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Application of Langmuir Isotherms to Describe Zinc and Copper Adsorption in Some Gypsiferous Soils

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Abstract

This study aims to evaluate and compare the adsorption behavior of copper and zinc in some gypsiferous soils using the linearization methods of the Langmuir equation. Six surface soil samples were taken from three different sites in Salah al-Din and Najaf governorates. Coefficient of determination (R^2) was high for both ions, except for zinc in Salah al-Din site T3. Langmuir equation constants showed maximum adsorption values (b) higher for copper than zinc, reaching 476.19 mg kg-^{1} in Salah al-Din site T3 and 1666.66 mg kg^{-1} in Najaf site N3. Zinc's highest values were 181.81 mg kg^{-1} in Salah al-Din site T2 and 666.66 mg kg^{-1} in Najaf N3. The results indicated that the high maximum adsorption values (b) for both ions are associated with a relatively low binding energy (k). The results also confirmed that copper ions had much lower binding energy values than zinc ions, with copper at 15 L mg^{-1} in Salah al-Din site T1 soil and 4 L mg^{-1} in Najaf site N2 soil. In contrast, zinc showed higher binding energy, with 122.54 L mg^{-1} in Salah al-Din T3 and 143.33 L mg^{-1} in Najaf N1. Copper's distribution coefficient values are generally higher than zinc's, except in Salah al-Din T3 and Najaf N1 soils. The results regarding the constants of the Langmuir equation for both ions indicated that the maximum adsorption value (b) indicates the soil's capacity to adsorb metals. Thus, the soil has a higher affinity for copper than for zinc.

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Introduction

Adsorption is a fundamental soil process; it determines the retention of nutrients, minerals, radionuclides, pesticides, and organic chemicals on soil surfaces. It significantly impacts nutrient and pollutant transport and also influences the electrostatic properties of suspended colloidal particles. Heavy metals are a group of chemical elements that have a density greater than five (>5 g cm^{-3}), as well as a high atomic number. They are found naturally in soil as a result of the erosion of rocks, and can also be added to soil by human or natural agents (Ahmed *et al.,* 2022).

Copper and zinc are essential elements involved in many biochemical processes of plants and animals. However, knowing the movement and retention of these ions in the presence of other metals is essential to predicting their fate in the soil system (Neves-Merlo *et al.,* 2024). Although they are essential micronutrients for plants and animals, they can become toxic at high concentrations (Guzman-Rangell *et al.,* 2018).

Soil adsorption capacities are commonly studied through experimental conditions designed to achieve equilibrium between soil solid and soil solution phase (Shaheen *et al.,* 2015), providing information on the soil affinities and therefore on the potential mobility of metal in concern. in a related context. Padilla *et al.* (2023) stated that the process of adsorption and desorption is one of the main processes responsible for the fate of minerals in the soil, as the movement of mineral ions is directly related to their distribution between the solid solution phases. Uygur *et al.* (2017) indicated that soil is an infinite number of complex mixtures of components, and these components have mutual relationships that lead to distinctly different physical and chemical properties that can characterize the nature of the interactions of trace elements with the soil.

The availability of copper to plants is directly related to the zinc content in the soil. Copper is absorbed in the same form as zinc, so an excess of one of these two elements in the soil makes the other unavailable to plants (Lisetskii *et al.,* 2020b). On the other hand, due to its very low mobility, copper is classified as a poorly mobile element in soil, as it is strongly bound to organic matter (Rashad *et al.,* 2014). About 50% of copper is closely bound to organic matter and becomes available to crops only after mineralization (Breus and Olha, 2022). As previously mentioned, copper and zinc are absorbed through highly complex physical and chemical bonds, the affinity of which depends on the binding capacity as well as the contents of clay minerals, iron oxide, aluminum, manganese, and carbonates (Brunetto *et al.,* 2014).

clay minerals are effective surfaces for heavy metal adsorption but involve a series of complex adsorption mechanisms such as direct binding, surface complexation, and ion exchange between metal cations and clay minerals (An *et al.*, 2019). Baghernejad *et al.* (2014) showed in their results that the adsorption of copper on clay minerals led to a reduction in the space between the mineral layers as the concentration of copper in the equilibrium solution increased, while the effect of zinc adsorption on clay minerals was less than that of copper.

The sorption isotherms are fundamental and play a key role in the determination of themaximum capacity of nutrient or pollutant sorption onto soil (Baghernejad *et al.,* 2014). To describe the adsorption and release capacities different mathematical models such as Freundlich and Langmuir are used which are subsequently statistically related to the soil components and their properties which are routinely analyzed (Campillo *et al.,* 2020). Mishra *et al.* (2013) found that both Langmuir and Freundlich equations effectively describe copper adsorption on biomass-packed soil. However, the Langmuir equation was found to be more suitable.

