

Removal of Pb(II) from water by natural zeolitic tuff: Kinetics and thermodynamics

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ARTICLE INFO

Article history:

Received 18 July 2011

Received in revised form 31 October 2011

Accepted 7 November 2011

Available online 15 November 2011

Keywords:

Volcanic tuff

Lead removal

Adsorption

Isotherms

Reaction kinetics

ABSTRACT

The present study was aimed at examining the ability of a natural zeolitic volcanic tuff to remove Pb(II) ions from aqueous solutions under various conditions. The effects of various parameters such as optimum adsorbent mass, contact time, pH of the medium, Pb(II) concentration, and temperature were investigated. In addition, different adsorption isotherms were obtained using concentrations of Pb(II) ions ranging from 1 mg/L to 200 mg/L. The adsorption process follows second-order reaction kinetics and follows the Langmuir adsorption isotherm. The thermodynamic parameters are discussed in this article, including changes in Gibbs free energy, entropy, and enthalpy, for the adsorption of Pb(II) on tuff, and it is revealed that the adsorption process was spontaneous and exothermic under natural conditions. The maximum removal efficiency of 92% was obtained at a pH of 5 with a 25-min contact time for a 10 g/L solid-to-liquid ratio and an initial heavy metal concentration of 100 mg/L.

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1. Introduction

The removal of heavy metals from waters and wastewaters is important in terms of protecting public health and environment owing to their accumulation in living tissues throughout the food chain as non-biodegradable pollutants [1,2]. Heavy metal pollution is found to occur in various types of industrial wastewater such as those produced by metal plating facilities, mining operations, metallurgical engineering, battery manufacturing processes, the production of paints and pigments, electroplating, nuclear power plants, and ceramic and glass industries. The wastewater commonly includes Ni, Cu, Cd, Cr, and Pb. These heavy metals are not biodegradable and their presence in streams and lakes leads to bioaccumulation in living organisms, thereby causing health problems in animals, plants, and human beings. Excessive intake of Pb by humans causes disruption in the biosynthesis of the hemoglobin level, a rise in blood pressure, kidney damage, miscarriages and abortions, brain damage, and diminished learning abilities of children [3–6]. Further, Pb is a known carcinogen. Therefore, the removal of excess Pb ions from wastewater is essential for protecting human health as well as the environment.

The most commonly used methods for removing heavy metals are chemical or electrochemical precipitation, both of which

pose a significant problem in terms of the disposal of precipitated wastes [7,8]. Further, ion-exchange treatments are also available, which do not appear to be economical [9]. It has been reported that some aquatic plants [10,11], wood materials [12–14], agricultural by-products [15], clay [16], natural zeolite [17], turba (partially decomposed vegetable matter) [18,19], microorganisms [20–22], and other low-cost adsorbents [23] have the capacity to adsorb and accumulate heavy metals. The adsorption capacities are found to be ranging from 3.04 mg/g to 425 mg/g for Pb(II) (Table 1). However, the uses of aquatic plants, microorganisms, and wood-based materials such as sawdust and bark have the disadvantage of increasing the chemical oxygen demand (COD) of water [20]. As a result of this problem with the aforementioned solutions, it becomes necessary to develop a low-cost, easily available sorbent for wastewater treatment that could remediate the environmental problems in developing countries. The clay- and zeolite-based adsorbents described in this article have satisfactory adsorption capacity and are of low cost, are abundant in nature, and are not toxic [24]. Since the original discovery of zeolitic minerals in a volcanogenic sedimentary rock, zeolitic tuffs have been found in several areas of the world. In the past decades, natural zeolites have found a variety of applications in adsorption, catalysis, building industry, agriculture, soil remediation, and energy [25–27]. It was estimated that the world natural zeolite consumption was 3.98 Mt, which would reach 5.5 Mt in 2010 [28]. In recent years, further research has been focused on the effects of various adsorbents that have been used for the removal of Pb(II) [29–34] from aqueous solution. However, new adsorbents made of locally

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Table 1
Removal capacities of some adsorbents for Pb(II).

Materials	mg/g	Sources
Poly2-hydroxyethyl methacrylate (PHEMA)	3.04	[67]
Maple sawdust	3.19	[68]
Chemical precipitation (NaOH)	8.0	[8]
Kaolinite	11.1	[69]
Sphagnum moss peat	12.3	[70]
Clinoptilolite	27.7	[71]
Copolymer 2-hydroxyethyl methacrylate with monomer methyl methacrylate P(MMA-HEMA)	31.45	[67]
<i>Ceratophyllum demersum</i>	44.8	[10]
Clinoptilolite	64.0	[72]
Natural zeolite	80.9	[43]
Phillipsite	104.0	[73]
Ion-exchange resin (Dowex50W)	425	[9]
Volcanic tuff	15.79	This study

available and economic materials, with high adsorption capacity are still required.

