

LEAD REACTIONS IN SOME CALCAREOUS SOILS OF NINEVEH GOVERNORATE

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ABSTRACT

The adsorption experiment of three different calcareous soils (two loam and one clay textures) for Nineveh governorate (Tel Aakoub, Ibrahim Al-Khalil, and Tel Kaif) was classified under Aridsol-Calciorthis with a slight slant to alkaline (7.43), non saline (3.24 dS m⁻¹), Low content of organic matter (17.3 kg⁻¹), cation exchange capacity (42 Cmol_c kg⁻¹), high content of carbonate minerals (409 g kg⁻¹). Lead adsorption was studied by batch equilibrium method at a temperature of (298 Kelvin) for lead solutions (5,10,20,40,80,100 mg L⁻¹). For 48 hours, the lead was measured in equilibrium solutions and the adsorption criteria were calculated according to Langmuir, Freundlich and the DR equations. The results of the mathematical description of lead adsorption showed high efficiency in the use of Langmuir, Freundlich and the DR equations at the concentrations used. The lead added to the soil was also distributed between the equilibrium solution and the solid soil phase in terms of propagation coefficient values (Kd), which ranged from (111.8) to (255.5 l kg⁻¹) with an average of 169 l kg⁻¹. The exceeded the Langmuir and Freundlich equivalents in the description of lead adsorption to obtain the highest coefficient of determination (R²) and a lesser standard error (SE). The adsorption capacity (qm) of the lead ion in the study of soil (13.63 - 41.48 mol g⁻¹). The K value associated with the adsorption capacity ranged from (-0.44) to (- 1.24) (mol² KJ⁻²). The value of (E) is the free energy rate of the reaction ranged from the lead adsorption values (0.63 - 1.06 KJmol⁻¹).

Keywords: lead, adsorption, calcareous, Langmuir, Freundlich, D-R equations.

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INTRODUCTION

Recently, heavy metal interactions in soils have come under scrutiny, mainly as a result of the increasing emphasis on the disposal of sewage sludge, fules ,industrial, war wors, The adsorption of Pb by calcareous soils is poorly understood in contrast to adsorption by noncalcareous soils. Carbonate minerals are major components of calcareous soils and may represent potential adsorption surfaces for heavy metals (Kabata-Pendias ,2011; Das ,2011). It is, therefore, expected that the presence of carbonate minerals can have a great effect on Pb mobility and reactivity through their surface interactions with Pb and through their effect on soil pH The process of adsorption is influenced by several factors, the most important of which are clay because they are involved in the important chemical reactions.

The properties of electrochemical properties such as the exchange of ions and their stabilization, which are very important in determining the chemical soil properties (Abdelwaheb et al,2019). The ion adsorbs by exchange and specific

adsorption, and ion adsorption by the clay surface is adsorption of hydroxyl groups followed by ion retention by clay; either by bonding with the hydroxyl adsorbent or in the sites that arise as a result of the proton removal and the predominance of extruded clay minerals such as semicite in the soils. A large proportion of the adsorption capacity is the result of the permanent charge on its surfaces. The outer sphere of the Kaolinite is the main cause, (Ebrahimi et al., 2018).

The environmental importance of metal minerals lies in their ability to capture part of lead ions at specific adsorption sites, thereby reducing the risk of these ions absorbed by the plant and reaching the food chain. Illites have a strong tendency to adsorption of lead compared with the rest of the other clay minerals. Lead adsorption is based on the bonds of the lead hydroxide complexes such as $PbOH^+$, $Pb_4(OH_4)^{+4}$ and its adsorption on the surfaces of the smectite that can be interpreted as simple ion exchange, adsorption of lead on the capacitor. kaolinite and illite is competitive adsorption. The forces associated with the heavy elements such as lead and clay particles depend on the degree of interaction and characteristics of the ion (charge and ionic radius) (Karak et al, 2005). Differences in the soil adsorption tendency of adsorption and its concentrations in equilibrium solutions may be related to soil content of organic matter, iron oxides and mineral composition of soils, (Sparks, 2003) show that the electrolytic exchange is made up of outer-sphere complexes in soils containing kaolinite and illite predominate, and the adsorption of lead in the form of external complexes is moving, leading to a high percentage of it in the solution of the washing filtration, whereas the high tendency of the heavy minerals is due to the internal surface complex(inner sphere) in the soil where metals predominate (Serrano et al., 2005).

The high concentration of carbonates in the soil solution leads to the deposition of lead (Al-Hayani and Al-Obaidi,2019). Also, Das,2011 noted that decreasing the lead movement in calcareous soils where carbonate minerals are dominated is by adsorption on the surfaces of those minerals or by rising the pH in those soils. Also, (Al-Hayani and Al-Obaidi,2018) pointed out that the difference in the content of calcium carbonate in soils leads to a difference in the ability of adsorption of lead. Organic matter plays an important role in the overall biological, physical and chemical processes of the soil. (Basta et al. 2005) noted that the electrical properties of the lead are a strong tendency towards organic matter to establish and form external surface surfaces (outer-sphere). Lead adsorption increases on the organic matter with increased pH. Organic matter is an important reservoir of lead in contaminated soils (Weirich, 2000 ,Evans et al. 2003) The lead complexes with the humatic parts of the soil are essential in determining the fate of the polluting element in the environment adsorption on organic matter surfaces and iron oxides have more specific complexities that require a longer reaction time to reach equilibrium, (Langmuir ,Freundlich and Dobbenen-Radushkevich DR) are used to describe the interaction behavior between adsorbent ion and adsorption surface (Kabata-Pendias 2011). The use of these equations can be used to predict the soil susceptibility to ion adsorption which reflects a part of the soil's ability to capture and retain these ions these equations have been used to predict the soil susceptibility to the adsorption of various ions and it reflects part of the soil's susceptibility to the retention of these ions. In the application of these equations on

the soil of Iraq it is clear that these soils have high adsorption capacity and low bond strength. (Al-Hayani and Al-Obaidi,2019). The objectives of this research were to determine how well the Langmuir, Freundlich and Dobbenen-Radushkevich DR equations can describe Pb sorption by three calcareous soils with contrasting physical and chemical characteristics and determine the Pb sorption parameters of the soils.

MATERIALS AND METHODS

Three surface soils samples (0-0.3 m) which differed in location, texture and calcium carbonate content, were used. One was (Till Aakoub) with GPS(MGRS) (38 SLF 5312002957) loam, the second was (Ibrahim Al-Khalil) (38SLE 5799389154) sandy clay soil and the third was (Tel Kaif) (38SLF 3256438608) sandy loam, the soils will be referred to as, CaCO₃-rich, respectively. Study soils are classified as Aridisols, Calciorthiss according to the US soil taxonomy (Survey Staff, 2017). Several random samples were taken for each of the study sites in order to obtain a composite soil sample and an excited soil sample with the soil classification below the level the soils sample were air-dried, passed through a (2mm) sieve and stored in plastic containers for analysis.

The physicochemical characteristics of the soil samples were estimated according to standard method (Carter and Gregarich 2008). in Table (1), Isotherm adsorption studied by using Batch technique, 2 g soil was shaken with 40 ml 0.01M CaCl₂ containing Pb concentrations of (0, 10, 20, 40, 80, and 100 mg Pb l⁻¹) for 24 hours at 298K. This process proceeded for each soil. After shaking, soil solution was filtered through Whatman No.42 filter paper. After filtration Pb concentration was determined by atomic absorption spectrophotometer, the wavelengths (405.8 nm) (Perkin Elmer A Analyst 100 U.S.A). adsorption isotherms were constructed following the methods described by (Elsheikh et al ,2018).

