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# Effect of organic matter on the adsorption and release of copper in some gypsiferous soils in Salah al-Din Governorate

**Basim S. Obaid , Ragaa S. Salih*, and Yasir H. Ajrash**
[1]*Department of Soil Sciences and Water Resources - College of Agriculture – Tikrit University – Iraq*

* *Corresponding author: E-mail*: ragaa0016@gamil.com

**KEY WORDS:**
Adsorption, release, copper, organic matter, gypsum soil

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**ABSTRACT**

A laboratory experiment was conducted to study the behavior of copper in gypsum soils of different organic sources through a number of experiences, and knowledge of copper adsorption and release conditions in it, and used three equations physicochemical Langmuir, Freundlich, and Temkin. It was adopted The coefficient of determination ($R^2$ ) is a better choice equation to describe the adsorption of copper, the results showed that the Langmuir equation was enough for the description and evaluation of copper adsorption compared to the rest of the physicochemical equations used according to the highest coefficient of determination $R^2$, and the efficiency of R2 was (92, 87, 65) % for each of the Langmuir and Freundlich equations and Temkin, respectively. The maximum adsorption values of the Langmuir equation were (61.728 - 25,906) mg.kg$^{-1}$ and a bonding energy (0.731 - 0.128) L.mg$^{-1}$, and Freundlech's equation showed the maximum adsorption values (1.346 - 0.855) L.mg$^{-1}$ and a bonding energy (15.160 - 4.010) mg.kg$^{-1}$, while the maximum adsorption values were to equation Temkin range between (35 - 29) mg.kg$^{-1}$ energy connectivity ranging what between (0.495-0.185) L.kg$^{-1}$, and from equation Temkin can that define type adsorption physical or a chemist and on the most chemical calendar for height valuable heat interaction bT, which ranges from (84.86 - 70.34). As for the results of liberating copper adsorbed, the highest values of liberated copper were recorded at. Levels add high from copper (50,100,150) mgkg$^{-1}$ and at levels low add from copper (2,5,10) mgkg$^{-1}$ be valuable Liberation copper zero (nill).

# تأثير نوع المادة العضوية على امتزاز وتحرر النحاس في بعض الترب الجبسية في محافظة صلاح الدين

**باسم شاكر عبيد وياسر حمود عجرش ورجاء سامي صالح**
**قسم التربة والمياه ، كلية الزراعية ، جامعة تكريت ، العراق**

**الخلاصة**

اجريت تجربة مختبرية لدراسة سلوك النحاس في ترب جبسية ذات مصادر عضوية مختلفة من خلال عدد من التجارب , ومعرفة ظروف امتزاز وتحرر النحاس فيها , واستعملت ثلاث معادلات فيزيوكيميائية لانكماير وفروندلخ وتمكن . تم اعتماد معامل التحديد $R^2$ في اختيار افضل معادلة لوصف امتزاز النحاس ،اظهرت النتائج ان معادلة لانكماير كانت هي الاكفأ في وصف وتقييم امتزاز النحاس مقارنة ببقية المعادلات الفيزيوكيميائية المستعملة تبعا لاعلى معامل تحديد $R^2$ ، وبلغت كفاءة $R^2$ (92)، (65،87 ) %لكل من معادلة لانكماير وفروندلخ وتمكن على الترتيب. اذ بلغت قيم الامتزاز الاعظم لمعادلة لانكماير(61.728 – 25.906) ملغم.كغم-1 وبطاقة ربط (0.731 – 0.128) لتر.ملغم-1 ،كما اظهرت معادلة فروندلخ قيم الامتزاز الاعظم (1.346 – 0.855) لتر .ملغم-1 وبطاقة ربط (15.160 – 4.010) ملغم.كغم-1 ،في حين كانت قيم الامتزاز الاعظم لمعادلة تمكن تتراوح ما بين (35 – 29) ملغم.كغم-1 وطاقة الربط تتراوح ما بين (0.185-0.495) لتر.كغم-1، ومن معادلة تمكن يمكن ان نحدد نوع الامتزاز فيزيائي ام كيميائي وعلى الاغلب كيميائي نتيجة لارتفاع قيم حرارة التفاعل $b_T$ والتي تتراوح مابين (84.86 – 70.34). اما نتائج تحرر النحاس الممتز سجلت اعلى قيم للنحاس المتحرر عند مستويات الاضافة العالية من النحاس (50،100،150) ملغم.كغم-1 وعند مستويات الاضافة المنخفضة من النحاس (2،5،10 ) ملغم.كغم-1 تكون قيم تحرر النحاس صفر (nill).

**الكلمات المفتاحية:** امتزاز ، تحرر ، نحاس ، مادة عضوية ، ترب جبسية.

## INTRODUCTION

Copper is one of the essential micro-nutrients for most economic agricultural crops, so it plays a major role in agricultural production in terms of quantity and quality, which necessitates the need to study the condition and behavior of this element in the soil in order to raise its productivity. Quick and accurate To analyze and detect the levels of this element in order to accurately express the readiness and estimate the need for fertilization with fertilizers containing this element. Copper plays a major role in a number of vital processes of the plant, as it is involved in the composition of chloroplasts, and therefore it affects the process of photosynthesis of the plant and is involved in the synthesis of a number of enzymes, as it participates in The vital processes of proteins, as it stimulates the formation of RNA and DNA, as well as participates in the vital processes of carbohydrates, as the levels of reduced sugar decrease with the deficiency of this element (Barker and Pilbeam, 2006). Although most soils contain a good level of copper, readiness is the determining and important factor, as this element can be exposed For factors and processes that may reduce or increase its readiness, such as the presence of organic matter in a high percentage or the presence of high levels of phosphorus, and symptoms of copper deficiency appear in calcareous soils fertilized with high amounts of phosphorus. Also, high levels of organic matter negatively affect the readiness of copper because of the strong bonding of copper with the material. Organic (formation of complexes with it) and thus its liberation is difficult and its readiness is reduced (Johnston and Tombacz, 2002).

