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Copper adsorption Behavior in some Calcareous Soils using Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich Models

Kamal Hama Karim*

Department of Natural Resources, College of Agricultural Engineering Sciences, Sulaimani University, Sulaimani, Kurdistan Region, Iraq.

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ABSTRACT

This study conducted to characterize copper adsorption behavior and determination sorption thermodynamic parameters in some calcareous soil from Sulaimani Governorate, Iraqi Kurdistan region. Copper adsorption studied in five calcareous soils includes (Sharazor, Qaradagh, Bazian, Mawat, and Surdash) varying in total calcium carbonate, organic matter and a cation exchange capacity of Sulaimani governorate in Iraqi - Kurdistan region. The adsorption isotherms of the Copper metal by the soil carried out using a batch method. One gram of each soil sample, in duplicate, was placed in plastic bottles and equilibrated with 50 ml of solution $CaCl_2$ (0.01*M*), containing a series of Cu concentrations (0, 2.5, 5, 10, 20, and 40 mg Cu L^{-1}) in the form of ($CuSO_4$). The concentration of Cu determined in a solution using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The amount of Cu adsorbed by the sample determined by subtracting the equilibrium Cu concentration in the solution from the added Cu. The equilibrium isotherm data used to describe Cu adsorption in the five different soils using the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) isotherm model. Freundlich model compared to the various models considered as the best model for describing copper adsorption at both temperatures (298 and 318^{o}K) to describe the isotherm models in the studied soils depending on the highest value of the determination coefficient (R^2), and the least value of root mean square error (RMSE), and Akaike information criterion (AIC).

Keywords: Adsorption, Calcareous Soils, Copper, Dubinin-Radushkevich, Freundlich, Langmuir, Temkin.

INTRODUCTION

Copper inadequacy is basic in plants developed on calcareous soil because of high soil pH, generally reflected to be the purpose behind the low Copper accessibility in these dirts. Copper takes up plants by means of the dirt arrangement. Notwithstanding, the measure of Copper in the dirt arrangement can be insufficient to keep up sufficient plant development, and accordingly soil arrangement Copper will be recharged by the dirt Copper saves (McLaren, and Crawford, 1973). Numerous components, for example, pH, cation trade limit, CaCO3, earth, natural issue, free iron and free manganese substance of the dirt impact the adsorption of copper on the strong soil stage. Parched soils are generally calcareous, containing a higher measure of free carbonates. Higher measures of CaCO3 may cause precipitation of copper as carbonate or hydroxide (Misra, and Tiwari, 1966). The marvel adsorption of applied micronutrient cations by soil called as explicit adsorption. This is shown by all the critical kinds of soil colloids that are by earth minerals (Tiller,1968). In calcareous soils, Cu2+ hold by a particular adsorption response and nearness of carbonates immobilizes Cu2+ by buffering the dirt pH (Dudley *et al.*,1991). Copper in soils can happen in a wide range of structures: (an) in the dirt arrangement ionic and complexed; (b) on standard trade destinations; (c) on explicit sorption locales that is copper adsorbed by a few soil constituents that can't be dispensed with by the reagents for the most part utilized for deciding the interchangeable particles (McLaren, and Crawford, 1973). Isotherm is a numerical condition depicting the connection between a measure of adsorbed adsorbate and its harmony focus in mass arrangement at a steady temperature. The isotherm used to describe and appraise the most significant properties of an adsorbent, for example, adsorbent proclivity, adsorption limit, adsorption component and quantitative circulation of adsorbate on the adsorbent and mass arrangement (Yang *et al.*, 2013). Langmuir Adsorption Isotherm portrays the development of a monolayer adsorbate on the external surface of the adsorbent quantitatively, and from that point onward, no more adsorption happens. Subsequently, the Langmuir speaks to the harmony appropriation of metal particles between the strong and fluid stages. The Langmuir isotherm is legitimate for monolayer adsorption onto a surface containing a limited number of indistinguishable destinations (Hall *et al.*, 1966). Langmuir isotherm states to homogeneous adsorption, which every particle claim consistent enthalpies and sorption actuation vitality (all destinations have an equivalent liking for the adsorbate) (Kundu, and Gupta, 2006). Freundlich isotherm is the main realized relationship depicting the non-perfect and reversible adsorption, not repressed to the arrangement of the monolayer (Freundlich, 1906). This observational model can apply to multilayer adsorption, with non-uniform circulation of adsorption warmth and affinities over the heterogeneous surface (Adamson, and Gast, 1967). Temkin condition portrayed by a uniform circulation of restricting energies (up

* **Corresponding author.**
E-mail address: kamal.hamakarim@univsul.edu.iq
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to some most extreme restricting vitality). It is fantastic for anticipating the gas stage harmony (when the association in a fixed direction isn't required), in actuality, complex adsorption frameworks including the fluid stage adsorption isotherms are generally not suitable to be spoken to (Kim *et al*., 2004). Dubinin-Radushkevich isotherm is an observational model right off the bat considered for the adsorption of subcritical fumes onto micropore solids following a pore-filling instrument. (Dubinin and Radushkevich, 1947). It is typically applied to communicate the adsorption component (Günay *et al*., 2007). Langmuir and Freundlich's isotherms don't give any thought regarding the sorption instrument, yet Dubinin-Radushkevich (D-R) isotherm characterizes sorption on a solitary kind of uniform pores. Right now, D-R isotherm is like the Langmuir type, yet it is increasingly broad since it doesn't assume a homogeneous surface or consistent sorption potential (Ünlü, and Ersoz, 2006). Adsorption increment with expanding temperature as a result of the ascent in the quantity of dynamic locales (Yavuz *et al*., 2003; Bouberka *et al*., 2005). The principle goals of this examination were: To utilize diverse scientific models to depict copper adsorption in the contemplated soils. To locate the best model thinking about the standard of the decency of attack of the bends.

MATERIALS AND METHODS

Soil samples taken at the depth (0-30) cm in five calcareous soil include (Sharazor, Qaradagh, Bazian, Mawat, and Surdash) in Sulaimani Governorate, Iraqi Kurdistan region. The study area lies between (longitudes 35°15′ 27″ N; and latitudes 45° 07′ 37″ E) as shown in (Fig.1).