Table (1): Some physiochemical characteristics of the study soil

Locations	EC (dS m ⁻¹)	pH	CEC Cmmol _c kg ⁻¹	Soil content (g kg ⁻¹)					
				Organic matter	carbonate Calcium	sand	Clay	Silt	
Till Aakoub	0.33	7.02	42	17.3	331	314	252	434	
Ibrahim Al-Khalil	0.49	7.11	27.3	16.2	376	452	177	371	
Tel Kaif	2.92	7.12	33.6	9.6	332	198	429	373	

Pb adsorption capacity was determined by the following equation:-

$$Pb_{ad} = (Pb_i - Pb_f) V/W.....(1)$$

where:- Pb_{ad} is the amount of adsorbed metal (mg kg⁻¹), Pb_i is the initial concentration of Pb in solution (mg L⁻¹), Pb_f is the concentration of Pb in solution after equilibrium (mg L⁻¹), V is the solution volume, and W is the weight of air-dried soil sorption data were described by the following equations:

Langmuir single - surface equation:

$$C_e/q = 1/Kb + C_e/b \dots\dots\dots(2)$$

Freundlich equation .

$$\log q = \log K_f + n \log C_e \dots\dots\dots(3)$$

Where C_e is the Pb concentration in the equilibrium solution (mg/l), q is the amount of Pb sorbed by the soil (mg kg^{-1}), b is the sorption maxima (mg kg^{-1}), and K is the bonding energy coefficient (L mg^{-1}), K_f is the Freundlich distribution coefficient, and n is an empirical constant.

Dubin-Radushkevich equation:

Langmuir and Freundlich isotherms don't give any idea about the sorption mechanism but Dubinin-Radushkevich (D-R) isotherm describes sorption on a single type of uniform pores. In this respect, the D-R isotherm is analogous of Langmuir type but it is more general because it does not assume a homogeneous surface or constant sorption potential (Al-Hayani and Al-Obaidi,2018). In order to understand the adsorption type, D-R isotherms were determined. The D-R isotherm has the form:

$$\ln q = \ln q_m - k\varepsilon^2 \dots\dots\dots(4)$$

$$\varepsilon = [RT \ln (1 + (1/C_e))] \dots\dots\dots(5)$$

where ε is Polanyi potential, q is the amount of Pb sorbed by the soil (mol g^{-1}), k is a constant related to the adsorption energy ($\text{mol}^2 \text{kJ}^{-2}$) and q_m is the adsorption capacity (mol g^{-1}). The mean free energy of adsorption (E) was calculated from the k values using the equation:

$$E = (-2k)^{-0.5} \dots\dots\dots(6)$$

The magnitude of E is useful for estimating the type of adsorption process. If this value is between 8 and 16 kJ mol^{-1} , the adsorption process can be explained by ion exchange (Al-Hayani and Al-Obaidi,2018). The analysis of correlation coefficient was performed by Excel (2010).: In order to determine the best mathematical equation for describing the adsorption process, the highest value of the R^2 parameter and the lowest standard error SE.

The thermodynamic parameters of the adsorption process:

The thermodynamic parameters of the adsorption process were calculated using the correlation coefficient of the single-core Lancer equation (K) Agencies: -

Free energy (ΔG)

$$\Delta G = - RT \ln K \dots\dots\dots (7)$$

ΔG = free energy (KJ^{-1}). And R = constant gases. And T = absolute temperature (Kelvin) and K = binding energy.

Adsorption energy (E) can be calculated for K values calculated from the D-R equation by which the adsorption type can be detected.

$$E = \frac{1}{\sqrt{-2K}} \dots\dots\dots(8)$$

Minerals controlling the solubility of lead in the soil solution:

In order to identify the predominant lead minerals that controlling insolubility in the soil solution,by making a semi equilibrium by using a water suspension (soil: distilled water) (1:20) left 48 hours after that were separated by a filter paper, in which the electrical conductivity, Soil reaction, lead ions concentration, sulfate, phosphates, carbonates, and bicarbonates were used for the calculations. The

thermodynamic parameters of the equilibrium solutions were used to calculate the ionic activity. The ionic coefficient of activity is calculated according to the following context:- Ionic Strength (I). The ionic strength in equilibrium solutions in mole L^{-1} , which is calculated indirectly from electrical conductivity, the solubility diagram were used according to (Lindsay, 2014).

RESULTS AND DISCUSSION

Physiochemical properties of the study soil:

Table (1) showed that the carbonate minerals were ranged (189 to 409)g kg^{-1} . The results in Table (1) showed that pH values in the soil ranged between (7.02 – 7.12). These results indicate that the studied soil slightly alkaline and may be due to certain factors and processes (Olorunfemi et al (2016). Alkalinity of the study soils due to carbonate mineral content. Carbonates have the regulatory capacity to resist changes in pH in those soils (Kassim, 2013) (Al-Hayani and Al-Obaidi, 2019), the electrical conductivity values ranged between (0.33-2.9 $dS.cm^{-1}$). The results in Table (1) showed also that the amount of organic matter ranged between 9.6 - 17.3 $g\ kg^{-1}$, and cation exchange capacity for the study soil ranged between (33.6-42) $Cmol_c.kg^{-1}$. This is due to the difference in the low content of the organic matter and the clay content of the soil of the study, which is within the arid and semi-arid regions and characterized by the prevailing environmental conditions from the increase in the annual temperature which increases the effectiveness of microorganisms that decomposes organic matter as well as the lack of the moisture in the soil, as well as the lack of precipitation that does not lead to the formation of a good vegetation help to build organic soil (Olorunfemi et al ,2016).

Adsorption reactions:

Table (2) showed the remaining quantities in the soil solution after the thermodynamic equilibrium was obtained at 298 ° Kelvin which was increased by increasing the initial added concentration (from 1.4 to 3.3), (3.5 to 5.6) and (4.1 to 9.6) $mg\ l^{-1}$. The difference in the residual quantity after adsorption is due to the different nature of the lead ion bonding and the competition among the different ion species to occupy the exchange sites on the surface of the soil granules (Al-Hayani and Al-Obaidi, 2019). This explains the role of soil textures and its physicochemical properties in the retention of ionic species and leaves part of it in the equilibrium solution after solid soil surfaces retain a quantity of this element as these values differed from one location to another.

It is clear from Figure (1) that there is a sharp increase in the amount of lead remaining after equilibrium, followed by a very small presence and as a straight line parallel to the X-axis which clearly indicates a great passion for the solid phase surfaces to retain the ionic species of lead and contain it within this phase. Ionic to a certain extent (the point of the reversal in the course of the curve) (Break throw).

Table (2): Change the lead concentration at equilibrium with the initial concentration at a temperature of (298°) Kelvin.