Represent the soils of the study sites on its gypsum covers large areas of Salah al-Din and Najaf governorates, which reflects a negative impact on many of the soil's physical and chemical properties, in addition to containing large amounts of lime, so these soils are often classified as calcareous gypsum soils. Many studies have confirmed that carbonates can encapsulate gypsum and reduce its solubility in the soil solution. Therefore, both lime and gypsum have a negative and positive impact on many of the soil properties, the most important of which are the absorption and release of trace elements and their readiness (Schonsky *et al.,* 2013). As a result of the peculiarity of gypsiferous soils in Iraq, Langmuir adsorption curves were fitted to the experimental data, and their coefficients were determined, in order to model the adsorption properties of zinc and copper in the studied soils.

Materials and Methods

Study area

Two different gypsum soil paths were chosen depending on the geographic location, the nature of sedimentation of the Tigris and Euphrates rivers, and the relative gypsum content in the surface horizons distributed in six locations, and the locations of the models were determined using a GPS device. The first path represents Salah al-Din Governorate and is located within the deposits of the Tigris River.

- The first site (T1) is located on the Tikrit-Mosul Road and is exploited for wheat and corn crops. The irrigation used is surface irrigation.
- The second location (T2), the Al-Alam area, east of the Tigris River, is unexploited land.
- The third site (T3), Tikrit University (College of Agriculture fields), a crop research station, is used for cultivating wheat crops, and the irrigation method used in it is sprinkler irrigation.

The second track, which represents the soil of Najaf Governorate which is located within the deposits of the Euphrates River was distributed over three sites.

The Zarka region included two sites N1, N2 located on the Karbala-Najaf Road. The first is developed by growing various vegetable crops and the second is unexploited. The third site N3 located in the Bahr al-Najaf region is also unexploited.

Soil Sampling

After collecting the samples from each site. They were air-dried in the laboratory on pieces plastic and grounded with a wooden hammer, then sieved with a 2 mm sieve and saved in plastic boxes for further analysis. Some physical and chemical properties of soil in the study sites are shown in Table 1.

Table 1. Some physicochemical characteristics of the study soil sites

Soil	**Location**	**Sand**	**Silt**	**Clay**	**Class texture**	**EC (dS m^{-1})**	**PH**	**Gypsum**	**CaCO$_3$**	**Organic Carbon**	**CEC (Cmol$_c$ kg^{-1})**
		(g kg^{-1})						**(gm kg^{-1})**			
Salah Al-Din Soils											
T1	Al- Fursan exploited	581	272	147	**S**	4.00	7.38	22.92	355.83	15.4	8.56
T2	Al-Alam non expoited	640	235	125	**S**	2.41	7.49	2.62	235.44	6.18	4.28
T3	Tikrit University exploited	597	250	153	SL	2.91	7.95	198.49	319.95	14.68	8.02
Najaf Soils											
N1	Zarka exploited	697	190	113	SL	4.38	7.64	52.19	101.28	6.95	4.81
N2	Zarka non exploited	723	177	100	SL	3.70	7.70	313.92	72.17	3.09	3.21
N3	Bahr Al-Najaf non exploited	808	128	64	LS	2.41	7.52	143.93	328.50	386	4.28

Soil analysis

The soil particle size distribution was determined using the international pipette method as described by black, (1965). The electrical conductivity and soil pH were measured using a distilled water soil: water ratio (1:1) according to the procedure described by Page *et al.* (1982). Gypsum content was determined using the gravimetric method according to the procedure reported by Omran (2016). Carbonate minerals were determined by the gravimetric method as described by Richard (1954). Organic matter content by wet oxidation according to the Walkley and Black method described in Jackson (1959). The cation exchange capacity of the soil samples was measured using the method described by Savant (1994).

Adsorption isotherm experiment

About 5 g of air-dried soil from all samples added to the universal tube, and 49 mL of Zn $(NO_3)_2$ solution was added to each soil sample in the following concentrations (0, 2, 4, 8, 10, 30, and 50) mg L^{-1} with 1 mL of 0.005 M $MgCl_2$ solution. The suspensions were shaken with a shaking device DRAGONLAB SK-330-Pro for an hour and left to stabilize for 24 h, then filtered Whatman No. 42 filter paper and the concentration of zinc in the equilibrium solution was measured. The soil was retained to study the released zinc. As for copper, 49 mL of Cu $(NO_3)_2$ solutions was used at the following concentrations (0, 5, 10, 20, 30, 40, and 50) mg L^{-1} with 1 mL of 0.005 M $MgCl_2$ solution. The suspensions were shaken with the above shaker for one hour and left to equilibrate for 24 h, then it was Nominated Whatman No. 42 filter paper was used, and the copper adsorbed concentration in the equilibrium solution was measured. The soil was retained to study the released copper.

The amount of adsorbed trace elements at equilibrium was calculated using the equation (1) described by Peng *et al.* *(*2021):

$$q\ (Zn^{+2} \text{ or } Cu^{+2}) = \frac{ci-ce}{W} * V \qquad (1)$$

Where:

Zn^{+2} or Cu^{+2} q = the amount of adsorbed ions in (mg kg^{-1})
Ci = initial concentration of added ions (mg L^{-1})
Ce = the concentration of ions in the equilibrium solution (mg L^{-1})
W =weight of the soil sample, V = volume of solution added.