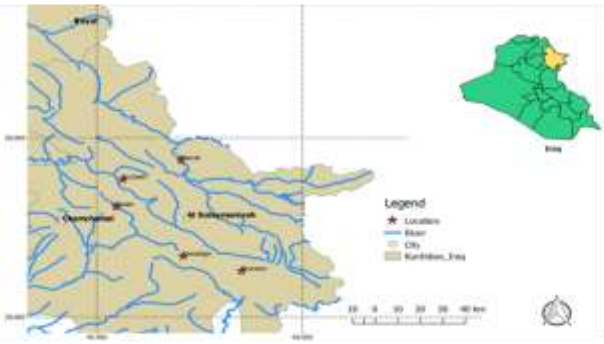

Fig. 1. The location of the studied area

The soil samples air-dried, crushed, and passed through a 2-mm sieve before soil analysis and adsorption studies. Some basic physicochemical properties of the studied soil including particle size distribution, pH, EC, organic matter %, calcium carbonate %, and CEC determined according to the methods of soil analysis as described by (Page *et al.* (1982); and Rayan *et al.* (2001), available concentration of Copper in studied soil as defined in DTPA method (1978). The adsorption isotherms of the Copper metal by the soil carried out using a batch method. Subsamples (1 g) of each soil sample, in duplicate, was placed in plastic bottles (100 ml) and equilibrated with 50 ml of solution $CaCl_2$ (0.01*M*) as a background electrolyte to keep the ionic strength almost constant, containing a series of Copper concentrations (0, 2.5, 5, 10, 20, and 40 mg Copper L^{-1}) in the form of ($CuSO_4$). Two drops of toluene added to each suspension to inhibit microbial activity. The suspension shaken for 30 min and then kept it overnight for attaining equilibrium at two different temperatures (298°K and 318°K). The soil suspension immediately filtered through Whatman paper No.42, then the concentration of Copper determined in a solution using Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES). The amount of Copper adsorbed by the sample determined by subtracting the equilibrium Copper concentration in the solution from the added Copper. SuiTable sorption model that best describes the adsorption of the cation. The parameters attained from the different models provide essential information on the adsorption mechanisms. (Jalali *et al*., 2002). Langmuir, Freundlich, Temkin and Dubinin-Radushkevich models used to describe Copper adsorption in the studied soils.

The Langmuir isotherm model:

The Langmuir adsorption equation is applied to interpret the reaction of copper with soil.

The linear form of Langmuir isotherm given in equation 1:

$$\frac{1}{q_{eq}} = \frac{1}{q_{max}\, k_L\, C_e} + \frac{1}{q_{max}} \qquad (1)$$

Where

q_{eq} is the amount of Copper adsorbed (mg g^{-1}), q_{max} is the maximum adsorption capacity (mg g^{-1}), k_L is an equilibrium constant (L mg^{-1}) related to energy of adsorption which quantitatively reflects the affinity between the adsorbent and adsorbate, and C_e is the equilibrium concentration of Copper in (mg L^{-1}). The Langmuir adsorption isotherms drew by plotting the ratio of one over the amount of Copper adsorbed against one over equilibrium Copper concentration.

The Freundlich isotherm model:

The Freundlich isotherm model applied to non – ideal sorption on various surfaces, and the linear form of the equation given in equation 2:

$$log\, qe \ = \ log\, Kf \ + \frac{1}{n} log\, Ce \quad (2)$$

Where

q_e is an amount of Copper adsorbed (mg g^{-1}), K_f is the Freundlich constant related to sorption capacity in (mg g^{-1}), n is related to the adsorption intensity of the adsorbent, and C_e equilibrium constant of Copper (mg L^{-1}). The constants determined by the linear plot of log q_e versus log C_e.

The Temkin isotherm model:

The Temkin isotherm takes into consideration the interactions between adsorbents and metal ions to be adsorbed (Das *et al*.,2014). The linear form of the Temkin isotherm elucidated in equation 3.

$$qe \ = \ B\, ln\, AT \ + \ B\, ln\, Ce \qquad (3)$$

q_e is the amount of Copper adsorbed at equilibrium (mg g^{-1}), A_T & B are constant, B is related to the heat of adsorption and A is the equilibrium binding constant (L mg^{-1}) conforming to the maximum binding energy, and C_e is the concentration of Copper at equilibrium (mg L^{-1}). The plot of q_e versus lnC_e enables the determination of A and B.

The Dubinin-Radushkevich isotherm model:

The Dubinin– Radushkevich (D - R) isotherm model (Dubinin and Radushkevich, 1947; Tempkin, and Pyzhev,1940) was used to explain the adsorption technique in the different surface (Dabrowski, 2001) The linear form written as following equation 4.

$$\boldsymbol{ln\, qe \ = \ ln\, qD \ - \ 2BD\, RT\, ln\left(1 + \frac{1}{Ce}\right) \quad (4)}$$

Where,

q_e is the amount of Copper adsorbed (mg g^{-1}) at equilibrium per unit weight of soil, q_D is the maximum adsorption capacity (mg g^{-1}), B_D constant of Dubnin-Radushkevich, R the gas constant (8.314 kj / mol K), T the absolute temperature (K), and C_e is the equilibrium concentration of Copper in solution (mg L^{-1}). The sorption energy can also work out using the following equation 5:

$$E \ = \ 1\sqrt{2\beta} \qquad (5)$$

Where,

E is the mean adsorption energy (kJ / mol), and β is the activity coefficient related to mean adsorption energy (mol^2/kJ^2)

Where,

q_e is the amount of Copper adsorbed ($mg\ g^{-1}$) at equilibrium per unit weight of soil, q_D is the maximum adsorption capacity ($mg\ g^{-1}$), B_D constant of Dubnin-Radushkevich, R the gas constant (8.314 kj / mol K), T the absolute temperature (K), and C_e is the equilibrium concentration of Copper in solution ($mg\ L^{-1}$). The sorption energy can also work out using the following equation: The mathematical expression of Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich isotherm models presented in (Table 1).