The concentration of initial lead added (mg l ⁻¹)	The concentration of remaining lead after equilibrium (mg l ⁻¹)		
	Till Aakoub	Ibrahim Al-Khalil	Tel Kaif
5	1.4	3.5	4.1
10	2.1	4.3	5.3
20	2.9	4.9	5.9
40	3.1	5.3	6.2
80	3.2	5.5	6.6
100	3.3	5.6	6.9

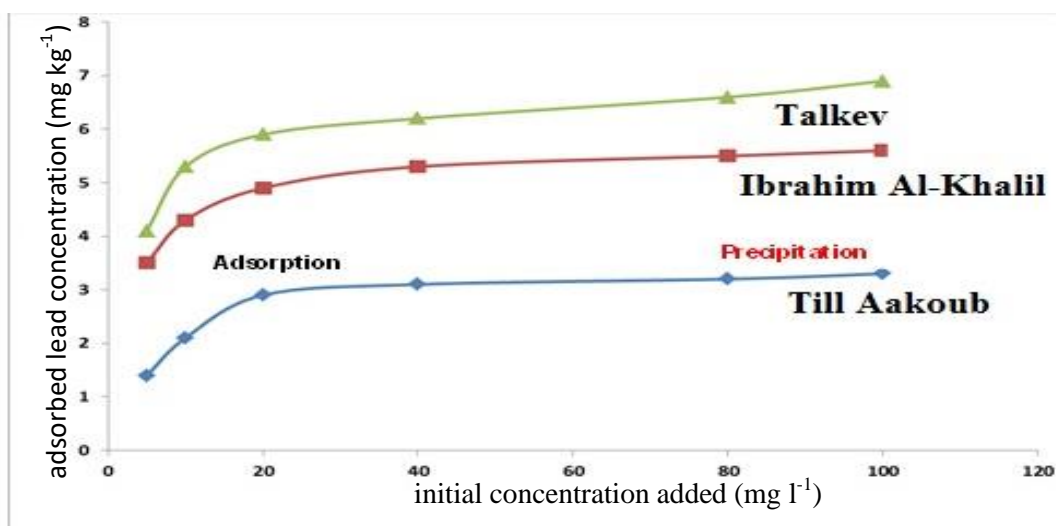


Figure (1): The effect of initial concentration added on the amount of lead remaining after equilibrium in the study soil.

This ion then moves to another process whose values are fixed in the solution through the deposition processes obtained as a result of exceeding the added concentrations of the dissolved values of the metals that may be formed in the soil solution.

Figure (1) showed the effect of the initial concentration of the lead added on the amount of lead taken. The measured lead ions show a similar tendency to adsorption on the solid soil surface. The number of adsorbent material increases with the increase in the initial concentration of the lead element. The initial concentration of a fixed number of effective sites available for adsorption makes the amount of material remaining larger. Figure (1) showed the variation and difference in the amount of the lead in the adsorbed lead. This is due to the nature of the soil under study. Surface soil adsorption has a specific number of active sites at the concentration of some active saturated sites (Isak,2019) However, increasing the concentration of adsorbed lead ion with increased initial lead concentration increases the concentration of the precipitation (Selim, 2013) This reduces the

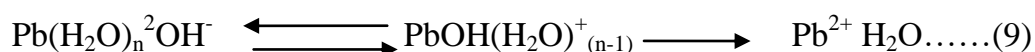
bonding power between the metal ion and the active site due to the increase in the efficiency of the surface of the soil (Selim ,2013).

In addition, the lead ions vary in their preference for soil surfaces and are highly concentrated on the soil surface. The variation in lead affinity towards adsorption sites of soil surfaces is due to the (Electrolysis), hydrolysis constant (PKH), electronegativity, acidity of Lewis, charge density, solubility of sediments containing hydroxide and carbonates (Fontes and Santos, 2010 Chen et al., 2012).

The variation in the amounts absorbed between the three soils can be attributed to different mechanics (exchange) Ionization and adsorption). In the ion exchange process, the ion penetrates into the crystalline clay network through the gaps on the surface and the channels leading to the grid. Thus, lead ions are substituted for existing ions, which are often sodium or calcium (Erdem et al., 2004; Selem and Spark, 2001). This process of propagation through the gaps is rapid but is delayed when the diameter of the channel or gap is relatively smaller than the metallic ion. The adsorption process occurs due to the bonding of the metal lead ions with the effective and available adsorption sites on the different surfaces in the soil. A factor that hinders this correlation as vacuum interference, especially when the ionic metal is large and when the active sites on the surface are close together (Selim, 2013).

The high density of the clay makes the amount used smaller and less surface area compared with carbonate minerals. Therefore, increasing the clay content and its quality, as well as increasing the content of both carbonate and organic matter as additional surfaces will increase the efficiency of adsorption (Das and Mondal, 2011; Ibrahim et al, 2013) in Figure (1) showed the close correlation between the initial concentration and the amount of adsorbent material in the study soil. It is observed from this form that the adsorption is of (H-Type) and the lead in this path Rapidly interacting with the solid soil phase and thus adsorption with the possibility of deposition in high concentration concentrations If we take into account that these soils have a high degree of reaction, which provides significant amounts of carbonate and bicarbonate in the equilibrium solution (Adhikari and Singh, 2003; Kadirvelu et al,2001),the soil is adsorbed into several factors, primarily soil content of clay, surface area, calcium carbonate, organic matter and the exchange capacity of positive ions (Jiang et al.,2011; Nhapi et al.,2011; Ghormi et al.,2013) in a study of calcareous soils (Das, 2011) to the role of physical and chemical properties in the process of adsorption.

This difference between soils may be due to the role of minerals in the process of adsorption. As the soil minerals adsorption of metal ions from the solution of soil after it gets hydrolysis (in this case, for example, lead metal added to the soil and because of the above process will be The result is a number of dissolved ion species as shown in the following equation:



The adsorption is dependent on the positive ionic capacitance and the negative electrical charge of the soil resulting from the substitution process. Isomorphous substitution. The second process consists of the formation of internal surface complexes (inrespher) and external (outer sphere), a mechanism independent of the

fixed charge of the soil and closely linked to the variable capacity acquired by the ionized laminate. It is seen in some of its surface sites. This adsorption has a significant effect on the physical properties of the soil such as zero point of charge and electrostatic junction point (Sparks, 2003, Al-Hayani and Al-Obaidi, 2019).

After this stage, precipitation reactions occur as it precipitates from ionic dissolved in solution or occurs on surface. The solid phase after adsorption, which is the beginning to be a complete deposit over time, the sedimentation process is similar to the process of adsorption as they are identical in the energy stock to become the separation between them is concentrated on the spatial extension of each of the adsorption phenomenon is two-dimensional while deposition is a three-dimensional phenomenon (Sharami et al., 2010). The results obtained are consistent with Gharaie (2009) finding of the lead element in Iranian calcareous soil which retained large quantities of lead - lead carbonate.

Lead Distribution Coefficient (Kd):

The relationship between the concentration of the adsorbed ion on the solid soil and its concentration in the soil solution is called equilibrium or the distribution coefficient (Kd). This coefficient reflects the soil's ability to retain the ion and is related to the movement of the ion in the soil solution (Kabata-Pendias, 2011). Also it makes it possible to compare the behavior of ions in different soil systems. The movement and behavior of the heavy elements in the soil environment are directly related to its distribution between the soil and soil solution and is therefore associated with the value of the distribution coefficient. The distribution coefficient is a useful tool to compare the adsorption capacity of different soil or material to ion when measured under the same experimental conditions (Alloway, 2013). The results are shown in Figure (2) indicate the values of the Kd between the soil solution and the solid phase of the lead ions differed Soil textures between (111.8 to 255.5) $l\ Kg^{-1}$ with an average of 169 $l\ Kg^{-1}$.

