



Adsorption of Lead and Cadmium Ions onto Soils: Isotherm Models, and Thermodynamic Studies

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Highlights

- Research focused on the Pb reactivity with Cd during their transferal in the different soils.
- Results revealed used models could describe an adsorption-isotherm parameter.
- The adsorption ability of the heavy metal ions decreased once temperatures increased.

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Abstract

The source of pollution of both underground-water and water is the existence of heavy metals in such an environment. constitutes. This research sheds light on the lead (Pb) reactivity with Cadmium (Cd) throughout their transferal in the different soils. The batch technique was used in order to demonstrate the influence of temperature, initiate concentration, adsorption-isotherm. The consequences reveal that the Freundlich model, Langmuir model, Harkin-Jura model, and Halsey model are able to adequately describe the adsorption-isotherm parameter. The adsorption ability of the heavy metals decreased once temperatures increased. On the bases of the highest ability of adsorption (Q_m), the order of affinity of Lead and Cadmium for the investigated soil occurred at $Pb > Cd$, and the maximum capacities of adsorption of competition of two cations are decreased for the same effective sites. The change in the thermodynamic state functions such as standard free-energy (ΔG°), standard entropy (ΔS°), and standard enthalpy (ΔH°) were investigated. The interaction of adsorption is revealed to be exothermic in nature

1. INTRODUCTION

Heavy metals are considered as one form of toxins that commonly contaminate industrial and wastewaters [1]. In soils, the ions of heavy metals have been used as an appropriate valuable indicator of the quality of the environment worldwide. These heavy metals are considered as the stable elements and the most harmful-inorganic pollutants. They could take place naturally or unnaturally in the soil [2–4]. They produce from a diversity of industrial facilities, such as the process of the electrochemical metal, the process of dying, mining, battery storage, plating, and the activity of humans [5]. Also, it is important to mention that heavy metals are not able to be degraded or terminated. Wastewater which is not properly treated results in accumulation and residue metals' heavy in the environment. Inappropriate treatment for the discharged wastewater leads up to residue and accumulation of these metals in such an environment. These metals could be in the ground, underground water, residues, plants, and also in dust [6-15].

Since lead and cadmium are poisonous to humans, their contamination of soil is of high concern to researchers [16]. Dosages of these heavy metals might be transferred to the polluted site at different times. For example, soils could have high dosages of lead from the batteries of the cars

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at one time at the centers of recycling of batteries. Then, it could have also high dosages of cadmium from the batteries of the household. The main interest of those who involve in the remediation of the environment is to understand how specific metals might interact and contest for sites of soil sorption while entering a system of soil at various times. In addition, verifying the reaction's mechanisms between the surface of soils and these metals is useful due to shedding light on the stability and strength of the surface's metal bonding in such soils. Using the relative distribution of the adsorbed metal kept at interchange sites and in non-interchange soil fractions such as particularly adsorbed versus non-particularly adsorbed could obtain clear information about how cations of metals adsorbed on the surfaces of soils [17].

The set of serious dangerous heavy metals (copper, cadmium, and lead) are mostly hazardous to ecosystems and health of human due to their possibly extraordinary poisonousness [18]. That leads to several health troubles such as the damage of lung, damage of renal, liver disease, insomnia, headache, cancer of coughing, dizziness, etc. [19]. Several chemical mechanisms like the formation of surface complex, processes of adsorption, ionic exchange, and sedimentation are used to control the mobility of such heavy metals in the soils. Nevertheless, adsorption is considered as the most effective chemical process on the obtainability of metals' heavy on solid phases of soil [20].

Many studies have been conducted concerning the actions of adsorbed heavy metals by the soils. However, limited soils were studied in these researches. Moreover, they mimic actual conditions where wastewater was discharged into the ground were not inclusive. This work studies the adsorption of the utmost common heavy metals (Pb, and Cd) in several soils. Both the column and batch techniques were utilized in this work. In order to discover the influence of adsorption isotherm, contact time, and also the effect of temperature on the process of adsorption, the batch technique was used.

2. MATERIAL

2.1. Adsorbent

The used adsorbents in this work consists of four samples of several soils gathered from different areas in Basra. They were mined from several depths, varying from 20 to 50 cm beneath the surface of soils. The areas adjacent rivers and industries or societies were chosen as locations from which to mine the samples of soil. The samples of soils were dehydrated by using an oven at 383.15 °F for 2 days and afterward passed throughout mesh (2 mm) [21].

2.2. Heavy Metal Solutions

Heavy metals which are Pb^{2+} and Cd^{2+} were selected as the adsorbed materials in this work. The laboratory grades of lead (II) nitrate ($Pb(NO_3)_2$), and cadmium (II) nitrate hexahydrate ($Cd(NO_3)_2 \cdot 6H_2O$) were all utilized in such investigation. Metal ion stock-solutions of Pb^{2+} , and Cd^{2+} of 100 mg l⁻¹ have been made by dissolving 0.01 g in 100 mL de-ionized water. Five working solutions with metal as the initial concentrations of 10, 20, 30, 40, 50 μg L⁻¹ were used throughout the research. A standard curve of all used metal has been established by using 10-50 μg mL⁻¹. The prepared stock solutions were analyzed by UV-visible spectrophotometer. The measured maximum wave lengths of lead (530nm) and cadmium are illustrated with a maximum peak of (370 nm) [22].