Tuff is one of the most abundant forms of zeolite in Turkey, with a wide geographic distribution and large deposits. The general composition of the zeolites can be represented by $M_{y/z}[(SiO_2)_x(AlO_2)_y]nH_2O$, where, M is the exchangeable cation with a valency z. [35]. However, the chemical composition of a zeolite is usually variable in both its framework part and the extra-framework cation population. The microporosity and relatively high surface area of zeolites have been utilized extensively in applications that require ion exchangers, adsorbents, catalysts, and separation media [36]. The use of zeolites as adsorbents for environmental protection and other applications has been stimulated by the good results obtained in testing and by the non-toxic nature of these materials. Tuff is particularly interesting owing to its availability and low cost.

Thus, the present study was aimed at determining whether volcanic tuff would have acceptable adsorption efficiency for removing Pb(II) and thereby offer an effective and economical alternative to more expensive treatments. In the present study, the batch adsorption characteristic of Pb(II) on volcanic tuff is described by concentrating on various operational parameters such as contact time, initial Pb(II) concentration, and the effect of the pretreatment of volcanic tuff on adsorption capacity. Experimental data have been analyzed by adsorption isotherms, kinetics, and thermodynamic parameters.

2. Materials and methods

2.1. Adsorbents and reagents

Volcanic tuff was obtained from natural zeolites extracted from deposits at Aksaray, in the middle Anatolia part of Turkey. The chemical properties of the volcanic tuff used in this study are given in Table 2. In accordance with the ASTM Method D4749 [37], crushed particles were sieved through a range of sieves, and only the particles that passed through a 0.25-mm mesh were used in this study. The sieves were shaken for approximately 15 min, and then the separated particles were stored. The zeolite materials were washed with distilled water three times to avoid any effects from dissolved salts in the equilibrium solution. Subsequently, the adsorbents were oven-dried at 70 °C for 2 h. In this study, an initial Pb(II) concentration of 100 mg/L was selected. A stock solution of Pb(II) (1000 mg/L) was prepared by dissolving a weighed quantity of $Pb(NO_3)_2$ salts in twice-distilled water. The stock solution was then used for preparing solutions with Pb(II) concentrations ranging from 1 mg/L to 200 mg/L. Prior to adding the adsorbents, the pH

of each solution was adjusted to the required value by adding 0.1 M NaOH or 0.1 M HNO_3 . All chemical compounds used for preparing the reagent solutions were of analytic grade (Merck, Whitehouse Station, NJ).

2.2. Instruments

The chemical compositions of the zeolite samples were determined using a Rigaku RIX 3000 X-ray spectrometer according to the Rietveld method [38]. A thermal stirrer (ZHWHY-200B, ZHICHENG Analytical Co., Ltd.) was used for the batch adsorption experiments. The metal solution was filtered through 0.45- μ m membrane filters after settling. The filtrates were then analyzed using an inductively coupled plasma spectrometer (Optima 2100DV ICP, Perkin-Elmer, Boston, MA). The pH measurements were performed using a digital ion analyzer with a combination electrode (WTW, Weilheim, Germany).

2.3. Batch sorption experiments and model equations

The metal concentration in the liquid phase was determined at the beginning (C_0) and at the end (C_e) of the agitation. The following equation was used for computing the percentage uptake of the metal by the sorbent:

$$\text{Sorption \%} = \frac{(C_0 - C_e) * 100}{C_0} \quad (1)$$

The data obtained were applied to the Langmuir adsorption isotherm using the following linear expression of this model [39]:

$$\left(\frac{C_e}{q_e}\right) = \left(\frac{1}{bK}\right) + \left(\frac{C_e}{b}\right) \quad (2)$$

where q_e is the amount of Pb(II) ions adsorbed per unit weight of clinoptilolite at the equilibrium (mg/g) and is expressed as $q_e = [(C_0 - C_e) * V] / M$; V (L) is the volume of the solution; M (g) is the amount of adsorbent added to the solution; C_e (mg/L) is the metal concentration in the aqueous phase; and b (mg/g) and K (L/mg) are the Langmuir constants related to the sorption capacity and the energy of adsorption, respectively.