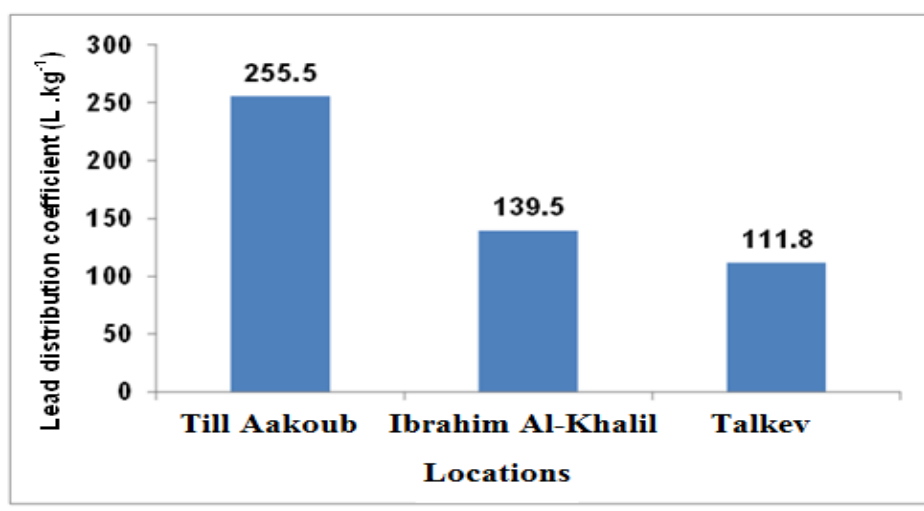


Figure (2): The lead distribution coefficient in calcareous soils

Our results indicate that there is a consensus with the global research presented by Soares (2006), which estimated the distribution coefficient (Kd) of the lead to (30) representative soil for the study of the correlation of heavy elements. The distribution coefficient (Pb) 121-7020 Lkg^{-1} , is consistent with Gharaie (2009) of

the lead element in Iranian calcareous soil, which retained large quantities of lead carbonate, that reached the values of the distribution factor (403-956) Lkg^{-1} because of the complexity of the soil components and the competition between the different elements, the coefficient of distribution (Kd) can not be estimated as a line-line because the adsorption or soil retention of heavy elements is usually the same at low concentrations. The distribution coefficient (Kd) of these elements was calculated to determine their adsorption capacity.

The values of the distribution coefficient ranged from 9.4 to 217. Lkg^{-1} that is affected by the initial concentration of the solution, due to the difference in the lead tendency of the soil components to the hydrolysis of the lead (pKH), the electrolysis, acidity, the charge density and the solubility (Ksp) of the sediments (Sparks, 2003). The high values of Kd are the role of mineral and organic colloids in soils, especially crystallized and non-crystallized iron oxides and calcium carbonate that may cause oxidation The deposition of these elements within those colloids. The order agrees to some extent with the findings (Hooda,2010; Al-Hamandi et al,2019)

MATHEMATICAL MODELS DISCRETION

LANGMUIR EQUATION:

Langmuir equation is based on a simple theoretical basis that the ion that is adsorbed on the surface forms a single layer and the adsorption surface has a specific number of adsorption sites that have identical energy with no movement of adsorbed ion at the adsorption level (Vasanthaiyah,2011) The linear formula of the equation for the purpose of detecting the reaction path as well as the determination of the adsorption constants were explained just as follows:

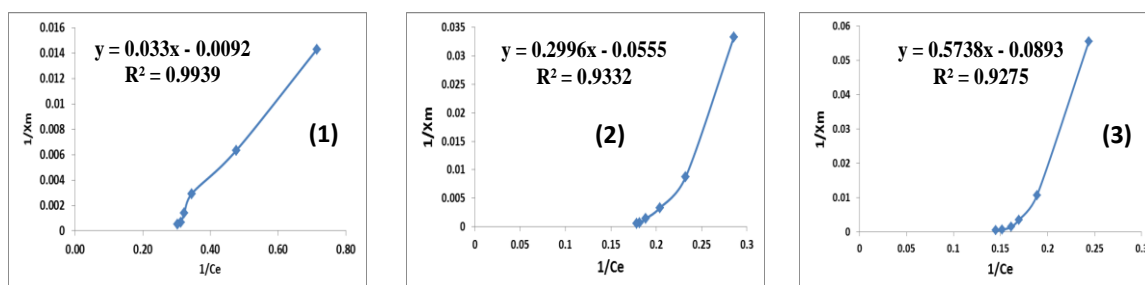


Figure (3): The pathway of the lead reaction according to the Langmuir1 equation

It is clear from Figure (3) that the process of adsorption of the first soil differed from the second and third soil pathways, which clearly reflects the role of the physical and chemical properties of the soil on the adsorption process. Furthermore, the second and third soil types clearly reveal the two surfaces of the adsorption process (H-Carve). The adsorption constants of the linear relationships of the single-scale Lancemeer equation could be calculated.

MAXIMUM ADSORPTION CAPACITY:-

Table 4 shows the adsorption parameters of the single-surface Langmuir equation, as it is clear that the adsorption capacity ranged from 11 to 1087 $mg\ kg^{-1}$. This clearly reveals the difference in the soil's adsorption potential due to the different content of the soft particles (sand, clay, carbon, organic matter and calcium carbonate) in addition to the ionic strength and the degree of reaction of the

equilibrium solution, which increases the absorbed amount. This is consistent with what was obtained by (Al-Hasson et al,2019) which gives an idea of the amount of plant ready-available element as well as a clear perception of contamination of the environment of lead soils indicating low values. The higher adsorption capacity increases the dissolved amount of lead in the soil solution. More precisely, the lead ion is more readily available for transition, adsorption and other chemical processes. In contrast, the higher the value of this standard indicates the lower ion movement and increased adsorption in the soil.

Table (4): adsorption parameters calculated according to Langmuir - Freundlich - D - R equations

No	Connecting energy l mg ⁻¹	Adsorption capacity l mg ⁻¹	MBC	Diffusion coefficient K _L	ΔG (K mol ^o)	K mol ² KJ ⁻²	q _m mol g ⁻¹	E KJ mol ⁻¹	Connecting energy l mg ⁻¹	Adsorption capacity l mg ⁻¹
Equivalents of the one - dimensional Langmuir equation					D-R Equations			Elements of the equation of Freundlich		
1	0.028	1087	30.44	1.03	-2.12	-0.44	13.6 3	1.06	3.56	15.84
2	0.185	18	3.33	1.19	-1	-1.15	39.4 4	0.66	8.65	2137
3	0.156	11	1.716	1.16	-1.1	-1.24	41.4 8	0.63	9.23	33113

BONDING ENERGY: -

Table 4 shows the binding energy was (0.028-0.185) and with a mean (0.12) l mg⁻¹. These values reflect the ability of calcium carbonate in adsorption of ionic species of lead. This can be explained by the presence of electrical charges on the surfaces of carbon metal. Charges on carbonate surfaces result from the refraction of the edges of the calcite metal. In this theory, it is assumed that relatively small and positive calcium ions are carried out within the crystalline and the large charge negative carbonate ions rush outwards, resulting in a negative charge on crystalline surface or calcium carbonate. The second is the amphoteric behavior of carbonate minerals. The type of surface charge depends on the degree of soil reaction and the zero point of the charge is within the reaction range (8-9.5). Thus the carbonate charge is positive when the reaction is less than (8) Negative when the reaction is more than (9.5).

