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Adsorption and physicochemical release of iron ions in soils with different content of Calcium Carbonate and Calcium Sulfate

ABSTRACT

Three soils of different content of gypsum and lime were selected, the first soil (G1) and the second soil (G3), were obtained near the fields of the Faculty of Agriculture, Tikrit University. As for the third soil (G5), was taken from the AL-alam Village side east of Tikrit city to a depth of (0-10)cm. the proportions of gypsum were 5%, 15%, 25%, and the proportions of lime were 25%, 20%, and 10% for soils G1, G3, and G5, respectively. Ferrous sulfate was added as a source of iron ions added to the three soils in the following proportions (0,10,25,50,100,150,250,500,750) mg.L⁻¹ The concepts of isotherm were tested by using the physicochemical Freundlich and Langmuir adsorption equations. The results of the study showed the success of both equations in describing of iron ion adsorption process for all three soils, because They achieve a high (R²) but Langmuir's equation showed a greater superiority due to its decreasing (SE). As it appears from the results of the study, the superiority of treatment (G1) over treatments (G3) and (G5) in the maximum adsorption values, binding energy, (PBC_{Fe})(KG) and (Kd) for adsorption and release. As for the values of Labale iron, the lowest value was in treatment (G1) then it began to increase until it reached its value in treatment (G5). The (Δf) values for the three soils were positive, and that the highest value was in soil (G1), and starts declining to reach its value for soil (G5).

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INTRODUCTION

Gypsiferous soils represent wide areas of Salah al-Din governorate, the high amount of gypsum in the soil has a negative impact on many soil properties, whether chemical, physical or fertile. Also, these gypsum lands contain significant amounts of calcium carbonate, so these lands are often classified as Calcigypsid, which bear the specifications of Gypsiferous and Calcareous soils at the same time, according to the morphological classification approved in classification books. (AL-Tarbouli 2019; Schonsky et al, 2013; AL-Barrak and Rowell, 2006) confirmed that lime can encapsulate gypsum and thus reduce its solubility in the soil solution. Both components (lime and gypsum) have negative and positive effects on many soil properties, the most important of which are adsorption and desorption processes of microelements and the level of their readiness in the soil. Many researchers have mentioned that calcium carbonate has an important and prominent role in the processes of adsorption and deposition of microelements in the soil, including iron and copper ions. (Al-Tarbouli, 2019; Al-Janabi, 2017). reported that (Jelić et al., 2011) Iron is present in the crystalline structure of the primary and secondary minerals of clay, and its presence in the soil is affected by many chemical and physical properties of soil such as (pH), (CEC) and the proportion of clay and silt. Barker & Pilbeam (2007) confirmed that the ionic formulas of ready-made iron in the soil include dissolved (Fe²⁺) and (FeOH⁺) in addition to exchangeable iron and iron in some organic complexes. Iron is one of the heavy elements of biological importance in the life of plants,

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as it is considered one of the nutrients necessary for plant growth, which it needs in small quantities compared to the major elements, and its deficiency in the soil leads to an imbalance in the vital functions of the plant growing in that soil. The case of iron deficiency in calcigypsid soils is common, as it is believed that this deficiency occurs as a result of interactions between dissolved iron and calcium carbonate in the soil, which leads to a decrease in the iron availability, as the adsorption and sedimentation reactions on the surfaces of carbonates are what reduce the concentration of iron in Soil solution, such as , iron carbonate, iron hydroxides, and iron phosphates (David and Uygun, 2000). Gypsum also has a high ability to adsorb and precipitate these heavy elements in these soils (Hashemi and Baghernejad, 2010). The processes of adsorption and Release of microelements in the soil are very complex, as they are subject to several factors, including the ionic strength of the element, its dominant ionic formula, and other chemical and physical properties, in addition to the nature of the adsorbent surface and its chemical properties. Due to the different nature of the adsorbing surface of gypsum and lime in the soil, this results in overlapping conditions for the adsorption and desorption processes of the microelements. In the absence of detailed studies related to the effect of the interaction of these two components in the soil on the processes of adsorption and desorption of iron, we proposed this study. This study aimed to describe adsorption and desorption behavior of iron in the three Calcigypsid Soils .

MATERIALS AND METHODS

Soilsampling

Three soils with different gypsum and lime content were selected, the first soil (G1) and the second soil (G3), which were obtained near the fields of the Faculty of Agriculture, Tikrit University. As for the third soil (G5), it was taken from the Al-Alam Village side east of the city of Tikrit to a depth of 10-0) cm. After removing the upper crust from the soil and taking into account the accuracy, more than one sample was taken for the studied site in order to obtain a representative sample of the site. The soil was pneumatically dried and crushed with a wooden hammer and then sieved with a sieve 2 mm a diameter of, for the purpose of conducting all chemical and physical analysis, according to the methods described by (Alison and Richards, 1954), (Handbook 60, 1954 USDA), (Verma et al ., 1977), (Walkley, 1947, FAO, 1974), (Lagerwerff et al., (1965),(Carter & Gregorich,2007) as shown in Table. (1). Where it was found that the proportions of gypsum were 5% 15% 25% and the proportions of lime were 25% 20% 10% for soils G1, G3, and G5, respectively.