2.3. Experimental Work

2.3.1. Batch Test

The adsorption kinetics was studied with four different concentrations of each heavy metals Pb^{2+} and Cd^{2+} (10, 20, 30, 40, and 50 $\mu g\ mL^{-1}$) have been prepared in duplicate for standard batch equilibration technique. The soil to water solution ratio in the experiments was 1:10 for lead and cadmium. Fifteen-milliliter glasses, blank centrifuge tubes with Teflon screw caps were washed with acetone, and finally rinsed with de-ionized water and dried and the same is done for UV-visible spectrophotometer. Duplicate samples of air-dried soil were equilibrated with a minimum volume of de-ionized water overnight (24 h) before the day of the experiment. Afterward, a certain volume of the stock solution of a metal ion is added in order to adjust the final volume and concentration. Each test tube was placed in a thermo-stated shaker at $25\pm 1^{\circ}C$ after equilibration for 6 h for lead and cadmium. Afterward, the suspension was centrifuged for thirty minutes at 3500 rpm, and 1 ml aliquot of each clear supernatant solution was detached and added indicator (dithiazol 1 mL) and analyzed on UV-visible spectrophotometer for the metal concentration. In every experiment, there was a blank measurement without test substance with the same amount of soil and total volume in H_2O is subjected to the same test procedure. [23,24].

2.3.2. Determination of Equilibrium Time

The adsorption time takings to obtain the state of equilibrium is called an equilibrium time. The batch technique was carried out by using concentration (100 mg/L) of solution having heavy metal with several intervals of time (0.5, 1, 3, 6, 12, 24, 48, and 72 h). The equilibrium time of adsorption can be achieved since it is easy to know the solutions' concentration by utilizing the batch technique [25].

2.3.3. Determination of Adsorption Isotherm

The adsorption isotherm can be determined once obtaining the equilibrium time of adsorption. The experiments were conducted by utilizing the batch technique, with preliminary concentrations of solutions varying from 10-50 $\mu g/ L$. these experiments were carried out until the adsorptions obtained equilibrium. The relation between the quantities of adsorbed metals' heavy by such soil (q) the concentrations of solutions having heavy metal at equilibrium C_e is known as an adsorption isotherm [26].

3. RESEARCH AND DISCUSSION

3.1. Coefficient of Linear Adsorption (Distribution Coefficient)

The coefficient of distribution (K_d) was computed employing the following Equation (1) [27].

$$q_e = K_d \times C_e \quad (1)$$

The coefficient of distribution (K_d) was computed by means of taking the proportion of concentration of adsorption in soil (q_e) and concentration of equilibrium in solution (C_e). The consequences are shown in Tables 1 and 2.

It is significant to mention that the adsorption isotherm is essential to be studied in the state of equilibrium. Thus, the contact time that is utilized for determined the adsorption isotherm was at 48 hr. The initial concentrations' solutions having Pb^{2+} and Cd^{2+} ions were at 10, 20, 30, 40, and 50 $\mu\text{g/L}$.

Figures 1 and 2 show the quantities of the equilibrium concentrations ' C_e ' and adsorbed heavy metals. It can be realized that the adsorption's quantity increased with enhancing the equilibrium concentrations.

This almost certainly happened when enhancing the metals' driving force toward the soils' active sites, and consequently the enhancing of concentrations [28-30]. The enhancing rate of the adsorbed quantity tends to progressively reduce and converge to the highest value. It may be attributed that there were adequate adsorption sites for adsorbed of heavy metal at lower preliminary concentrations; however, the quantity of heavy metal was overmuch as compared to the sites of adsorption at higher concentrations [31].

Table 1. Coefficients of adsorption distribution for Pb^{2+} ion adsorption on soils sample

Pb^{2+} at 25°C	Parameter	S1	S2	S3	S4
	K_d	1.0633	1.0557	1.079	1.0091
	R^2	0.9981	0.9525	0.9684	0.9918
at 35°C	K_d	1.1251	1.0989	1.1203	1.1729
	R^2	0.9848	0.9846	0.9865	0.9943
at 45°C	K_d	1.2556	1.2232	1.3568	1.5344
	R^2	0.9961	0.9779	0.998	0.9843
at 55°C	K_d	1.5152	1.3914	1.4463	1.5969
	R^2	0.9895	0.9915	0.9921	0.9719

Table 2. Adsorption distribution coefficients for Cd^{2+} ion adsorption on soils sample

Cd^{2+} at 25°C	Parameter	S1	S2	S3	S4
	K_d	1.846	1.0296	1.0437	5.1221
	R^2	0.9979	0.9941	0.9956	0.9913
at 35°C	K_d	2.0581	1.0786	1.0664	5.6187
	R^2	0.9899	0.9943	0.9909	0.9976
at 45°C	K_d	2.2036	1.1029	1.1058	5.8928
	R^2	0.9976	0.9963	0.9819	0.9951
at 55°C	K_d	3.1184	1.2632	1.2189	7.4251
	R^2	0.9894	0.9794	0.9995	0.9891

