

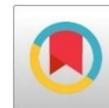


## Modeling the Sorption of Industrial Wastewater Heavy Metals in Two Different soils

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**ABSTRACT:** The sorption characteristics of the most common heavy metals; cadmium, cobalt, nickel, and lead have been investigated by two different natural soils; sandy and sandy loam soils. The soil samples used in the present experiment were taken from the surface layer (0-30 cm depth) of the El-Hammam region, Matrouh Governorate (sandy loam soil), and Nubaria region for sandy soil. The synthetic industrial wastewater was prepared from the stock solution of heavy metals compatible with industrial wastewater of the Paper industry wastewater company and Food industry Wastewater Companies. To study and compare the sorption of heavy metals on sorbent materials, the sorption data were fitted to some sorption isotherm models using the software IsoFit such as Linear, Freundlich, Langmuir, Langmuir-Freundlich, Generalized Langmuir-Freundlich, and proposed new models. Measured and simulated data were compared statistically for evaluating model reliability. It was observed that both soils sorbed about 63 to 85% (sandy soil) and about 75 to 87% (sandy loam soil) of the initial concentration of the heavy metal ions from the aqueous solution. The sorption of heavy metals is more pronounced in sandy loam soil than in sandy soil. The sorption percentage was decreased by increasing the initial concentration. The average sorption percentage overall initial concentrations were 74.18 (Cd), 66.17 (Co), 80.25 (Ni), and 79.78% (Pb) for sandy soil and 80.84 (Cd), 77.50 (Co), 84.96 (Ni), and 86.79% (Pb) for sandy loam soil. In the present study, experimental data were analyzed to examine the adsorption isotherm models. The distribution coefficients,  $K_d$  determined from the linear part of the sorption isotherm varied within a wide range, from 44.65 to 95.42 L/kg for sandy soil and from 83.82 to 178.73 L/kg for sandy loam soil. Metals can be arranged according to their  $K_d$  values, i. e. their affinities for the soil, there resulting in the following relative sequence:  $Pb > Ni > Cd > Co$ . This general sequence tends to vary slightly for different soil types. The present study recommends future studies are needed to verify the competitive mechanism of heavy metals sorption correlated to the soil characteristic parameters.

**Keywords:** industrial wastewater – sorption – transport- batch sorption- heavy metals- sorption isotherm models.

### NOTATIONS

Terms used in the various equations of this paper are defined as follows:

qe	Sorption capacity at equilibrium, mg/kg
Ce	The equilibrium concentration of sorbate in solution, mg/l
Kd	Henry's law constant, L/kg (Partition or Distribution coefficient)
KF	Freundlich isotherm constant
n	Exponent in Freundlich isotherm
C0	Initial concentration
qm	The maximum sorption capacity, mg/kg
bL	The affinity of adsorbent to the adsorbate L/mg
KGK1	GK1 isotherm constant
nGK2	Exponent in GK2 model
bGK2	Affinity constant of GK2 model
KGK2	GK2 isotherm constant
bGLF	The affinity constant in Generalized Langmuir- Freundlich isotherm

## INTRODUCTION

Human activity affects the wastewater that affects water supplies. **Tilley et al. (2016)** state that wastewater can arise from residential, commercial, industrial, or agricultural operations, surface runoff or stormwater, and sewer discharge or seepage. The use of untreated industrial wastewater for domestic, agricultural, and other purposes poses health risks. Due to their toxicity, durability, and propensity to bioaccumulate, heavy metals in wastewater pose one of the most difficult environmental issues.

Heavy metals in wastewater are one of the most challenging environmental concerns due to their toxicity, persistence, and propensity to bioaccumulate (**Mwangi et al., 2012**). Many companies discharge heavy-metal wastewater into the soil and water. This can lead to serious environmental damage and harm to human health. Governments should implement regulations to limit the amount of heavy metals discharged into the environment, and companies should invest in technologies to treat wastewater before discharging it. This reduces water quality and increases metal content (**Yu et al., 2013**). These heavy metals include Cd, Pb, Cu, Fe, Ni, Mn, and Cr. Heavy metal contamination is not a recent problem, but its control remains a worldwide concern (**Monachese et al., 2012**).

Among the sources of environmental pollution associated with heavy metals are heavy metal mining, the metal industry, foundries, plating, painting, battery making, tanning, textiles, papermaking, and other similar industries that repel and release elements such as cadmium, mercury, nickel, lead, zinc, chromium, copper, and silver. Heavy metals in municipal wastewater disrupt the wastewater treatment system, reduce purification efficiency, and, in acute cases, stop biological activities in treatment systems. The cationic heavy metal retention in soils is due to its strong adsorption onto negatively charged soil surfaces, the ability to form complex molecules with organics found in the soil, and the formation

of oxides, hydroxides, and other insoluble minerals in the soil (**Stewart, et al., 2003**).

One of the biggest environmental issues today is heavy metal contamination. Three types of heavy metals are of concern, including toxic metals “such as Hg, Cr, Pb, Zn, Cu, Ni, Cd, As, Co, Sn, etc.”, and precious metals “(such as Pd, Pt, Ag, Au, Ru, etc.”, and radionuclides “such as U, Th, Ra, Am, etc.” (**Wang and Chen, 2006**).

When wastewater is discharged into soil, it seeps through the soil before progressing downward into groundwater, or it flows past surface soil to lowland. According to numerous research, heavy metals can be taken out of soils (**Abat et al., 2012**). Soils are a crucial natural resource that treats wastewater. They act as filters, preventing harmful metals from seeping into groundwater or flowing into other areas and rivers. This process is essential for maintaining our environment and communities health and safety. By utilizing the soil's natural properties, we can effectively treat wastewater and protect our precious water resources. (**Srivastava et al., 2005**).

In this study, the sorption characteristics of the most common heavy metals; cadmium, cobalt, nickel, and lead by two different natural soils; sandy and sandy loam soils have been investigated. These heavy metals are found in the effluent of almost every industry and hence were selected for the study.

## MATERIALS AND METHODS

### Soil

The soil used in the present experiment was taken from the surface layer (0-30 cm depth) of the El-Hammam region, Matrouh Governorate (sandy loam soil), and Nubaria region for sandy soil. The soils were air-dried and passed through a 2.0 mm sieve. Some physicochemical properties of the soil samples are reported in Table (1). The soil properties were performed according to the procedures outlined in Carter and Gregorich (2008).

