorption was almost constant at higher dosages than 0.1 g. With increasing adsorbent dosage, more surface area is available for adsorption due to increase in active sites on the adsorbent and thus making easier penetration of metal ions to the sorption sites.

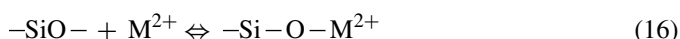
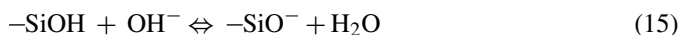
3.3. Effect of pH

The pH of solution has been identified as the most important variable affecting metal adsorption onto adsorbent. This is partly because hydrogen ions themselves are strongly competing with adsorbate. The removal of Pb(II) as a function of hydrogen ion concentration was examined at pH 2–9. The removal efficiency was found to be highly dependent on hydrogen ion concentration of solution. The effect of pH on adsorption efficiency is shown in Fig. 4. The high adsorption was obtained at pH 5–9. At higher pH values than 9, metal precipitation was observed. The maximum adsorption efficiency was 97% at pH 5 and this pH value was selected as optimum pH for further studies.

The effect of pH can be explained considering the surface charge on the adsorbent material. At low pH values (pH 2–6), the low adsorption observation was explained due to increase in positive charge (protons) density on the surface sites and thus, electrostatic repulsion occurred between the metal ions (M²⁺:Pb²⁺) and the edge groups with positive charge (Si–OH²⁺) on the surface as follows:



In an alkaline medium (pH > 7), the surface of kaolinite clay becomes negatively charged and electrostatic repulsion decreases with raising pH due to reduction of positive charge density on the sorption edges thus resulting in an increase metal adsorption. This mechanism can be shown as follows:



A similar theory was proposed by several earlier workers for metal adsorption on different adsorbents [4,17,19].

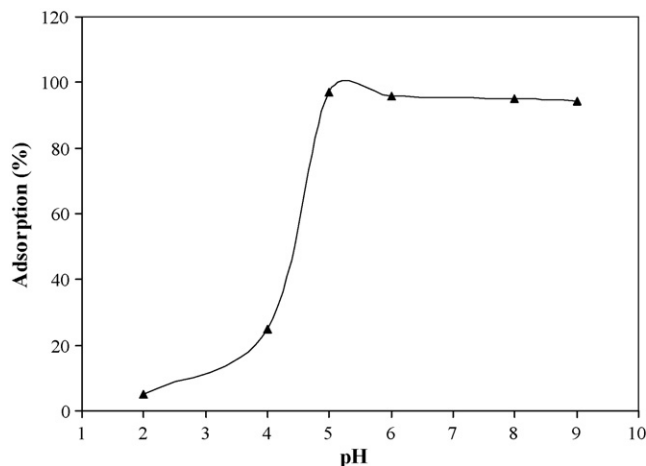


Fig. 4. Effect of pH on the adsorption of Pb(II) onto kaolinite clay. (Metal concentration: 10 mg/L; adsorbent dosage: 0.1 g; temperature: 20 °C.)

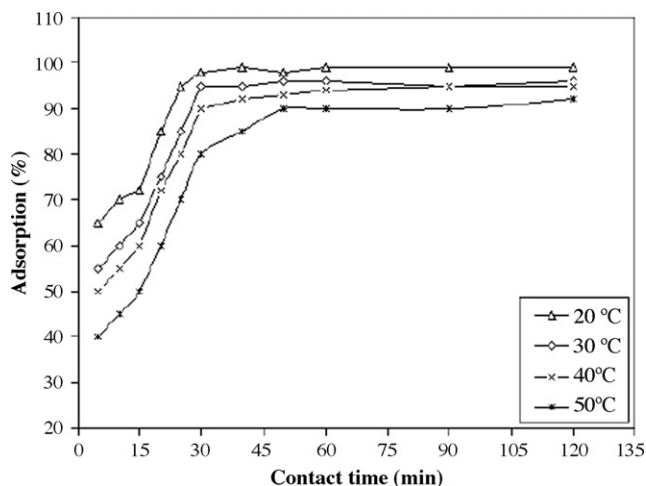


Fig. 5. Effect of contact time and temperature on the adsorption of Pb(II) onto kaolinite clay. (Metal concentration: 10 mg/L; adsorbent dosage: 0.1 g; pH 5.)