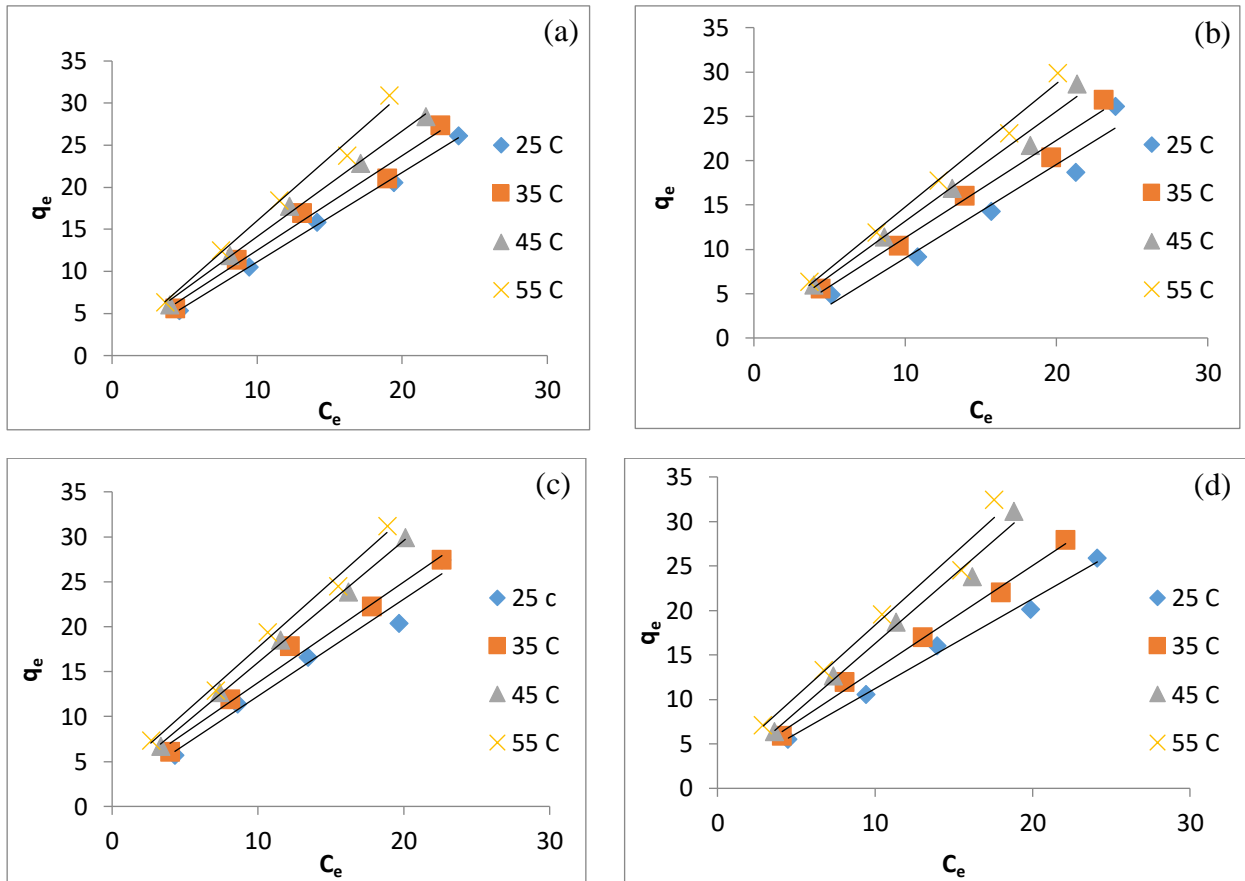
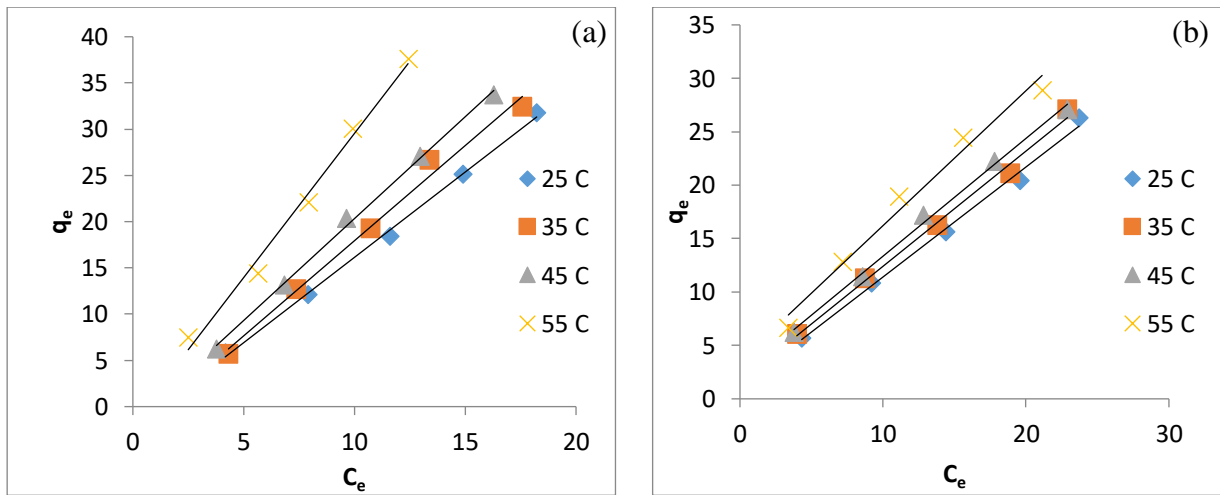


Figure 1. Distribution coefficients for Pb^{2+} ions on; a)S1, b)S2, c)S3,d) S4 soils sample