Table 1. Lists of adsorption isotherms models

Isotherm	Linear form	Plot	Parameters	Reference
Langmuir	$\frac{1}{q_{eq}} = \frac{1}{q_{max}\, k_L\, C_e} + \frac{1}{q_{max}}$	$\frac{1}{q_{eq}} vs \frac{1}{C_e}$	qmax = 1 / Intercept kL = 1 / (slope / intercept)	(Langmuir,1916)
Freundlich	$log\ qe = log\ Kf + \frac{1}{n} log\ Ce$	$log\ qe\ vs\ log\ Ce$	n = 1 / slope Kf = exp (intercept)	(Freundlich ,1906)
Temkin	$qe = B\ ln\ AT + B\ ln\ Ce$	$qe\ vs\ ln\ Ce$	B = slope A = exp (intercept / slope)	(Tempkin, and Pyzhev,1940)
Dubinin	$ln\ qe = ln\ qD - 2BD\ RT\ ln\left(1 + \frac{1}{Ce}\right)$	$ln\ qe\ vs\ ln\left(1 + \frac{1}{Ce}\right)$	q_D exp (intercept) B_D = - slope / 2RT	(Dubinin and Radushkevich, 1947)

Four models are used to describe copper adsorption in the studied soil, including Langmuir, Freundlich, Temkin, and Dubinin- Radushkevich. The model that gives the highest value of determination coefficient (R^2) and the minimum value of (root mean square error - RMSE), and Akaike information criterion (AIC) was considered the best model equation. The value of determination coefficient, (root mean square error), and Akaike information criterion calculated according to the following equations: The determination coefficient (R^2) and Root mean square error (RMSE)

$$(\boldsymbol{R^2}) = \sum (\boldsymbol{q_{cal}} - \boldsymbol{q_{aemeas}})^2 / \sum(\boldsymbol{q_{cal}} - \boldsymbol{q_{aemeas}})^2 + (\boldsymbol{q_{cal}} - \boldsymbol{q_{aemeas}})^2$$

$$(\mathbf{RMSE}) = \{\sum (\boldsymbol{q_{cal}} - \boldsymbol{q_{aemeas}})^2 / \mathbf{n} - \mathbf{2}\}^{1/2}$$

Where

q_{calc} = the theoretical concentration of adsorbate on the adsorbent, which has been calculated from one of the isotherm models q_{emeas} = the experimentally measured adsorbed solid-phase concentration of the adsorbate adsorbed on the adsorbent.

q_{aemeas} = the average value of q_{emeas}

n = number of measurement

Akaike information criterion(AIC) generally calculated with the software.

The basic formula of AIC = AIC = 2K− 2(ln L) (Mirzaei *et al*., 2017)

Where

K indicates the number of parameters and L indicates a probability of the data given a model (likelihood).

Statistical Analysis

Statistical operations performed using the statistical software XLSTAT software package (Version, 2016)

RESULTS AND DISCUSSION

Physicochemical properties of the soil

Some chemical and physical properties of the soils presented in (Table 2) showed that the soils vary in their texture from silty clay to loam, with a range of organic matter, and total calcium carbonate content, from 90 to 25, and 25 to 430 g kg $^{-1}$ respectively. Most of the soil had a neutral reaction (7.48 to 7.90). EC of the soil ranged from 0.40 to 0.90 dS m $^{-1}$. The extracTable Copper by DTPA varied from 0.12 to 0.51 g kg $^{-1}$, whereas the CEC values ranged from 26.93 to 41.57 cmolc kg $^{-1}$.

Table 2. some chemical and physical properties in the studied soils.

Soil No.	pH	EC (dS m $^{-1}$)	T. $CaCO_3$ (g kg $^{-1}$)	O.M (g kg $^{-1}$)	Sand	Silt	Clay	Textural class	DTPA Copper mg kg $^{-1}$	CEC $cmol_c$ kg $^{-1}$
						g kg $^{-1}$				
Sharazor	7.49	0.60	180	25	37.20	475.10	487.70	Silty clay	0.51	41.15
Qaradagh	7.65	0.70	25	17	383.50	370.30	246.20	loam	0.47	26.93
Bazian	7.78	0.60	100	15	55.80	430.50	513.70	Silty clay	0.20	41.57
Mawat	7.48	0.9	25	16	161.90	434.20	403.90	Silty clay	0.38	39.42
Surdash	7.90	0.40	430	9	91.60	490.40	418.00	Silty clay	0.12	36.39

Effect of the initial concentration of the adsorbate in the adsorption process

With the increasing addition of Copper from 2.5 to 40mg L^{-1}, there was a slight increase in the equilibrium concentrations (Tables 3 and 4). Addition of 2.5 mg L^{-1} Copper resulted in higher equilibrium concentration in Bazian and Qaradagh soil (0.012and 0.025mg L^{-1}) than in Surdash, Mawat and Sharazor soil (0.001 to 0.008mg L^{-1}) at temperature 298 ^oK. There was no increase in the Copper adsorbed among the five soil at 2.5mg L $^{-1}$ Copper addition at two different temperatures (298, and 318 ^oK) (Table 3, and 4). The amount of Copper adsorbed by the five soil with 2.5mg L^{-1} Copper concentration was low (0.123 to 0.124mg g $^{-1}$) which increased with copper additions up to 40mg L^{-1} (1.997mg g^{-1}). The amount of Copper adsorbed by the five soil increased with the increasing level of applied Copper. These results are in agreement with (Misra and Tiwari, 1966) who reported that might be due to specific adsorption of Copper on $CaC0_3$ crystal and relatively to its precipitation as carbonate/hydroxide. Similarly, (Abat *et al.* 2012) indicated that copper and zinc adsorption increased gradually with increasing levels of added Copper and Zn in both control and limed soil.

Table 3. Influence of Copper additions on the equilibrium concentration (C_e, mg L^{-1}) and adsorption (q, mg g^{-1}) of copper at temperature 298°K in the studied soils.