Study of the adsorption phenomenon: - Preparation of equilibrium solutions: -

1 liter of aqueous ferrous sulfate solution ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) with a concentration of 1000 mg.L^{-1} iron was made by dissolving 2.489 g of aqueous ferrous sulfate containing 1 g of iron ion in a volume of distilled water with shaking to ensure Complete solubility and complete volume to 1000 ml with distilled water. Then the following series of dilutions (0,10,25,50,100,150,250,500,750) mg.L^{-1} iron solution was added 40 ml were made to 2 grams of soil and for all soil treatments with 2:1 Soil:Water a ratio two duplicates,. solution. After that, it was shaken for Two hour with on a shaker device)) and then left for 24 hours to ensure that a state of dynamic equilibrium was obtained. More than one shaking device was used to ensure smooth work and similarity of equilibrium conditions and time.

Calculation of the dissolved iron ion concentrations:

The concentration of dissolved iron in the equilibrium solution was calculated by using atomic absorption spectroscopy (AAS) after filtering the studied soil extracts using micro-elements filter paper. Then the aforementioned device was calibrated by making multiple iron solutions of different concentrations, using Buffer for iron with a concentration of 1000ppm, where the Standard Curve of the device was made to ensure the correct reading. The adsorbed amount of iron ions was calculated after taking the reading from atomic absorption spectroscopy (AAS)) using the equation below.

(Altarboli,2020)

$$\text{Fe}^{+2} - \text{ad} = \frac{(\text{Cin} - \text{Cfin})V}{w} \dots (1)$$

Since:-

Fe-ad = iron ion adsorbed in mg.kg-1

Cin = Initial iron concentration added to soil mg.L-1

Cfin = Iron concentration in equilibrium after filtering mg.L-1

V = volume of equilibrium leachate l

W = weight of soil kg.

Mathematical description of the adsorption process:

The following physicochemical equations were used to describe the results of the iron adsorption process for this study, which is Freundlich, because it has a single surface, according to (Al-Obaidy, 2013); (Qadeer, 2005).

1- Freundlich equation:

$$\text{Logx} = \text{Logk} + b \text{Logc} \dots (2)$$

where:-

x = the amount of iron adsorbed on the exchange surfaces mg.kg-1

C = iron ion concentration in equilibrium solution mg.l-1

b = hypothetical constant, sometimes called adsorption intensity l.mg-1

K = constant and is sometimes called adsorption capacity or distribution coefficient mg.kg-1.

2- Langmuir equation 1:-

$$x = \frac{Kcb}{(1+Kc)} \dots (3)$$

where:-

x = the amount of iron adsorbed on the exchange surfaces mg.kg-1

C = iron concentration in equilibrium mg.L-1

b = maximum adsorbed iron, mg.kg-1

K = binding energy of iron adsorbed on the exchange surfaces l. mg-1.

Thermodynamic criteria used in the study of the phenomena of adsorption and release of iron ion

This substitution energy has been calculated according to the equation proposed by (Woodruff, 1955)

$$\Delta F = - 2.303 R T \log ARFe^{\circ} \dots (4)$$

where:-

ΔF = substitution free energy kilojoules.mol-1

R = gas constant

T = absolute temperature

$AR Fe^{\circ} \log$ = represents the logarithm of the relative effectiveness of the iron ion, which represents the point of intersection of the relationship Q/I with the x-axis, where neither gain nor loss occurs, which is when the value of the y-axis is equal to zero.

Procedures for the release experiment for iron ions.

Upon completion of the adsorption experiment, all three soil treatments were re-extracted with extraction solution (0.005)M Di ethylene triamine penta acetic acid (DTPA). and (0.01) molar calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) and 0.1) molar triethanolamine (TEA) at pH equal to 7.3, according to (Lindsay & Norvell, 1978) method. Where 1 liter of extraction solution, 1.967 gm of DTPA and 1.47 gm of calcium chloride were prepared in 100 ml of distilled water, then stirred to dissolve and then transferred to a volumetric flask with a capacity of 1000 ml. We also dissolved 13.38 ml of TEA in a certain volume of water, then It was transferred with distilled water to a volumetric flask containing and DTPA $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, then diluted with distilled water to 900 ml, the pH of the extraction solution was adjusted by adding a volume of hydrochloric acid (HCl N6), so the pH of the solution became 7.3, then the final volume was completed to liters of distilled water. Extraction was added to 2 g of the remaining soil and for all studied soils with a frequency of 40 ml and it

shook for 3 hours, then left to equilibrate for 24 hours at a laboratory temperature of 298 K and filtered by filter paper. Then the filtrate was measured in the atomic absorption device.

Thermodynamic calculations required for Quantity and intensity curves Q/I:-

The amounts of calcium, magnesium, electrical conductivity (Ec) and pH values were measured in each of the equilibrium the following concentrations (750,500,250,150,100,50,25,10,0) iron mgL⁻¹. After that, special tables were made for each soil, showing the concentrations and effectiveness coefficient and effectiveness of calcium and magnesium ions in addition to the values of electrical conductivity, pH, concentration and coefficient of effectiveness and ionic activity of iron, as well as ionic strength of iron ion for the purpose of obtaining the relative effectiveness of iron ion for all equilibrium solutions. and belonging to each soil of the study soil for the purpose of drawing the relationship between the intensity of iron and the capacity of iron Q/I and thus calculating the constants of this relationship.