**Table (1). Physical and chemical analysis of soils used in the present study**

Parameters	Sandy soil (Nubaria)	Sandy loam soil (El-Hammam)
<b>Particle-size distribution, %</b>		
Sand	91.12	74.32
Silt	4.00	16
clay	4.88	9.68
Textural grade	Sand	Sandy loam
<b>Water retention parameters</b>		
$\theta_r$ , cm <sup>3</sup> /cm <sup>3</sup>	0.0529	0.0477
$\theta_s$ , cm <sup>3</sup> /cm <sup>3</sup>	0.3758	0.4409
$\alpha$ , 1/cm	0.0323	0.0328
n	2.6491	1.5277
Ks, cm/day	382.80	125.51
OM, %	0.42	0.81
CaCO <sub>3</sub> , %	2.63	1.06
pH	8.00	8.10
EC, dS/m	0.58	4.00
<b>Soluble cations, me/l</b>		
Ca	2.33	13.28
Mg	3.01	24.72
Na	0.32	1.53
K	0.11	0.48
<b>Soluble Anions, me/l</b>		
CO <sub>3</sub> +HCO <sub>3</sub>	0.33	3.78
Cl	4.49	12.75
SO <sub>4</sub>	0.93	23.47
<b>Available nutrients, mg/kg</b>		
N	14.2	18.7
P	60.0	80.5
K	600	800
Pb	0.11	0.22
Ni	0.09	0.18
Cd	0.17	0.27
Co	0.02	0.03

**Reagents**

In the present study, we used only analytical-grade chemical reagents. The reagents were Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, and Pb(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O were purchased from Al-Gomhoria Chemical Co., Alexandria, Egypt, Also NaOH and HNO<sub>3</sub> which were used for pH adjustment were bought from Al-Gomhoria Company for the trade of medicines, chemicals and medical supplies, Alexandria, Egypt. The stock solutions of Cd(II), Co(II), Ni(II), and Pb(II) with a concentration of 1000 mg/L were prepared by dissolving a confirmed amount of corresponding reagent into a 1000 mL volumetric flask, respectively. The stock solutions and the working solutions diluted from the stock solutions were stored at 4°C under HNO<sub>3</sub> (5% w/w) conditions to prevent the heavy metal ions from hydrolysis. Deionized (DI) water was used throughout the experiment.

**The batch sorption of heavy metals:**

The synthetic industrial wastewater was prepared from the stock solution of heavy metals compatible with industrial wastewater of the Paper industry wastewater company and Food industry wastewater companies.

Stock solutions of the Pb<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup> and Co<sup>2+</sup> 1000 mg/l were prepared from analytical grade of high purity salts (Pb(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in 5% HNO<sub>3</sub>). Subsequent dilutions of (0.0 to 6.23 mg/l for Cd<sup>2+</sup>, (0.0 to 5.146 mg/l) for Co<sup>2+</sup>, (0.0 to 9.449 mg/l) for Ni<sup>2+</sup> and (0.0 to 10.039 mg/l) for Pb<sup>2+</sup>, respectively were prepared by suitably diluting the stock solution with distilled water. The experiments were performed in 100 ml flasks containing 50 ml of heavy metals solution with different concentrations plus 2.0 g of soil (sandy or sandy loam soil) with three replicates for each experiment. The mixture was shaken in a rotary

shaker at 200 rpm for one hour followed by filtration using Whatman filter paper (No.1). The filtrate containing the residual concentration of heavy metals was stored for analysis. The filtrate was analyzed for the tested heavy metals using Inductively Coupled Plasma=Emission Spectrometry, ICP (Ultima 2 JY Plasma) according to Ivajlo et al. (2008). The data were fitted using some sorption models.

The capacities of the sorbents were calculated after equilibrium was attained. The metal sorbed capacity for each sample was calculated according to a mass balance of the metal ion using the following equation (Vijayaraghavan et al., 2006):

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (1)$$

Where:  $C_0$  is the initial concentration of metal ( $\text{mg L}^{-1}$ ),  $C_e$  is the equilibrium metal concentration ( $\text{mg L}^{-1}$ ) and  $q_e$  is the quantity of metal sorbed at equilibrium ( $\text{mg kg}^{-1}$ ).  $m$  is the mass of the adsorbent (g), and  $V$  is the amount of the solution (L). The percent sorbed of metals from the solution was calculated by the following equation (Sethuraman and Balasubramanian, 2010):

$$\% \text{ sorbed} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

#### Mathematical modeling

To study and compare the heavy metals sorption on sorbent materials, the sorption data were fitted to some sorption isotherm models using the

software IsoFit (Matott, 2004; Matott and Rabideau, 2008). The software package IsoFit offers three options for weighted least squares fitting of the sorption models to experimental data: uniform weighting, sorbed relative (weights are inversely proportional to sorbed concentrations), and solute relative (Weights and solute concentrations have an inverse relationship).

Isotherm sorption models have been used to predict the ability of a certain adsorbent to remove a pollutant down to a specific discharge value. When a mass of adsorbent and a waste stream are in contact for a sufficiently long time, an equilibrium between the amount of pollutant adsorbed and the amount remaining in the solution will develop.

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Adsorption isotherm is the mathematical representation of adsorption capacity ( $q_e$ ) versus equilibrium concentration of the solute ( $C_e$ ). Modeling adsorption isotherm data is important for prediction or comparison among adsorption performances. One, Two, three, and four - parameters isotherm models are suggested to model the sorption data (Table 2).