3.4. Effects of contact time and temperature

The effect of contact time on the adsorption of Pb(II) ion onto kaolinite clay at the temperature range, 20–50 °C is shown in Fig. 5. It can be seen that the adsorbed amount of Pb(II) increased with contact time up to 30 min, after that a maximum removal is attained. There was no big difference between the adsorption percentage (98%) during first 30 and 60 min (99%) at 20 °C. Therefore, 30 min was selected as the optimum contact time for all further experiments. The almost same equilibrium time was reported in several earlier works made on the adsorption of Pb(II) onto various adsorbents [17,25]. Fig. 5 also shows the effect of the temperature on the adsorption of Pb(II) onto kaolinite clay. The maximum adsorption was found as 98, 95, 90, and 80% at 20, 30, 40, and 50 °C, respectively. A decrease in the adsorption of Pb(II) with the rise in temperature was due to the increasing tendency to desorb from the interface to the solution. This result also indicated that the adsorption process of Pb(II) onto kaolinite clay was exothermic in nature. The optimum temperature for further experiments was selected as 20 °C.

3.5. The adsorption isotherms

The equilibrium data obtained for the adsorption of Pb(II) onto kaolinite clay were fitted to linear Langmuir equation (Eq. (2)). Linear plot of C_e/q_e versus C_e (Fig. 6) was examined to determine q_m and K_L values. The Langmuir adsorption maxima q_m was quite high with the values of 31.75 mg/g, and the Langmuir equilibrium constant K_L , had a value of 0.049 L/g. The high coefficient of determination ($R^2 = 0.996$) of the plot (Fig. 6) shows that the linear Langmuir equation gives a good fit to the adsorption isotherm for the adsorption of Pb(II) onto kaolinite clay at 20 °C.

The variation of the adsorption intensity (R_L) with the initial concentration of the solution (C_0 ; mg/L) is shown in Fig. 7. The R_L value ranges from 0.049 to 0.67 between 10 and 400 mg/L and approaches zero with increase in the C_0 value. This param-

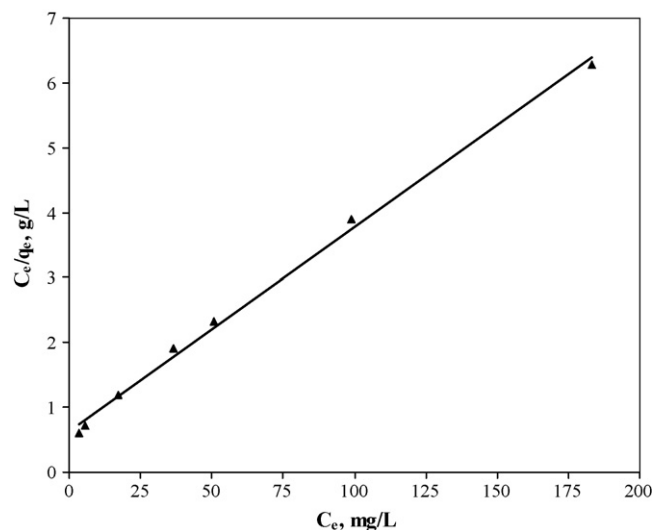


Fig. 6. Langmuir isotherm plot for the adsorption of Pb(II) onto kaolinite clay. (Adsorbent dosage: 0.1 g; contact time: 30 min; pH 5; temperature: 20 °C.)

eter ($0 < R_L < 1$) indicates that the kaolinite clay is a suitable adsorbent for the adsorption of Pb(II) from aqueous solution.

The equilibrium data were also fitted to linear Freundlich equation (Eq. (4)) for the adsorption of Pb(II) onto kaolinite clay. A fairly satisfactory empirical isotherm can be used for non-ideal adsorption because the coefficient of determination (R^2) was 0.992 (Fig. 8). From the linear plot of Freundlich isotherm, K_F and n were found as 0.175 L/g and 0.38, respectively. The Freundlich constant n smaller than 1 indicates that the adsorption of Pb(II) onto kaolinite clay was favorable under studied conditions.