Another adsorption isotherm, the Dubinin–Radushkevich (D–R) isotherm, was calculated from the adsorption data. This isotherm is more general than the Langmuir isotherm as it does not assume a homogeneous surface or constant sorption potential. The D–R equation is expressed as follows [40]:

$$q_e = X'_m \exp(-K' \varepsilon^2) \quad (3)$$

where ε (the Polanyi potential) = $RT \ln(1 + 1/C_e)$, q_e and C_e are as described under Eq. (2) (mg/g and mg/L, respectively), X'_m is the maximum adsorption capacity of the sorbent (mg/g), K' is a constant related to the adsorption energy (mol^2/kJ^2), R is the gas constant ($\text{kJ}/\text{K mol}$), and T is the temperature (K). The D–R isotherm can be expressed in linear form as follows:

$$\ln q_e = \ln X'_m - K' \varepsilon^2 \quad (4)$$

The Freundlich isotherm was also applied to the adsorption data. This model has the following linear expression [41]:

$$\log q_e = \log K_f + \left(\frac{1}{n}\right) * \log C_e \quad (5)$$

where K_f (mg/g) is the Freundlich constant related to the sorption capacity of the sorbent, and $1/n$ is the Freundlich constant related to the energy heterogeneity of the system and the size of the adsorbed molecule.

The kinetic parameters for the adsorption process were studied for the trial of adsorption at 100 mg/L of Pb(II) at 293 K and pH 5.40. The contact time was varied between 1 min and 120 min and the

Table 2

The chemical composition of Aksaray (Turkey) volcanic tuff used in the present study (wt%).

SiO ₂	Al ₂ O ₃	CaO	K ₂ O	Na ₂ O	Fe ₂ O ₃	MgO	TiO ₂	Loss on ignition (LoI)
69.57	10.59	2.23	5.37	1.50	1.33	0.77	0.22	7.62

percent removal of Pb (II) was monitored. The pseudo-first order ([42]; Eq. (6)) and pseudo-second order ([19]; Eq. (7)) kinetic models were selected for testing the adsorption dynamics in this study owing to their good applicability in most cases in comparison with the first and second order models:

$$\log(q_e - q_t) = (\log q_e) - k_1 t \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \left(\frac{1}{q_e}\right) t \quad (7)$$

where q_t is the amount of Pb(II) removed at time t (mg/g), and k_1 (1/min) and k_2 (g/mg min) are the rate constants of the first- and second-order kinetic equations for adsorption.

The changes in Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) for the adsorption process were obtained using the following equations [43]:

$$\Delta G = -RT \ln b \quad (8)$$

$$\ln b = \left(\frac{\Delta S}{R}\right) - \left(\frac{\Delta H}{RT}\right) \quad (9)$$

The enthalpy change (ΔH) and the entropy change (ΔS) can be calculated from a plot of $\ln b$ (Langmuir constant) versus $1/T$.

2.4. General procedures

The effects of adsorbent mass, contact time, pH, and initial metal ion concentration on the adsorption of Pb(II) were studied using the experimental conditions shown in Table 3. The sorption experiments were performed in a batch reactor using stoppered Pyrex glass flasks.

Each experiment was replicated three times, and the mean values were used in the analyses. If the standard errors (SE) were greater than 0.01, the test was repeated to control for errors. The deviation of the metal uptake per unit weight of clinoptilolite (Δq_e) was calculated as follows:

$$\Delta q_e(\%) = \frac{\sum_{i=1}^N |(q_e)_{cal} - (q_e)_{exp}|}{N (q_e)_{exp}} \times 100 \quad (10)$$

where the subscripts “exp” and “cal” indicate the experimental and calculated values of q_e and N specifies the number of measurements.

3. Results and discussion

3.1. Effect of the mass of adsorbent

The effect of the mass of adsorbent on the retention of Pb(II) was studied using 100 mL of 100 mg/L Pb(II) solution treated with 0.05–2.5 g of volcanic tuff for 60 min. It can be seen in Fig. 1 that the Pb(II) retention increased gradually with increasing mass of adsorbent and that the optimum volcanic tuff concentration was 10 g/L. This optimum volcanic tuff dosage decreased the Pb(II) concentration to 6.469 mg/L, which is less than the discharge limit for wastewater. After this maximum equilibrium value, it was observed that the removal efficiency did not increase with increasing adsorbent mass. Thus, this concentration was used for the following experiments. These results suggested that the proportional increase between adsorbent dosage and removal efficiency was related to an increase in the number of adsorption sites.