The ionic strength (Ionic Strength I) where the ionic strength was calculated in equilibrium solutions according to what was mentioned (Griffin & Jurinak, 1973).

$$I = E_c \times 0.013 \dots (5)$$

where:-

Ec = electrical conductivity of the equilibrium solution ds.m⁻¹, measured at 25°C

constant = 0.013

The activity coefficient of iron ion was calculated using the modified Davies equation as mentioned by (Sposito.2008) and for all equilibrium solutions of the parameters used in the study and its replicates.

$$(7) \dots -0.3 I) \text{Log } f_i = -A Z i^2 \left(\frac{\sqrt{I}}{\sqrt{1+I}} \right)$$

Where:-

-Log fi = the negative logarithm of the ionic reactivity factor

A = a constant of 0.509

Zi² = square of ion charge

I = ionic strength mol.L⁻¹

Ionic activity

The ionic activity of the iron ion was calculated for all equilibrium solutions in the coefficients used in the study and their replicates according to the equation proposed by Lewis.

$$a_i = c_i \times f_i \dots (6)$$

where:-

ai = ionic activity mol.l-1

ci = ion concentration in solution mol.l-1

fi = efficiency factor

Quantity – Intensity relationship Q/I

The relationship between the adsorbed amount of iron, which represents the quantity of iron in the solid soil phase (Quantity) on y-axis vis a function of the intensity of iron in the liquid phase (Intensity), x- axis expressed in ARFe (the relative effectiveness of the iron ion), which is placed on the x-axis For the purpose of obtaining a graphical description of the iron adsorption behavior.

Gapon constant:

The adjusted Gapon constant was calculated according to the equation below (Diatta et al.,2000)

$$KG = \frac{PBC}{CEC} \dots (8)$$

Where:-

KG = Modified Gapon constant

PBC = Potential Buffering Capacitance of Iron

CEC = Soil cation exchange capacity

Distribution Coefficient (Kd)

The distribution coefficient values were calculated for all the studied soil for the adsorption and release processes, after taking the reading of the atomic absorption spectroscopy (AAS)), and then using the following equation: (Chakrapani & Subramanian, 1990).

$$K_d = \frac{S}{C} \dots \dots \dots (9)$$

where:-

kd = diffusion coefficient or distribution l.kg-1

S= iron adsorbed concentration mg.kg-1

C = iron concentration in aqueous solution mg.L-1.

Determine the best mathematical description equation:

The value of the best statistical determination coefficient R2 and the lowest value of Standard Error (S.E) were adopted to determine the best mathematical description equation for the adsorption process, according to(Ghasemi-Fasaei & Jarrah, 2013).

$$SE = \left[\frac{\sum(q - \hat{q})^2}{n - 2} \right] \dots \dots \dots (10)$$

where:-

S.E = standard error

q = the practically measured amount of iron adsorbed, mg.kg-1

q* = the amount of iron calculated from the equation of the straight line

n = number of observations or repetitions

RESULTS AND DISCUSSION

Table (1): Chemical and physical properties of the study soils

Adjective	Measuring Unit	G1	G3	G5
pH		7.82	7.76	7.39
Ec	dS.m ⁻¹	1.59	2.03	2.12
CaSO ₄ .2H ₂ O	g.Kg ⁻¹	60.2	153	245
CaCO ₃	g.kg ⁻¹	243	219	101
O.M	g.kg ⁻¹	11	10	8
CEC	Cmol.kg ⁻¹	12.3	11	10.82
Sand	g.Kg ⁻¹	650	590	739
Silt	g.kg ⁻¹	72	190	75
Clay	g.kg ⁻¹	278	220	186
Texture		Sandy Clay loam	Sandy Clay loam	Sandy loam
Na	Mmol.l ⁻¹	1.34	1.39	2.2
K	Mmol.l ⁻¹	0.81	0.78	0.54
Ca	Mmol.l ⁻¹	5.314	8.965	12.814
Mg	Mmol.l ⁻¹	4.32	4.11	3.16
Cl	Mmol.l ⁻¹	2.02	1.68	1.27
HCO ₃	Mmol.l ⁻¹	1.25	1.44	2.5
SO ₄	Mmol.l ⁻¹	10.3	13.36	16.32