Confirmed Singh *et al* (1994) indicated that the adsorption and liberation of copper from the exchange complex and the crystalline structure of the metals to the solution and vice versa is the process responsible for the movement of copper and the relative distribution of soil copper and its readiness for plants. The adsorption behavior of copper is important both from an environmental and fertility point of view, as the availability of copper in the soil depends on the state of its

presence in the soil in different states, which are adsorbed and dissolved in solution and are exchangeable (Maftoon,2002).
The use of concepts of thermodynamic chemistry is one of the important and modern means in determining the readiness of soil copper when it interferes with organic matter, which explains the nature of adsorption or liberation to which it is exposed. Due to the lack of studies on the behavior of the copper element in gypsum soils, this study was conducted with the aim of:
1_ Studying the behavior of the copper element in gypsum soils. 2_ The effect of the type of organic matter added on the adsorption and liberation of copper. 3_ Calculation of thermodynamic parameters using physiochemical ion exchange equations. 4- Study of the interaction between copper and organic matter in the growth and yield of barley plant in gypsum soil.

## MATERIAL AND METHODS

Three samples of different gypsum content were selected, the low gypsum symbolized by it (G1), medium gypsum symbolized by (G2), high gypsum symbolized by (G3), taken from separate areas and for different depths, gypsum increases with increasing depth in most gypsum soils of Tikrit University. The representative samples of gypsum were transferred from the three sites to the laboratory for processing. When grind and dried I passed it through a sieve with a diameter of its holes (2 mm) and then kept it in plastic containers. In order to determine some of the chemical and physical properties of soil and conduct a laboratory experiment, Table (1) shows some of the chemical and physical properties of the research soil.

Table (1) Some physical and chemical properties of the study soils

| Samples adjectives | Measruing unit | G1 | G2 | G3 |
|---|---|---|---|---|
| pH | | 7.63 | 7.82 | 7.84 |
| EC | ds. $m^{-1}$ | 2.56 | 2.34 | 2.35 |
| $CaSO_4$ | g.kg-1 | 50 | 150 | 250 |
| $CaCO_3$ | | 262 | 321 | 104 |
| O.M | | 10.1 | 9.1 | 9.2 |
| Available N | mg $kg^{-1}$ | 6. 18 | 4.17 | 12.4 |
| Available P | | 0.55 | 3.24 | 1.3 |
| Available K | | 112.62 | 81.61 | 5.336 |
| Melted copper | m.cu.$kg^{-1}$ | 0.23 | 0.39 | 0.41 |
| Available Cu | Mg.cu.$kg^{-1}$ | 1.36 | 1.17 | 0.97 |
| Total Cu | | 27.21 | 26.43 | 25.5 |
| dissolved ions | | | | |
| Na | m mol $L^{-1}$ | 1.22 | 1.46 | 2.22 |
| K | | 0.89 | 0.75 | 0.53 |
| Ca | | 5.44 | .669 | 3.331 |
| Mg | | 6.48 | 4.45 | 3.14 |
| Cl | | 2.86 | 1.91 | 1.64 |
| $CO_3$ | | Nile | Nile | Nile |
| $HCO_3$ | | 1.35 | 1.64 | 2.32 |
| $SO_4$ | | 8.89 | 12.75 | 15.32 |
| CEC | C mol $kg^{-1}$ | 13.27 | 12.28 | 6.710 |
| Sand | g.$kg^{-1}$ | 662 | 548 | 744 |
| Silt | | 85 | 224 | 53 |
| Clay | | 253 | 228 | 203 |
| Texture | | SCL | SCL | SCL |

Three types of organic waste were selected: (Remnants of Sheep, cows and poultry)It was collected from field livestock in Ishaqi district and it was dried pneumatically, then passed through a sieve with a diameter of its orifices 2mm for the purpose of conducting some chemical analyzes shown in table (2).

. Table 2.Some chemical properties of the organic waste used in the study

| | pH | EC | N% | P% | M% | C% | N/C | C/P |
|---|---|---|---|---|---|---|---|---|
| sheep waste | 7.57 | 8.02 | 2.65 | 0.62 | 1.71 | 46.90 | 17.70 | 75.66 |
| poultry waste | 7.01 | 6.94 | 3.98 | 0.91 | 2.69 | 42.73 | 10.74 | 46.96 |
| cow waste | 7.64 | 9.31 | 2.44 | 0.57 | 1.58 | 41.57 | 17.04 | 72.93 |

**Laboratory experiments**

Adsorption the copper at the state of dynamic equilibrium was weighed (2gm) from air-dry soil from the model and placed in plastic tubes (50 ml), then guest for her (40ml) solution copper ($CuSO_4.2H_2O$), in concentrations (2,5,10,25,50,100 and 150) mg $kg^{-1}$ for each level of gypsum (5, 15 and 25) i.e. with gypsum content (low, medium, high), respectively. The organic waste was added according to the recommendations then the tubes were closed and agitated for (24) hours using a vibrator and at a constant temperature (298)°kelvin at 25 C°. After It was left for 24 hours for the purpose of equilibrium, and then run on her centrifugation for a period of (15) minutes after that It was completed Teton the balanced solution of the soil was for the purpose of estimating the concentration of copper in which on Atomic Absorption Spectroscopy AAS.
In order to characterize interactions, adsorption of the copper at grow up study use (3) equations, according to (Qadeer,2005; Al-Obaidi, 2013) the Langmuir equation and the Freundlich and Temkin equation and let's go and an equation that enables applying the formulas of these equations to the data for adsorption of copper in the soil by using a linear regression analysis program for the actual (estimated) and calculated adsorption values against soil and for the purpose of choosing the best equivalent has been compared between the three equations above-mentionedabasedto standard coefficient of statistical determination(R2).

The Langmuir equation was used to describe the adsorption of copper on the study soil samples:

$$X=(K\ b\ C)/(1+KC) \ldots\ldots.(1)$$

The Laungmiur equation n the following form:

$$1 \ldots\ldots.(2)/Xm = 1 / Kb + b / C$$

Where:

X = the amount of adsorbed ion mg. $kg^{-1}$

C = ion concentration in mg equilibrium solution. $L^{-1}$

k = a constant representing the binding energy $l.mg^{-1}$

Xm = a constant that expresses the maximum adsorption of the amalgam ion. $kg^{-1}$

Fraundlich equation was used to describe the adsorption of copper on the study soil samples

$$X=KC^{b} \ldots\ldots\ldots(3)$$

$$\text{Log } X = \log K + b \log C \ldots\ldots\ldots\ldots(4)$$

Where:

X=The amount of the adsorbed element on the adsorbent surface is mg. $kg^{-1}$

C = the concentration of the element in the mg equilibrium solution. $L^{-1}$

B= constantIt has to do with the greatest adsorption$L.mg^{-1}$

K= constantIt has to do with the link cardmg.$l^{-1}$

Temkin equation equation was used to describe the adsorption of copper on the study soil samples

$$qe= B \ln AT + B \ln C \ldots\ldots.(5)$$

$$B=RT/ bT \ldots\ldots(6)$$

Where:

qe= The adsorbed quantity of the element mg. kg-1

B= Adsorption capacity mg. kg-1

C=Copper concentration in equilibrium solution mg. $L^{-1}$

AT=Constant represents binding energy L. $kg^{-1}$
R=gas constant
T=temperature atK298
bT=A constant related to the temperature of reaction.