On the other hand, the adsorption data were also applied to the D–R isotherm model based on the heterogeneous surface of the adsorbate in order to distinguish between physical and chemical adsorption. Fig. 9 shows the D–R isotherm plot ($R^2 = 0.985$) for the adsorption of Pb(II) onto kaolinite clay at 20 °C. The β constant and monolayer sorption capacity (q_m) were calcu-

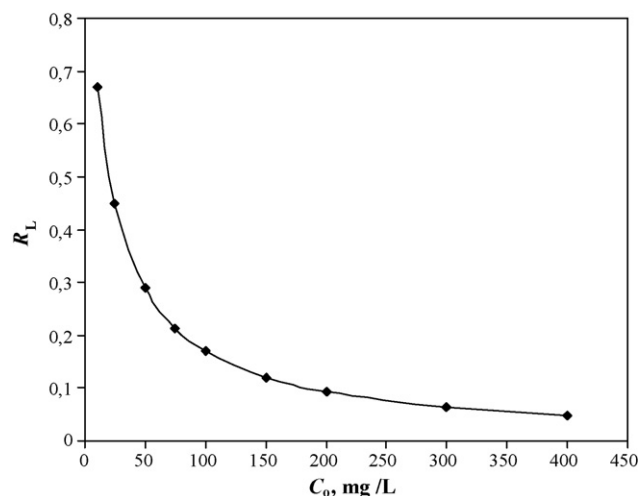


Fig. 7. Variation of adsorption intensity (R_L) with initial metal concentration (C_0 ; mg/L).

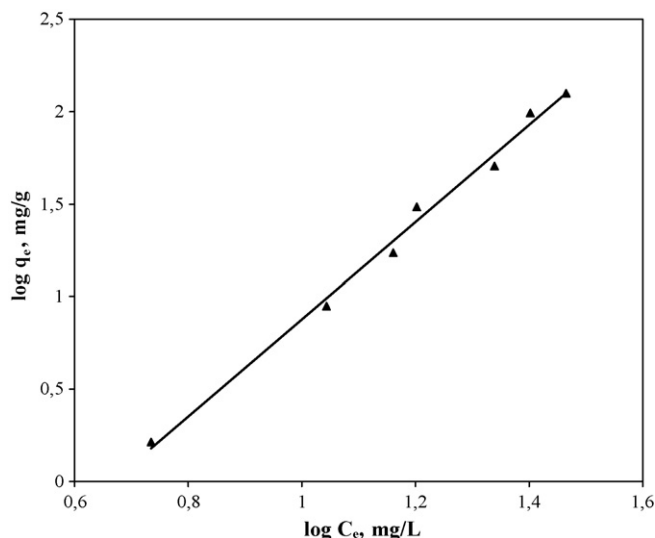


Fig. 8. Freundlich isotherm plot for the adsorption of Pb(II) onto kaolinite clay. (Adsorbent dosage: 0.1 g; contact time: 30 min; pH 5; temperature: 20 °C.)

lated from the slopes and intercept of the plot. The β constant and the q_m value were found to be $2.63 \times 10^{-6} \text{ mol}^2/\text{kJ}^2$ and $2.96 \times 10^{-4} \text{ mol/g}$, respectively.

The mean free energy of adsorption E , gives information about adsorption mechanism as chemical ion-exchange or physical adsorption. If E value is between 8 and 16 kJ/mol, the adsorption process follows by chemical ion-exchange, and if $E < 8 \text{ kJ/mol}$, the adsorption is physical in nature [42,43]. From Eq. (6) the numerical value of E was calculated as 13.78 kJ/mol, indicating the adsorption process may be carried out via chemical ion-exchange mechanism.