Adsorption Equations Constants

Freundlich and Langmuir equations of one surface were used to describe the adsorption process. Freundlich's equation was built on the basis of multilayer adsorption to describe the

adsorption of gases on heterogeneous surfaces, and the heat of adsorption is also heterogeneous in distribution (Bahl and Toor, 2002). As for the Langmuir equation, it assumes the adsorption of one molecular layer on the adsorption surfaces, so that each molecule has one position on the homogeneous surface. Figures (2,1) and Table.(2) showed that the soil (G1) with a high content of calcium carbonate and a lower content of calcium sulfate has high adsorption capacity and binding energy compared to soils (G3 and G5). While as the quantities of lime decrease and the quantities of gypsum increase, as in soils (G3 and G5), we notice a decrease in the adsorbed quantities binding energy of iron ions, increase in the solubility, and readiness of iron in the soil solution. The values of maximum adsorption and binding energy, according to Freundlich's concept, ranged between (366.859) to (70.696) until and from (1.1397) until to (1.4572) until for soils (G1 and G5) respectively. As for their values according to Langmuir concept, they ranged between (277.777) to (217) until and from (0.379) until to (0.130) until for soils (G1 and G5) respectively. we mentioned before and according to Table.(2) that the calcium carbonate salt absolutely controls iron adsorption process at different levels of calcium sulfate. Where calcium sulfate, is a salt with good solubility and free of surface charge, and its dissolution process provides large amounts of calcium and sulfate, and affects to a limited extent the ability of carbonate to adsorb iron in addition its of calcium competition with iron on the effective adsorption sites surfaces of clay minerals , organic matter and gypsum coating surfaces. Effective adsorption on the surfaces of clay minerals, which leads to a reduction in the adsorption capacity of iron and makes it and other cations more ready, even to a limited extent, in the soil solution containing lime. The lime in the soil acts as a proton receptor during its interaction with the ferric in the soil, which leads to the deposition of ferric goethite on the surfaces of calcium carbonate, and this deposition process increases as the surface area of the lime increases (active lime) (Junagadh, 2000). The high content of calcium carbonate leads to a high degree of soil reaction (pH) and thus increase alkalinity of the solution These conditions lead to the precipitation of iron in the form of ferric hydroxide as well as another precipitate is iron carbonate (Siderite) Our results are in agreement with the findings of many researchers that reported the presence of calcium carbonate in the soil leads to a decrease in the availability of iron as a result of adsorption on the surfaces of active carbonate such as calcite, magnesite and dolomite, in addition to adsorption on the surfaces of mineral and organic colloids, lime works to further improve soil aeration and these conditions are suitable for the oxidation of ferrous to ferric, which is less ready for easy sedimentation in soil solution. Also The presence of phosphorous lead to iron phosphate formation which is not a available form, and this condition is formed in Calcareous soils (Moraghan et al.; 2002 Lahav & Zipori, 1978; Ryan & Hariq, 1983; Sheta et al., 2003;.) We also note that Both equations gave a similar description of the adsorption process in spite of the different adsorption values and binding energy. Also, both equations had a high correlation coefficient (R^2) and a little value of standard Error (SE). as shown in table (2) the superiority of Langmuir equation over Freundlich's equation in describing the adsorption process (Al-Tarbouli, 2019). It is worth noting that the binding energy according to Freundlich's concept is opposite to the binding energy of Langmuir's concept, where we notice in Freundlich's equation that the values of $(1/n)$ increase, indicates a decrease in the binding energy, unlike the binding energy values in Langmuir, whose increase means an increase in the binding energy. The adsorption of iron in the presence of calcium carbonate in the soil pass through two stages. first stage is rapid, its duration does not exceed several hours, in which the iron ions are adsorbed until the saturation of the colloidal surfaces completely, The second stage begins, in which the iron ions in the solution undergo a process similar to precipitation, and this requires several days.