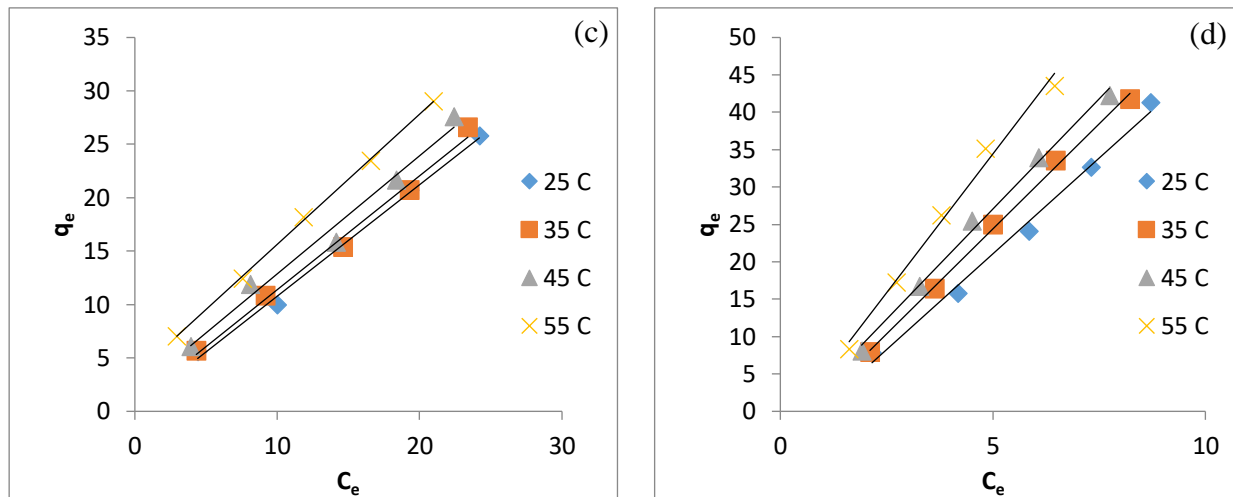
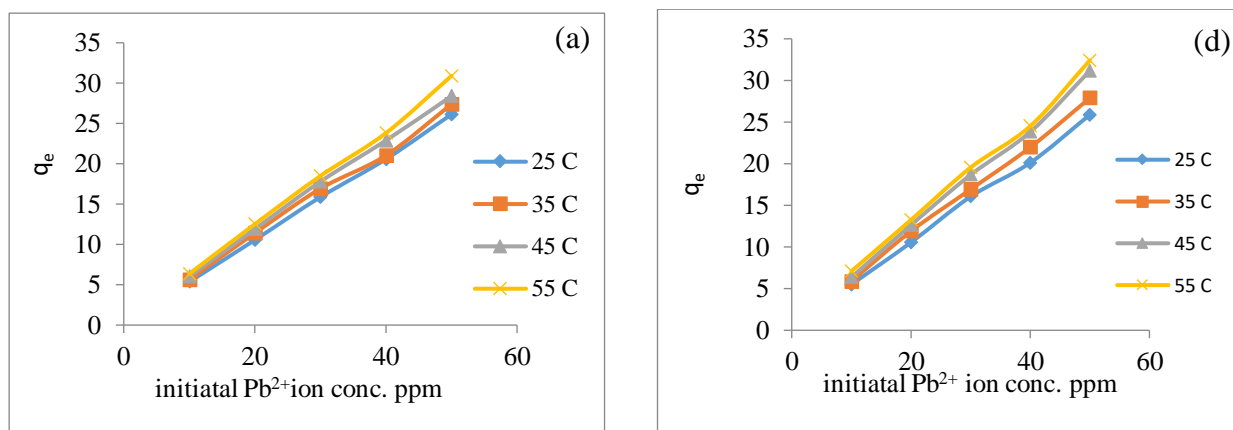


Figure 2. Distribution coefficients for Cd^{2+} ions on; a)S1, b)S2, c)S3,d) S4 soils sample

3.2. Influences of the Initial Adsorbate Concentration

The effect of lead and cadmium ions concentration was deliberated by batch adsorption experimentations carried out at 25°C by means of a concentration range of 10 – 50 $\mu\text{g/L}$. The adsorptions of lead ion on soil samples with different initial concentrations are shown in Figure 4.

The initial Pb and Cd ions concentration generates a significant-gradient driving strength to overwhelm the resistance of mass transfer to the metal between the liquid and solid phases. The collected data shows that Pb^{2+} and Cd^{2+} ions adsorption capability of soil sample was increased with Pb^{2+} and Cd^{2+} ions concentration enhancing from 10 to 50 $\mu\text{g/L}$, and adsorption capacity of soil sample was increased with increased temperature from 298K to 328K as shown in Figures 3 and 4. This may be attributed to the high mass transfer force [32].



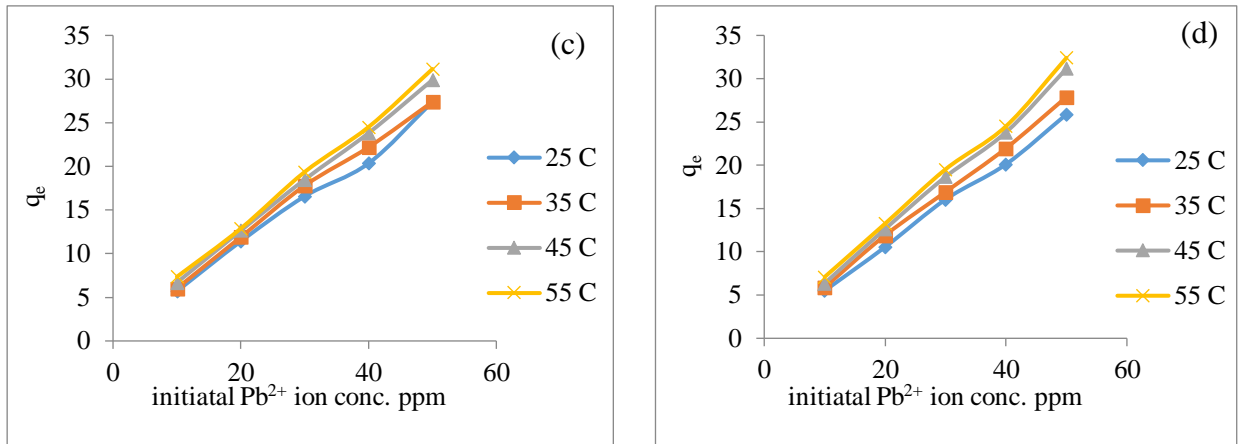


Figure 3. Effect of Pb^{2+} ion concentration on the; a)S1, b)S2, c)S3,d) S4 soil adsorption capacity of the soil