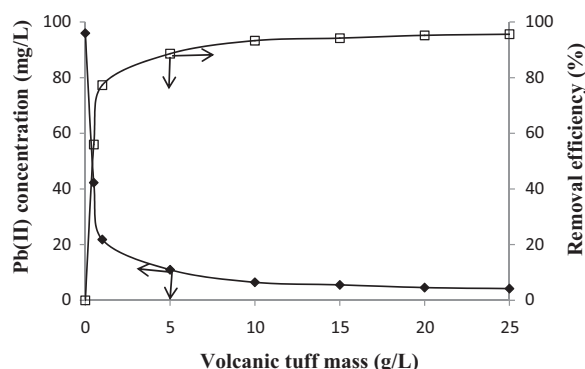


Fig. 1. Effect of the mass of adsorbent on the removal of Pb(II) (initial concentration of Pb(II), 100 mg/L; shaking speed, 250 rpm; contact time, 60 min.; temperature, 293 K).

3.2. Effect of contact time

The effect of contact time was studied using a constant concentration of Pb(II) solution at room temperature. The adsorption of Pb(II) ions was examined on volcanic tuff as a function of time in the range of 1–120 min. The removal of Pb(II) as a function of contact time is shown in Fig. 2. As shaking consumes energy, and the cost increases with increase in shaking time, it is important to determine the optimal contact time that maximizes the removal efficiency without unacceptably increasing the cost. The graph indicates that initially the adsorption efficiency increased rapidly and the equilibrium was attained at 120 min with an adsorption efficiency of 94%. Although the highest value of adsorbed Pb(II) ions on tuff was reached at 120 min there was no significant difference between the data obtained for 25 min (93%) and 120 min. On the basis of these results, a 25 min shaking period was selected for all further studies. Nevertheless, for isotherm experiments, a 120 min contact time was chosen as the equilibrium time is more important in this case. This is probably a result of the saturation of adsorbent surfaces with heavy metals followed by adsorption and desorption processes that occur after saturation [24]. Almost similar equilibrium time values were reported in several earlier works that examined the adsorption of Pb(II) ions on various adsorbents [32,33,44].

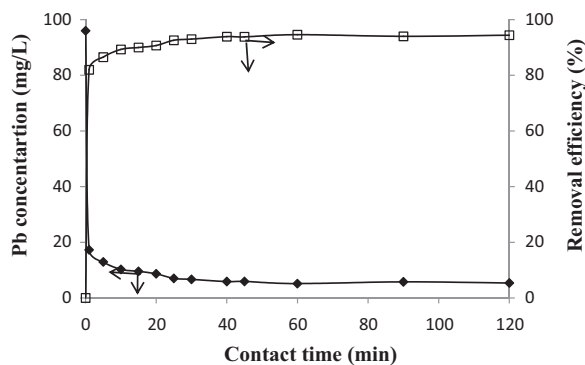


Fig. 2. Effect of contact time on the removal of Pb(II). The volcanic tuff concentration was 10 g/L, the initial concentration of Pb(II) was 100 mg/L, the shaking speed was 250 rpm, and the temperature was 293 K.

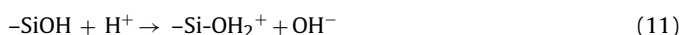
Table 3
Experimental conditions for the adsorption of Pb(II) by ions on the volcanic tuff.

	S (rpm)	M _s (g/L)	t (min)	pH	C ₀
Effect of adsorbent mass, M _s (g)	250	0.5–25	60	5.40	96
Effect of contact time, t (min)	250	10	0–120	5.40	96
Effect of pH	250	10	25	2–6	96
Effect of metal concentration, C ₀ (mg/L)	250	10	120	5	1–200