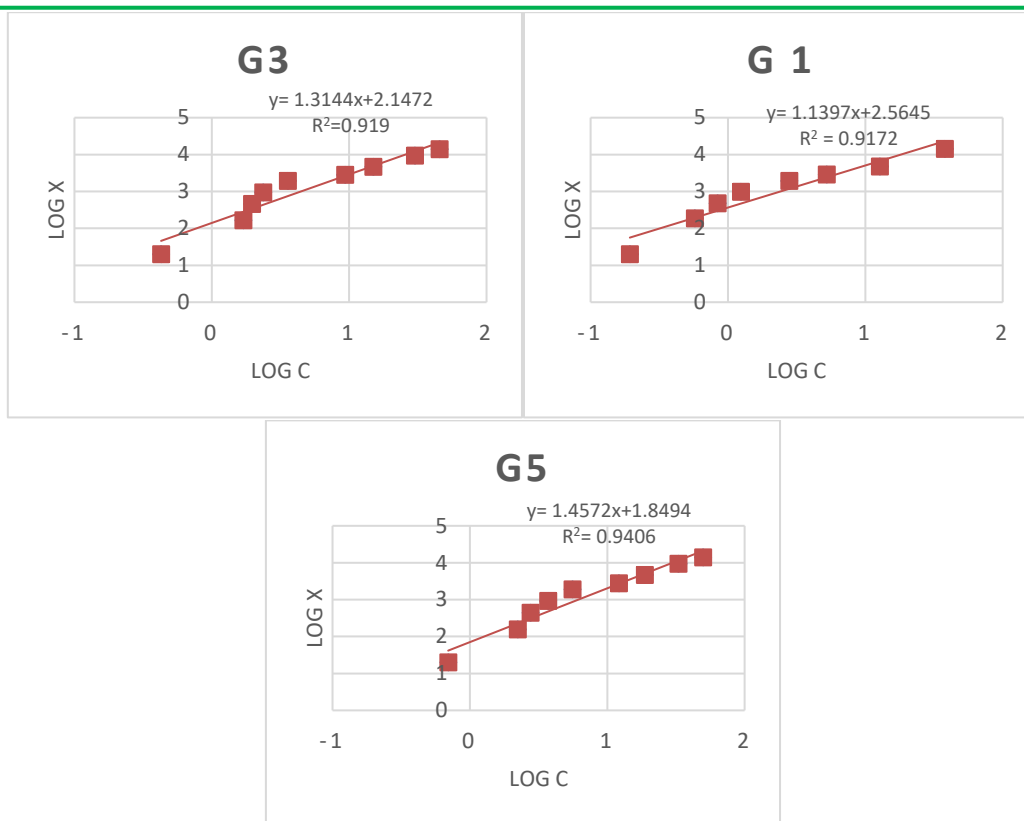


Figure (1): The adsorption curves of the three soils according to Freundlich's equation

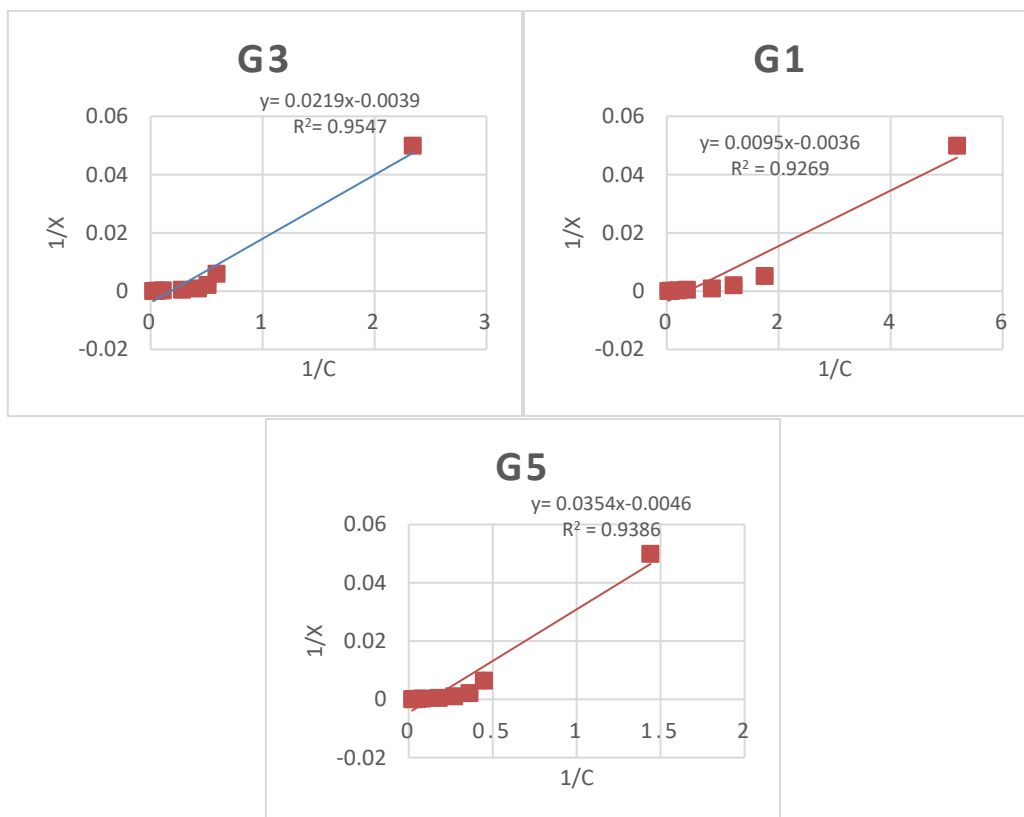


Figure (2): The adsorption curves of the three soils according to Langmuir equation (1).

Table (2): values of Thermodynamic parameters for studied soils according to Freundlich and Langmuir (1) concept

Treatments for Freundlich equation	maximum adsorption (kf)	Binding energy (1/n)	R ²	S.E
G1	366.859	1.1397	0.9172	0.274
G3	140.345	1.3144	0.919	0.252
G5	70.696	1.4572	0.9406	0.243
Treatments for Langmuir equation	(b) maximum adsorption	Binding energy (k)	R ²	S.E
G1	277.777	0.379	0.9269	0.054
G3	256.410	0.178	0.9547	0.036
G5	217	0.130	0.9386	0.028

Distribution coefficient (Kd) for iron adsorption and release

Table No.(3) shows the values of the distribution coefficient for studied soils upon adsorption and desorption of iron. The highest(Kd) value was for soil (G1) in the case of adsorption, which amounted to (467,890) We also note that with the increasing in the proportions of gypsum in soils (G3 and G5) occurs A decrease in the values of the distribution coefficient average, as its value decreased to (283.992) and (209.433) for soils (G3 and G5) respectively. This is due to the solubility of gypsum, which provides large amounts of calcium ions, which will compete with iron ions on the effective adsorption sites, which leads to a decrease in the adsorbed amount of iron and an increase in the relatively dissolved iron, or because of the gypsum encapsulation of effective adsorption sites in the soil, such as clay (Al-Tarbouli, 2019). While in the process of iron release, the highest values of distribution coefficient average are in soil (G1) as its value is (49.858), and then these values begin to decline until soil (G5) where its value is (40.001) and this is due to the high susceptibility of lime present in the soil to sediment Iron in the form of iron carbonates and hydroxides, and what is liberated from iron adsorbent on the surfaces of organic matter and clay, and from it adsorbed in the form of multi-layered adsorption (physical adsorption). Our results are on the line of many researchers have mentioned that iron adsorption in soil is affected by soil chemical properties, including pH, organic carbon content, CEC, added iron level, total and active carbons, in addition to primary and secondary minerals of clay (Kang et al., 2010).