Soil No.		Initial concentration of Copper in solution (mg L^{-1})					
		0	2.5	5	10	20	40
Sharazor	Ce	0	0.008	0.007	0.011	0.019	0.066
	q	0	0.124	0.2496	0.499	0.999	1.996
Qaradagh	Ce	0	0.025	0.026	0.034	0.046	0.095
	q	0	0.123	0.248	0.498	0.997	1.995
Bazian	Ce	0	0.012	0.021	0.021	0.031	0.065
	q	0	0.124	0.248	0.498	0.998	1.996
Mawat	Ce	0	0.003	0.072	0.039	0.061	0.073
	q	0	0.124	0.246	0.498	0.996	1.996
Surdash	Ce	0	0.001	0.002	0.013	0.021	0.052
	q	0	0.124	0.249	0.499	0.998	1.997

Table 4. Influence of Copper additions on the equilibrium concentration (C_e, mg L^{-1}) and adsorption (q, mg g^{-1}) of copper at temperature 318 °K in the studied soils.

Soil No.		Initial concentration of Copper in solution (mg L^{-1})					
		0	2.5	5	10	20	40
Sharazor	Ce	0	0.018	0.024	0.041	0.076	0.109
	q	0	0.124	0.248	0.497	0.996	1.994
Qaradagh	Ce	0	0.027	0.039	0.058	0.094	0.127
	q	0	0.123	0.248	0.497	0.995	1.993
Bazian	Ce	0	0.018	0.035	0.046	0.082	0.127
	q	0	0.124	0.248	0.497	0.995	1.993
Mawat	Ce	0	0.014	0.024	0.077	0.092	0.108
	q	0	0.124	0.248	0.496	0.995	1.994
Surdash	Ce	0	0.002	0.004	0.008	0.026	0.047
	q	0	0.124	0.249	0.499	0.998	1.997

Adsorption Isotherms:

Langmuir adsorption isotherm

The Langmuir equation optimised by the linear regression method, useful in the analysis of the reaction mechanism. Moreover, the Langmuir equation explains the formation of a monolayer of adsorbate on the adsorbent surface, which inhibits more adsorption (Dada *et al*.,2012). The values of maximum adsorption capacities estimated from the Langmuir model (q_m) of the soils at temperature 298 °K ranged between 0.359 to 1.344 mg g^{-1} soil, the highest value of (q_m) was observed at Sharazor soil, while the lowest value was recorded at Qaradagh soil as shown in (Table 5). On the other hand, the values of (q_m) of the soil at temperature 318 °K ranged between 0.522 to 6.579 mg g^{-1} soil.

On the contrary, the highest value of (qm) recorded at Mawat soil, and the lowest value was noticed in Qaradagh soil at temperature 318 °K respectively, as shown in the (Table 6). This low value of maximum adsorption in Qaradagh soil might relate to the effect of the low content of clay, total calcium carbonate, and CEC in the soil. These results were in close agreement with obtained by (Khan and Khattak, 1992) who stated that lower adsorption of Copper might be attributed to the precipitation of Copper ions like $Cu(OH)_2$. The values of bonding energy constant (K_L) calculated from the Langmuir model of the soils at temperature 298 °K ranged between 13.188 to 108.429 (L mg $^{-1}$). Moreover, the highest value of (K_L) recorded in the Surdash soil, while the lowest value of (K_L) noticed in Qaradagh soil (Table 5).

On the other hand, the values of (K_L) of the soils at temperature 318 °K ranged between 1.357 to 13.063 (L mg $^{-1}$). The highest value of (K_L) recorded in Surdash soil, and the lowest value of (K_L) noticed in Mawat soil (Table 6). High values of K_L indicate a strong attraction between sorbed Cu and soil surface. These results indicate that changes in temperature led to a decreasing in the value of bonding energy constant. Similar results were reported by (Pila *et al*., 2015), who reported that one of the basic requirements for an excellent production of adsorption isotherm is temperature. According to (Del-Bubba *et al*.,2003), K_L is a measure of the affinity of the adsorbate to the adsorbent.

Freundlich adsorption isotherm

Freundlich adsorption isotherm is mainly used to describe the adsorption properties of the homogeneous surface ((Dada *et al*.,2012). The (K_f) constant can provide an evaluation of the amount of adsorbed metal in (mg kg $^{-1}$) at a solution concentration of (1 mg L $^{-1}$) (Welp, and Brümmer, 1999). The values of the Freundlich constant related to sorption capacity (K_f) of the soils at temperature 298 °K ranged between 3.631 to 237.137 (L mg $^{-1}$), the highest value of (K_f) was observed at Bazian soil, while the lowest value was recorded at Mawat soil as shown in (Table 5). On the other hand, the values of (K_f) of the soil at temperature 318 °K ranged between 15.812 to 68.077 (L mg $^{-1}$). The highest value of (K_f) recorded at Qaradagh soil. Similarly, the lowest value was noticed in Mawat soil at temperature 318 °K, respectively, as shown in the (Table 6). In general, with increasing temperature, the values of (K_f) was decreased for all soils except Mawat and Surdash soils. The low value of K_f indicates low adsorption capacity and vice versa. These results also indicated that the Surdash and Mawat soils had a high capability to Copper adsorption when compared with other soils at different temperature 298°K and 318 °K respectively. K_f characterises the sorption attraction of the metal cations in the solution for the solid soil phase and can be used to characterise the mobility and retention of Copper in a soil system. K_f can be concerned about both plant uptake and environmental pollution. The low value of K_f indicates that most of the metals present in the system stay in the solution and are obtainable for transport, chemical processes and plant uptake (Jalali, and Moharrami, 2007), whereas higher values designate lower mobility and higher retention of metal in the soil. Therefore, Copper in Bazian soil had the lowest mobility, while, Copper in Mawat soil had the highest mobility. Freundlich constant related to sorption capacity K_f could place according to the following sequence: Bazian > Qaradagh > Sharazor > Surdash > Mawat, as shown in the (Table 5).On the other hand, these results of the value of K_f presented in Table (6) are in agreement with the finding of Pattamat and Pavarajarn, 2016) claims that temperature influences the value of Kf and as the temperature became higher, the adsorption increase more slowly, and higher concentration is requiring in order to saturate the surface. Variation in K_f value is dependent on the variation of soil properties like $CaCO_3$, clay content and organic matter (Hussain *et al*.,2003).