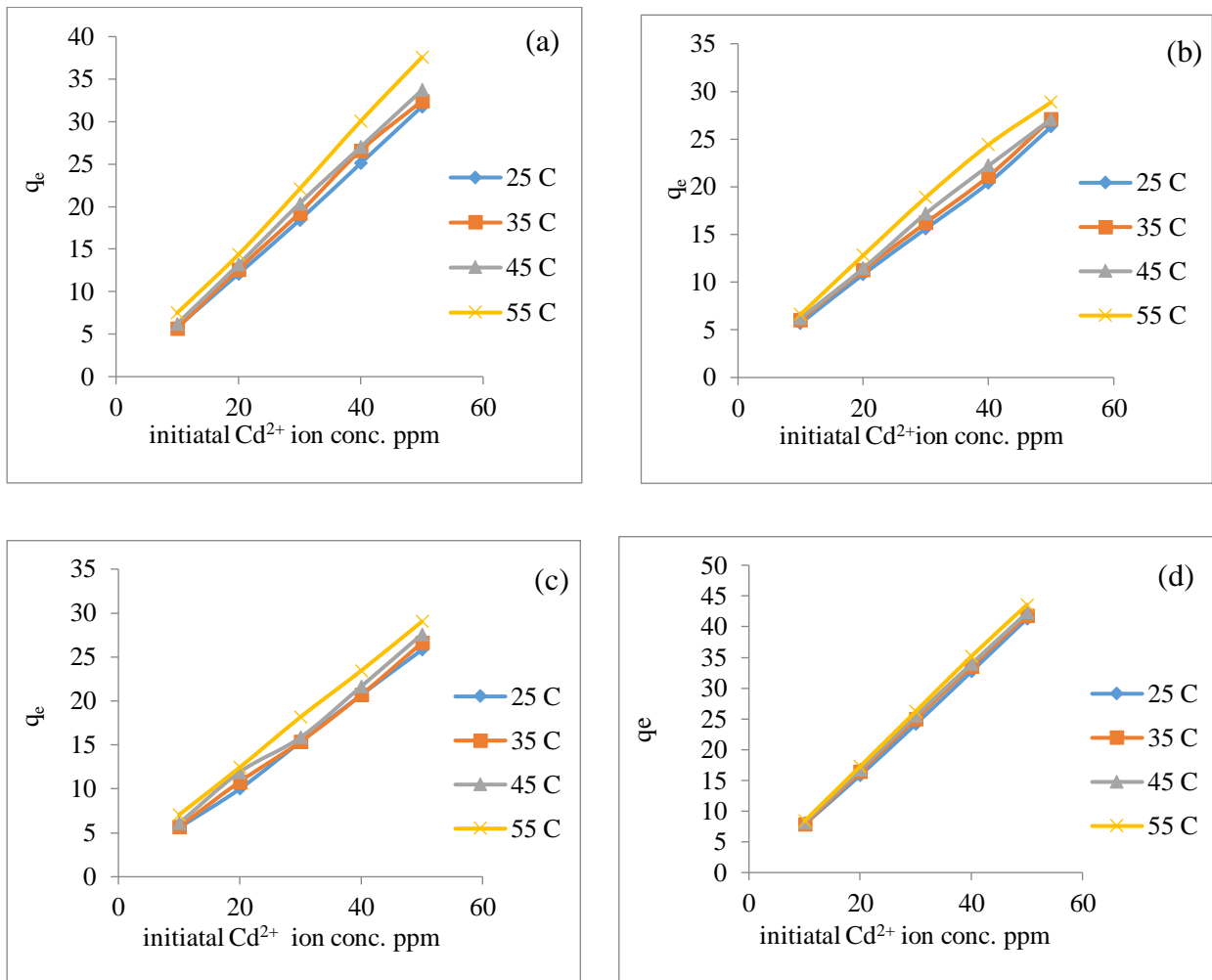


Figure 4. Effect of Cd^{2+} ion concentration on the; a)S1, b)S2, c)S3,d) S4 soil adsorption capacity of the soil

3.3. Adsorption Isotherm

In the equilibrium state, it is important to study the adsorption isotherm. Thus, the contact time utilized for investigating it was 2 days. In order to explain the isotherm, models of Freundlich and Langmuir adsorption isotherms have been adopted. Table 3, and Table 4 displays the parameters of the Freundlich and Langmuir isotherms [31].

Assessment of sorption performance Freundlich (Equation (2)), Langmuir (Equation (3)) isotherm was graphed employing equation of the standard straight line and related two factors for lead (II) and Cadmium (II) ions were computed from their corresponding plots [33]

$$\ln q_e = \ln K_E + \left(\frac{1}{n}\right) \ln C_e \quad (2)$$

$$\frac{1}{q_e} = \frac{1}{Q_{\max}} + \left(\frac{1}{Q_{\max} K_L}\right) \left(\frac{1}{C_e}\right) \quad (3)$$

where q_e (mg g^{-1}) is the quantity of adsorbed metal and C_e (lg mL) is the concentration of equilibrium. q_m (mg g^{-1}) and b (L g) are parameters of Langmuir isotherm. ' K_F ' and ' n ' are parameters of Freundlich isotherm [34, 35].

The model of Harkin-Jura (H-J) isotherm presumes the probability of multilayer adsorption on the adsorbent surface containing a distribution of heterogeneous pore [36]. Mathematically, such a model could be shown as in the following Equation (4).

$$\frac{1}{q_e^2} = \frac{B}{A} - \left(\frac{1}{A}\right) \log C_e \quad (4)$$

where B and A are constants of H -J achieved from graph $1/q_e$ versus $\log C_e$.