**Reversal of adsorption (release) of copper at dynamic equilibrium:**

To study the reversal of copper adsorption and reveal the ability of soil to retain copper, (40) ml of. The solution was added to extraction calcium chloride ($CaCl_2$) at a concentration of (0.01) N in the soil in the tubes and agitated for (24) hours using a circular vibrator, at a constant temperature (298 )˚Kelvin, 25 ˚C, then separate the solution with a centrifugal use the solution was separated for estimation of copper in it.

**Determination of the amount of copper ion adsorbed**

The amount of adsorbed copper ion was estimated by the difference between the concentrations before and after equilibrium, using the equation below, according to what was mentioned (Fasaei and Jarrah, 2013) :

$$Cu^{+2}\text{-ad}=\frac{(Cin-Cfin)}{W}\times V\ldots\ldots(7)$$

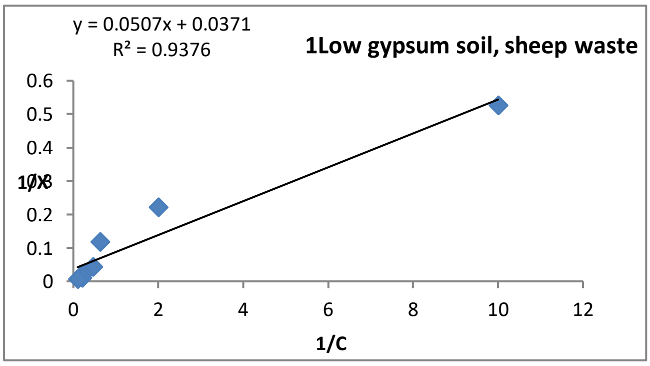
Where:
Cu-ad = Cu ion adsorbent ($\mu g.gm^{-1}$)
Cin = Initial copper concentration added ($mg.l^{-1}$)
Cfin= concentration of copper in equilibrium solution ($mg.l^{-1}$)
V = volume of solution added (ml)
W= weight of soil (g)

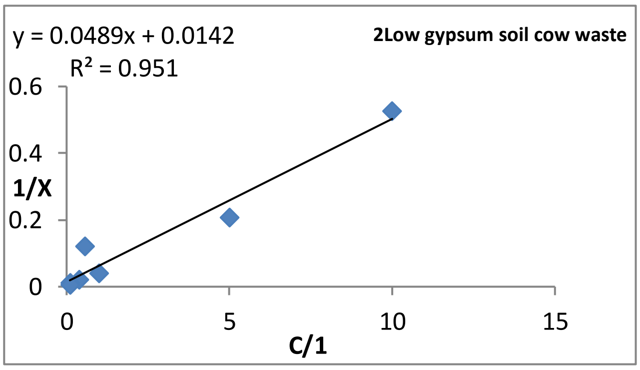
**RESULTA AND DISCUSSION**

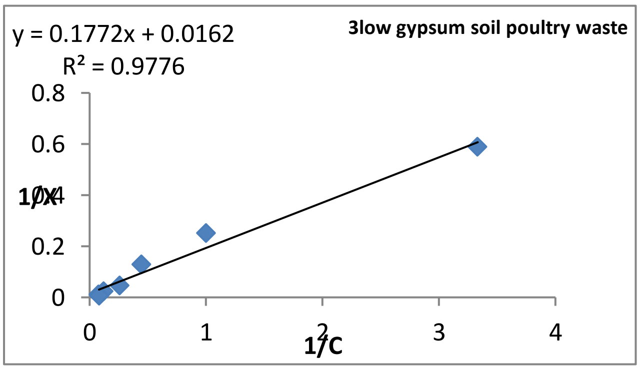
Notes from table (3) the maximum adsorption value is (b) the Langmuir equation ranged between (61.728-25,906) $mg.kg^{-1}$, as the low gypsum soil of poultry residues recorded the highest values of adsorption in this surface, while the lowest values of adsorption in gypsum soil were medium for poultry residues, while the binding energy values were (K) for these equation getting between(0.731-0.128) $L.mg^{-1}$For the low gypsum soil of poultry residues, the lowest values of the binding energy were recorded, while the low gypsum soil of sheep wastes recorded the lowest values of the binding energy. Top binding energy values. This increase in the maximum adsorption values and the decrease in the binding energy values for low gypsum soil with poultry waste may be due to the occurrence of adsorption on non-specialized sites. For example, adsorption on clay surfaces, while the values of the binding energy increased in low gypsum soil with sheep residues as returns the reason for the difference in the type of organic matter or to the adsorption of copper ions on the specialized sites, and this is associated with the content of those soils of clay with the behavior of the organic matter, the behavior of the specialized sites, which leads to an increase in the binding strength in these soils. Or perhaps because of the high levels of organic matter, which will bind strongly with copper and thus form complexes with it, and thus its release will be difficult, and its readiness will decrease. The decrease in the maximum adsorption values in gypsum soil medium of poultry waste maybe is due to the increase in calcium sulfate in the soil to the fact that gypsum particles do not carry negative electrical charges on their surface and are a source of calcium and sulfate ions(Elrashidi *et al.*, 2007) and thus increasing the competition of calcium ions for copper ions on the adsorption surfaces, and perhaps the gypsum coated the effective adsorption surfaces of the folding minerals.