In the Freundlich equation, (n) values clarify the strength of held cations by the soil and the stability of forming complexes between cations and soil constituent (Buchter *et al*.,1989). The values of (n) of the soils at temperature 298 ^oK ranged between 0.533 to 1.721, the highest value of (n) was observed at Mawat soil, while the lowest value was recorded at Qaradagh soil as shown in the (Table 5). On the other hand, the values of (n) of the soil at temperature 318 ^oK ranged between 0.574 to 1.195. The highest value of (n) recorded at Surdash soil. Similarly, the lowest value was noticed in Mawat soil at temperature 318 ^oK, respectively, as shown in the (Table 6). Our finding is in agreement with Amjad *et al*., 2003) who reported that the Freundlich equation parameters (1/n) positively correlated with $CaCO_3$, and not with other soil characteristics (pH, EC, ESP, SAR, and TSS).

Temkin adsorption isotherm

The Temkin isotherm model supposes that the adsorption energy decreases linearly with the surface coverage owning to adsorbent–adsorbate interactions (Boparai *et al*., 2011). In contrast to the Langmuir and Freundlich equation, the Temkin isotherm takes into consideration the interactions between adsorbents and metal ions to be adsorbed and based on the hypothesis that the free energy of sorption is a function of the surface coverage (Chen *et al*., 2008). The values of constants related to heat sorption (B) of the soils at temperature 298^oK ranged between 0.298 to 1.387 mg g^{-1} soil, the highest value of (B) was observed at Qaradagh soil, while the lowest value was recorded at Mawat soil as shown in the (Table 5). On the other hand, the values of (B) of the soil at temperature 318 ^oK ranged between 0.545 to 1.115 mg g^{-1} soil. The highest value of (B) was recorded at Qaradagh soil, similarly, and the lowest value was noticed in Surdash soil at temperature 318 ^oK respectively, as shown in the (Table 6).

In the Temkin equation, the value of (A_T) is the equilibrium binding constant, which indicates the maximum bonding energy. The values of constants related to heat sorption (A_T) of the soils at temperature 298 ^oK ranged between 44.138 to 856.155 L mg $^{-1}$, the highest value of (A_T) was observed at Surdash soil, while the lowest value was recorded at Qaradagh soil as shown in the (Table 5). On the other hand, the values of (A_T) of the soil at temperature 318 ^oK ranged between 33.669 to 435.748 L mg $^{-1}$. The highest value of (A_T) recorded at Surdash soil. Similarly, the lowest value was noticed in Qaradagh soil at temperature 318 ^oK, respectively, as shown in the (Table 6).

Dubinin-Radushkevich isotherm

The Dubinin-Radushkevich adsorption isotherm usually used to distinguish the physical or chemical adsorption process (Dubinin,1975). The values of constants related to the maximum adsorption capacity (qD) of the soils at temperature 298 oK ranged between 3.888 to 324.083 mg g-1 soil, the highest value of (qD) was observed at Qaradagh soil, while the lowest value was recorded at Mawat soil as shown in the (Table 5). On the other hand, the values of (qD) of the soil at temperature 318 oK ranged between 19.713 to 105.004 mg g-1 soil. The highest value of (qD) recorded at Qaradagh soil. Similarly, the lowest value was noticed in Mawat soil at temperature 318 oK, respectively, as shown in the (Table 6). Our finding is in agreement with Mehmedany *et al*., 2016) who reported that the values of qm constant in (D-R) isotherm which represented the adsorption capacity vary from (1.139 to 214.344 mg g-1) in some calcareous soil of Duhok governorate. Qaradagh and Bazian soil had the highest copper adsorption capacity, as shown in the (Table 5). This is in agreement with the result gained from the Freundlich equation. The values of constants related to the maximum adsorption capacity (BD) of the soils at temperature 298 oK ranged between 0.120 to 0.399 (mole2kJ-2), the highest value of (BD) was observed at Qaradagh soil, while the lowest value was recorded at Mawat soil as shown in the (Table 5). On the other hand, the values of (BD) of the soil at temperature 318oK ranged between 0.161 to 0.350 (mole2kJ-2). The highest value of (BD) recorded at Qaradagh soil, and the lowest value was noticed in Surdash soil at temperature 318 oK, respectively, as shown in the (Table 6). The values of constants related to the maximum adsorption capacity (E) of the soils at temperature 298 oK ranged between 1.119 to 2.044 (kJ mol -1), the highest value of (E) was observed at Mawat soil, while the lowest value was recorded at Qaradagh soil as shown in the (Table 5). On the other hand, the values of (E) of the soil at temperature 318 oK ranged between 1.195 to 1.765 (kJ mol-1). The highest value of (E) recorded at Surdash soil. Similarly, the lowest value was noticed in Qaradagh soil at temperature 318 oK respectively, as shown in the (Table 6). The magnitude of (E) which calculated from D-R isotherm is useful for estimating the type of adsorption process. If the value of (E) is in the range of 8 -16 KJ mol-1, the adsorption type is ion exchange, and if it is < 8 KJ mol-1, then the adsorption is physical. The E values calculated in the studied soils ranged between 1.119 to 2.044 (kJ mol-1) and 1.195 to 1.765 (kJ mol-1) at different temperatures 298oK and 318 oK respectively (Table 5, and 6); therefore, it can be concluded that the adsorption mechanism of Copper ions in the studied soils can be explained with Phys-sorption (Bering *et al*., 1972).

Table 5. Langmiur, Freundlich, Temkin, and Dubinin-Radushkevich constants of Copper sorption at temperature 298°K in the studied soils.

Soil No.	Langmuir		Freundlich		Temkin		Dubinin-Radushkevich		
	q_{max} ($mg\ g^{-1}$)	K_L ($L\ mg^{-1}$)	K_f ($L\ mg^{-1}$)	n	B ($mg\ g^{-1}$)	A_T ($L\ mg^{-1}$)	q_D ($mg\ g^{-1}$)	B_D ($mole^2\ kJ^{-2}$)	E ($kJ\ mol^{-1}$)
Sharazor	1.344	16.497	48.195	0.919	0.830	168.679	56.109	0.225	1.488
Qaradagh	0.359	13.188	213.255	0.533	1.387	44.138	324.083	0.399	1.119
Bazian	0.468	18.405	237.137	0.596	1.177	75.812	306.433	0.350	1.195
Mawat	0.642	80.725	3.631	1.721	0.298	410.255	3.888	0.120	2.044
Surdash	1.318	108.429	11.800	1.536	0.408	856.155	12.330	0.133	1.940

Table 6. Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich constants of Copper sorption at the temperature 318 °K in the studied soils.