3.6. Comparison of Turkish kaolinite clay with various adsorbents

The comparison of adsorption capacity of the Turkish kaolinite clay with that of various adsorbents is given in Table 1. The kaolinite clay has a high adsorption capacity as comparable with

Table 1

Comparison of adsorption capacity of Turkish (Bandırma region) kaolinite clay with various adsorbent

Adsorbent	Adsorption capacity (mg/g)	Reference
Sawdust	21.05	[6]
Modified peanut husk	29.14	[6]
Montmorillonite	31.05	[15]
Modified kaolinite	23.10	[15]
Turkish clay (Celtek)	18.08	[13]
Turkish siderite	10.32	[12]
Turkish bentonite (MTA)	16.66	[14]
Rice husk ash	10.86	[19]
Tree fern	39.80	[20]
Peat	28.30	[22]
Activated carbon prepared from coconut shell	12.64	[17]
Olive cake	19.53	[18]
Biopolymeric sorbent	12.85	[1]
Biosorbent (<i>Cephalosporium aphidicola</i>)	0.924	[16]
Turkish kaolinite (Bandırma region)	31.75	Present study

that of the other adsorbents. Therefore, considering the low cost of this natural adsorbent, it can be used as an alternative material to minimize the concentration of Pb(II) in wastewater.

3.7. Kinetics of adsorption

The adsorption of Pb(II) onto kaolinite clay was investigated in terms of the kinetics of the adsorption mechanism by using three models: Lagergren-first-order, pseudo-second-order, and intraparticle diffusion models.

The plots of $\ln(q_e - q_t)$ versus t for the Lagergren-first-order model were not shown as figure because the coefficients of determination for this model at studied temperatures is low ($R^2 = 0.821\text{--}0.890$) for the Pb(II) adsorption at 20–50 °C. The adsorption of Pb(II) onto kaolinite clay does not follow the Lagergren-first-order model because the coefficients of determination are low.

The linear plots of t/q_t versus t for the pseudo-second-order model in Eq. (10) were obtained at 20–50 °C (Fig. 10). As shown in Table 2, the rate constant ($k_1; \text{min}^{-1}$) was decreased from 8.38×10^{-2} to $4.33 \times 10^{-2} \text{ g/mg min}$ when the temperature was raised from 20 to 50 °C. The R^2 value was determined as 0.990, 0.994, 0.992, and 0.993 for 20, 30, 40, and 50 °C, respectively. These results indicate that the pseudo-second-order kinetics is expected to be followed in the adsorption of Pb(II) onto kaolinite clay since it has higher R^2 values than that obtained from the Lagergren-first-order model. The similar results were reported for the adsorption of Pb(II) onto modified kaolinite clay [26].

The plots of q_t versus $t^{1/2}$ for the intraparticle diffusion model given in Eq. (11) were obtained at 20–50 °C (Fig. 11). The intraparticle rate constant k_{ip} ($\text{mg/g min}^{1/2}$) and intercept C (mg/g) parameters are given in Table 3. The R^2 values were found to be 0.962, 0.967, 0.880, and 0.889 for the plots, which represent 20, 30, 40, and 50 °C, respectively. The intraparticle diffusion can not be accepted as the only rate controlling step for the adsorption of Pb(II) onto kaolinite clay due to the deviation (C value