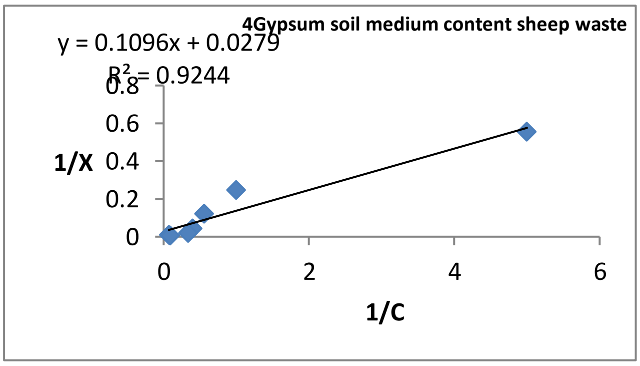
Table (3) Maximum adsorption and binding energy of the Langmuir equation for the study soils.

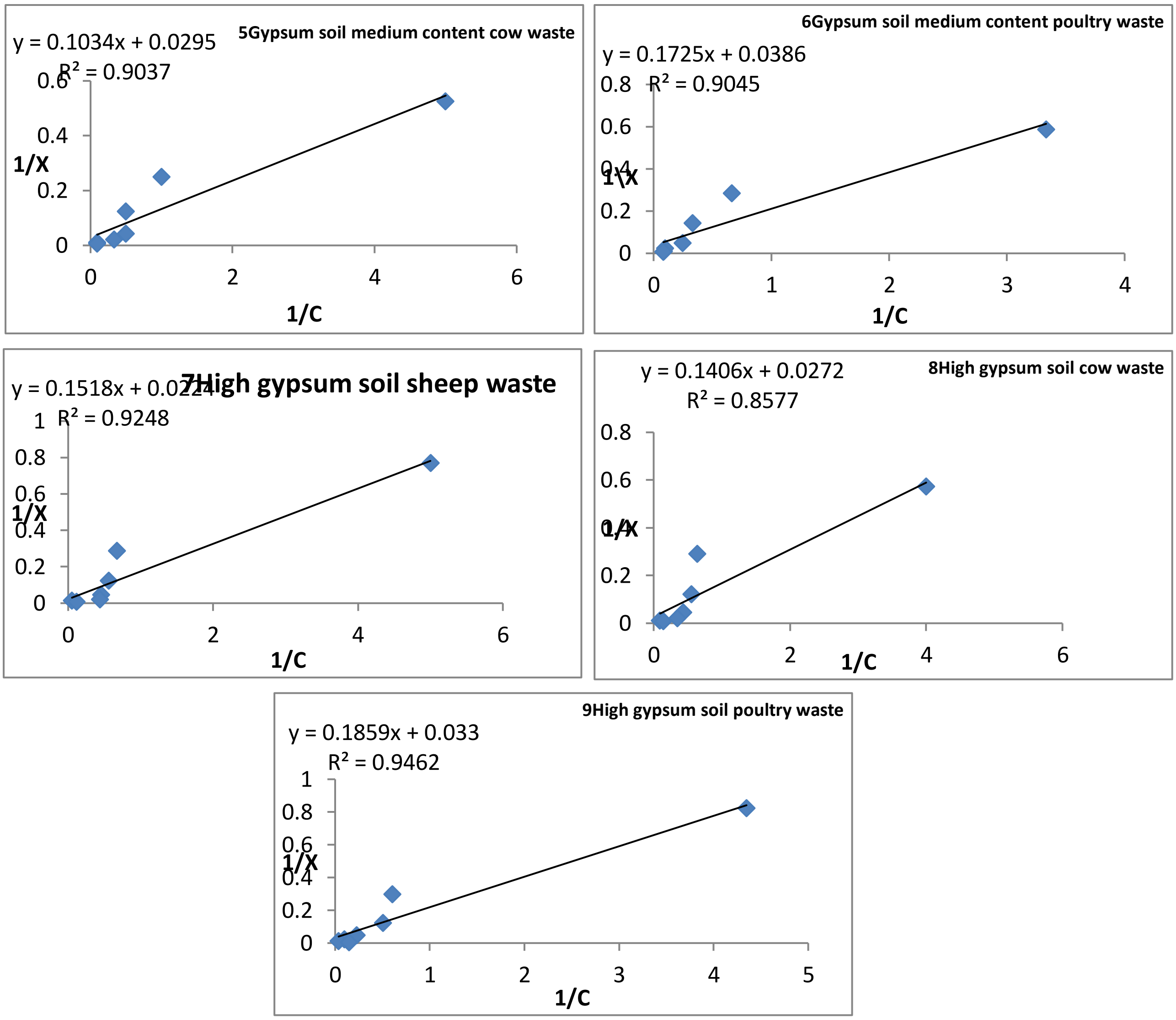
| **Standards** / **soil parameters** | **Straight-line equation to the Langmuier equation** | **The coefficient of determinationR2 (%)** | **(b) the greatest adsorption ($mg.kg^{-1}$)** | **(K) binding energy ($L.mg^{-1}$)** |
|---|---|---|---|---|
| Low gypsum soil, sheep waste | Y=0.0507x+0.0371 | 93 | 26,954 | 0.731 |
| Low gypsum soil cow waste | Y=0.0489x+0.0142 | 95 | 30.120 | 0.653 |
| low gypsum soil poultry waste | Y=0.1772x+0.0162 | 97 | 61.728 | 0.128 |
| Gypsum soil medium content sheep waste | Y=0.1096x+0.0279 | 92 | 35.842 | 0.254 |
| Gypsum soil medium content of cow waste | Y=0.1034x+0.0295 | 90 | 33.898 | 0.285 |
| Gypsum soil medium content poultry waste | Y=0.1725x+0.0386 | 90 | 25,906 | 0.223 |
| High gypsum soil, sheep waste | Y=0.1518x+0.0224 | 92 | 44.642 | 0.147 |
| High gypsum soil cow waste | Y=0.1406x+0.0272 | 85 | 36.764 | 0.193 |
| High gypsum soil poultry waste | Y=0.1859x+0.033 | 94 | 30.303 | 0.177 |