Table (2). Isotherm sorption models used in the present study

Sorption isotherm models	Equation
<b>Single parameter model</b>	
Linear or Henry isotherm Xue et al. (2001)	$q_e = K_d \times C_e$ (3)
<b>Two parameters model</b>	
Freundlich isotherm Freundlich (1906) Jain et al. (2003)	$q_e = K_F \times C_e^{1/n}$ (4)
Langmuir isotherm Langmuir (1916) Chen (2013)	$q_e = \frac{q_m \times b_L \times C_e}{1 + b_L \times C_e}$ (5)
A new model (GK1)	$q_e = q_m (1 - EXP(-K_{GK1} \times C_e))$ (6)
A new model (GK2)	$q_e = \frac{K_{GK2} \times C_e}{b_{GK2} + C_e^{n_{GK2}}}$ (7)
<b>Three parameters model</b>	
Langmuir-Freundlich isotherm Azizian and Eris (2021)	$q_e = \frac{q_m \times b_{LF} \times C_e^{1/n}}{1 + b_{LF} \times C_e^{1/n}}$ (8)
Generalized Langmuir-Freundlich isotherm Ayawei et al.(2017)	$q_e = \frac{q_m (b_{GLF} \times C_e)^{1/n}}{1 + (b_{GLF} \times C_e)^{1/n}}$ (9)

#### Performance evaluation of sorption models

A statistical comparison of measured and simulated data is used to assess the reliability of the model (D'Agostino and Stephens, 1986). Agreement between predicted and measured values was determined by calculating the determination coefficient ( $R^2$ ), the Root Mean Square Error (RMSE), the Normalized Root Mean Square Error, NRMSE (Jacovides and Kontoyiannis, 1995), Nash-Sutcliffe Efficiency (EF), (Nash and Sutcliffe, 1970) and the Index of Willmott (d), (Willmott, 1982,1985&2012).

## **RESULTS AND DISCUSSION**

### Sorption of heavy metals

The equilibrium isotherms for every single heavy metal ( $Pb^{+2}$ ,  $Ni^{+2}$ ,  $Cd^{+2}$ , and  $Co^{+2}$ ) onto both sandy and sandy loam soils are presented in Tables (3 and 4), respectively, and Figures 1 to 8. From the results, it was observed that both soils sorbed about 63 to 85% (sandy soil) and about 75 to 87% (sandy loam soil) of the initial concentration of the heavy metal ions from the aqueous solution. The sorption of heavy metals is more pronounced in sandy loam than in sandy soil. The sorption percentage was decreased by increasing the initial concentration. The average sorption percentage overall initial concentrations were 74.18 (Cd), 66.17 (Co), 80.25 (Ni), and 79.78(Pb) for sandy soil and 80.84(Cd), 77.50 (Co), 84.96 (Ni), and 86.79(Pb) for sandy loam soil.