The absorption curves corresponding to each metal were quantitatively described by the parameters of the experimental data with the Langmuir curve described by the following equation (Kibreselassie *et al.,* 2018).

$$\frac{1}{x/m} = 1lKbc + 1/b \qquad (2)$$

Where:

C = ions concentration in equilibrium solution (mg L^{-1})
X/m = amount of adsorbed per unit mass of soil ions (mg kg^{-1})
k = Constant related to the bonding energy of ions to the soil (L
b = maximum ions adsorption capacity of the soil (mg kg^{-1})

The reverse adsorption process of both ions was studied using 40 ml of 0.1 N CaCl2 solution, shaken for 24 hours, left to equilibrate, and then filtered to measure the released zinc and copper for both adsorption and desorption was measured by using a Shimadzu AAS-6300 atomic absorption spectrophotometer.

Results and Discussion

Zinc ion adsorption

To evaluate the adsorption of zinc, the widely used single-plane Langmuir adsorption equation was chosen. As being it gives good agreement in modeling the adsorption reactions (Bhattacharya *et al.,* 2006). As shown in Table (2) and Figures (1) and (2), the equation produced high coefficient of determination (R^2) values, indicating a strong fit. To describe zinc adsorption in soils, R^2 values were high and greater than 0.90 for all samples, except site T3 soil from Salah al-Din, where R^2 was 0.84.

The study showed variation in the maximum adsorption capacity (b) values among the soils, a key constant in the Langmuir equation. This value gives a clear picture of the element's availability for plant absorption. A lower (b) value indicates an increase in the dissolved amount of the element in the soil solution, making it more available for transport, absorption, and chemical processes. Conversely, a higher (b) value suggests reduced element movement and greater retention in the soil. In Salah al-Din soils, (b) values ranged from 102.04 to 181.81 mg kg^{-1}, with the lowest in T3 soil and the highest in soil T2.

In Najaf soils, the lowest adsorption capacity (b) was observed in soil N1, with a value of 116.27 mg kg^{-1}, while the highest was in soil N3, at 666.66 mg kg^{-1}. This high adsorption capacity was accompanied by relatively low binding energy (K), as shown in Table (2). This indicates that most of the zinc adsorbed at low concentrations was bound to non-specialized sites with low binding energy, such as those associated with carbonate ($CaCO_3$) and gypsum ($CaSO_4 \cdot 2H_2O$), as noted in Table 1. Therefore, (Peng *et al.,* 2010; Fu, 2012) indicated that high pH discourages adsorption, resulting in precipitation between metal ions on the one hand and carbonates or sulfates on the other. This type of zinc can potentially be released back into the soil solution. However, in soil T3 from Salah al-Din and soil N1 from Najaf, the adsorbed zinc was associated with higher binding energy, indicating that zinc occupied more active sites in these soils.

This type of zinc can potentially be released back into the soil solution. However, in soil T3 from Salah al-Din and soil N1 from Najaf, the adsorbed zinc was associated with higher binding energy, indicating that zinc occupied more active sites in these soils. Figure 1 (T1, T2, T3) of the Salah al-Din soil shows that the adsorption process took a sharp upward curve after the concentration reached 10 mg L^{-1}, indicating that adsorption began to follow a specific pattern, as suggested by the one-plane Langmuir equation, particularly at low concentrations (Reyhanitabar, 2010). The variation in maximum adsorption capacity (b) between the study soils can be attributed to differences in their physicochemical properties.

This is due to the presence of lime and gypsum in these soils, which act as barriers to specific adsorption, making it difficult for zinc ions to reach specialized sites. Calcium ions, derived from the cation exchange complex of aluminosilicate clay and the dissociation of soil carbonates primarily compete with zinc for adsorption sites (Dandanmozd and Hosseinpur, 2010).