Table (3): Average of distribution coefficient values for iron adsorption and desorption

Treatment	Average values Adsorption (Kd)	Average values release (Kd)
G1	467.890	49.858
G3	283.992	45.733
G5	209.433	40.001

Quantity and intensity relationship Q/I

The relationship between the relative effectiveness of iron in the soil solution and the adsorbed amount of iron was drawn for the purpose of obtaining the thermodynamic parameters accompanying the adsorption process. Figures (3) and Table (4) showed that the values of the regulatory capacitance potential and the Gapon constant (KG) for iron are the highest in soil (G1) with a high content of calcium carbonate and a low content of calcium sulfate. This indicates that this soil prefers iron ions at the due to its content of high lime, which works on the formation of iron carbonates, and this rise is due to the high adsorption capacity with the increase of specialized and non-specialized sites located on the surfaces of the internal adsorption sites between the layers and the outer On surfaces of clay minerals in limestone soils (Agib and Jarkass.2008). also these values begin to decrease gradually with the decrease in the quantities of lime and the increase in gypsum quantities for soils (G3 and (G5) respectively. As for the values of iron that could be returned to the solution, their values start to rise with the increase in the proportions of gypsum and the decrease in the content of these soils of clay and organic matter.As for the substitutive free energy values, the highest value is in the soil (G1), then its value begins to decrease to reach soil (G5) a positive value

which indicates that the interaction is not spontaneous and that decrease in the positive values of (Δf) indicates an increase in the availability of iron, The higher value of free energy with a positive sign, indicates the lack of iron availability in that soil and that needs more energy for the replacement to occur between the heavy element and calcium (Al-Tarbouli; 2019). This reason is due to the association of iron with non-specialized adsorption sites, that means physical adsorption with a multi-layered form, perhaps as a result of gypsum encapsulating the effective adsorption sites of clay minerals, and the occupation of those active sites by calcium brought by gypsum solubility Soil solution again. The results of intensity and Quantity (Q/I) are consistent with the results we reached in the adsorption equations mentioned before in the research in terms of the nature of the adsorbed quantities and the binding energy for the three soils. It also in agreement of with (Al-Tarbouli 2019) found when studying the effect of the interaction between calcium carbonate and calcium sulfate on adsorption and release Copper in the soil and Beckett mentioned. (1972).

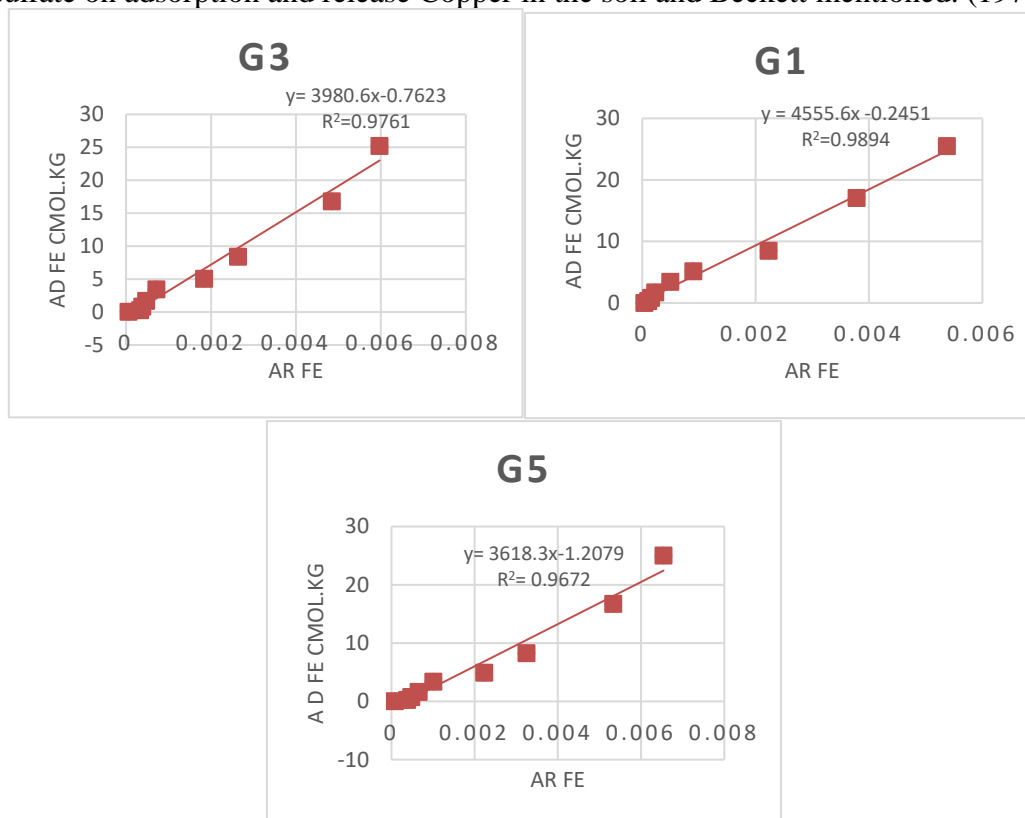


Figure (3): Intensity and amplitude curves for the three soils

Table (4): The intensity and capacity values of iron ions for the three soils.