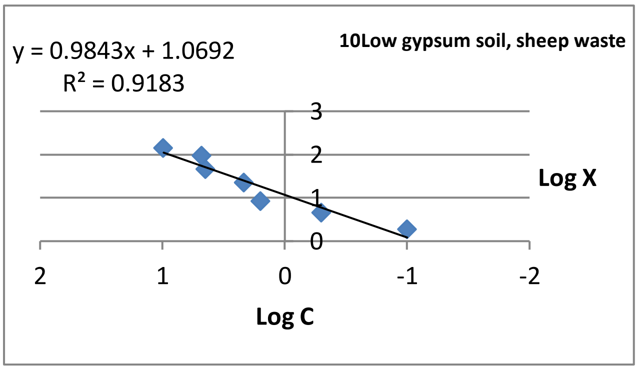

Figures (9-1) adsorption curves of the Langmuier equation for the study soils

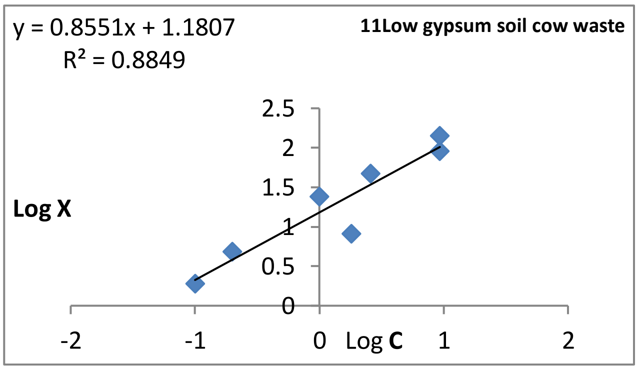
Table (4) shown the maximum adsorption values (b) and the binding energy (K) for copper ions obtained from Freundlech equation. The values of the maximum adsorption (b) range between (1.346 - 0.855) L. $Mg^{-1}$ The highest values of the greatest adsorption were in high gypsum soil with cow waste, and the lowest values of maximum adsorption were in soil Low gypsum cow waste. As for the binding energy (K) values, it ranged between (15.160 - 4.010) $mg.kg^{-1}$ the highest values of binding energy in gypsum soil with low cow residues and the lowest values of binding energy in gypsum soil medium poultry offal, and this difference between the valuesmay beThis is due to a decrease in the quantities of adsorbed copper as we tend to increase the quantities of gypsum in the soil, due to the increase in the quantities of calcium ions competing for the adsorption sites, so that the copper ions associated with a lower binding energy remain, and this is confirmed by the decrease in the binding energy with an increase in the quantities of gypsum in the soilwhere copper is deposited in the form of copper sulfate ($CuSO_4$).

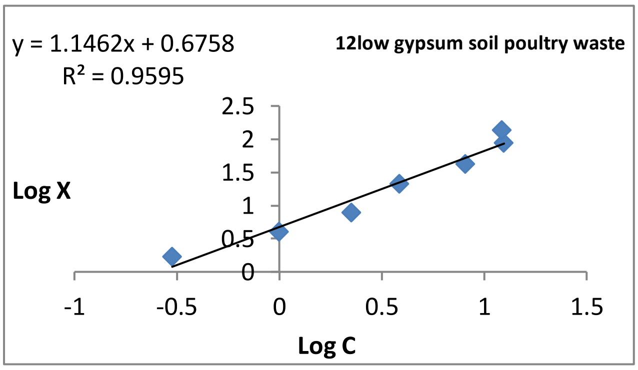
Table (4) values of maximum adsorption and binding energy from Freundlech equation for the study soils.

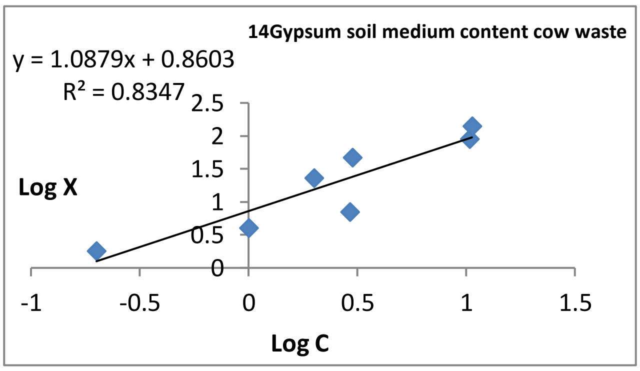
| **Standards** / **soil parameters** | **Straight-line equation For Frendlech's equation** | **The coefficient of determinationR2 (%)** | **(b)(L.mg$^{-1}$)** | **(K)(mg.kg$^{-1}$)** |
|---|---|---|---|---|
| Low gypsum soil, sheep waste | Y=0.9843x+1.0692 | 91 | 0.984 | 11.727 |
| Low gypsum soil cow waste | Y=0.8551x+1.1807 | 88 | 0.855 | 15.160 |
| low gypsum soil poultry waste | Y=1.1462x+0.6758 | 95 | 1.146 | 4.704 |
| Gypsum soil medium content sheep waste | Y=1.067x+0.8871 | 89 | 1.067 | 7.710 |
| Gypsum soil medium content of cow waste | Y=1.0879x+0.8603 | 83 | 1.087 | 7.249 |
| Gypsum soil medium content poultry waste | Y=1.1822x+0.6032 | 89 | 1.182 | 4.010 |
| High gypsum soil, sheep waste | Y=1.2916x+0.7527 | 84 | 1.291 | 5.658 |
| High gypsum soil cow waste | Y=1.3467x+0.7586 | 85 | 1.346 | 5.735 |
| High gypsum soil poultry waste | Y=1.154x+0.7781 | 82 | 1.115 | 5.999 |