3.3. Effect of pH

The effect of pH on lead (II) adsorption onto natural volcanic tuff was investigated in the range of 2–6 for an initial lead concentration of 100 mg/L. The experimental results of pH on the adsorption of Pb(II) by the volcanic tuff are presented in Fig. 3. The pH of the aqueous solution is an important variable for the adsorption of metals on the adsorbents. Under acidic conditions, the tuff mineral surface will be completely covered with H⁺ ions and the Pb(II) ions cannot compete with them for adsorption sites. However, with increasing pH, the competition from the hydrogen ions decreases and the positively charged Pb(II) ions can be adsorbed at the negatively charged sites on the adsorbent [45]. Under these circumstances, the adsorbing cation might be species such as Pb²⁺, Pb(OH)⁺, Pb(OH)₂, Pb(OH)₃⁻, Pb(OH)₄²⁻ [46]. At pH lower than 8, Pb(II) ions were the dominant species; Pb(OH)₂ was present at pH higher than 8 [47]. Adsorption occurs at a comparatively low pH (~6.0) for Pb(II) ions [48]. Based on these results, it can be mentioned that natural volcanic tuff exhibited a good capacity for removing Pb(II) from solution at pH values ranging from 4 to 6. The optimum adsorption (8.80 mg/g and 91.7%) was at a pH value of 5 with a 25-min contact time, a 10 g/L solid-to-liquid ratio, and an initial heavy metal concentration of 100 mg/L.

The effect of pH can be explained by considering the surface charge on the adsorbent material. At low pH values (pH 2–6), the low adsorption observation was explained owing to the increase in positive charge 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 explained below [49].



In an alkaline medium (pH > 7), the surface of volcanic tuff clay becomes negatively charged and electrostatic repulsion decreases with increasing pH owing to the reduction of positive charge density on the sorption edges, thereby resulting in an increase in metal adsorption [49]. This mechanism can be shown as follows:

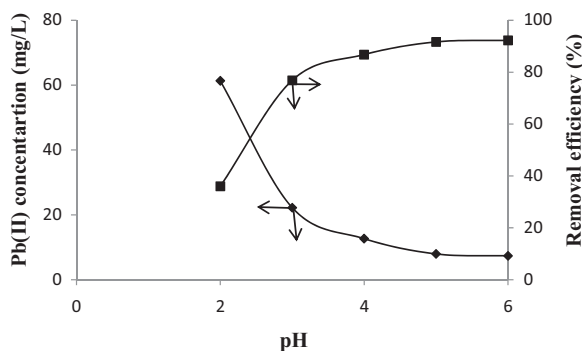
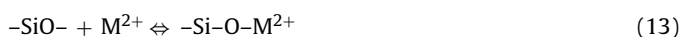


Fig. 3. Effect of pH on the removal of Pb(II) (initial concentration of Pb(II), 100 mg/L; volcanic tuff concentration, 10 g/L; shaking speed, 250 rpm; contact time, 25 min.; temperature, 293 K).

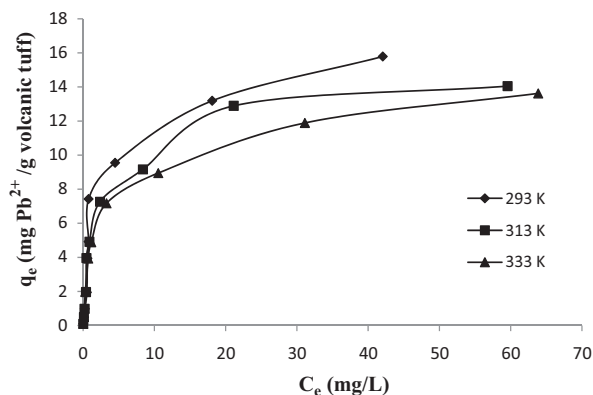


Fig. 4. Adsorption isotherm for volcanic tuff using different initial Pb(II) concentrations ranging from 1 mg to 200 mg Pb(II)/L. The volcanic tuff concentration was 10 g/L, and the contact time was 120 min at pH 5.

A similar theory was proposed in several earlier works for metal adsorption on different adsorbents [2,50–52].

3.4. Determination of adsorption isotherms

Adsorption isotherms or capacity studies are of fundamental importance in the design of adsorption systems as they indicate how the metal ions are partitioned between the adsorbent and liquid phases at equilibrium as a function of increasing metal concentration. When an adsorbent comes into contact with a metal ion solution, the concentration of metal ions on the adsorbent will increase until a dynamic equilibrium is reached; at this point, there is a defined distribution of metal ions between the solid and the liquid phases. Heavy metal ion concentrations range from 1 mg/L to 200 mg/L with a fixed adsorbent mass and pH for heavy metal. As metal concentrations increase, the removal efficiencies decrease from 97% to 79% for Pb(II). Thus, increasing the initial heavy metal concentrations in the solutions decreases the removal efficiency. The Pb adsorption capacities at pH 5 were calculated by means of least-squares regression using Eqs. (2), (4) and (5). The resulting adsorption isotherms for the volcanic tuff used in this study are shown in Figs. 4–7.