The model of Halsey isotherm (Equation (5)) is appropriate for multilayer adsorption. if this model well satisfies the equilibrium data, the adsorbent is non-homogeneous in nature. The Halsey isotherm is mostly showed as in the following Equation (5):

$$q_e = \exp\left(\frac{\ln K_H - \ln C_e}{n_H}\right). \quad (5)$$

Equation (5) can be written in a linearized form as Equation (6):

$$\ln q_e = \frac{1}{n_H} \ln K_H - \frac{1}{n_H} \ln C_e \quad (6)$$

where k_H and n are the constants of Halsey's isotherm and computed from the slope and intercept of the plot $\ln q_e$ vs. $\ln C_e$ [37]. As compared between Figures 5 and 6, the result shows that the more suitable model for fitting such data is the Halsey isotherm model based on the correction factor than Freundlich, Barkinn, and Langmuir isotherm model.

The isothermal factors for the four applied isotherms are stated in Table 3. On evaluation values of R^2 for the investigational points, the obtained coefficients of correlation were observed to be the greatest for the Halsey isotherm model and between 0.9784-0.9992 for Pb^{2+} ion and 0.9886-0.9998 for Cd^{2+} ion.

Table 3. Parameters of Langmuir, Freundlich, Halsey, and Harkins-Jura isotherm model and correlation coefficients for adsorption of lead ion

Models	Parameter	S1	S2	S3	S4
Freundlich	k_f	1.233389	1.202264	1.592575	1.394119
	n	1.043841	1.090037	1.120825	1.098901
	R^2	0.9992	0.9583	0.9865	0.9962
Langmuir	k_l	0.003616	0.004106	0.011404	0.008189
	Qm	322.5806	212.766	123.4568	151.5152
	R^2	0.6383	0.1266	0.5069	0.6605
Harkins-Jura	A	21.64502	16.83502	25.7732	23.36449
	B	1.313853	1.340067	1.304124	1.32243
	R^2	0.87	0.9203	0.8475	0.876
Halsey	k_h	1.244959	823.56	1.684586	1.440751
	1/n	0.958	1.0339	0.8922	0.91
	R^2	0.9992	0.9784	0.9865	0.9962

Table 4. Langmuir, Freundlich, Halsey, and Harkins-Jura isotherm model parameters and correlation coefficients for adsorption of cadmium ion

Models	Parameter	S1	S2	S3	S4
Freundlich	k_f	1.130577	1.802188	1.372777	2.868138
	n	0.872448	1.212562	1.101807	0.81666
	R^2	0.9998	0.9929	0.9886	0.9989
Langmuir	k_l	0.017199	0.010912	0.013831	0.034163
	Qm	102.0408	120.4819	47.61905	97.08738
	R^2	0.9699	0.6748	0.8102	0.9784
Harkins-Jura	A	25.5102	38.31418	23.64066	38.31418
	B	1.329082	22.77904	1.333333	0.885057
	R^2	0.8629	0.8914	0.9281	0.8972
Halsey	k_h	1.112989	1.65617	1.41788	2.364184
	1/n	1.1462	0.8763	0.9076	1.2245
	R^2	0.9998	0.9965	0.9886	0.9989