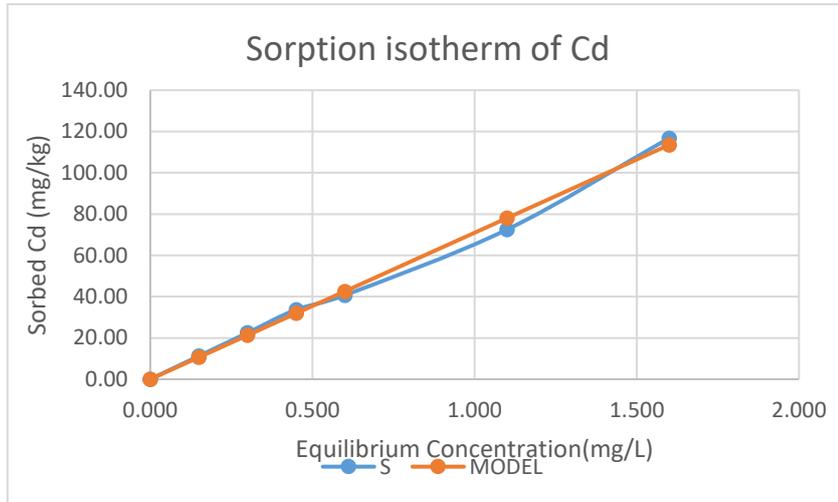


Figure (1). Linear sorption isotherm of Cd on sandy soil

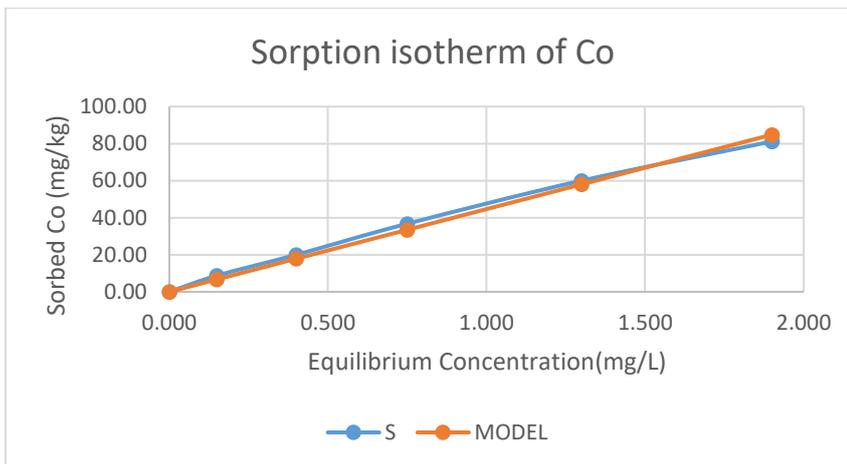


Figure (2). Linear sorption isotherm of Co on sandy soil

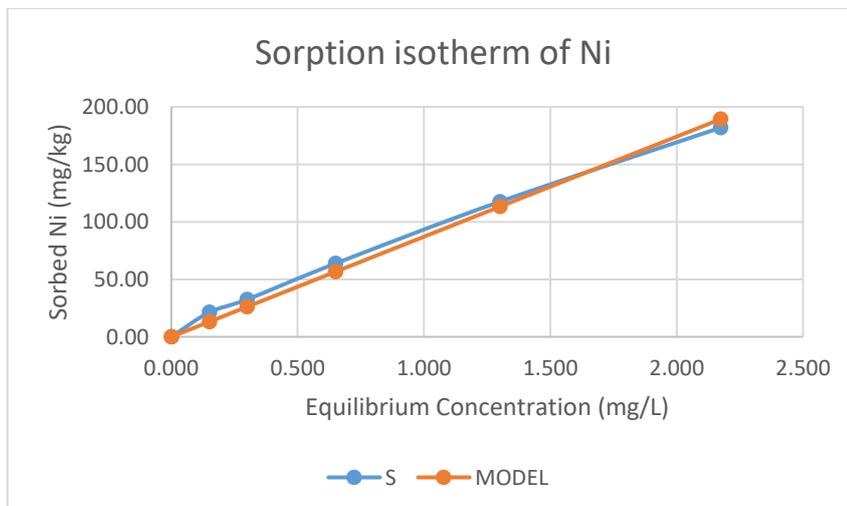


Figure (3). Linear sorption isotherm of Ni on sandy soil

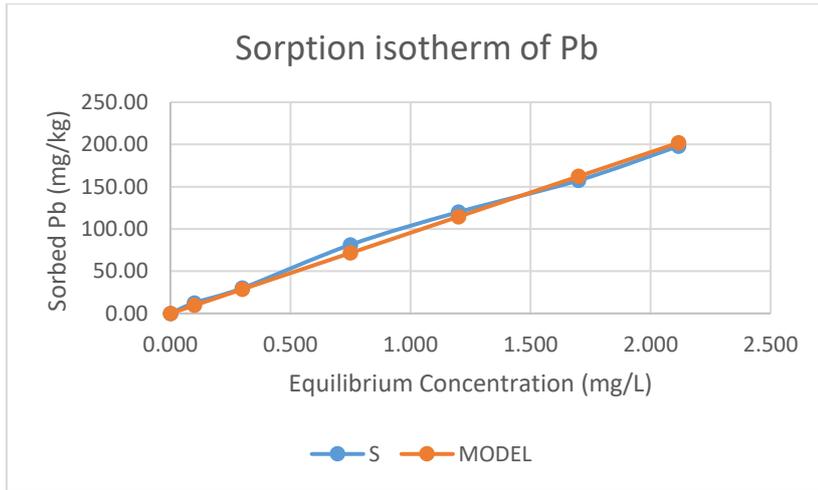


Figure (4). Linear sorption isotherm of Pb on sandy soil

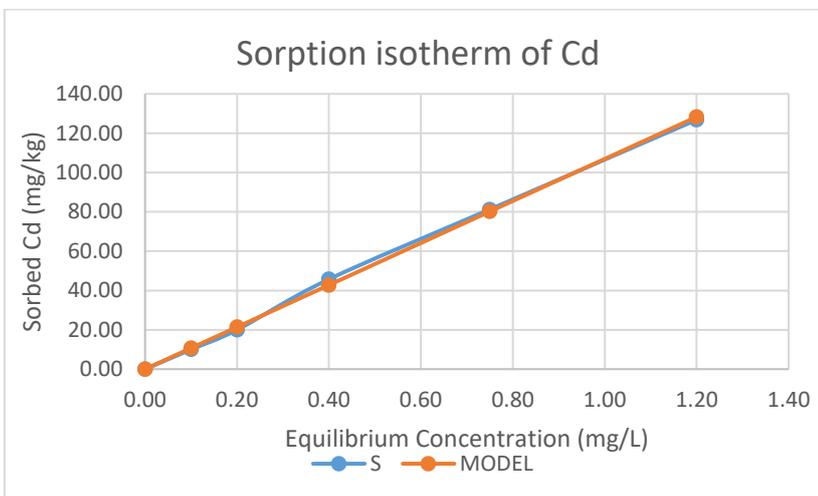


Figure (5). Linear sorption isotherm of Cd on sandy loam soil

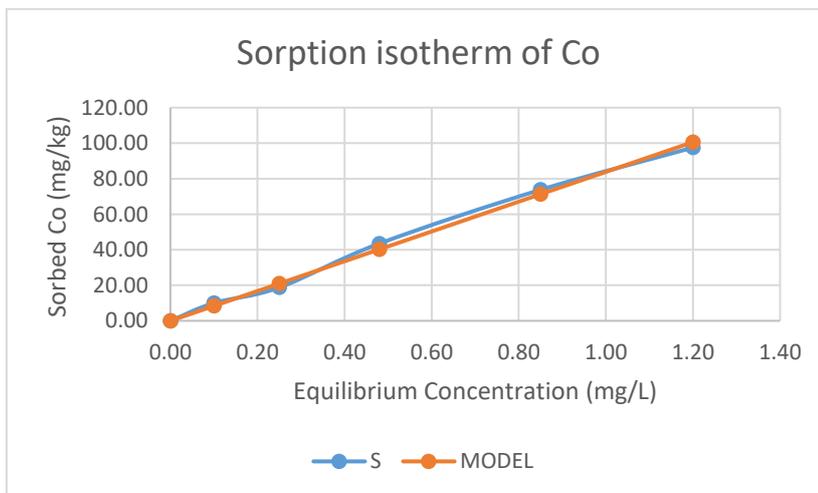


Figure (6). Linear sorption isotherm of Co on sandy loam soil

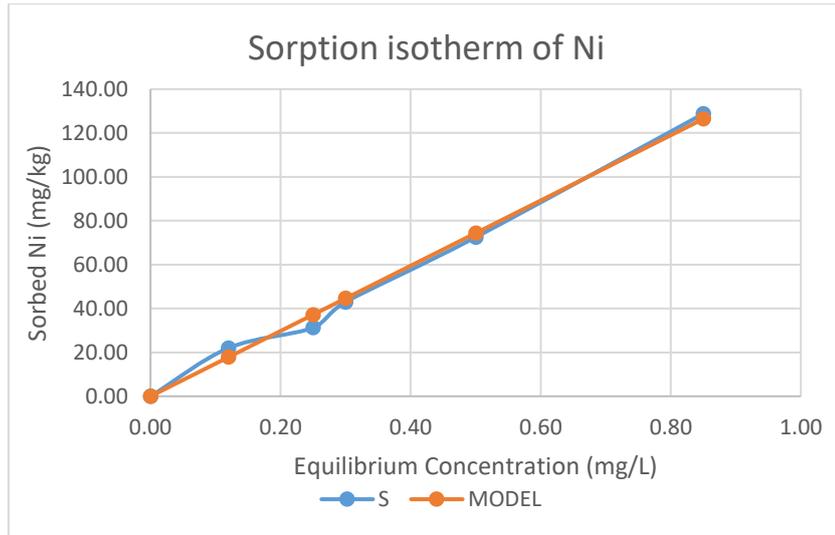


Figure (7). Linear sorption isotherm of Ni on sandy loam soil

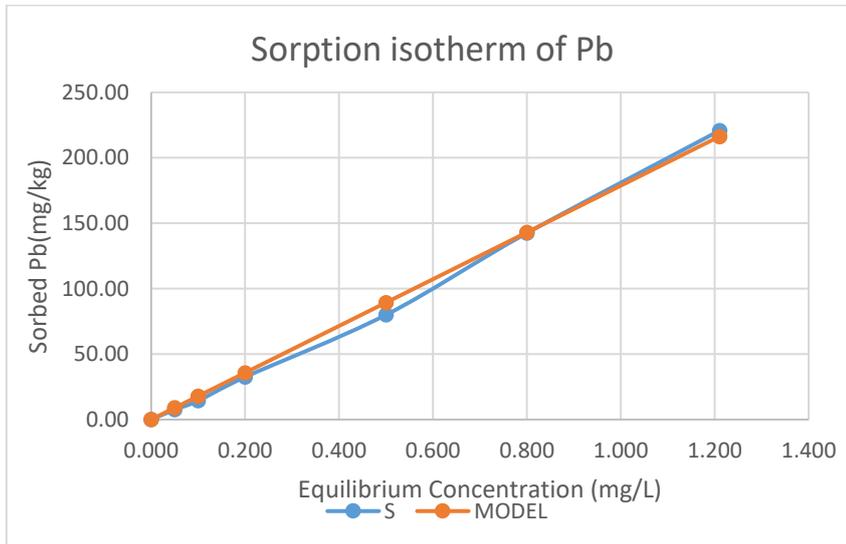


Figure (8). Linear sorption isotherm of Pb on sandy loam soil

**Table (3). Equilibrium sorption of heavy metals on the sandy soil**

<b>Cd<sup>2+</sup></b>			<b>Co<sup>2+</sup></b>		
<b>C<sub>e</sub> mg/l</b>	<b>q<sub>e</sub> mg/kg</b>	<b>% sorbed</b>	<b>C<sub>e</sub> mg/l</b>	<b>q<sub>e</sub> mg/kg</b>	<b>% sorbed</b>
0.000	0.00		0.000	0.00	
0.150	11.25	75.00	0.150	8.75	70.00
0.300	22.50	75.00	0.400	20.00	66.67
0.450	33.75	75.00	0.750	36.75	66.22
0.600	40.73	73.08	1.300	60.00	64.86
1.100	72.50	72.50	1.900	81.15	63.08
1.600	116.83	74.49			

<b>Ni<sup>2+</sup></b>			<b>Pb<sup>2+</sup></b>		
<b>C<sub>e</sub> mg/l</b>	<b>q<sub>e</sub> mg/kg</b>	<b>% sorbed</b>	<b>C<sub>e</sub> mg/l</b>	<b>q<sub>e</sub> mg/kg</b>	<b>% sorbed</b>
0.000	0.00		0.000	0.00	
0.150	21.25	85.00	0.100	12.50	83.33
0.300	32.50	81.25	0.300	30.00	80.00
0.650	63.75	79.69	0.750	81.25	81.25
1.300	117.50	78.33	1.200	120.00	80.00
2.174	181.88	76.99	1.700	157.50	78.75
			2.117	198.05	78.91

Since only a particular amount of adsorbent can adsorb a specific quantity of heavy metal ions, the initial concentration of heavy metal ions is a crucial factor in adsorption. The data shown in Tables (3 and 4) demonstrate that as starting concentration increased, the percentage of ions that were adsorbed dropped. However, as shown in Tables (3 and 4), the actual number of ions adsorbed per unit mass of the adsorbent increased with increasing initial ions concentration in the test solution. At low concentrations, all metal ions interact with the soil and are swiftly removed from the solution due to the high ratio of surface active sites to total metal ions in the solution. The initial concentration of heavy metal ions is a key component in adsorption because only a specified amount of adsorbent can adsorb a specific amount of heavy metal ions. The information in Tables (3