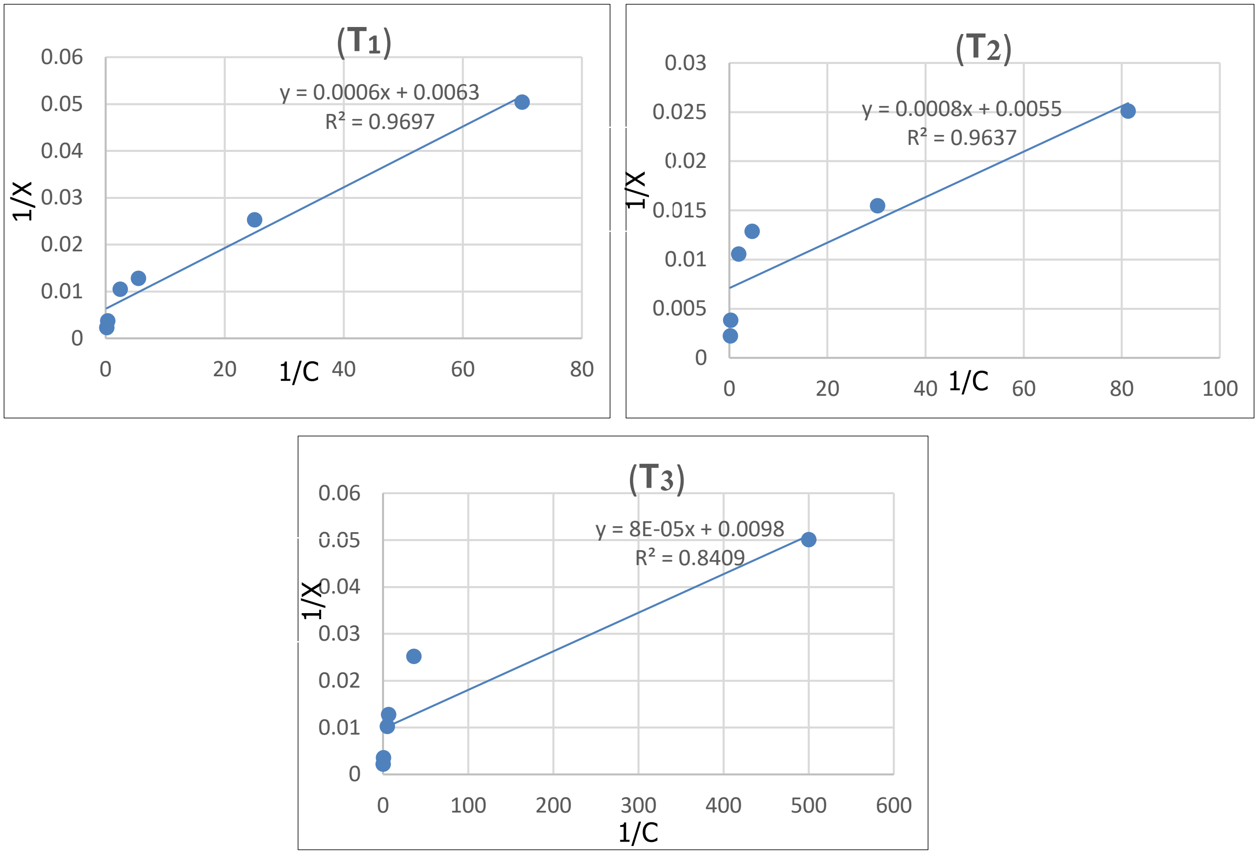
Table 2 shows the distribution coefficient (Kd) values for the studied soils. In Salah al-Din soils, Kd values ranged from 1,666.66 L kg^{-1} lowest in soil T1 to 12,503.98 L kg^{-1} highest in soil T3. In Najaf soils, Kd values ranged from 666.23 L kg^{-1} to 16,664.93 L kg^{-1}. These values were not affected by the adsorption capacity, but were affected by the binding energy, as is the case in Tikrit T3 and Najaf N1 soils. May be Kd value can reflect the extent of adsorption /dissolution equilibrium and is not only affected by binding energy (K). Kd values can also be affected by soil properties, such as the presence of clay minerals or organic matter.

The binding energy (K) values for Salah al-Din soil were highest in soil T3, at 122.54 L mg^{-1}. For Najaf soil, the highest binding energy was observed in the exploited soil N1, at 143.33 L gm^{-1}, while a significant decrease was noted in soil N3, with a value of 5 L mg^{-1}. The results suggest a correlation between the values of K and the adsorption capacity (b). That higher value of K usually mean more selective adsorption sites but fewer, resulting in a lower maximum capacity b. According to Al-Janabi *et al.* (2023) indicated, the high binding energy in this soil may be due to the relative increase in the organic matter content, as it contains active surfaces for absorption in addition to its high calcium carbonate content., the high binding energy in this soil may be due to the relative increase in the organic matter content, as it contains active surfaces for absorption in addition to its high calcium carbonate content, but with a greater potential for release of the adsorbed element.

Table 2 shows that the Desorption Index (DI) values were less than 1 (DI < 1) in some cases, such as in Salah al-Din soil at the T3 site (0.75) and the T2 site (0.875), as well as in Najaf soil at the N3 site (0.666). These DI values indicate that the adsorbed zinc in these soils can return to the soil solution. Lindsay (1980) highlighted those minerals like $ZnCO_3$, ZnO, and Zn $(OH)_2$ are highly soluble, being up to five times more soluble than zinc bound in the soil (Soil-Zn). Conversely, higher DI values (greater than 1) suggest that the soils in those locations are more prone to leach the adsorbed zinc, meaning the element is less likely to be retained in the soil and more likely to be lost through leaching.