(MBC):

This value is mathematically expressed as the product of the maximum adsorption capacity of the surface (X_m) with the binding energy (K) of the Langmuir equation, which is a characteristic of the adsorption of ionic soil. Table 4 shows the difference in the values of the regulatory capacity in the soil the MBC ranged from 30.44 to 1.716. This clearly reveals the difference in the soil's adsorption potential due is due to the different nature of the adsorption of the lead, and the difference of the values of adsorption to the greatest and the energy of the bonding in the high energy sites led to different readiness ion at different locations of the adsorption curve The high amount of ion adsorption and low bonding of ion

in such soils clearly means that it is easily released from adsorption surfaces to soil solution, increasing the propagation rates of this ions and more abundances for absorption by the plant (Krishnamurti and Naidu, 2008; Al-Hayani and Al-Obaidi,2018). In the opinion of (Krishnamurti and Naidu, 2008) the values of (MBC) is an important criterion in the characterization of contamination of lead soils and high values indicate that the type of ionic adsorbent characterized by a low link card and thus easy movement and migration (Heavy Metals Migration) to the depths of the soil and thus make these soils With self-purification capacity and high regulation capacity to cope with pollution.

Thermodynamic Parameters Of Lead Adsorption:

The results are shown in Table (4) indicate that the free energy values of the adsorption reaction were all negative ranging from (1) to (2.12), which clearly indicates that the adsorption process is an automatic thermodynamic process. The values (1.03) and (1.19) indicate that the reaction process is also automatic and does not require the energy to initiate the reaction. It is consistent with its findings (Das, 2011) in a calcareous soil study from India as agreed with Matawl (Al-Hayani and Al-Obaidi,2019).

Freundlich equations:

This equation assumes a heterogeneous distribution of energy on the active sites in the adsorption surface with overlapping molecules that are surface-based and multi-layered. However, this model is experimentally the mathematical description and the adsorption parameters according to the Frundelkh equation. In order to detect the process of lead adsorption according to the equation of Freundlich, the following forms are considered:

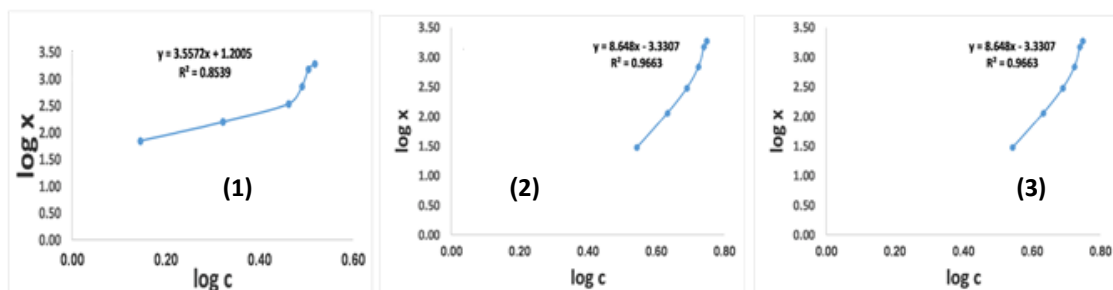


Figure (4): The relationship between the logarithm of the concentration of equilibrium and the adsorbed logarithm of the three sites

The values of the adsorption factor or the coefficient of the Friedlkh equation (Kf) reflects the adsorption capacity of the soil ranged from 15.84 to 33113 mg/kg⁻¹ Soil. These values indicate the large variation in the adsorption of lead to adsorption sites or the restriction of lead in the soil which shows that these three values differed in their ability to absorb lead. As the soil was characterized by (3) low value indicating that most of the amount of lead is present in free and dissolved in the solution and that the amount of adsorption is low, The results also showed an increase in the average binding power factor values of the lead element in its logarithmic form from (3.56) to (9.22) Lmg⁻¹, and that the increase of the exponent value (n) greater than (1) indicates the high adsorption capacity of the soil so that any change in The concentration of equilibrium will not lead to a significant change

in the amount of adsorbed ion. (Kumar et al,2019). This may be due to the distribution of surface sites or any other work that may be reduced of the overlap between the adsorbent ion and the mazze material when increasing the surface density (Kalalagh et al., 2011) as it is clear with lead in Table (4) (Karak et al., 2014). Brann for measuring the intensity of global capacity and adsorption respectively, the researcher has suggested that the value of the exponent (n) confined between (1 to 10) represents good adsorption material adsorbent effort (Ugochukwu et al., 2012).

It is clearly indicated that the deposition process of lead overcomes the adsorption process and this is due to the values of the constant very low emission (ksp) of the lead and the exchange capacity of positive ions in the second phase in the adsorption process (Sparks, 2003).

D-R equation:-

Thermal model (DR) gives a good description of adsorption in a single model that assumes the adsorption surface is heterogeneous as well as the uncertainty of the adsorption voltage based on a boolean voltage which can be calculated by balancing the chemical voltage of the ion near the surface and the chemical agent at a certain distance away from the surface (Kilislioglu, and Bilgin, 2003).Figure (5) showed the isotherm D-R model similar to the Lancmair model, but this model is the most comprehensive one that the adsorption surface is more heterogeneous surface and the adsorption voltage is unstable.In order to detect the path of lead adsorption according to the equation, (D-R) has been clarified just as follows :

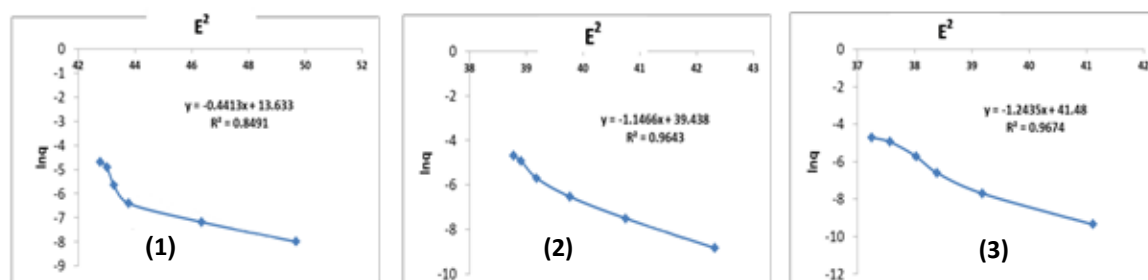


Figure (5): The relationship between the square of the Boolean potential and the natural logarithm of the amount of lead adsorbed to the three positions.

(K)was associated with adsorption capacity, ranging from (-0.44) to (-1.24). The value of E^2 is the energy rate of the reaction in order to determine the type of adsorption process. The values of lead adsorption for the studied soil ranged from 0.63-1.06 (KJ mol^{-1}). If the value is (16- 8), the process of adsorption is subject to the concept of ion exchange (ion exchange energy) but if it is less than (8), adsorption is a physical one. As shown in Table (4), the value of adsorption energy is the decrease in the free energy value of the reaction (8). (KJ mol^{-1}) leads to the conclusion that the lead is weak in the solid soil phase and therefore pollution of groundwater occurred by lead.