and 4) shows that the percentage of ions that were adsorbed decreased as the initial concentration rose. The actual amount of ions adsorbed per unit mass of the adsorbent did, however, increase with increasing initial ions concentration in the test solution, as shown in Tables (3 and 4). Due to the large ratio of surface active sites to total metal ions in the solution, all metal ions interact with the soil at low concentrations and are quickly eliminated from the solution. However, the amount of metal ions adsorbed per unit weight of adsorbent,  $q_e$ , is higher at high concentrations. According to these results, the initial ions concentration plays an important role in the adsorption capacities. Higher concentrations of metal ions were used to study the maximum adsorption capacity of the adsorbent (Karthikeyan et al., 2004; Mohanty et al., 2005).

**Table (4). Equilibrium sorption of heavy elements on sandy loam soil**

<b>Cd<sup>2+</sup></b>			<b>Co<sup>2+</sup></b>		
<b>C<sub>e</sub> mg/l</b>	<b>q<sub>e</sub> mg/kg</b>	<b>% sorbed</b>	<b>C<sub>e</sub> mg/l</b>	<b>q<sub>e</sub> mg/kg</b>	<b>% sorbed</b>
0.00	0.00		0.00	0.00	
0.10	10.00	80.00	0.10	10.00	80.00
0.20	20.00	80.00	0.25	18.75	75.00
0.40	45.73	82.05	0.480	43.50	78.38
0.75	81.25	81.25	0.850	73.75	77.63
1.20	126.83	80.87	1.200	97.50	76.47

<b>Ni<sup>2+</sup></b>			<b>Pb<sup>2+</sup></b>		
<b>C<sub>e</sub> mg/l</b>	<b>q<sub>e</sub> mg/kg</b>	<b>% sorbed</b>	<b>C<sub>e</sub> mg/l</b>	<b>q<sub>e</sub> mg/kg</b>	<b>% sorbed</b>
0.00	0.00		0.000	0.00	
0.12	22.00	88.00	0.050	7.50	85.71
0.25	31.25	83.33	0.100	14.35	85.16
0.30	42.95	85.13	0.200	32.50	86.67
0.50	72.50	85.29	0.500	80.00	86.49
0.85	128.75	85.83	0.800	142.50	87.69
1.40	201.23	85.18	1.210	220.73	87.95

Adsorption isotherms are typically used to characterize the adsorption mechanism for the interaction of cations on the adsorbent surface. The equilibrium in the sorption study is vital for an adsorption process as it reveals the capacity of the adsorbent. In this study, the adsorption isotherm was investigated using experimental data and several isotherm models, including the linear, Freundlich, Langmuir, Langmuir-Freundlich,

Generalized Langmuir-Freundlich, and two New models (Tables 5 and 6).