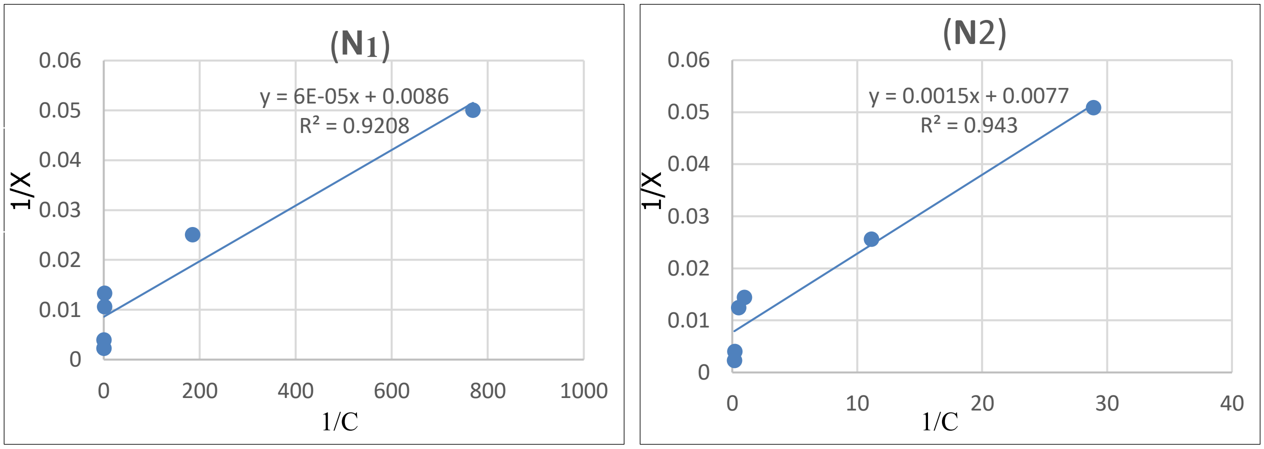
Table 2. Values of zinc adsorption equation constants for the study soil samples

Soil	Location	Maximum adsorption(b) (mg kg^{-1})	Binding energy(k) (L mg^{-1})	distribution coefficient (kd) (L kg^{-1})	Adsorption index (DI)	Correlation coefficient (R^2)	Adsorption equations
							Desorption
Salah Al-Din Soils							
T1	Al- Fursan exploited	158.73	10.50	1666.66	1.16	0.96	$y=0.0006x+0.0063$ $y=0.0007x+0.0166$
T2	Al-Alam non expoited	181.81	6.87	1249.03	0.875	0.96	$y=0.0008x+0.0055$ $y=0.0007x+0.0166$
T3	University exploited	102.04	122.54	12503.98	0.75	0.84	$y=0.00008x+0.0098$ $y=0.00006x+0.0202$
Najaf Soils							
N1	Zarka exploited	116.27	143.33	16664.97	1.16	0.92	$y=0.00006x+0.0086$ $y=0.00007x+0.0183$
N2	Zarka non exploited	129.87	5.13	666.23	1.6	0.94	$y=0.0015x+0.0077$ $y=0.0024x+0.0166$
N3	Bahr Al-Najaf non exploited	666.66	5	3333.3	0.666	0.97	$y=0.0003x+0.0015$ $y=0.0002x+0.0168$



1/C = reciprocal of the equilibrium concentration (L mg^{-1})
1/X = reciprocal of the amount adsorbed (kg mg^{-1})

Figure 1. Schematics (T_1, T_2, T_3) zinc adsorption curves for Saladin Al-Din soils



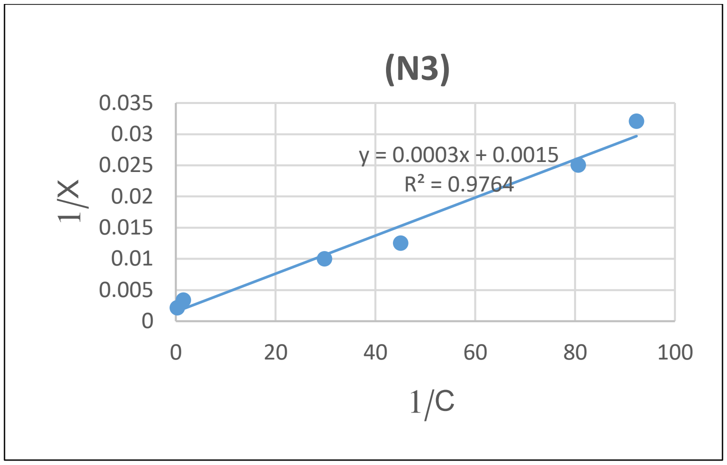


Figure 2. Schematics (N_1, N_2, N_3) zinc adsorption curves for Al-Najaf soils

Copper ion adsorption

Table 3 presents the determination coefficient (R^2) for copper. The results and Figures 3 and 4 indicate that R^2 was high in Salah al-Din soil, ranging from 0.97 to 0.99. In Najaf soil, it ranged from 0.86 to 0.99.