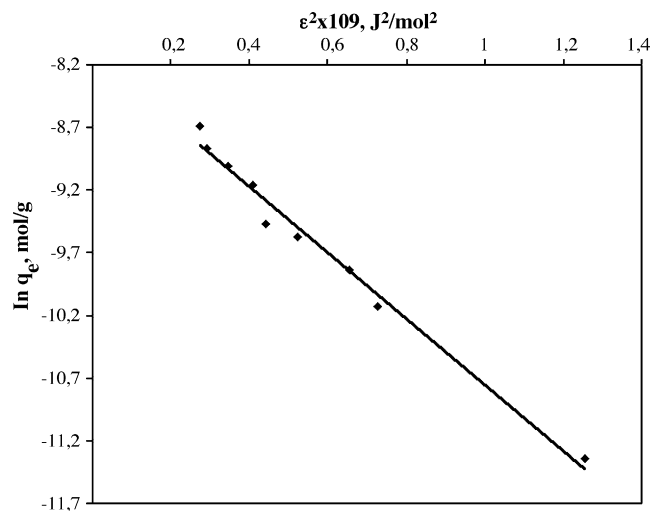
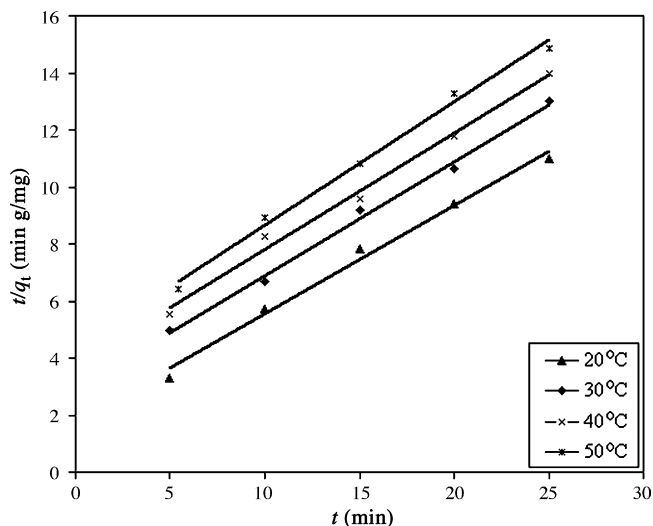


Fig. 9. D–R isotherm plot for the adsorption of Pb(II) onto kaolinite at 20 °C.

Table 2

Lagergren first-order and pseudo-second-order parameters for the adsorption of Pb(II) onto kaolinite clay at various temperatures

T (K)	Lagergren-first-order		R^2	Pseudo-second-order		R^2
	k_1 (min^{-1})	q_e (mg/g)		k_2 (g/mg min)	q_e (mg/g)	
293	7.22×10^{-2}	1.21	0.821	8.38×10^{-2}	2.62	0.990
303	4.49×10^{-2}	1.12	0.823	5.52×10^{-2}	2.50	0.994
313	3.36×10^{-2}	1.10	0.890	2.45×10^{-2}	2.45	0.992
323	2.79×10^{-2}	1.09	0.884	4.33×10^{-2}	2.31	0.993

Fig. 10. Plot of $\ln K$ vs. $1/T$ for estimation of thermodynamic parameters for the adsorption of Pb(II) onto kaolinite clay.

in Table 3) of the plots from the origin. The same type results were also given in some works [4,6].

Based on all the kinetic data, it is assumed that a surface reaction adsorption mechanism may take place as a result of an interaction, specifically, between negatively charged groups of ($\text{Si}-\text{O}^-$, $\text{Al}-\text{O}^-$) and the positively charged metal ion (Pb^{2+}) or

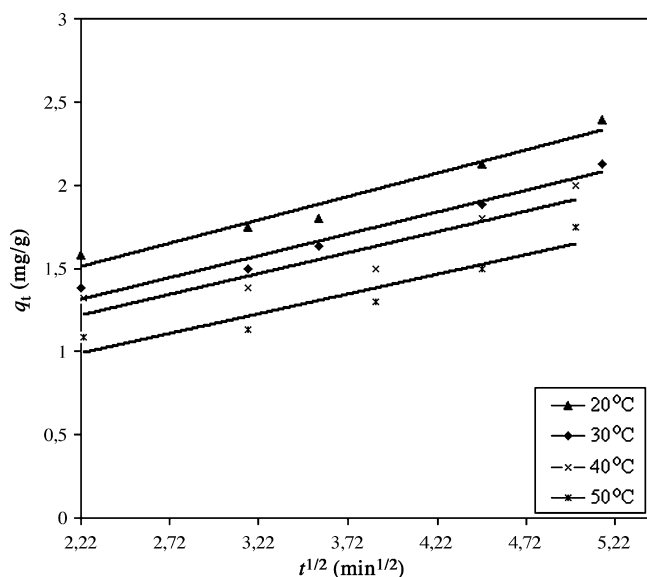


Fig. 11. Pseudo-second-order kinetic plots for the adsorption of Pb(II) onto kaolinite clay at different temperatures.