In the present study, the experimental data were analyzed to examine the sorption isotherm models. All sorption isotherm models used in this study apply to monolayer adsorbate coverage on the soil surface (**Abdulrasaq and Basiru, 2010**).

Table (5). Sorption isotherm parameters of some models for heavy metals sorption on sandy soil

Sorption model	Parameters	Cd <sup>2+</sup>	Co <sup>2+</sup>	Ni <sup>2+</sup>	Pb <sup>2+</sup>
Linear	K <sub>d</sub>	70.96	44.65	87.06	95.42
	R <sup>2</sup>	0.9939	0.9931	0.9911	0.9960
Freundlich	K <sub>f</sub>	70.52	46.78	93.67	100.34
	1/n	1.0323	0.8726	0.8540	0.8982
	R <sup>2</sup>	0.9949	0.9993	0.9996	0.9983
Langmuir	q <sub>m</sub>	1595.78	980.88	788.64	1159.38
	B	0.0470	0.1428	0.1372	0.0958
	R <sup>2</sup>	0.9916	0.9998	0.9987	0.9984
Langmuir-Freundlich isotherm	q <sub>m</sub>	790.48	583.43	1958.68	1848.02
	B	0.0991	0.0881	0.0507	0.0578
	1/n	1.1213	0.9520	0.9993	0.9578
	R <sup>2</sup>	0.9928	0.9997	0.9996	0.9984
Generalized Langmuir-Freundlich Isotherm	q <sub>m</sub>	613.38	408.39	732.52	1548.07
	B	0.1720	0.1290	0.1482	0.0644
	1/n	1.1517	0.9897	0.9916	0.9697
	R <sup>2</sup>	0.9920	0.9998	0.9984	0.9984
New model (GK1)	q <sub>m</sub>	896.09	210.87	445.37	637.27
	K	0.0836	0.2561	0.2403	0.1732
	R <sup>2</sup>	0.9919	0.9998	0.9984	0.9984
	K	178.19	475.42	166.70	565.41
New model (GK2)	B	1.5109	8.9666	0.7739	4.5929
	N	0.0000	1.1951	0.2567	0.5522
New model (GK2)	R <sup>2</sup>	0.9945	0.9998	0.9996	0.9985

Table (6). Sorption isotherm parameters of some models for heavy metals sorption on sandy loam soil

Sorption model	Parameters	Cd <sup>2+</sup>	Co <sup>2+</sup>	Ni <sup>2+</sup>	Pb <sup>2+</sup>
Linear	K <sub>d</sub>	106.92	83.82	148.72	178.73
	R <sup>2</sup>	0.9987	0.9963	0.9963	0.9971
Freundlich	K <sub>f</sub>	106.75	83.53	145.66	179.33
	1/n	0.9765	0.9482	0.9904	1.1014
	R <sup>2</sup>	0.9990	0.9962	0.9933	0.9995
Langmuir	q <sub>m</sub>	2275.72	888.12	8447.11	7136.97
	B	0.0493	0.1041	0.0176	0.0256
	R <sup>2</sup>	0.9992	0.9977	0.9974	0.9967
Langmuir-Freundlich Isotherm	q <sub>m</sub>	592.66	268.18	944.91	1149.78
	B	0.2218	0.4603	0.1860	0.0967
	1/n	1.1116	1.2118	1.1309	1.0004
	R <sup>2</sup>	0.9996	0.9980	0.9974	0.9984
Generalized Langmuir-Freundlich Isotherm	q <sub>m</sub>	594.04	268.11	1189.48	1178.61
	B	0.2572	0.5274	0.0920	0.0932
	1/n	1.1111	1.2119	0.9944	0.9960
	R <sup>2</sup>	0.9996	0.9980	0.9984	0.9988
New model (GK1)	q <sub>m</sub>	1162.25	461.22	4227.41	637.23
	K	0.0965	0.2003	0.0351	0.1732
	R <sup>2</sup>	0.9992	0.9970	0.9974	0.9984
	K	130.13	98.83	181.54	503.73
New model (GK2)	B	0.2191	0.1831	0.2465	3.9831
	N	0.0289	0.0621	0.0075	0.5045
	R <sup>2</sup>	0.9990	0.9963	0.9973	0.9985

The sorption isotherm parameters of all models are illustrated in Tables (5 and 6). The results indicated that all tested models accurately fitted the sorption data where the determination coefficient ( $R^2$ ) was more than 0.99. The sorption capacity was in the order of  $Pb > Ni > Cd > Co$  for both soils. Also, the ability of used soils was in the order of sandy loam soil > sandy soil where the average sorption percent was 82.52 and 75.10%, respectively (Maftouh et al., 2023)

The results indicated that sandy loam soil has a high affinity for heavy metals ( $Pb^{2+}$ ,  $Ni^{2+}$ ,  $Cd^{2+}$ , and  $Co^{2+}$ ) sorption comparable with sandy soil. Sandy loam soil is high in surface area and has negative surface charge density (Lehmann, 2006).

These properties increase the capacity of the soil to hold nutrients and become more stable. The new model (GK, two-parameters model) proved to be more accurate and stable for describing the sorption of heavy metals on the soil. For sandy soil and sandy loam soil, respectively, the distribution coefficients (Figure 9) calculated from the linear component of the sorption isotherm ranged from 44.65 to 95.42 L/kg and 83.82 to 178.73 L/kg. According to their  $K_d$  values, or affinities for the soil, metals can be grouped in the following relative order:  $Pb > Ni > Cd > Co$ . Figure(9). Soares et al.(2021) illustrate how this broad sequence tends to change slightly for various soil types.