Table 3 shows some indicators for copper adsorption, including the adsorption capacity (b). This capacity varied across the soils studied. The lowest value was in Salah al-Din soil T2, at 322.58 mg kg^{-1}, while the highest was in T3, at 476.19 mg kg^{-1}. In Najaf soil, the lowest was in N1 at 312.5 mg kg^{-1}, and the highest was in Bahr al-Najaf soil at 1666.66 mg kg^{-1}.

The reason for the increased adsorption of copper on the solid phase compared to zinc can be explained by the high content of calcium carbonate in the study soils, as shown in the table 2 and according to what was indicated by (Flogeac *et al.,* 2007) that copper has a higher selectivity than zinc for adsorption with soil carbonate since the electric negativity of copper is greater than of zinc. This is consistent with what was found by (AL-Hamandi *et al.,* 2024). It is believed that the exchange capacity of zinc and copper adsorption is not always directly related to the b values.

The binding energy (K) ranged from 5.16 to 15 L mg^{-1} for Salah al-Din soil, with the lowest value in soil T2 and the highest in soil T1. In contrast, the K values for Najaf soil were significantly lower, ranging from 1.57 to 4 L mg^{-1}, with the lowest value in soil N1 and the highest in soil N2. The decrease in binding energy values and increase in maximum adsorption values may be due to adsorption occurring at non-specific sites (Obaid *et al.,* 2023).

Several studies have shown that lower K values indicate that a greater amount of adsorbed zinc will become non-exchangeable either by crystalline zinc formation or by entrapment and is therefore a measure of the affinity of the adsorbent to the sorbent.

When comparing the binding energy of zinc and copper, zinc adsorption was generally higher than copper adsorption, with the exception of soil T1, where copper adsorption was higher. This indicates that zinc adsorption is stronger than copper on clay minerals in the studied soils. This is consistent with the findings of (Akrawi *et al.,* 2021), possibly due to the strong affinity or attraction between adsorbed zinc and clay minerals. As the surfaces of clay minerals contain negative charges, which encourage further zinc adsorption and thus lead to a strong bond between them (Violante *et al.,* 2010; Samadi *et al.,* 2013).

Table 3 shows that the distribution coefficient (Kd) for copper ions was notably lower compared to zinc. In Salah al-Din soil, Kd ranged from 1664.51 to 4999.99 L kg^{-1}, with the lowest value in the Al-Alam soil and the highest in the University soil. The Kd values for the same exploited soils in Salah al-Din were relatively similar.

Table 3. Values of copper adsorption equation constants for the study soils

Soil	Location	Maximum adsorption (b) (mg kg^{-1})	Binding energy (k) (L mg^{-1})	distribution coefficient (kd) (L kg^{-1})	Adsorption index (DI)	Correlation coefficient (R^2)	Adsorption equations
							Desorption
Salah Al-Din Soils							
T1	Al- Fursan exploited	333.33	15	4996.61	14	0.97	$x+0.0032y=0.000$
							$761x+0.028y=0.00$
T2	Al-Alam non expoited	322.58	5.16	1664.51	13.33	0.98	$31x+0.0006y=0.000$
							$82x+0.08y=0.000$
T3	University exploited	476.19	10.5	4999.99	1	0.99	$y=0.0002x+0.0021$
							$y=0.0002x+0.0071$
Najaf Soils							
N1	Zarka exploited	909.09	1.57	1427.27	19.57	0.90	$y=0.0007x+0.0011$
							$y=0.0137x+0.0325$
N2	Zarka non exploited	312.5	4	1250	15.5	0.99	$y=0.0008x+0.0032$
							$y=0.0124x+0.0856$
N3	Bahr Al-Najaf non exploited	1666.66	2	3333.32	35	0.86	$60y=0.0003x+0.00$
							$1730.0-x105y=0.0$

In Najaf soil, the Kd values varied more: the lowest was 1250 L kg^{-1} in the unexploited Zarka soil, while the highest was 3333.32 L kg^{-1} in N3 soil.

The results indicated that a high Kd value for Cu ions was associated with the adsorption capacity (b) of the solid phase. Conversely, a low Kd value corresponded to a low maximum adsorption of Cu ions. This is in line with the results of Gomes *et al.* (2001). In general, the distribution coefficients for Cu were somewhat higher than those for Zn in the studied soils. However, exceptions were observed in soil T3 from Salah al-Din and soil N1 from Najaf, where the distribution coefficients for Cu were lower compared to Zn. As indicated in Tables 2 and 3, low distribution coefficients for both metals remain in solution and are available for transport, chemical processes, and plant uptake Morera *et al.* (2001); while higher values indicate reduced movement and retention of metals in the soil.

Lower distribution coefficients for both zinc and copper indicate that most of the metals remain in solution, making them available for transport, chemical processes, and plant uptake (Jalali and

Moharrami, 2007). In contrast, higher distribution coefficients suggest less mobility in the soil solution and greater retention of metals in the soil (Jalali and Zinli, 2012).