Soil No.	Langmuir		Freundlich		Temkin		Dubinin-Radushkevich		
	q_{max} ($mg\ g^{-1}$)	K_L ($L\ mg^{-1}$)	K_f ($L\ mg^{-1}$)	n	B ($mg\ g^{-1}$)	A_T ($L\ mg^{-1}$)	q_D ($mg\ g^{-1}$)	B_D ($mole^2\ kJ^{-2}$)	E ($kJ\ mol^{-1}$)
Sharazor	0.790	8.313	46.345	0.694	0.938	52.936	62.615	0.286	1.322
Qaradagh	0.522	7.477	68.077	0.574	1.115	33.669	105.004	0.350	1.195
Bazian	1.030	5.957	37.757	0.694	0.926	46.333	52.102	0.287	1.319
Mawat	6.579	1.357	15.812	0.877	0.656	67.484	19.713	0.225	1.491
Surdash	4.785	13.063	24.604	1.195	0.545	435.748	26.327	0.161	1.765

Comparison of Isotherms

Several equations have been used to compare the goodness of fit of different mathematical models to describe the copper adsorption; these models include Langmuir, Freundlich, Temkin, Dubinin-Radushkevich. (Table7, and 8) shows the values of determination coefficient (R^2), root means square error (RMSE), and Akaike information criterion (AIC) of these various mathematical models for all the five soils at both temperatures 298 °K and 318 °K. Freundlich model compared to the other models is considered as the best model to describe copper adsorption since it has given the highest R^2 and the lowest RMSE, and AIC, which were (0.987 , 0.099 , -21.725) , (0.963,0.105 , -21,084) , (0.912 , 0.164 , -16.659), (0.874 , 0.195 , -14.883) ,and (0.518 , 0.382 , -8.177)for (R^2), RMSE, and AIC at Sharazor, Surdash , Bazian , Qaradagh, and Mawat soils respectively(Table 7). It can conclude that the Freundlich model is the best model to describe the isotherm models. Effectiveness in these models depending on R^2, RMSE, and AIC at 298°K to describe Copper adsorption for the studied soils can arrange as follows:

Freundlich > Temkin > Dubinin-Radushkevich > Langmuir.

Whereas effectiveness in these models depending on R^2, RMSE, and AIC at 318°K to describe Copper adsorption for the studied soils can arrange as follows: Freundlich > Dubinin-Radushkevich > Langmuir > Temkin. (He *et al*.,2006) reported similar results who indicated that the isotherms of Cu^{2+}, Pb^{2+}, or Cd^{2+} adsorption fit well with some physical-chemical models, such as the Freundlich and the simple Langmuir equation. The determination coefficient (R^2), root mean square error (RMSE), and Akaike information criterion (AIC) of various models used to describe the copper adsorption at temperature (298 °K) in studied soils presented in (Table 7 and 8).

Table 7. The determination coefficient (R^2), root mean square error (RMSE), and Akaike information criterion (AIC) of various models used to describe the copper adsorption at temperature (298°K) in studied soils.

Soil No.	Langmuir			Freundlich			Temkin			Dubinin-Radushkevich		
	RMSE	AIC	R^2	RMSE	AIC	R^2	RMSE	AIC	R^2	RMSE	AIC	R^2
Sharazor	2.252	9.566	0.594	0.234	-3.085	0.819	0.099	-21.725	0.987	0.534	-4.832	0.822
Qaradagh	1.947	8.109	0.701	0.195	-4.883	0.874	0.052	-28.205	0.997	0.441	-6.739	0.879
Bazian	1.104	2.440	0.903	0.164	-6.659	0.912	0.2319	-13.1699	0.9304	0.372	-8.450	0.914
Mawat	1.580	6.022	0.800	0.382	-8.177	0.518	0.744	-1.509	0.284	0.880	0.164	0.518
Surdash	0.505	-5.380	0.970	0.105	-1.084	0.963	0.410	-7.472	0.783	0.246	-2.574	0.970
Min.	0.505	-5.38	0.594	0.105	-1.084	0.518	0.052	-28.205	0.284	0.246	-2.574	0.518
Max.	2.252	9.566	0.97	0.382	-8.177	0.963	0.744	-1.509	0.997	0.88	0.164	0.97
Mean	1.477	4.152	0.794	0.216	-4.778	0.817	0.307	-14.416	0.796	0.495	-6.486	0.821

Table 8. The determination coefficient (R^2), root mean square error (RMSE), and Akaike information criterion (AIC) of various models used to describe the copper adsorption at temperature (318 °K) in studied soils.

Soil No.	Langmuir			Freundlich			Temkin			Dubinin-Radushkevich		
	RMSE	AIC	R^2	RMSE	AIC	R^2	RMSE	AIC	R^2	RMSE	AIC	R^2
Sharazor	0.870	0.054	0.940	0.063	-6.235	0.987	0.316	-10.061	0.870	0.143	-8.005	0.987
Qaradagh	0.603	-3.620	0.971	0.034	-2.278	0.996	0.337	-9.423	0.852	0.083	-3.446	0.996
Bazian	0.396	-7.829	0.988	0.059	-6.777	0.988	0.341	-9.321	0.849	0.144	-7.947	0.987
Mawat	0.561	-4.340	0.975	0.181	-5.650	0.892	0.545	-4.618	0.614	0.423	-7.164	0.889
Surdash	0.152	-17.378	0.998	0.058	-7.060	0.989	0.319	-9.992	0.869	0.132	-8.775	0.989
Min.	0.152	-17.378	0.94	0.034	-2.278	0.892	0.316	-10.061	0.614	0.083	-3.446	0.889
Max.	0.87	0.054	0.998	0.181	-15.65	0.996	0.545	-4.618	0.87	0.423	-7.164	0.996
Mean	0.516	-6.623	0.974	0.079	-25.6	0.9704	0.381	-8.683	0.812	0.185	-7.067	0.970