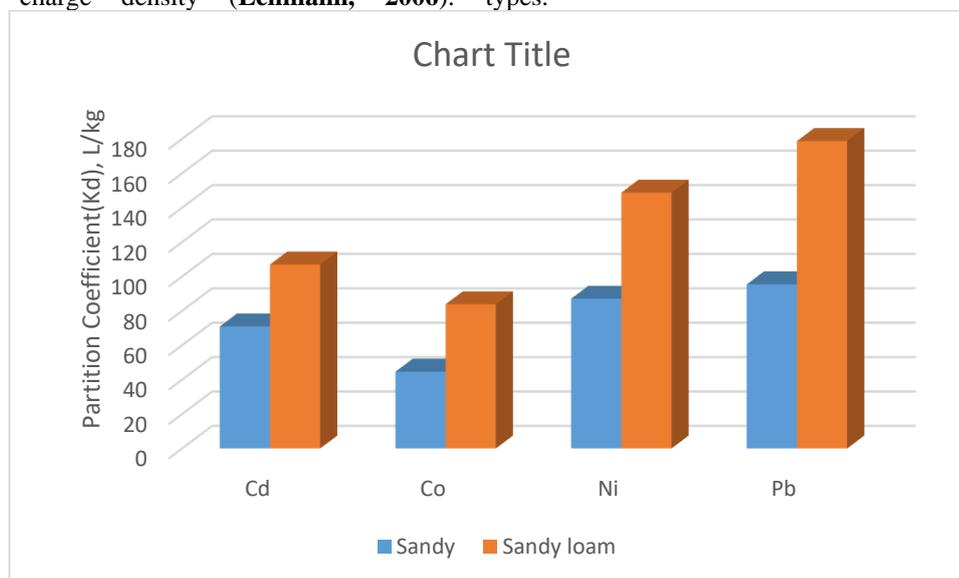


Figure (9). Affinities of heavy metals to two types of soil

In the recent study, the observed sequence of heavy metals was  $Pb > Ni > Cd > Co$ . This general sequence tends to be compatible with ionic radii  $Pb(202 \text{ pm}) > Ni(163 \text{ pm}) > Cd(158 \text{ pm}) > Co(126 \text{ pm})$  or with the sequence of electronegativity  $Pb(2.33) > Ni(1.91) > Co(1.88) > Cd(1.69)$ . The present results are in agreement with **Abd-Elfattah and Wada (1981)** as reported that most of the observed sequences are not correlated either with the sequence of ionic radii, which is  $Pb(1.20) > Cd(0.97) > Cr(0.75) > Zn(0.74) > Cu(0.72) > Ni(0.69)$  or with the sequence of electronegativity given by  $Cu(1.9) > Pb(1.8) = Ni(1.8) > Cd(1.7) > Zn(1.6)$ .

Soil Heavy metals are primarily sorbed to soil particles. Adsorbed heavy metals can dissolve in soil water, where they can then travel into plants, and lower soil layers, or groundwater. A distribution coefficient, which is the ratio of the metal concentration in the solid phase to that in the liquid phase at equilibrium, can be used to model the heavy metals' mobility in soil (**Anderson et al., 1988; Khater, 2007**). From the slopes of the

adsorption isotherms, distribution coefficients can be calculated.

The sorption greatly affects the metal's bioavailability, or how much of it can be absorbed by plant roots and how far it can go in the soil profile. The most mobile metals being studied right now are those with low distribution coefficient values, like Co. The degree of precision obtained from adsorption operations is significantly influenced by the performance of adsorption isotherm modeling and interpretation.

As a result of its broad applicability to a variety of adsorption data, linear regression has been used frequently to assess the goodness of fits and performance. However, nonlinear regression analysis has also been used extensively by many researchers to bridge the gap between predicted and experimental data. As a result, it is important to recognize and explain the value of both linear and nonlinear regression analysis in distinct adsorption systems.

**Performance evaluation of sorption models**

The statistical description of the goodness of fit is illustrated in Tables (7 and 8). It can be concluded that all isotherm models used in the

present study are good for describing the sorption process of heavy metals, but both the Generalized Langmuir-Freundlich and the new model (GK2) were more suitable than other isotherm models.

**Table (7). The goodness of fit techniques for tested sorption isotherm models of sandy soil**

<b>Isotherm</b>	<b>Element</b>	<b>RMSE</b>	<b>AAE</b>	<b>d</b>	<b>NRMSE%</b>
<b>Linear</b>	Cd	1.1816	2.3880	0.9983	2.38
	Co	1.2138	2.6196	0.9975	2.94
	Ni	3.0493	6.6898	0.9970	3.66
	Pb	2.1890	4.6966	0.9984	2.23
<b>Freundlich</b>	Cd	1.1601	2.4574	0.9984	2.34
	Co	0.3573	0.7018	0.9998	0.86
	Ni	0.6216	1.0311	0.9999	0.75
	Pb	1.2026	2.5221	0.9995	1.20
<b>Langmuir</b>	Cd	1.4182	2.5458	0.9975	2.86
	Co	0.2077	0.3907	0.9999	0.50
	Ni	1.1832	2.0091	0.9995	1.42
	Pb	1.1900	2.5422	0.9995	1.19
<b>Langmuir-Freundlich</b>	Cd	1.2511	2.7092	0.9982	2.52
	Co	0.2827	0.5550	0.9999	0.82
	Ni	0.7098	1.1851	0.9998	0.85
	Pb	1.1677	2.5043	0.9995	1.17
<b>Generalized Langmuir-Freundlich</b>	Cd	1.4488	0.2070	0.9975	2.92
	Co	0.2072	0.3953	0.9999	0.50
	Ni	1.1974	2.2827	0.9995	1.44
	Pb	1.1701	2.5173	0.9995	1.17
<b>A new model (GK1)</b>	Cd	1.2653	2.4579	0.9981	2.55
	Co	0.2028	0.3653	0.9999	0.49
	Ni	1.2201	2.0598	0.9995	1.46
	Pb	1.2026	2.5622	0.9995	1.20
<b>A new model (GK2)</b>	Cd	1.1815	2.3886	0.9983	2.38
	Co	0.2041	0.3512	0.9999	0.49
	Ni	0.6216	1.0299	0.9999	0.75
	Pb	1.1519	2.4952	0.9995	1.15