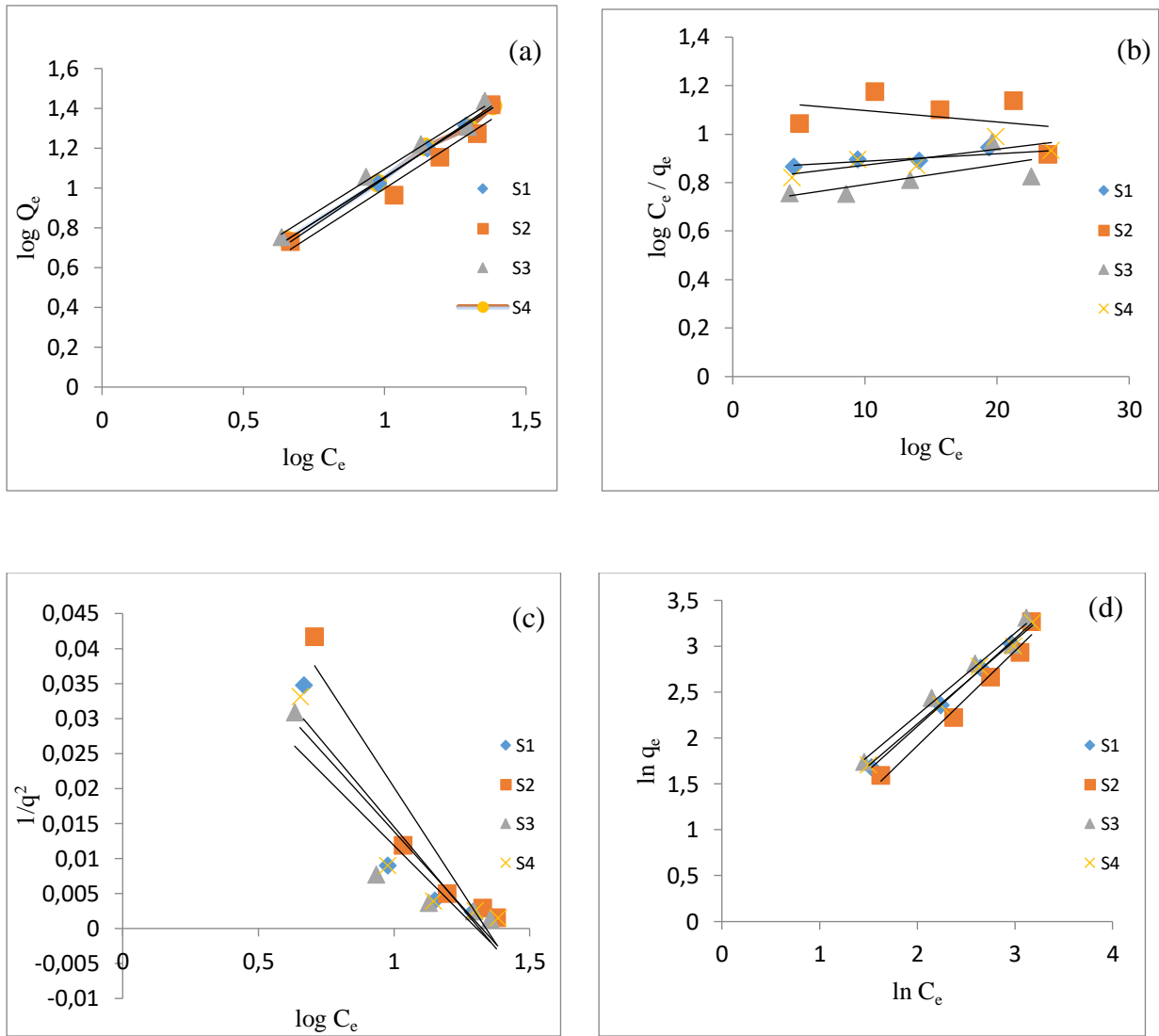
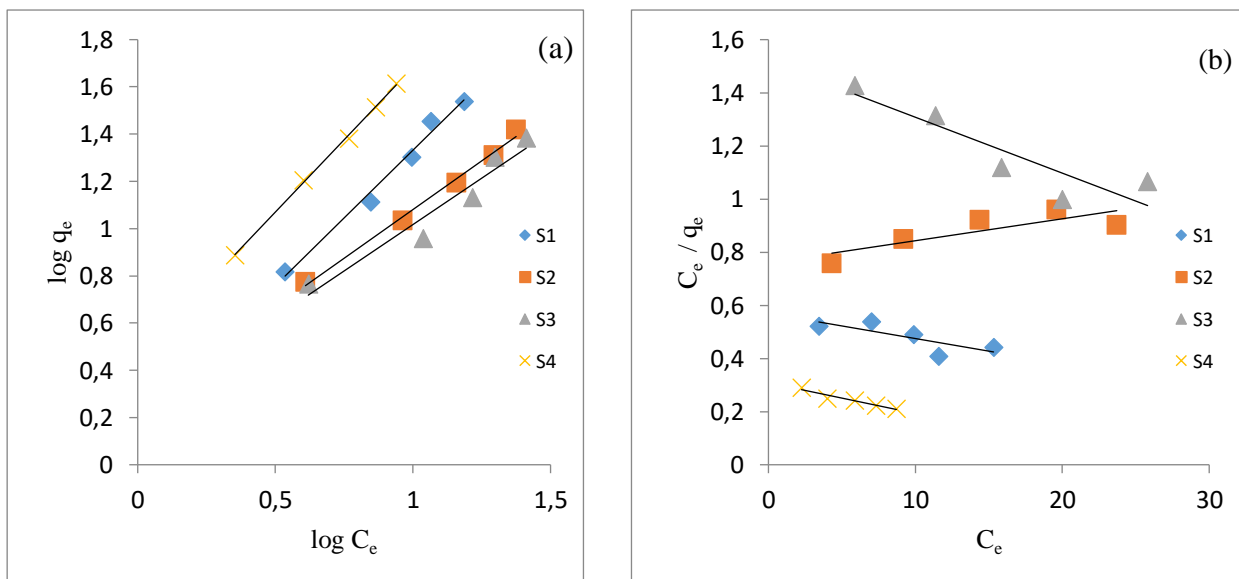


Figure 5. Adsorption Isotherm; a) Freundlich model b) Langmuir model c) Harkin model d) Halsey model for adsorption of Pb^{2+} ions on the soils



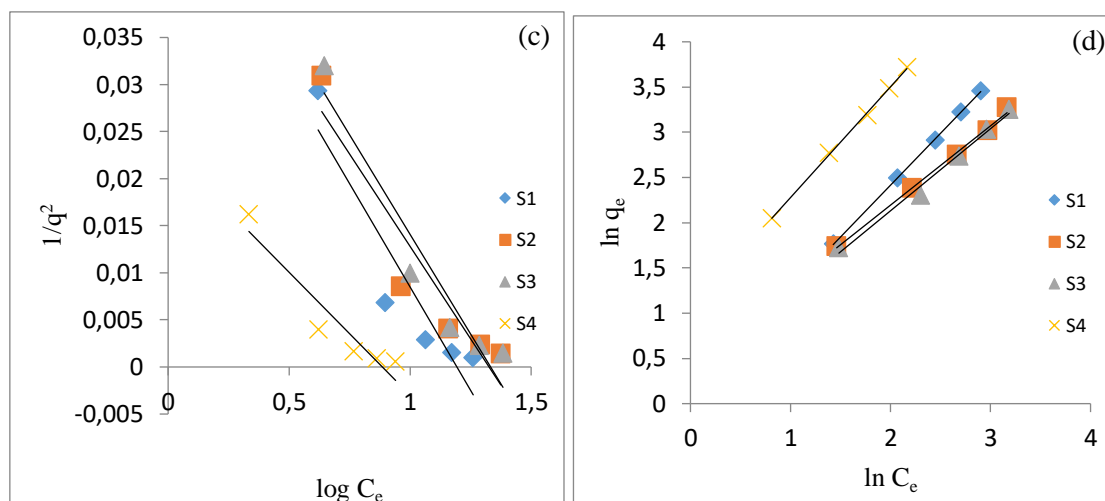


Figure 6. Adsorption Isotherm a) Freundlich model b) Langmuir model c) Harkin model d) Halsey model for adsorption of Cd^{2+} ions on the soils