CONCLUSION

Results showed that the amount of Copper adsorbed by the five soil increased with the increasing level of applied Copper. Copper in Bazian soil had the lowest mobility, while, Copper in Mawat soil had the highest mobility. Freundlich constant related to sorption capacity (K_f) could place according to the following sequence: Bazian > Qaradagh > Sharazor > Surdash > Mawat. The magnitude of (E) which calculated from D-R isotherm in the studied soils ranged between 1.119 to 2.044 (kJ mol $^{-1}$) and 1.195 to 1.765 (kJ mol $^{-1}$) at different temperatures 298^{o}K and 318 ^{o}K; therefore, it can conclude that the adsorption mechanism of Copper ions in the studied soils can explain with physisorption. Several models such as Langmuir, Freundlich, Temkin, Dubinin-Radushkevich were used to compare the goodness of fit to describe the copper adsorption. Freundlich model compared to the other models is considered as the best model at both temperatures (298 and 318^{o}K) for describing copper adsorption since it has given the highest value of R^2 and the lowest RMSE and AIC.

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REFERENCES

Abat, M., McLaughlin, M. J., Kirby, J. K., & Stacey, S. P., 2012. Adsorption and desorption of copper and zinc in tropical peat soils of Sarawak, Malaysia. Geoderma 175: 58-63.

Adamson, A. W., & Gast, A. P., 1967. Physical chemistry of surfaces (Vol. 150, p. 180). New York: Interscience publishers.

Amjad H., Abdul G., Anwar U., and Muhammad N., 2003. Application of the Langmuir and Freundlich Equations for P Adsorption Phenomenon in Saline-Sodic Soils. Int. J. Agri. Biol.5, (3). 349–356.

Bering, B. P., Dubinin, M. M., & Serpinsky, V. V., 1972. On the thermodynamics of adsorption in micropores. Journal of Colloid and Interface Science, 38(1), 185-194.

Boparai, H. K., Joseph, M., & O'Carroll, D. M., 2011. Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles. Journal of hazardous materials, 186(1), 458-465.

Bouberka, Z., Kacha, S., Kameche, M., Elmaleh, S., & Derriche, Z., 2005. Sorption study of an acid dye from aqueous solutions using modified clays. Journal of Hazardous Materials, 119(1-3), 117-124.

Buchter, B., Davidoff, B., Amacher, M. C., Hinz, C., Iskandar, I. K., & Selim, H. M., 1989. Correlation of Freundlich Kd and n retention parameters with soils and elements. Soil Sci, 148(5), 370-379.

Chen, Z., Ma, W., & Han, M., 2008. Biosorption of nickel and copper onto treated alga (Undaria pinnatifida): application of isotherm and kinetic models. Journal of hazardous materials, 155(1-2), 327-333.

Dąbrowski, A., 2001. Adsorption—from theory to practice. Advances in colloid and interface science, 93(1-3), 135-224.

Dada, A. O., Olalekan, A. P., Olatunya, A. M., and Dada, O. J. I. J. C., 2012. Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of Zn^{2+} unto phosphoric acid modified rice husk. IOSR Journal of Applied Chemistry, 3(1), 38-45.

Das, B., Mondal, N. K., Bhaumik, R., & Roy, P., 2014. Insight into adsorption equilibrium, kinetics and thermodynamics of lead onto alluvial soil. International Journal of Environmental Science and Technology, 11(4), 1101-1114.

Del Bubba, M., Arias, C. A., & Brix, H., 2003. Phosphorus adsorption maximum of sands for use as media in subsurface flow constructed reed beds as measured by the Langmuir isotherm. Water Research, 37(14), 3390-3400.

Dubinin M.M., and Radushkevich L.V.,1947. The equation of the characteristic curve of the activated charcoal, Proc. Acad. Sci. USSR Phys. Chem. Sect. 55: 331-337.

Dubinin, M. I.,1975. Physical adsorption of gases and vapors in micropores. In Progress in surface and membrane science (Vol. 9, pp. 1-70). Elsevier.

Dudley, L. M., McLean, J. E., Furst, T. H., and Jurinak, J. J.,1991. Sorption of cadmium and copper from an acid mine waste extract by two calcareous soils: Column studies. Soil Science, 151(2), 121-135.

Freundlich, H. M. F.,1906. Over the adsorption in solution. J. Phys. Chem, 57(385471), 1100-1107.

Günay, A., Arslankaya, E., & Tosun, I., 2007. Lead removal from aqueous solution by natural and pretreated clinoptilolite: adsorption equilibrium and kinetics. Journal of hazardous materials, 146(1-2), 362-371.

Hall, K. R., Eagleton, L. C., Acrivos, A., and Vermeulen, T., 1966. Pore-and solid-diffusion kinetics in fixed-bed adsorption under constant pattern conditions. Industrial & Engineering Chemistry Fundamentals, 5(2), 212-223.

He, Z., Yu, S., Yang, J., Yang, X., Xu, H. and Stoffella, P.J., 2006, July. Adsorption-Desorption Characteristics of Copper, Lead, and Cadmium at Contaminated Levels in Variable Charge Soils. In The 18th World Congress of Soil Science.

Hussain, A., Ghafoor, A., Anwar-Ul-Haq, M., & Nawaz, M., 2003. Application of the Langmuir and Freundlich equations for P adsorption phenomenon in saline-sodic soils. International Journal of Agriculture and Biology, 5(3), 1560-8530.

Jalali, M., & Moharrami, S., 2007. Competitive adsorption of trace elements in calcareous soils of western Iran. Geoderma, 140(1-2), 156-163.

Jalali, R., Ghafourian, H., Asef, Y., Davarpanah, S. J., & Sepehr, S., 2002. Removal and recovery of lead using nonliving biomass of marine algae. Journal of Hazardous Materials, 92(3), 253-262.

Kahn, M. A., & Khattak, Y. I.,1992. Adsorption of copper from copper sulfate solution on carbon black "Spheron 9"—II. Carbon, 30(7), 957-960.