**Table (8). The goodness of fit techniques for tested sorption isotherm models of sandy loam soil**

Isotherm Models	Element	RMSE	AAE	d	NRMSE
<b>Linear</b>	Cd	0.7602	1.5142	0.9996	1.34
	Co	1.1650	2.5353	0.9985	2.39
	Ni	1.8874	5.3160	0.9988	2.65
	Pb	0.7437	0.7437	0.9999	0.90
<b>Freundlich</b>	Cd	0.6835	1.3861	0.9997	1.20
	Co	1.0034	1.9945	0.9988	2.06
	Ni	3.0460	4.6495	0.9920	3.66
	Pb	0.8000	1.5620	0.9997	0.96
<b>Langmuir</b>	Cd	0.6104	1.0691	0.9997	1.08
	Co	0.8984	1.6158	0.9991	1.84
	Ni	1.5959	3.5876	0.9991	1.92
	Pb	2.0663	4.1026	0.9989	2.49
<b>Langmuir-Freundlich</b>	Cd	0.5924	1.0906	0.9998	1.04
	Co	0.9434	1.8749	0.9990	1.94
	Ni	2.6701	4.2955	0.9975	3.21
	Pb	1.1124	2.1495	0.9993	1.11
<b>Generalized Langmuir-Freundlich</b>	Cd	0.4715	0.8312	0.9998	0.83
	Co	0.7406	1.2815	0.9995	1.52
	Ni	1.1852	2.5267	0.9995	1.19
	Pb	1.1860	2.5520	0.9995	1.19
<b>A new model (GK1)</b>	Cd	0.6103	1.0488	0.9997	1.08
	Co	0.8926	1.6455	0.9991	1.83
	Ni	1.4714	3.1086	0.9992	1.77
	Pb	1.2029	2.5584	0.9995	1.20
<b>A new model (GK2)</b>	Cd	0.6826	1.3797	0.9997	1.20
	Co	1.0030	2.0086	0.9988	2.06
	Ni	1.4751	3.0906	0.9992	1.77
	Pb	1.1513	2.4952	0.9995	1.15

Adsorption is one technique that has been used to describe the transport of pollutants in an aqueous medium and the subsequent creation of containment measures (Ayawei et al., 2005; Shooto et al., 2016; Yang, 2021).

The most crucial piece of knowledge required to fully comprehend an adsorption process is information on adsorption equilibrium.

From this study of the Cd, Co, Ni, and Pb adsorption rates by various soils, the results indicate that the equilibrium condition occurred within 2-5 hours. The adsorption isotherms can satisfactorily be described by both the Generalized Langmuir-Freundlich and newly proposed models. Sandy loam soil displayed the highest adsorption capacity, while sandy soil provided the lowest adsorption capacity. Almost all soils showed adsorption capacity in the order of Pb>Ni>Cd>Co. The adsorption capacity depends significantly upon the specific surface area of the soil.

## CONCLUSION

The current results are very useful in the industrial wastewater infiltration in the soil profile and into the groundwater. The behavior of heavy metals sorption in soil was studied by some sorption isotherm models, which have stated that monolayer adsorption was predominant in these soils. Also, sandy loam soil was found to have more sorption capacity than sandy soil. Also, the present study recommends future studies are needed to verify the competitive mechanism of heavy metals sorption correlated to the soil characteristic parameters.

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## الملخص العربي

### نمذجة ادمصاص العناصر الثقيلة لمياه الصرف الصناعي في تربتين مختلفتين

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خصائص الادمصاص للعناصر الثقيلة الأكثر شيوعاً مثل الكاديوم، الكوبلت، النيكل، الرصاص على نوعين من التربة الطبيعية تم دراستها للتربة الرملية واللومية الرملية. هذه العناصر موجودة في مياه الصرف الصناعي لمختلف الأنشطة الصناعية وبالتالي تم اختيارها للدراسة. تم جمع التربة المستخدمة في التجربة الحالية من الطبقة السطحية عمق (0-30 سم) لمنطقة الحمام محافظة مطروح (التربة اللومية الرملية) ومنطقة النوبارية للتربة الرملية. تم تحضير مياه الصرف الصناعي من المحلول المركز للعناصر الثقيلة المتوافقة مع مياه الصرف الصناعي لشركات صناعة الورق وشركات صناعة المواد الغذائية. لدراسة ومقارنة امتصاص العناصر الثقيلة على نوعي التربة، تم توفيق بيانات الادمصاص لبعض نماذج الادمصاص باستخدام برنامج isofit مثل: Linear، Freundlich، Langmuir، Langmuir-Freundlich، Generalized Langmuir-Freundlich ونماذج جديدة مقترحة. تمت مقارنة البيانات المقاسة والمحسوبة من النماذج إحصائياً لتقييم موثوقية النموذج. وقد لوحظ أن الكمية المدمصة تعادل حوالي 63 إلى 85 % (التربة الرملية) وحوالي 75 إلى 87 % (التربة اللومية الرملية) للتركيز الابتدائي للعناصر الثقيلة من المحلول المائي. يكون ادمصاص العناصر الثقيلة أكثر وضوحاً في حالة التربة اللومية الرملية عن التربة الرملية. انخفضت نسبة الادمصاص مع زيادة التركيز الابتدائي. كان متوسط النسبة المئوية التركيزات الأولية (Cd) 74.18، (Co) 66.17، (Ni) 80.25، و (Pb) 79.78 % للتربة الرملية و (Cd) 80.84، (Co) 77.50، (Ni) 84.96، و (Pb) 86.79 % للتربة اللومية الرملية. في هذه الدراسة، تم تحليل البيانات التجريبية لفحص نماذج الادمصاص حيث تبين انها تنطبق على جميع نماذج الادمصاص المستخدمة في هذه الدراسة تعتمد على ادمصاص أحادي الطبقة على سطح التربة. تختلف معاملات التوزيع، Kd المحددة من الجزء الخطي من نماذج الادمصاص المتنوعة على نطاق واسع من 44.65 إلى 95.42 لتر/كجم للتربة الرملية ومن 83.82 إلى 178.73 لتر/كجم للتربة اللومية الرملية. يمكن ترتيب العناصر الثقيلة المدروسة وفقاً لقيم Kd الخاصة بهم من حيث ارتباطاتهم بالتربة كما في التسلسل النسبي التالي:  $Pb > Ni > Cd > Co$ . هذا التسلسل العام يختلف قليلاً لأنواع التربة المختلفة. توصي الدراسة الحالية بالحاجة إلى دراسات مستقبلية للتحقق من الآلية التنافسية لادمصاص العناصر الثقيلة المرتبطة بالخصائص المميزة للتربة.