Treatment	Bc	ARFe°	Fe labile	ΔF	KG	R ²
G1	4555.6	0.000053	-0.2451	24.371	370.37398	0.98
G3	3980.6	0.00019	-0.7623	21.224	361.872	0.97
G5	3618.3	0.00033	-1.2079	19.846	334.408	0.96

CONCLUSIONS

- 1 - The success of the Freundlich and Langmuir equations in describing the iron adsorption process, but the Langmuir equation excelled with the highest correlation values and the lowest standard error values.
- 2- The presence of calcium carbonate in Gypsiferous soils is the dominant factor in the adsorption and liberation processes of heavy elements in these soils, including iron ions.
- 3- Soil G1 with high content of calcium carbonate, clay, organic matter and less content of calcium sulfate achieved the highest values in adsorbed quantities, binding energy, regulatory capacity voltage, substitutive free energy, Gapon's constant and distribution coefficient, and the lowest values in mobile or returnable iron to the soil solution.

REFERENCES

- Agib, A., & f.Jarkass, (2008). *Prediction of Zinc Precipitation Accompanying Sorption Process in Calcareous and Basaltic Soils*. *Jornal Tishreen University for Research and Scientific Studies* 30(5)
- Al-Barrak, K., & D.L. Rowell, (2006). The solubility of gypsum in calcareous soils. *Geoderma*, 136(3–4), 830–837.
- Al-Obaidy, B. S. O. (2013). Adsorption of Copper and Cobalt on Bentonite and Kaolinite. *Tikrit Journal for Agricultural Sciences*, 13(1).
- Al-Tarbouli, N. H. Y. (2019). Effect of the interaction between Calcium Carbonate and Calcium Sulfate on Adsorption and Release of Copper in Soil. *Tikrit University Journal of Agricultural Sciences*, 2019. (Arabic Master's Thesis)
- Allison, L. E., & L.A.Richards, (1954). *Diagnosis and improvement of saline and alkali soils* (Issue 60). Soil and Water Conservative Research Branch, Agricultural Research Service
- Altarboli, N. H. Y., & M.M.O.Aljumaili, (2020). Thermodynamic Criteria for Adsorption and Release of Copper in the Soil under the Influence of Different Levels of Calcium Sulfate. *Proceedings of the Eighth and Second International Scientific Conference of the College of Agriculture / Tikrit University*, 151–156.
- Bahl, G. S., & G.S. Toor, (2002). Influence of poultry manure on phosphorus availability and the standard phosphate requirement of crop estimated from quantity–intensity relationships in different soils. *Bioresource Technology*, 85(3), 317–322.
- Barker, A. V., & D.J. Pilbeam. (2007). *Handbook of plant nutrition*, CRC. Taylor & Francis Boca Raton, FL, USA:
- Beckett, P. (1972). Critical cation activity ratios. In *Advances in Agronomy* (Vol. 24, pp. 379–412). Elsevier.
- Carter, M. R., & Gregorich, E. G. (2007). *Soil sampling and methods of analysis*. CRC press.
- Chakrapani, G. J., & Subramanian, V. (1990). Preliminary studies on the geochemistry of the Mahanadi river basin, India. *Chemical Geology*, 81(3), 241–253.
- Diatta, J. B., Kocialkowski, W. Z., & Grzebisz, W. (2000). Copper distribution and quantity–intensity parameters of highly contaminated soils in the vicinity of a copper plant. *Polish Journal of Environmental Studies*, 9(5), 355–362.
- FAO. (1974). *The Euphrates pilot irrigation project. Methods of soil analysis. Gadeb soil laboratory (a laboratory manual)*. Food and Agriculture Organization Rome.
- Ghasemi-Fasaei, R., & Jarrah, M. (2013). Adsorption kinetics of cadmium and zinc as influenced by some calcareous soil properties. *International Journal of Agriculture and Crop Sciences*, 5(5), 479.
- Griffin, R. A., & Jurinak, J. J. (1973). The interaction of phosphate with calcite. *Soil Science Society of America Journal*, 37(6), 847–850.
- Hashemi, S. S., & Baghernejad, M. (2010). Zinc sorption by acid, calcareous and gypsiferous soils as related to soil mineralogy. *Iran Agricultural Research*, 27(1.2), 1–16.
- Jelić, M. Ž., Milivojević, J. Ž., Trifunović, S. R., Đalović, I. G., Milošev, D. S., & Šeremešić, S. I. (2011). Distribution and forms of iron in the vertisols of Serbia. *Journal of the Serbian Chemical Society*, 76(5), 781–794.
- Junagadh, G. (2000). *Balanced Nutrition of Groundnut and Other Field Crops Grown in Calcareous Soils of India*.
- Kang, D.-H., Schwab, A. P., Johnston, C. T., & Banks, M. K. (2010). Adsorption of iron cyanide complexes onto clay minerals, manganese oxide, and soil. *Journal of Environmental Science and Health Part A*, 45(11), 1391–1396.
- Lagerwerff, J. V., Akin, G. W., & Moses, S. W. (1965). Detection and determination of gypsum in soils. *Soil Science Society of America Journal*, 29(5), 535–540.