For the sake of distinction between the three models above, the linear relationship was determined for each model,i.e. each of which was evaluated by taking two criteria; the first(R^2) and the second-lowest value of (SE) between the actual and calculated adsorption values of each equation.Which shows the values of

these two criteria. It is clear from Table (5) that the values of the coefficient of determination were significant for all the equations ranging from (0.85) to (0.99), which gives a clear indication of the possibility of using any of these equations. The mathematical description of lead adsorption to have a less standard error which earns the advantage in the mathematical description on. The results of the equations are confirmed and consistent with the results o obtained by (Mouni et al., 2009; Gharaie, 2009). This is consistent with what (Safarzadeh et al., 2010; Al-Hayani and Al-Obaidi,2019).

Table (5): Standard error (SE) and coefficient of determination (R^2) for lead adsorption.

Langmuir equation				
Soil Number	(1)	(2)	(3)	Average
(SE)	0.99	0.96	0.92	0.95
(R^2)	0.009	0.0062	0.005	0.01
Freundlich equation				
(SE)	0.97	0.97	0.85	0.93
(R^2)	0.18	0.22	0.29	0.23
D-R equation				
(SE)	0.85	0.97	0.97	0.92
(R^2)	0.006	0.0058	0.004	0.005

Use of solubility diagram to determine the minerals controlling of lead precipitation in the soil:

The results shown in Tables (6) indicated that some thermodynamic parameters used in the solubility schemes to determine the type of metal controlling the thawing of lead-bearing metals. Note that the ionic strength of equilibrium solutions expressed as molten-1 was ranged from 0.0043 to 0.12. Clearly, increasing the added levels of added lead solution led to significant differences in the ionic strength values of equilibrium solutions that have a significant role in the solubility and deposition of lead depending on the melting value (Sparks, 2003). The table also showed that the values of the ionic efficacy coefficient ranged from (0.47 to 0.66). The ionic energy values expressed as (mol.l^{-1}) ranged from 4.46×10^{-6} to 15.65×10^{-6} . The ion voltage values ranged from (-3.35) to (-5.03). These results were used to determine the metals controlling the dissolving of lead-bearing metals using (Lindsay ,2014). by melting the values of the Logi voltage with the values of the reaction level of the equilibrium solution. The lead points of convergence that occurred under the line of lead sulfate metal controlling the process of melting and sedimentation in the soil of the study.

Table (6): Thermodynamic parameters of lead equilibrium in the study soil

Lead added mg L ⁻¹	I mol L ⁻¹	f	aPb mol L ⁻¹ (10 ⁻⁶)	-logP	pH
(1)					
0	0.0043	0.66	4.46	-3.35	7.10
100	0.0043	0.66	10.51	-4.90	7.02
(2)					
0	0.0064	0.55	9.29	-5.03	7.07
100	0.0064	0.55	10.86	-4.82	7.11
(3)					
0	0.012	0.47	9.30	-5.03	7.50
100	0.012	0.47	15.65	-4.80	7.12

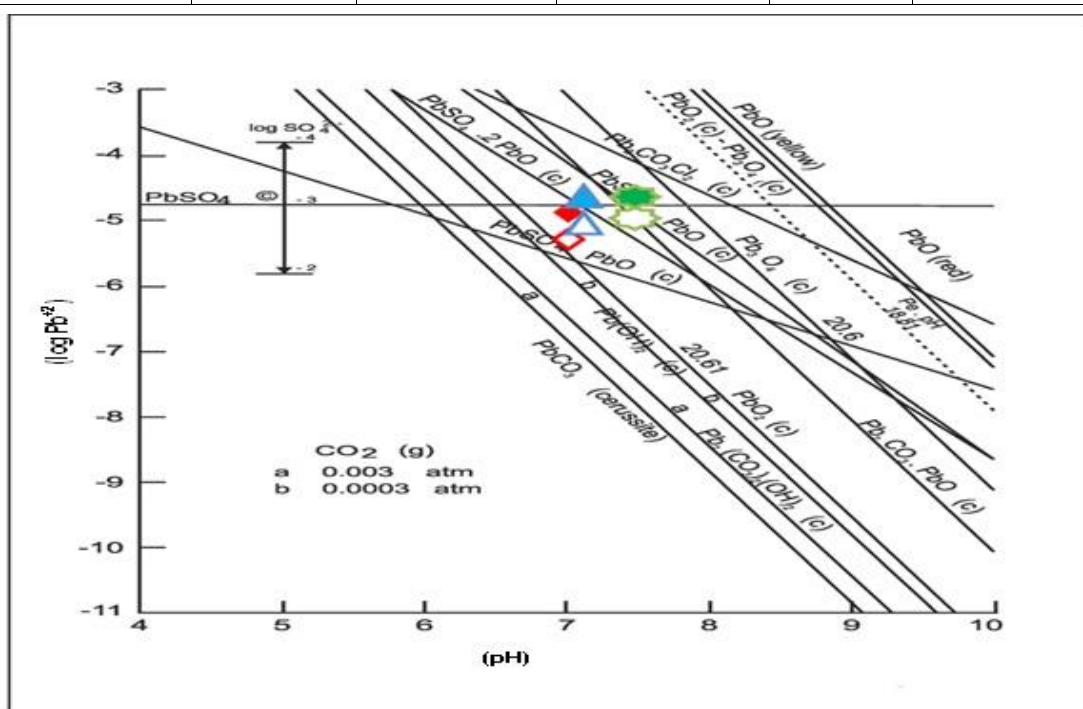








Figure (6): Solubility Diagram of lead in the soil

-  Soil No. 1 after lead addition 100 mg l⁻¹
-  Soil No. 1 Without lead Add
-  Soil No. 2 After addition of lead (100 mg l⁻¹)
-  Soil No. 2 without the addition of lead
-  Soil No. 3 After addition of lead 100 mg l⁻¹)
-  Soil No. 3 Without lead

تفاعلات الرصاص في بعض الترب الكلسية لمحافظة نينوى

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الخلاصة

اجريت تجربة الامتزاز لثلاثة ترب كلسية مختلفة النسجة (مزيجة - طينية) لمحافظة نينوى (تل عاكوب - ابراهيم الخليل - تلييف) مصنفة ضمن تحت الرتبة (Aridsol - Calciorthids) ذات تفاعل قليلة القاعدية (7.43), غير ملحية (3.24 ديسيمنز م-1), قليلة المحتوى من المادة العضوية (17.3 غم كغم-1) السعة التبادلية للأيون الموجب (42 سنتيمول شحنة كغم-1), محتوى عالي من معادن الكربونات (409 غم كغم-1). تم دراسة امتزاز الرصاص بطريقة الاتزان الهادئ على درجة حرارة (298 كلفن) لمحاليل الرصاص (0-10-20-40-60-80-100 ملغم رصاص لتر-1) ولمدة 48 ساعة قدر الرصاص في رواشح الاتزان وحسبت معايير الامتزاز حسب معادلة لانكماير ذات السطح الواحد - فرنديلخ - دوبيين (D-R), وقد اظهرت نتائج الوصف الرياضي لامتزاز الرصاص الكفاءة العالية في استخدام معادلات لانكماير وفرنديلخ و معادلة دوبيين (D-R) عند التراكيز المستخدمة, كما توزع الرصاص المضاف الى الترب بين طوري محلول الاتزان وطور التربة الصلب بدلالة قيم معامل الانتشار (Kd) الرصاص والتي تراوحت بين (111.8 إلى 255.5) لتر كغم-1 وبمتوسط قدره (169) لتر كغم-1. تفوقت معادلة (D-R) على معادلتها (لانكماير و فرنديلخ) في وصف امتزاز الرصاص لحصولها على أعلى معامل تحديد (R2) وأقل خطأ قياسي (SE). وقد بلغت السعة الامتزازية (qm) لايون الرصاص في ترب الدراسة والتي تراوحت (3.63-41.48 mol g-1) اما قيمة (K) المرتبطة مع طاقة الامتزاز تراوحت ((-1.24) - (-0.44)) (mol2 KJ-2), اما قيمة (E) هي معدل الطاقة الحرة للتفاعل تراوحت قيم امتزاز الرصاص (0.63-1.06) (mol-1 KJ). كما كشفت مخططات الاذابة بان المعدن المسيطر على تفاعلات الرصاص في ظروف الترب الكلسية هو معدن كاربونات الرصاص.