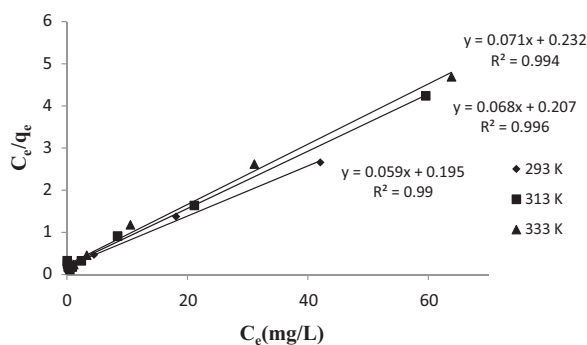


Fig. 5. The linearized Langmuir isotherm for adsorption of Pb(II) by volcanic tuff (tuff concentration, 10 g/L; contact time, 120 min.; shaking speed, 250 rpm at pH 5).

Table 4
Regression parameters for the Langmuir, D–R and Freundlich adsorption isotherms for solutions of Pb(II) at different temperatures.

T (K)	Langmuir isotherms			D–R isotherms			Freundlich isotherms		
	b	K	R^2	X'_m	K'	R^2	$1/n$	K_f	R^2
293	16.81	0.305	0.99	6.80	0.064	0.834	0.666	2.88	0.823
313	14.71	0.328	0.996	6.94	0.0593	0.881	0.617	2.50	0.835
333	13.99	0.308	0.995	6.71	0.0502	0.892	0.587	2.07	0.852

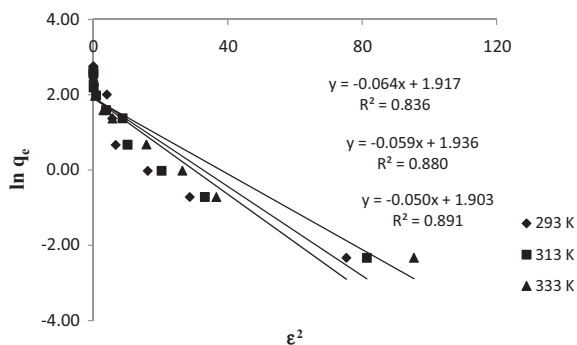


Fig. 6. The linearized D–R isotherm for adsorption of Pb(II) by volcanic tuff (tuff concentration, 10 g/L; contact time, 120 min.; shaking speed, 250 rpm at pH 5).

Several conceptual and empirical models such as Langmuir, D–R, and Freundlich have been used for describing the equilibrium phase distribution for the sorption of metal ions in surface systems. The Langmuir isotherm model suggests that uptake occurs on homogeneous surface by monolayer sorption without interaction between adsorbed metal ions [53]. This isotherm dictates a limiting sorption capacity. Once the monolayer coverage is achieved, the sorption is no longer influenced significantly by the solute transport. Such behavior is characteristic to the Langmuir type sorption, and a strong affinity of the solute on the solid phase at low concentration can be shown [54,55]. The adsorption isotherms for Pb(II) sorption on volcanic tuff were obtained from experimental data at various lead concentrations under optimum conditions. The regression parameters and correlation coefficients (R^2) presented in Table 4 indicate that the adsorption data for Pb(II) removal best fitted the Langmuir adsorption isotherm.

However, the D–R and Freundlich isotherms are also important as they do not assume a homogeneous surface. At 293 K, the adsorption capacity b (Langmuir isotherm) was 16.8 mg/g and the adsorption capacity X'_m (D–R isotherm) and K_f (Freundlich) were 6.80 mg/g and 2.88 mg/g, respectively. The applicability of all isotherm models to the Pb(II) volcanic tuff system implies that both monolayer adsorption and heterogeneous surface conditions exist under the experimental conditions studied. Thus, adsorption

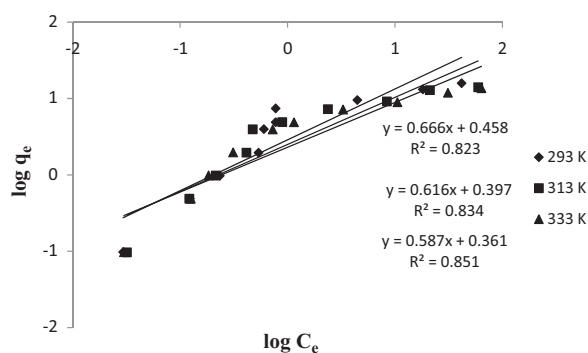


Fig. 7. The linearized Freundlich isotherm for adsorption of Pb(II) by volcanic tuff (tuff concentration, 10 g/L; contact time, 120 min.; shaking speed, 250 rpm at pH 5).