3.4. Adsorption thermodynamics

In order to determine the process, the parameters of thermodynamic that should be considered are: alterations in standard entropy (ΔS°), standard free energy (ΔG°), and standard enthalpy (ΔH°) because of transmission of a unit mole of solute from solution to the liquid-solid interface. The value of ΔH° and ΔS° were calculated employing the following Equation (7):

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (7)$$

The values of ΔH° and ΔS° were computed correspondingly from the slope and intercept of the van't Hoff plot of $\ln K_d$ versus $1/T$, where R (0.8314 KJ/mol K) is the constant of universal gas, T (K) is the absolute temperature of the solution, and K_d (l/mg) is the distribution coefficient constant. ΔG° was calculated using Equation (8) [38, 39]:

$$\Delta G^\circ = -RT \ln K_d \quad (8)$$

The calculated values of ΔH° , ΔS° , and ΔG° are listed in Tables 5 and 6.

The values of ΔG° , which is negative, spontaneity reveals for every process of sorption, with the spontaneity order Pb^{2+} ion > Cd^{2+} Cd ion. The value of ΔH° , which is negative, for the process of sorption of every ion's metal indicates the sorption processes' nature of exodo-thermic. Besides, the sorbent's capacity of sorption is reduced by increasing the temperature. The values of ΔS° , which is positive, noticed for such ion's metals of the soil show a rise in unpredictability at the interface of solid-solution through soils.

Table 5. Thermodynamic factors for adsorption of Pb^{2+} ion on soils sample

Soils	ΔG°				ΔH°	ΔS°	R^2
	25 ⁰ C	35 ⁰ C	45 ⁰ C	55 ⁰ C			
S1	-15.214	-30.198	-60.206	-113.37	-946.133	3.196151	0.9263
S2	-2.9814	-24.162	-53.291	-90.117	-860.915	2.885374	0.9841

S3	-18.8476	-29.103	-80.71	-100.67	-868.73	2.957124	0.9286
S4	-2.2455	-40.858	-113.25	-127.7	-1343.38	4.516664	0.9443

Table 6. Thermodynamic parameters for adsorption of Cd^{2+} ion on soils sample

Soils	ΔG°				ΔH°	ΔS°	R^2
	25 ⁰ C	35 ⁰ C	45 ⁰ C	55 ⁰ C			
S1	-151.957	-184.918	-208.987	-310.288	-1321.93	4.904927	0.8579
S2	-7.23081	-19.385	-25.907	-63.745	-512.226	1.728481	0.857
S3	-10.602	-16.47	-26.602	-54.005	-404.019	1.376133	0.8729
S4	-405.92	-442.22	-469.17	-546.98	-937.154	4.480165	0.8868

All the calculated values of ΔH° , ΔS° , and ΔG° for adsorption of Pb^{2+} and Cd^{2+} ions are presented in Tables 5 and 6. The consequences are demonstrated in the presented table denoted to a negative value of ΔH° (exothermic in nature) for adsorption of Pb^{2+} and Cd^{2+} ions on the soils. The positive value of ΔS° , which denotes that there increases in state of randomness in the molecules throughout the process [40].

An enhancing in temperature followed in a decrease in the rate of adsorption of lead, and cadmium demonstrating that such process is exothermic. The parameters of thermodynamic for Pb^{2+} and Cd^{2+} ions adsorption were quantified to enhance the utility of measured data and satisfying factors to a broader range of temperatures [41,42].

K_d decreased with temperature demonstrating that the adsorption was exothermic. Negative values of ΔG° show spontaneous adsorption and the degree of the spontaneity of the reaction decreases with increasing temperature [43]. The negative value of ΔH° indicated the exothermic nature of the adsorption interaction.

The negative standard enthalpy change of (-860.915 to -1343.38) kJmol^{-1} for Pb^{2+} and (-404.019 to -321.930) kJmol^{-1} for Cd^{2+} ion in such work proposes that the adsorption of ions are exothermic, which is supported by the decreasing adsorption of Pb^{2+} and Cd^{2+} ions with enhance in temperature. The positive standard entropy change (2.885374-4.51666432 Jmol K^{-1}) for Pb^{2+} ion, and (1.376133-4.104927 Jmol K^{-1}) for Cd^{2+} ion reflects the affinity of the particles of soil towards Pb^{2+} and Cd^{2+} ions [44].

4. CONCLUSIONS AND RECOMENDATION

The soil sample was positively employed for the study adsorption of lead and cadmium ions on an aqueous solution by batch adsorption method. The coefficient of distribution for adsorption of lead (Pb^{2+}) less than Cadmium (Cd^{2+}) in the different soils. In addition, it focuses on the behaviors of the adsorption of lead and cadmium in several environmental soils. The quantity of heavy metal was overmuch as compared to the sites of adsorption at higher concentrations. The equilibrium data were examined using the Langmuir, Freundlich, Harkin-Jura, Halsey isotherms. Correlation coefficients indicated the following order to fit isotherms Halsey > Freundlich > Harkin-Jura > Langmuir. Thermodynamic effect showed that the adsorption is exothermic, and the entropy is increasing and its spontaneous adsorption within the limits of chemical adsorption and the degree

of the spontaneity of the reaction decreases with enhancing temperature. The authors would recommend the following:

- 1- Study the desorption of lead and cadmium ions.
- 2- Study the impact of pH on the lead and cadmium ions.
- 3- Study the adsorption of other ions.

CONFLICTS OF INTEREST

No conflict of interest was stated by the authors.

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