Kim, Y., Kim, C., Choi, I., Rengaraj, S., & Yi, J., 2004. Arsenic removal using mesoporous alumina prepared via a templating method. Environmental science & technology, 38(3), 924-931.

Kundu, S., & Gupta, A. K., 2006. Arsenic adsorption onto iron oxide-coated cement (IOCC): regression analysis of equilibrium data with several isotherm models and their optimisation. Chemical Engineering Journal, 122(1-2), 93-106.

Langmuir, I., 1916. The constitution and fundamental properties of solids and liquids. Part I. Solids. Journal of the American chemical society, 38(11), 2221-2295.

Lindsay, W. L., & Norvell, W., 1978. Development of a DTPA soil test for zinc, iron, manganese, and copper 1. Soil science society of America Journal, 42(3), 421-428.

McLaren, R. G., & Crawford, D. V., 1973. Studies on soil copper I. The fractionation of copper in soils. Journal of Soil Science, 24(2), 172-181.

Mehmedany, L. A., Hashim, F. A., & Barwari, V. I., 2016. Adsorption behaviour of copper in some calcareous soils from Duhok Governorate. Science Journal of the University of Zakho, 4(2), 200-207.

Mirzaei, N., Ghaffari, H.R., Sharafi, K., Velayati, A., Hoseindoost, G., Rezaei, S., Mahvi, A.H., Azari, A. and Dindarloo, K., 2017. Modified natural zeolite using ammonium quaternary based material for Acid red 18 removals from aqueous solution. Journal of environmental chemical engineering, 5(4), 3151-3160.

Misra, S. G., and Tiwari, R. C., 1966. Retention and release of copper and zinc by some Indian soils. Soil Science, 101(6), 465-471.

Page, A. L.; Miller R. H.; Keeney D. R.,1982. Methods of soil analysis. Part 2. Chemical and microbiological properties.2nd edition Agronomy No.9. ASA, Madison, Wisconsin USA.

Pila, A. N., Jorge, M. J., Profeta, M. I., Romero, J. M., Jorge, N. L. and Castro, E. A., 2015. Adsorption isotherm the herbicide 2-methyl-4-chlorophenoxyacetic acid in the watery phase on soil with high contained organic matter. Asian Journal of Science and Technology Vol. 06, Issue 08, pp. 1647-1651.

Puttamat, S., and Pavarajarn, V., 2016. Adsorption study for removal of Mn (II) ion in aqueous solution by hydrated ferric (III) oxides. International Journal of Chemical Engineering and Applications, 7(4), 239-243.

Ryan J., Estefan G, and Rashid A., 2001 Soil and plant analysis laboratory manual.2nd edition. International centre for agriculture research in the dry areas (ICARDA).

Tempkin M.I., and Pyzhev V., 1940. Kinetics of ammonia synthesis on the promoted iron catalyst, Acta Phys. Chim. USSR 12: 327-356.

Tiller, K. G., 1968. Stability of hectorite in weakly acidic solutions. III. Adsorption of heavy metal cations and hectorite solubility. Clay Minerals, 7(4), 409-419.

Ünlü, N., & Ersoz, M., 2006. Adsorption characteristics of heavy metal ions onto a low-cost biopolymeric sorbent from aqueous solutions. Journal of hazardous materials, 136(2), 272-280.

Welp, G., & Brümmer, G. W., 1999. Adsorption and solubility of ten metals in soil samples of different composition. Journal of plant nutrition and soil science, 162(2), 155-161.

Yang, W., Ding, P., Zhou, L., Yu, J., Chen, X., & Jiao, F., 2013. Preparation of diamine modified mesoporous silica on multi-walled carbon nanotubes for the adsorption of heavy metals in aqueous solution. Applied Surface Science, 282, 38-45.

Yavuz, Ö., Altunkaynak, Y., & Güzel, F., 2003. Removal of copper, nickel, cobalt and manganese from aqueous solution by kaolinite. Water Research, 37(4), 948-952.

سلوك ادمصاص النحاس في بعض الترب الجيرية باستخدام نماذج Langmuirو Freundlich و Temkin و Dubinin-Radushkevich

كمال حمه كريم

قسم الموارد الطبيعية ، كلية علوم الهندسة الزراعية ، جامعة السليمانية ، السليمانية ، إقليم كوردستان ، العراق

تم دراسة ادمصاص النحاس في خمسة أنواع من ترب الجيرية (شهرزور ، قرداغ ، بازيان ، ماوت ، وسورداش) مختلفة في إجمالي كربونات الكالسيوم، المواد العضوية ، وقدرة التبادل الكاتيوني في محافظة السليمانية - إقليم كوردستان العراق. تم الإدمصاص المتساوي الحرارة من النحاس المعدني من قبل التربة باستخدام طريقة الدفعي. تم وضع غرام واحد من كل عينة من التربة ، بمكررين ، في زجاجات بلاستيكية وتم معايرتها بـ 50 مل من محلول $CaCl_2$ (0.01M)، حاوية على سلسلة من تركيزات النحاس (0 ، 2.5 ، 5 ، 10 ، 20 ، 40 ملغم من النحاس . لتر$^{-1}$) بشكل ($CuSO_4$) ، تم تحديد تركيز Cu في المحلول باستخدام (ICP-OES)، ومن ثم تم تقدير مقدار النحاس المدمص من قبل العينة المحددة بطرح تركيز توازن النحاس في المحلول من النحاس المضاف.استخدمت بيانات توازن الأيزوثرم لوصف ادمصاص النحاس في الترب الخمسة المختلفة باستخدام نموذج الأيسوثرم (لانجموير ، فروندليتش ، تيمكين ودوبنين - رادوشكيفيتش (D-R)). اعتبر نموذج Freundlich أفضل نموذج لوصف ادمصاص النحاس مقارنة مع النماذج المختلفة، لوصف نماذج الأيسوثرم اعتمادًا على أعلى قيمة لمعامل التحديد (R^2) ، وأقل قيمة لخطأ الجذر التربيعي المتوسط (RMSE) ، و معيار معلومات Akaike (AIC) .