The results indicate that a higher percentage of added copper was strongly adsorbed onto the clay minerals of the soil, making it less available for transport compared to the amount remaining in the equilibrium solution across all studied soils. However, this was not the case for soil T3 from Salah al-Din and soil N1 from Najaf, where copper showed higher mobility. In contrast, zinc exhibited greater mobility than copper in the studied soils, particularly in T1 and T2 from Salah al-Din and N2 from Najaf, where zinc was more capable of movement through the soil. Soil N3 exhibited similar behavior for both ions.

Regarding the adsorption or desorption index (Di) for copper ions, Table 3 shows that Di > 1 for all studied soils. In Salah al-Din soils, the values followed this pattern: 1 > 2 > 3, while for Najaf soils, the sequence was: 6 > 4 > 5. Notably, soil T3 from Salah al-Din had a Di value of 1, indicating that the soil's ability to adsorb and release copper is balanced.

Therefore, the maximum adsorption capacity (b) can be used with the Langmuir equation, along with Di, to assess the soil's ability to adsorb heavy metals. The results suggest a high preference for copper adsorption in the soils studied. This implies that copper retention in these soils is relatively high and is influenced by soil properties such as cation exchange capacity (CEC), soil texture, and mineral content. Consequently, copper has a greater affinity for adsorption in the soil compared to zinc.

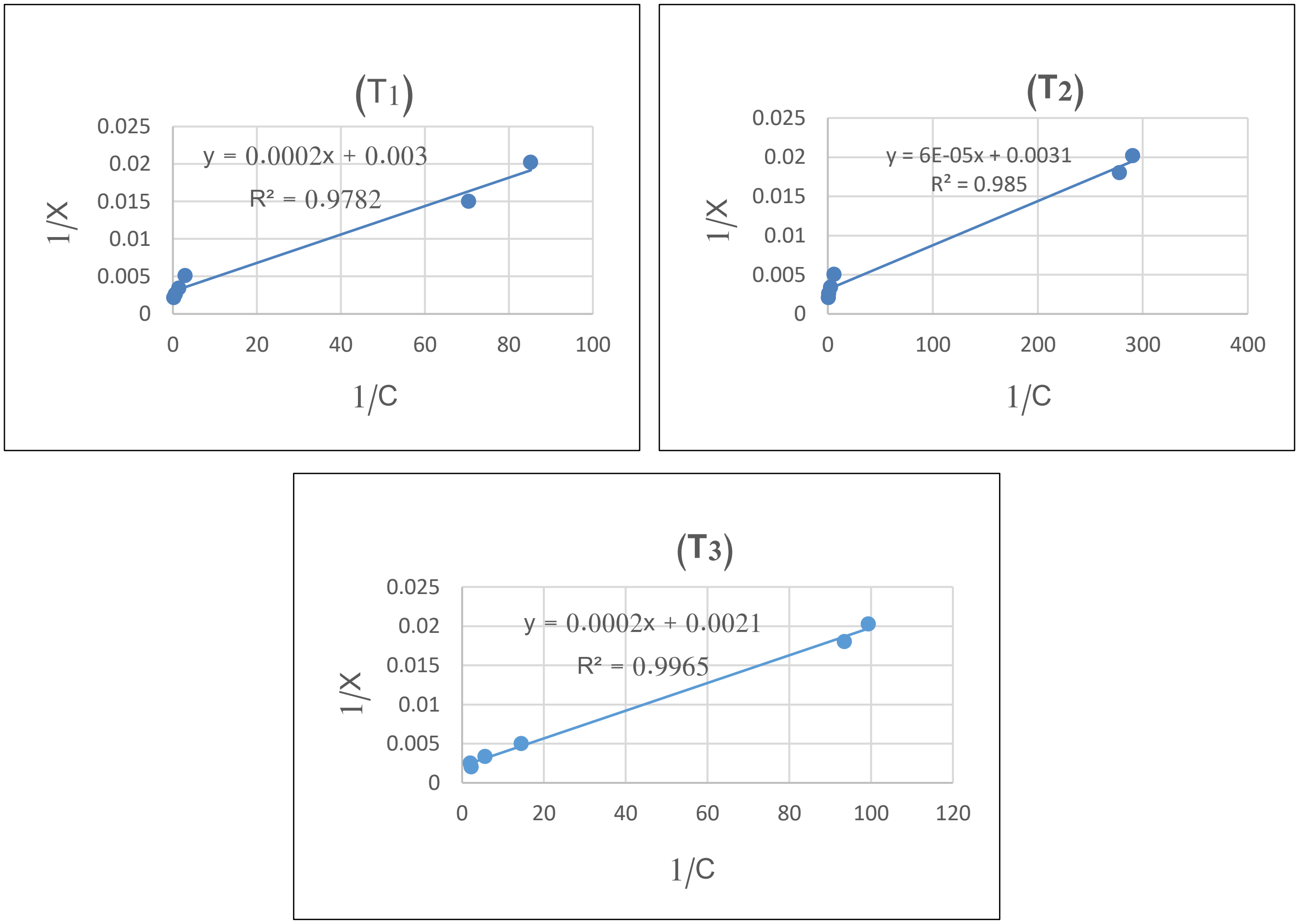


Figure 3. Schematics (T1, T2, T3) Copper adsorption curves for Salah Al-Din soils