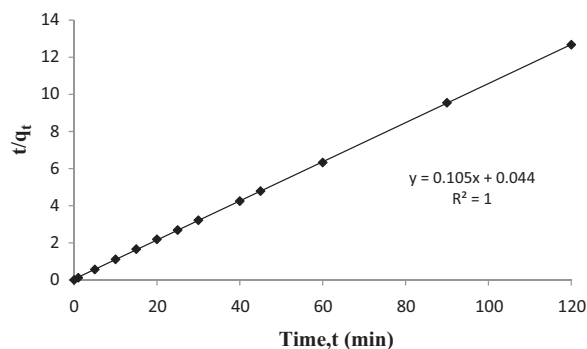


Fig. 8. Linearized pseudo-second-order kinetics plots for adsorption of Pb(II) by volcanic tuff. The volcanic tuff concentration was 10 g/L, the shaking speed was 250 rpm, and the temperature was 293 K.

of Pb(II) ions on the volcanic tuff is complex, which involves more than one mechanism [56]. This could occur if the adsorption of Pb(II) on the tuff surface forms a monolayer more often than it forms a bilayer and if the electron configuration of Pb(II) ions prevents a greater adsorption capacity. It is also possible that the adsorption occurs as a result of the interaction between the adsorbed molecule and an empty cation-exchange site. However, empty exchange sites are less common in a real-world solution; thus, ion exchange would more often require the replacement of an adsorbed charged species by another charged species from the surrounding solution. In addition, it was observed that increasing the initial Pb concentration in the solution decreased the removal efficiency. This could be owing to a progressive decrease in the proportion of covalent interactions and an increase in the proportion of electrostatic interactions at sites with a lower affinity for Pb(II) as the initial Pb(II) concentration increased [24].

3.5. Determination of adsorption kinetics

Two kinetic models, the pseudo-first order and the pseudo-second order equations were used for testing the experimental data to examine the adsorption kinetics. The slopes and intercepts of these curves were used for determining the pseudo-first-order and pseudo-second-order constants k_1 and k_2 and the equilibrium capacity q_e . The calculated (cal) value of q_e (Table 5) from the first-order kinetics model was observed to be dramatically lower than the experimental (exp) value. However, the pseudo-second-order kinetics model (Fig. 8 and Table 5) provided a near-perfect match between the theoretical and experimental q_e values. As a result, the sorption system appears to follow pseudo-second-order reaction kinetics. Similar results were reported for the adsorption of Pb(II) on different adsorbents with chemical structure similar to that of volcanic tuff [29–31,49].

The first- and pseudo-second-order kinetics rate constants for the adsorption of Pb(II) ions on volcanic tuff were $k_1 = 6.0 \times 10^{-4}$ 1/min and $k_2 = 0.252$ g/mg min, respectively. Similar results were also obtained in some works [2,50,57]. When the Pb(II) ion solution is mixed with the adsorbent, transport of the Pb(II) ions from the solution through the interface between the solution and the adsorbent and into the particle pores is effective.

Table 5
The kinetic constants for the adsorption of Pb(II) ions on the volcanic tuff.

T (K)	$(q_e)_{exp}$ (mg/g)	Pseudo-first-order kinetic			Pseudo-second-order kinetic		
		$(q_e)_{cal}$ (mg/g)	k_1 (1/min)	Δq_e (%)	$(q_e)_{cal}$ (mg/g)	k_2 (g/mg min)	Δq_e (%)
293	9.48	5.05	6.0×10^{-4}	43.8	9.49	0.252	11

Table 6
Thermodynamic parameters for the adsorption of Pb(II) on the volcanic tuff at various temperatures.

T (K)	$\ln b$	ΔG (kJ/mol)	ΔS (kJ/mol/K)	ΔH (kJ/mol)
293	2.823	-6.86		
313	2.688	-6.98	0.011	-3.75
333	2.638	-7.29		

There are essentially four stages in the process of adsorption by porous adsorbents [58]: (i) solute transfer from the bulk solution to the boundary film that borders the adsorbent's surface, (ii) solute transport from the boundary film to the adsorbent's surface, (iii) solute transfer from the adsorbent's surface to active intraparticle sites, and (iv) interactions between the solute molecules and the available adsorption sites on the internal surfaces of the adsorbent.