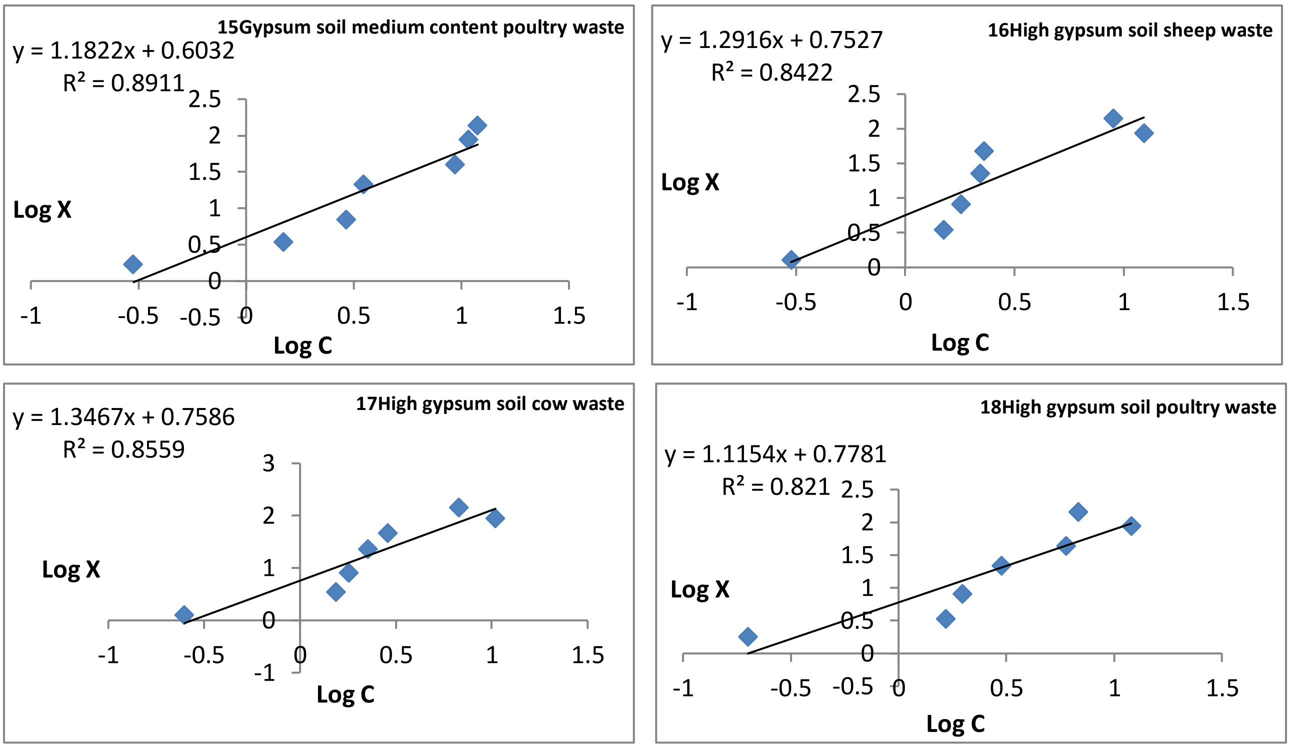
(b) a constant related to the maximum adsorption
(k) is a constant related to the bonding energy





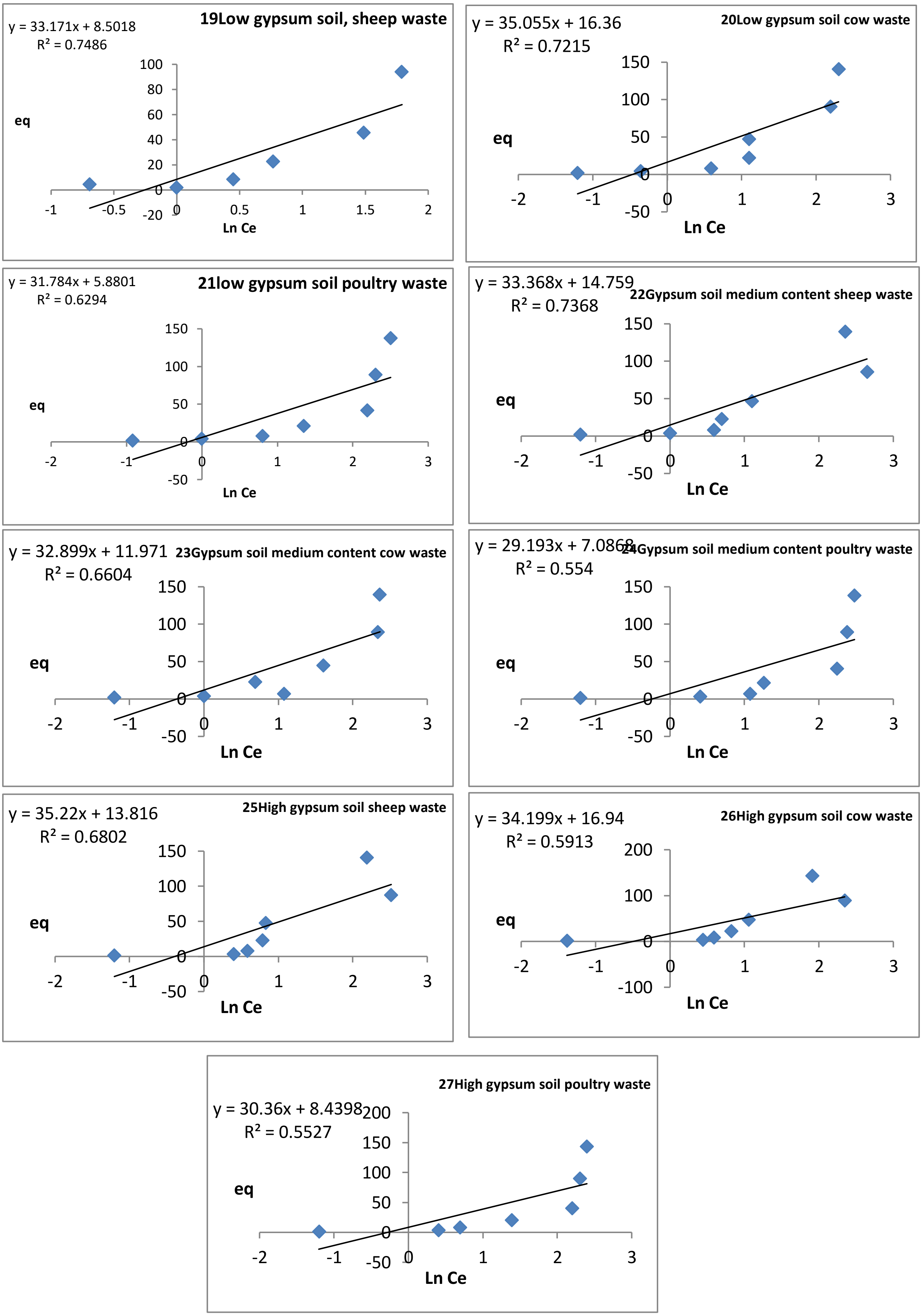

Shapes (18-10) the adsorption curves of Freundlech's equation for the study soils