- Lahav, N., & Zipori, I. (1978). Fixation of iron applied as FeEDTA: effect of calcium concentration and soil solid phase. *Soil Science Society of America Journal*, 42(2), 255–257.
- Lindsay, W. L., & Norvell, Wa. (1978). Development of a DTPA soil test for zinc, iron, manganese, and copper. *Soil Science Society of America Journal*, 42(3), 421–428.
- Moraghan, J. T., Padilla, J., Etchevers, J. D., Grafton, K., & Acosta-Gallegos, J. A. (2002). Iron accumulation in seed of common bean. *Plant and Soil*, 246(2), 175–183.
- Qadeer, R. (2005). Adsorption of erbium ions on activated charcoal from aqueous solutions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 254(1–3), 17–21.
- Rimmer, D., & Uygur, V. (2001). The effect of surface coatings of iron oxide on the sorption and precipitation of zinc on calcite surfaces. *Compte Rendu Du 16ième Congrès Mondial de Science Du Sol*.
- Ryan, J., & Hariq, S. N. (1983). Transformation of incubated micronutrient chelates in calcareous soils. *Soil Science Society of America Journal*, 47(4), 806–810.
- Schonsky, H., Peters, A., Lang, F., Abel, S., Mekiffer, B., & Wessolek, G. (2013). Sulfate transport and release in technogenic soil substrates: experiments and numerical modeling. *Journal of Soils and Sediments*, 13(3), 606–615.
- Sheta, A. S., Falatah, A. M., Al-Sewailem, M. S., Khaled, E. M., & A.S.H.Sallam, (2003). Sorption characteristics of zinc and iron by natural zeolite and bentonite. *Microporous and Mesoporous Materials*, 61(1–3), 127–136.
- Sposito, G. (2008). *The chemistry of soils*. Oxford university press.
- Verma, B. C., Swaminathan, K., & K.C.Sud, (1977). An improved turbidimetric procedure for the determination of sulphate in plants and soils. *Talanta*, 24(1), 49–50.
- Walkley, A. (1947). A critical examination of a rapid method for determining organic carbon in soils—effect of variations in digestion conditions and of inorganic soil constituents. *Soil Science*, 63(4), 251–264.
- Woodruff, C. (1955). The energies of replacement of calcium by potassium in soils. *Soil Science Society of America Journal*, 19(2), 167–171.

الامتزاز والتحرر الكيميوفيزيائي لايونات الحديد في ترب مختلفة المحتوى من كاربونات الكالسيوم وكبريتات الكالسيوم

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الخلاصة

تم اختيار ثلاثة ترب مختلفة المحتوى من الجبس والكلس التربة الاولى (G1) والتربة الثانية (G3) تم الحصول عليهما بالقرب من حقول كلية الزراعة جامعة تكريت اما التربة الثالثة (G5) فتم اخذها من ناحية العلم شرق تكريت ولعمق من 10-0 سم. وكانت نسب الجبس والكلس 5%، 15%، 25%، و 25%، 10%، 20% للترب G5، G3، G1 على التوالي. تم اضافة كبريتات الحديدوز كمصدر لايونات الحديد المضافة للترب الثلاثة وبالنسب التالية 0، 10، 25، 50، 100، 150، 250، 500، 750)) ملغم/كغم حديد تم اختبار مفاهيم التماثل الحراري وذلك عن طريق استخدام معادلات الامتزاز الفيزيوكيميائية فروندلخ ولانكماير. اظهرت نتائج الدراسة نجاح المعادلتين في وصف عملية امتزاز ايونات الحديد للترب الثلاثة وذلك حسب قيم (R²) لكن اظهرت معادلة لانكماير تفوق اكبر بسبب انخفاض قيم (SE) لها كما يتضح من نتائج الدراسة تفوق المعاملة G1 على المعاملات G3 و G5 في قيم اقصى امتزاز ، طاقة الربط، جهد السعة التنظيمية، ثابت كابون ومعامل التوزيع للامتزاز والتحرر اما بالنسبة لقيم الحديد القابل للعودة للمحلول فكانت اقل قيمة في المعاملة G1 ثم بدأت في الزيادة حتى وصلت الى قيمتها في المعاملة G5 كما كانت قيم الطاقة الحرة الاستبدالية للترب الثلاثة موجبة وان اعلى قيمة كانت في التربة G1 وتبدأ بالانخفاض وصولا الى قيمتها في التربة G5

الكلمات المفتاحية:
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