الكلمات المفتاحية: الرصاص, امتزاز, كلسية, لانكماير, فرنديلخ, دوبيين D-R.

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REFERENCES

- Abdelwaheb, M., Jebali, K., Dhaouadi, H., Dridi-dhaouadi, S., (2019). Ecotoxicology and Environmental Safety Adsorption of Nitrate , Phosphate ,Nickel and lead on soils :Risk of Groundwater Contamination. Ecotoxicol. Environ. Saf. 179, 182–187. <https://doi.org/10.1016/j.ecoenv.2019.04.040>
- Al-Hamandi H.M., Al-Obaidi M.A., Farhan M.J. (2019) .Study of successive lead recovery in some calcareous soils. *Journal of cellular Automata*.10(5):102-125
- Al-Hasson, N.H. , Al-Hayani, A.S.J.Z. , Al-Obaidi, M.A.J., (2019) . Adsorption Isotherm Of Lead On Calcium Carbonate. *I.J.AG.SC*. 50(2): 84-35 .
- Al-hayany ,A .J, Al-obaidi , M.A. ,(2018) . Lead adsorption in some calcareous soils in northern Iraq. *Iraqi J. soil Science*. 18(1) :204-246.
- Al-hayany ,A .J , Al-obaidi , M.A. ,(2019) . Chemical fragmentation and bioavailability for lead in some calcareous soils from the city of mosul.2nd in international scientific conference. (IOP Conf.Series: *Journal of physics* : 1294(2019)092048.
- Alloway, B. J. (2013). Heavy Metals in Soils. Third Edition ,Blackie Academic & Professional. London, Springer Science , Business Media Dordrecht.

- Altin,O.; O. Hozbelge and T. Pogu (1999b). "Effect of pH, Flow rate and concentration on the sorption of Pb and Cd on montemorillonite II-modeling". *J. Tech. Biotech.*, 74:1139-1144.
- Atkins, P. and J. de Paula (2001). Physical Chemistry. 7th Ed. Oxford: Oxford University Press.
- Basta,N.T.; J.A. Ryan and R.L. Chaney(2005).Trace element chemistry in residual-treated soil:key concepts and metal bioavailability. *J. Environ. Qual.* 34:49-63.
- Carter M. R and E. G. Gregorich (2008). Soil Sampling and Methods of Analysis 2nd. Ed. CRC Press is an imprint of Taylor & Francis Group, an Inform business.
- Chen, B.; R. Qu; J. Shi; D. Li; Z. Wei; X. Yang and Z. Wang (2012). Heavy metal and Phosphorus Removal from waters by optimizing use of calcium hydroxide and risk assessment. *Environment and Pollution Vol. 1, No. 1; January 2012,pp.:38-54.*
- Covelo,E.F.; F.A.Vega and M.L. Andrade (2007). Simultaneous sorption and desorption of Cd, Cr, Cu, Ni, Pb and Pb in acid soils II: soil ranking and influence of soil characteristics. *J. Hazard. Mater.*, 14 : 862-870.
- Das, B. and N.K. Mondal(2011).Calcareous soil as a new adsorption to remove lead from aqueous solution : equilibrium kinetic and thermodynamic study .*Universal Journal of Environmental Research and Technology .Vol.1,Issue 4: 515-530 .*
- Ebrahimi, R., Hayati, B., Shahmoradi, B., Rezaee, R., Safari, M., Maleki, A., Yetilmezsoy, K., 2018. Adsorptive removal of nickel and lead ions from aqueous solutions by poly. *Environ. Technol. Innov.* 12, 261–272. <https://doi.org/10.1016/j.eti.2018.10.001>.
- Elkhatib .E. A., G. M. Elshebiny and A. M. Balba (1991). Lead Sorption in Calcareous Soils . *Environmental Pollution* 69 ,269-276.
- Elsheikh, M.A., Muchaonyerwa, P., Johan, E., Matsue, N., 2018. Mutual Adsorption of Lead and Phosphorus onto Selected Soil Clay Minerals. *Adv. Chem. Eng. Sci.* 8 .81–67 ,<https://doi.org/10.4236/aces.2018.82005>
- Erdem,E.;N. Karapinar and R. Donat (2004). "The removal of heavy metal cations by natural zeolites". *Journal of Colloid and Interface Science*, 280, 309-314.
- Evans,L.J.;Sedy;Boua;D.G. Lumsdon and D.A. Stanbury (2003). Cadmium adsorption by an organic soil: a comparison of some humic-metals complexation models. *Chemical Speciation and Bioavailability*, 15(4):93-100.
- Fontes, M. P. F. and G. C. dos Santos(2010). Lability and sorption of heavy metals as related to chemical, physical, and mineralogical characteristics of highly weathered soils. *J. Soils Sediments* 10:774-786.
- Gharaie, H.A. (2009). Lead adsorption characteristics of selected calcareous soils of iran and their relationship with soil properties. *American-Eurasian J. Agric. and Environ. Sci.*,6(6):637-641.
- Ghormi, F.; A. Lahsini; Laajeb and A. Addaou (2013).The removal of heavy metals ions (Copper, Zinc, Nickel and Cobalt) by nature bentonite. Morocco.