Table (5) show the maximum adsorption values and the binding energy of the temkin equation, where a clear fluctuation is observed in the values, where the maximum adsorption values range between(35 - 29) mg.kg-1 and the binding energy values range between (0.495 - 0.185) liters.kg-1, and the highest values of maximum adsorption were in low gypsum soil with cow waste and the same value in high gypsum soil with sheep wasteThe lowest values were in the medium gypsum soil of poultry residues.As for the highest values of binding energy in high gypsum soil with cow litter, and the lowest values of binding energy in low gypsum soil with poultry offal, it is worth noting that through the high values of reaction temperature($b_T$) in an equation temkin which range from (34.70-86.84)It becomes clear to us that the adsorption is physical or chemical, and

Table (5) The values of the maximum adsorption and binding energy of the Equation temkin for the study soils

| **Standards / soil parameters** | **Straight-line equation for an equation that enables** | **R2 (%)** | **(b) the greatest adsorption (amalgam.kg-1)** | **(K) binding energy (Liter.mg-1)** | **reaction heat Bt** |
|---|---|---|---|---|---|
| Low gypsum soil, sheep waste | Y=33.1713x+8.508 | 74 | 33 | 0.256 | 74.69 |
| Low gypsum soil cow waste | Y=35.055x+16.36 | 72 | 35 | 0.466 | 70.67 |
| low gypsum soil poultry waste | Y=31.784x+5.8801 | 62 | 31 | 0.185 | 77.95 |
| Gypsum soil medium content sheep waste | Y=33.368x+14.759 | 73 | 33 | 0.442 | 73.84 |
| Gypsum soil medium content of cow waste | Y=32.899x+11.871 | 66 | 32 | 0.363 | 75.30 |
| Gypsum soil medium content poultry waste | Y=29.193x+7.0868 | 55 | 29 | 0.240 | 84.86 |
| High gypsum soil, sheep waste | Y=35.22x+13.816 | 68 | 35 | 0.392 | 70.34 |
| High gypsum soil cow waste | Y=34.199x+16.94 | 59 | 32 | 0.495 | 72.45 |
| High gypsum soil poultry waste | Y=30.36x+8.4398 | 55 | 30 | 0.278 | 81.61 |

through the results it appears to us that the adsorption is mostly chemicalmay return tohigh deposition of copper ions in the form of($CuSO_4$) where the greater the amount of gypsum, the greater the sedimentation due to the increase in sulfates.




Figures (27-19) adsorption curves for an equation temkin the study soils

In general, it is noted from the results that the soils showed a discrepancy in their response to the three equations (Lankemeyer Freundlich, Temkin ) because of the different chemical properties of soils according to their content of gypsum, organic matter, clay, and lime.

**Choosing the equation that best describes the adsorption process:**

Many researchers often resort to adopting some statistical criteria, including the coefficient of modification hand for the curve of the adsorption values for that equation(R2) In order to reach the best equation that describes the study of a specific characteristic or condition related to the reactions of the adsorption process or even ion exchange. The values of the statistical coefficient of determination (R2) are shown in Table No. (6), which was obtained by applying the Langmeier and Freundlich adsorption equations and Temkin, as the Langemeier equation outperformed the value of the determination coefficient for the straight line equation curve, which reached(92%) and for the Freundlich equation it reached (87%) and for the Temkin equation it reached (65%). It is noted from the values that the superiority is clear for the Langmuir equation and its precedence over the rest of the equations with the values of the coefficient of determination that gives it priority over the rest of the equations. This agrees with what Al-Jumaili *et al* (2016) in their study on the adsorption of zinc in the limestone and gypsum soils of Salah al-Din Governorate, and the graphic forms (9-1,18-10.27-19)It refers to the adsorption curves of the three equations through which we note the true agreement of the values obtained from the adsorption experiment with the mathematical formula of Lankmayr's equation.

Table (6) coefficient of determination ($R^2$) for the equations used to describe copper adsorptionto study.

| **Equations used** | **soil parameters** | | |
|---|---|---|---|
| | **Langmeier equation (%)** | **Freundlech's equation(%)** | **Equation temkin(%)** |
| Low gypsum soil, sheep waste | 93 | 91 | 74 |
| Low gypsum soil cow waste | 95 | 88 | 72 |
| low gypsum soil poultry waste | 97 | 95 | 62 |
| Gypsum soil medium content sheep waste | 92 | 89 | 73 |
| Gypsum soil medium content of cow waste | 90 | 83 | 66 |
| Gypsum soil medium content poultry waste | 90 | 89 | 55 |
| High gypsum soil, sheep waste | 92 | 84 | 68 |
| High gypsum soil cow waste | 85 | 85 | 59 |
| High gypsum soil poultry waste | 94 | 82 | 55 |

**The liberation of the adsorbed copper in the study soil sites**

Table (7) indicates the difference in the amount of copper released from the amount of copper adsorbed in the unit mg.kg-1, as it is observed at low levels of copper addition (10,5,2)$mgkg^{-1}$Its release values are zero (nill), but there is an increase in the values of liberation of adsorbed copper at high levels of copper addition (50, 100, 150).$mgkg^{-1}$Where the values for all types of soil range between (378.0-52.8) $mg.kg^{-1}$, as a sharp decrease in the liberation values is observed at low levels of copper addition. The reason may be due to the high content of the soil of organic matter, where organic complexes are formed with copper ions, so it is difficult to liberate it, or because of the connection of copper with specialized sites for adsorption, as the displacement force of it was insufficient. Which led to the soil holding it in addition to the deposition on the surfaces of minerals and oxides, especially with the pH value pH (7.82)Which encourages the precipitation of most micro-elements, including copper (Peltier et, al, 2004), where it is precipitated as copper sulfate($CuSO_4$)Because of the high percentage of gypsum and these factors combined gave the copper adsorbed in those soils a high binding energy, especially at low levels of addition..