Table 3

Intraparticle diffusion model parameters for the adsorption of Pb(II) onto kaolinite clay at various temperatures

T (K)	k_{id} (mg/g $\text{min}^{1/2}$)	C (mg/g)	R^2
293	0.28	0.89	0.962
303	0.26	0.74	0.967
313	0.25	0.66	0.880
323	0.24	0.46	0.889

take place via chemical ion-exchange mechanism between the hydrogen of edge OH groups onto surface of kaolinite clay and the Pb^{2+} ions.

3.8. Thermodynamic parameters of adsorption

From Eq. (12), Gibbs free energy change of adsorption (ΔG°) was calculated using $\ln K$ values for different temperatures. It was found as -19.82 , -18.70 , -18.05 , and -16.91 kJ/mol for the adsorption of Pb(II) onto kaolinite clay at 293, 303, 313, and 323 K, respectively. The negative ΔG° values indicated that the adsorption of Pb(II) onto kaolinite clay was feasible and spontaneous thermodynamically. In addition, the decrease in ΔG° values with increase in temperature shows that the adsorption was not favorable at higher temperatures. The enthalpy change (ΔH°) and entropy change (ΔS°) for the adsorption process were

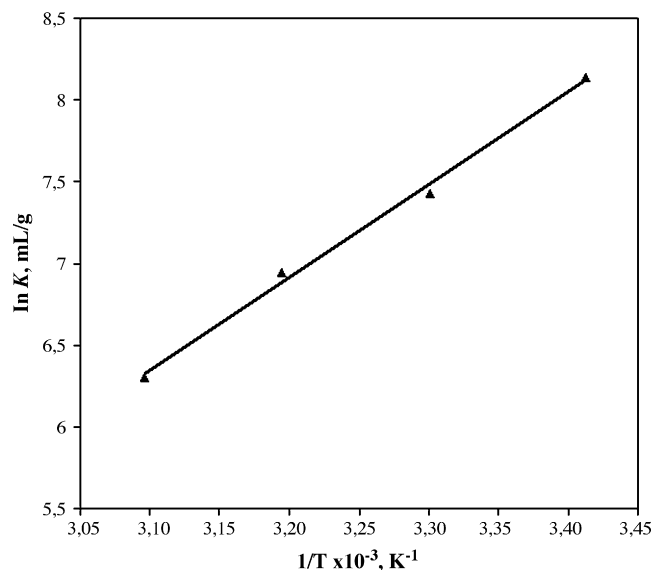


Fig. 12. Intraparticle diffusion kinetic plots for the adsorption of Pb(II) onto kaolinite clay at different temperatures.

obtained from the $\ln K$ versus $1/T$ plot (Fig. 12). The ΔH° parameter had a value of -47.21 kJ/mol. The negative ΔH° value indicated exothermic nature of the adsorption. The ΔS° parameter was found to be -93.61 J/mol K, implying that the Pb(II) in bulk phase (aqueous solution) were in a much more chaotic distribution compared to the relatively ordered state of solid phase (surface of adsorbent).

4. Conclusions

In this study, batch adsorption experiments for the removal of Pb(II) from aqueous solution by using Turkish (Bandırma region) kaolinite clay have been carried out. The obtained results can be summarized as follows:

- (1) For the maximum adsorption, the optimal operating parameters, pH of solution, adsorbent dosage, contact time and temperature was selected as pH 5, 0.1 g, 30 min and 20°C . The linear Langmuir and Freundlich isotherm models were used to represent the experimental data. Both models were fitted well. The monolayer adsorption capacity was obtained 31.75 mg/g at optimal experimental conditions.
- (2) The mean free energy of adsorption E (13.78 kJ/mol) calculated from examination of D–R isotherm indicated that the adsorption of Pb(II) onto kaolinite clay may be carried out via chemical ion-exchange mechanism. The negative ΔG° values showed that the adsorption of Pb(II) onto kaolinite clay was feasible and spontaneous. The negative ΔH° value depicted exothermic nature of the adsorption. The negative ΔS° values revealed that the orderliness of the adsorbed system was higher than the solution phase before adsorption.
- (3) By applying the kinetic models to the experimental data, it was found that the adsorption of Pb(II) onto kaolinite clay follows the pseudo-second-order rate kinetics.

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