- Grafe, M.; B. Singh and M. Balasubramanian (2007). Super face speciation of Cd(II) and Pb(II) on kaolinite by XAFS spectroscopy. *J. Colloid Interface Sci.* 315:21–32.
- Hooda, P.S., 2010. Trace Elements in Soils, This editi. ed. A John Wiley and Sons, Ltd., Publication. <https://doi.org/10.13140/RG.2.1.3377.1123>.
- Ibrahim, H.; A. El-Kady; N. Ammar; L. Meesuk; P. Wathanakul and M. Abdel-Wahhab (2013). Application of isotherm and kinetic models for the removal of lead ions from aqueous solutions." *J. Environ. Eng.*, 139(3):349–357.
- Isak, A.A., 2019. determination of lead level in soil for some areas at east gezira and khartoum-sudan, africa. *Int. J. Sci. Eng. Res.* 10, 1–6.
- Jabbar, K. Kassim (2013). Method for estimation of calcium carbonate in soils from iraq. *International Journal Of Environment . 1 (1) : 2091-2854*.
- Jiang, W.; T. Tao and Z. Liao (2011). Removal of heavy metal from contaminated soil with chelating agents. *Open J. Soil Sci.*, 1, :70–76.
- Kabata-Pendias, A. (2011). Trace Metals in Soils and Plants. CRC Press, Boca Raton, Fla, USA, 4th edition.
- Kadirvelu, K. ; K. Thamaraiselvi and C. Namasivayam (2001). Removal of heavy metal from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste. *Bioresour. Technol.*, Vol. 76(1), pp.: 63–65.
- Kalalagh S.; S.H. Babazadeh; A.H. Nazemi and M. Manshour (2011). Isotherm and kinetic studies on adsorption of Pb, Pb, and Cu by kaolinite caspan. *J. Env. sci.* 9:243-255.
- Karak T.; R.K. Paul; D.K. Das and I. Sonar (2014) . Thermodynamic of cadmium sorption on different soils of west Bengal, India. *The scientific world Journal. Article ID216451, 11 pages*.
- Karak, T.; D.K. Das; U.K. Singh and D. Maiti (2005). Influence of pH on soil charge characteristics and cadmium sorption in some noncontaminated soils of Indian subtropics. *The Scientific World Journal* 5:183–194.
- Kent, S.K. (2003). "Adsorbent Selection", Adsorption Research, Inc., Dublin, Ohio, 43016, pp.: 1-23.
- Kilislioglu, A. and B. Bilgin (2003). Thermodynamic and kinetic investigations of uranium adsorption amber lite IR-118H resin. *Applied Radiation and Isotopes*, 58:155-160.
- Krishnamurti, G.S.R. and R. Naidu (2008). Chemical Speciation and Bioavailability of Trace Metals.. In: Violante, A. ; P.M. Huang and G.M. Gadd (eds). Biophysico-Chemical Processes of Heavy Metals and Metalloids in Soil Environments Wiley Inter science, New York, pp.: 419-466.
- Kumar, P. S. and K. Kirthika (2009). Equilibrium and kinetic study of adsorption of nickel from aqueous solution onto bael tree leaf powder. *Journal of Engineering Science and Technology Vol.4, No.4, pp.:351- 363*.
- Kumar, V., Sharma, A., Kaur, P., Preet, G., Sidhu, S., Bali, A.S., Bhardwaj, R., Thukral, A.K., Cerda, A., (2019). Pollution assessment of heavy metals in

- soils of India and ecological risk assessment: A state-of-the-art. ECSN 216, 449–462. <https://doi.org/10.1016/j.chemosphere.2018.10.066>.
- Lindsay , W. L. (2014). Chemical Equilibria in Soils. John Wiley and Sons. New York.
- Merrikhpour,H. and M. Jalali (2013). Comparative and competitive adsorption of cadmium, copper, nickel, and lead ions by Iranian natural zeolite. *Clean Technologies and Environmental Policy, Volume 15, Issue 2, pp.:303-316*.
- Mouni, L; D. Merabet ; D. Robert and A. Bouzaza (2009).Batch studies for the investigation of the sorption of the heavy metals Pb^{2+} and Pb^{2+} on to Amizour soil (Algeria).*Geoderma,154,30-35* .
- Nhapi, I.; N. Banadda; R. Murenzi; C.B. Sekomo and U.G. Wali (2011). Removal of heavy metals from industrial wastewater using rice husks. *the open Environmental Engineering Journal,4 , pp. : 170 -180*.
- Olorunfemi , Idowu Ezekiel; Fasinmirin ,Johnson Toyin ; Ojo , Adefemi Samuel (2016). Modeling cation exchange capacity and soil water holding capacity from basic soil properties. *Eurasian J Soil Sci 2016, 5 (4) 266 – 274*.
- Page, A.L.(1982). Methods of Soil Analysis. Part 1. Chemical and Microbiological Properties. Amer. Soc. Agron. Madison, Wis.
- Pare, S.; I. Persson; B. Guel; D. Lundberg; L. Zerbo; S. Kam and K. Traoré (2012) . Heavy metal removal from aqueous solutions by sorption using natural clays from Burkina Faso. *Afr. J. Biotechnol., 11, 10395–10406*.
- Safarzadeh, S.; A. Ronaghi and N. Karimian(2010).comparison of Cadmium adsorption behavior in selected calcareous and acid soils. *Iran Agriculturalmal Research, Vol. 28, No. 2, 2009 and Vol. 29 No. 1-2, 2010,pp.:63-76* .
- Selim, H. M. (2013a). Transport and Retention of Heavy Metal in Soils: Competitive Sorption. *Advances in Agronomy. 119: 275-308*.
- Selim, H.M. and D.L. Sparks (eds), (2001). Heavy Metals Release in Soils. Lewis Publishers, Boca Raton, London, New York, Washington, D.C.
- Serrano,S.;F. Garrido; C. G. Campbell and M. T. Garcia-Gonzalez (2005). Competitive sorption of cadmium and lead in acid soils of Central Spain . *Geoderma 124:91-104*.
- Sharami, M.S; A. Forghani; A. Akbarzadeh and H.Ramezanzpour (2010).Mineralogical characteristics and related surface charge fluctuations of some selected soils of temperate regions of northern Iran. *Clay Minerals, 45., 327–348*.
- Shi, Z. ; D.M. Di Toro; H. E. Allen and D. L. Sparks (2013). A general model for kinetics of heavy metal adsorption and desorption on soils. *Environ. Sci. Technol., 47,pp.: 3761–3767*.
- Soares, M.R. (2006). Distribution Coefficient (Kd) of Heavy Metals in Brazilian Soils. *18th World Congress of Soil Science July 9-15, 2006 Philadelphia, Pennsylvania, USA*.
- Soil Survey Staff (2017). Keys to Soil Taxonomy 10th edition united states department of agriculture natural resources conservation service. SW .Washington DC.

- Sparks , D.L (2003). Environmental Chemistry of Soils .Academic Press ,Inc ,
.England.
- Sposito, G. (2008). The Chemistry of Soils. 2nd Ed. Oxford University Press, New
York.
- Sripathy, L., Pratima Rao, N.M. Ajay Kumar, S. Yashwanth, Jagadisha, N.
Divya and K.R. Sharada. (2015). Heavy metal contamination of soil due to
Vehicular Traffic: a case study across nelamangala-dabaspeta segment
of national highway no.4. *rasayan J.chem.Vol.8: No.2, 232-236.*
- Tsang, C.W. and M.C. Lo Irene (2006). Competitive Cu and Cd and transport in
Soils: A combined batch kinetics, column, and sequential extraction study.
Sci. Total Environ. 40:6655-6661.
- Ugochukwu,N.;I.Ali;Q.Fu;J.Zhu;G.Jiang and H.Hu(2012). Sorption of lead on
variable-charge soils in China as affected by initial metal concentration, pH
and soil properties. *Journal of Food, Agriculture & Environment Vol.10
(3&4) , July-October : 1014 - 1019 .*
- Vasanthaiyah, H.KN. and D. Kambiranda(2011). Plants and Environment. Published
by In Tech Janeza Trdine 9, 51000 Rijeka, Croatia.
- Weirich,D.A.(2000). Influence of Organic Ligands on the Adsorption of Copper,
Cadmium, and Nickel on Goethite. Ph.D. Thesis. Swiss Federal Institute of
Technology Zürich, Switzerland .