**Table (7) values of adsorption and release of copper mg.kg$^{-1}$ soil for study soil**

| **Levels** | **Adsorbent** | **Liberated** | **levels** | **adsorbent** | **liberated** | **Thelevels** | **Adsorbent** | **Liberated** |
|---|---|---|---|---|---|---|---|---|
| Low gypsum soil, sheep waste | | | Low gypsum soil cow waste | | | low gypsum soil poultry waste | | |
| **2mgkg$^{-1}$** | **1.9** | Nill | 2mgkg$^{-1}$ | 1.9 | Nill | 2mgkg$^{-1}$ | 1.23 | Nill |
| **5mgkg$^{-1}$** | **4.8** | Nill | 5mgkg$^{-1}$ | 4.8 | Nill | 5mgkg$^{-1}$ | 4.8 | Nill |
| **10mgkg$^{-1}$** | **9,432** | Nill | 10mgkg$^{-1}$ | 9.2 | Nill | 10mgkg$^{-1}$ | 7.756 | Nill |
| **25mgkg$^{-1}$** | **22.85** | Nill | 25mgkg$^{-1}$ | 24.036 | 4.332 | 25mgkg-1 | 21.13 | 0.378 |
| 50mgkg$^{-1}$ | 45,568 | 0.554 | 50mgkg$^{-1}$ | 47.452 | 0.6 | 50mgkg$^{-1}$ | 41.918 | 0.864 |
| 100mgkg$^{-1}$ | 97.244 | 0.906 | 100mgkg$^{-1}$ | 90,676 | 1.324 | 100mgkg$^{-1}$ | 77.49 | 2.136 |
| 150mgkg$^{-1}$ | 140.216 | 1.74 | 150mgkg$^{-1}$ | 143.75 | 1.72 | 150mgkg$^{-1}$ | 138.79 | 2.098 |
| Gypsum soil medium content of residue Sheep | | | Gypsum soil medium content of residue Cows | | | Gypsum soil medium content poultry waste | | |
| 2mgkg$^{-1}$ | 1.9 | Nill | 2mgkg$^{-1}$ | 1.9 | Nill | 2mgkg$^{-1}$ | 0.338 | Nill |
| 5mgkg$^{-1}$ | 3.1 | Nill | 5mgkg$^{-1}$ | 3.096 | Nill | 5mgkg$^{-1}$ | 2.446 | Nill |
| 10mgkg$^{-1}$ | 9.2 | Nill | 10mgkg$^{-1}$ | 7.068 | Nill | 10mgkg$^{-1}$ | 7.068 | Nill |
| 25mgkg$^{-1}$ | 23.594 | Nill | 25mgkg$^{-1}$ | 24,056 | Nill | 25mgkg$^{-1}$ | 21.486 | Nill |
| 50mgkg$^{-1}$ | 48.176 | Nill | 50mgkg$^{-1}$ | 48.5 | Nill | 50mgkg$^{-1}$ | 42,594 | Nill |
| 100mgkg$^{-1}$ | 85.906 | 0.636 | 100mgkg$^{-1}$ | 89.648 | 0.702 | 100mgkg$^{-1}$ | 85.202 | 2.122 |
| 150mgkg$^{-1}$ | 139,472 | 1.29 | 150mgkg$^{-1}$ | 139,356 | 1.426 | 150mgkg$^{-1}$ | 143.078 | 0.378 |
| High gypsum soil, sheep waste | | | High gypsum soil cow waste | | | High gypsum soil poultry waste | | |
| 2mgkg$^{-1}$ | 1.9 | Nill | 2mgkg$^{-1}$ | 1.9 | Nill | 2mgkg$^{-1}$ | 1.213 | Nill |
| 5mgkg$^{-1}$ | 3.5 | Nill | 5mgkg$^{-1}$ | 1.45 | Nill | 5mgkg$^{-1}$ | 3.352 | Nill |
| 10mgkg$^{-1}$ | 9.2 | Nill | 10mgkg$^{-1}$ | 9.2 | Nill | 10mgkg$^{-1}$ | 8.028 | Nill |
| 25mgkg$^{-1}$ | 22,801 | Nill | 25mgkg$^{-1}$ | 24.768 | Nill | 25mgkg$^{-1}$ | 20,658 | Nill |
| 50mgkg$^{-1}$ | 47,702 | 0.406 | 50mgkg$^{-1}$ | 47.122 | Nill | 50mgkg$^{-1}$ | 40.412 | \|8.52 |
| 100mgkg$^{-1}$ | 80.622 | 0.648 | 100mgkg$^{-1}$ | 89,554 | 1.202 | 100mgkg$^{-1}$ | 72.622 | 3.756 |
| 150mgkg$^{-1}$ | 141.044 | 1.636 | 150mgkg$^{-1}$ | 143.246 | 0.808 | 150mgkg$^{-1}$ | 143.184 | Nill |

As for the increase in the values of liberating copper adsorbed at high levels of copper addition, the reason may be attributed to the high amount of copper adsorbed in those soils or adsorption on non-specialized sites, which weakened the binding energy as it facilitated the process of returning copper to the soil solution when extracted with calcium chloride solution, and these factors combined, the Cu adsorbed in those soils gave low binding energy especially at high levels of addition. The difference in the amount of copper adsorbed on the surfaces of the soil under study was clear due to the characteristicsPhysical and chemical properties such as the organic matter content of those soils, the quality of the organic acids resulting from their decomposition, the clay, the different proportions of lime and gypsum minerals, and the variation in the pH value of these factors.They affect the amount of adsorbed copper and the binding energy values, and the difference in the amount of adsorbed copper and the different binding energy values resulting from different adsorption sites to specialized and non-specialized sites causes a difference in the amount of released copper, as the high binding energy reduces the released copper towards the soil solution, while it leads low bonding energy leads to an increase in liberated copper and ease of removal and movement into the soil solution. As well as the effect of the amount of adsorbed copper, as the amount of liberated copper increases with the increase in the amount of adsorbed copper, thus increasing the readiness of this element in the soil solution and its availability for absorption by the roots of the plant. It is noted from the special forms of adsorption that the different factors affecting the soil body, which were previously mentioned, which produced a different behavior of the soil and is not subject to a certain type of displacement recognized in the ion exchange process, because there is a clear discrepancy in the values of clay and organic matter (Dahiya *et al*. 2005).

## CONCLUSION

It is preferable to add copper spray on leaves or in an encapsulated form because the ground addition leads to difficulty in liberating copper ions. Adding poultry waste to the soil because it contains higher nutrients and less adsorption than the rest of the organic waste. It also contains humic acids, including fulvic acid, which in turn works to chelate nutrients and protect them from leaching and sedimentation instead of having organic complexes with them

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## CONFLICT OF INTEREST

The authors declare no conflicts of interest associated with this manuscript.

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