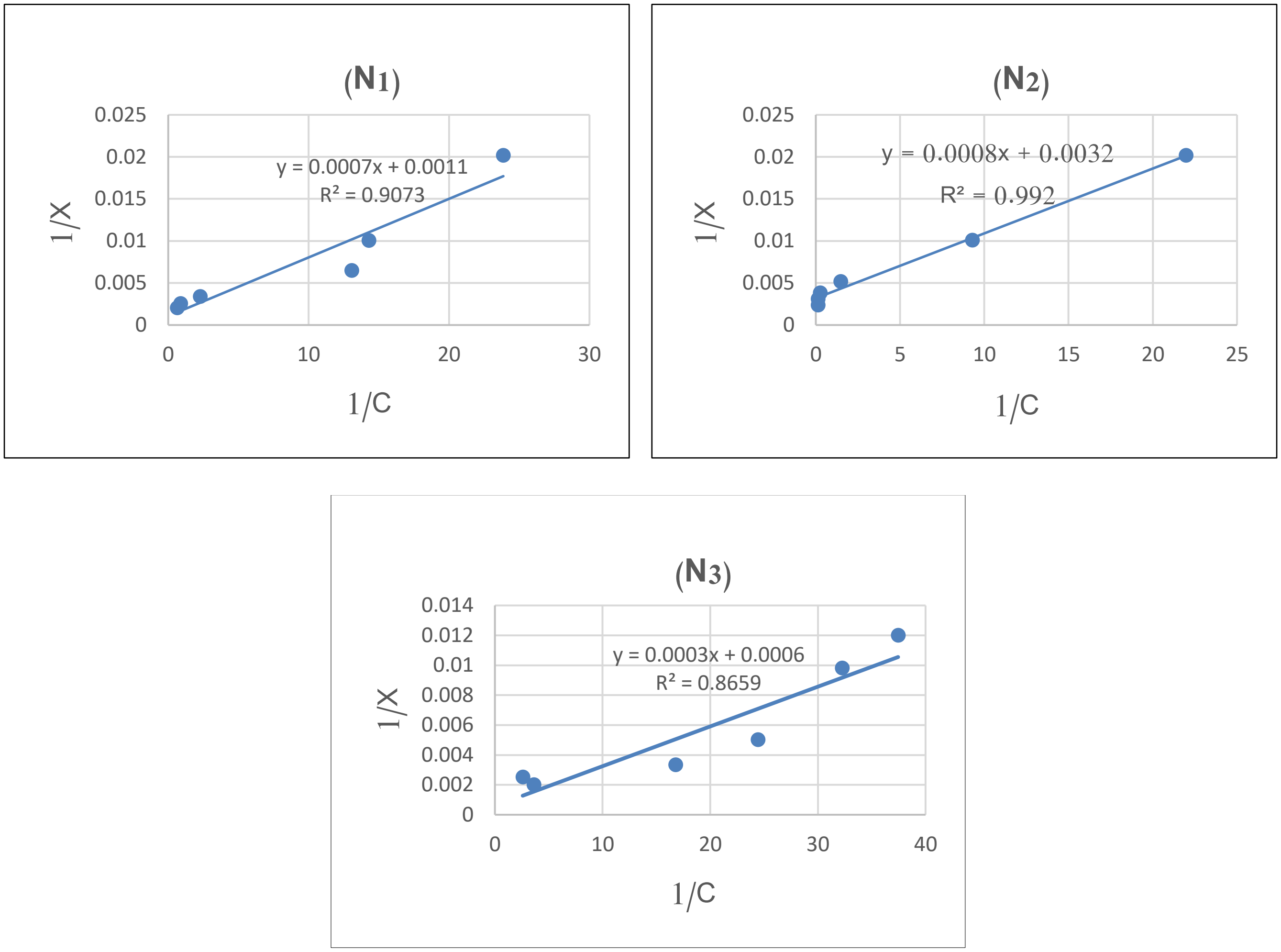


Figure 4. Schematics (N1, N2, N3) Copper adsorption curves for Al-Najaf soils

Conclusions

The soil properties that have the most influence on zinc and copper absorption in the studied soils are Gypsum, $CaCO_3$, OM and CEC. The results of sorption in this research showed that gypsiferous soils have a high capacity for trace elements. The adsorption capacity (b) for Cu was greater than Zn measured by the estimated Q parameter from the Langmuir equation. As for the distribution coefficient, this expresses the movement and retention of trace elements in the soil system. The results showed that the high values of the distribution coefficient indicated the presence of affinity between the metals in the solution for the soil solid phase, especially the copper element, while zinc had a high affinity only in the sites of Tikrit (T3) and Najaf (N1).

Conflicts of interest

The researchers declare that there are no conflicts of interest from the initial steps of preparing the research until this moment.

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