3.6. Effect of temperature and determination of adsorption thermodynamics

The results of the thermodynamic calculations are shown in Table 6. The Gibbs free energy of Pb(II) adsorption on volcanic tuff was -6.84, -6.98, and -7.29 kJ/mol for the temperature of 20, 40, and 60 °C, respectively. It was found that the negative Gibbs free energy indicating the adsorption process is spontaneous in nature and that the degree of spontaneity of the reaction decreases with increasing temperature, mainly owing to physisorption rather than chemisorption. The thermodynamic parameters are identical to those reported in the literatures [59–63]. These results are consistent with the Gibbs free energy for adsorption of Pb(II) on lateritic minerals ranging between -10.87 kJ/mol and -14.82 kJ/mol at a temperature range of 278–323 K [64]. Günay et al. [65] calculated the values of the Gibbs free energy as -8.86 and -8.89 kJ/mol for raw and pretreated Pb(II)-clinoptilolite system, respectively. Further, Yadava et al. [66] also calculated the Gibbs free energy of Pb(II) adsorption on China clay as -8.08, -4.53, and -3.07 kJ/mol for the temperature of 20, 30, and 40 °C, respectively. In addition, it is demonstrated in Fig. 9 that adsorption decreases with increasing temperature. The overall adsorption process seems to be exothermic ($\Delta H = -3.75$ kJ/mol). This result also supports the suggestion that the adsorption mechanism is primarily physisorption and that the resulting Pb-adsorbent complex is energetically stable. It can be

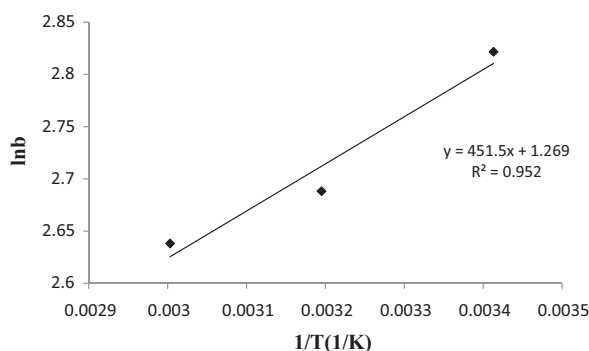


Fig. 9. Plot of the Langmuir constant ($\ln b$) versus temperature ($1/T$). The thermodynamic parameters in Table 6 are determined from this graph.

observed in Table 6 that the S values were positive (i.e., that entropy increases as a result of adsorption). This occurs as a result of the redistribution of energy between the adsorbate and the adsorbent. Prior to adsorption, the heavy metal ions near the surface of the adsorbent will be more ordered than in the subsequent adsorbed state and the ratio of free heavy metal ions to ions interacting with the adsorbent will be higher than in the adsorbed state. This results in an increase in the distribution of rotational and translational energy among a small number of molecules with increasing adsorption by producing a positive value of S as well as an increase in randomness at the solid solution interface during the process of adsorption.

4. Conclusions

This article presents the results of a detailed study of equilibrium and kinetics of the sorption process for removing Pb(II) ions from aqueous solution using a common, naturally occurring volcanic tuff. The maximum removal efficiency by the volcanic tuff was obtained as 92% for Pb at pH 5. These results provide a good indication of the different operating conditions that would be required for the efficient removal of Pb(II) from aqueous solution. It was also found that the Langmuir, D-R, and Freundlich isotherms could all be used to model the isothermal sorption of Pb(II) on volcanic tuff, and the kinetics data could be modeled by a pseudo-second-order kinetics equation. The negative value of change in the Gibbs free energy (ΔG) indicates that the adsorption process of Pb(II) on volcanic tuff was thermodynamically spontaneous under natural conditions. The results suggest that the capacity of adsorbents to adsorb certain metals can be calculated using the models described in this article. The adsorption capacity of the volcanic tuff adsorbent for Pb(II) was 16.81 mg/g and the adsorption rate (k_2) was 0.252 g/mg min. Thus, it can be concluded that volcanic tuff could be used as a low-cost and abundant source for the removal of Pb(II), and as an alternative to more costly materials such as ion-exchange resins and activated carbon.

Acknowledgment

I thank the Environmental Engineering Department of Aksaray University for providing laboratory equipment of the work described in this paper.

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