Evaluation of Langmuir and Freundlich isotherm equation for Zinc Adsorption in some calcareous soil of Erbil province north of Iraq.

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Abstract. The purpose of this study soil samples were to investigate of Zinc concentrations on the mechanism of adsorption phenomena in four calcareous soils (Choman, Qoshtepe, Herir, and Soran) from Erbil North Iraq classified (calciorthids). Isotherm adsorption was studied by using the Batch technique, 2 g soil was shaken with 40 ml 0.01M CaCl₂ containing Zn concentrations of 0, 1, 2, 4, 8, 16, 32, 64, 128, and 256 mg Zn l⁻¹ for 24 hours at 298K. Zn adsorption under isotherm reaction 298K. The adsorption data were described by using Langmuir and Freundlich equations. The results showed that the concentration of adsorption was increased by an increase of Zn level added to Soils. According to the Langmuir equation, the maximum adsorption capacity of Zn was higher in Qoshtepe, Herir Soils. 666 mg kg⁻¹ while the lower value was recorded in Soran soil. Bonding energy was higher in Soran 0.4050 mg L⁻¹, while the lower value was recorded in Choman Soils. 0.0184 mg L⁻¹ soil MBC was higher in Soran Soil. 134.87 mg kg⁻¹ while the lower value was recorded in Choman 7.65 soil, also the results showed that reaction was spontaneous with Negative free energy, were higher in Soil. -2.16 while the lower value was recorded in Herir soil -1.94 joule.mole⁻¹.degree⁻¹ for Soil. And RL value was higher in Choman Soil 0.71, while the lower value was recorded in Soran soil 0.32. The values of qm constant Dubinin-Radushkevich (D-R isotherm) which is the adsorption capacity mol g⁻¹ ranged from -2.3007 to -3.6758

1- Introduction
Zinc is the essential element for natural growth and plant development, Zinc deficiency is very common in many crops, especially in the calcareous soil (high pH and carbonate minerals). The calcareous soils that suffer from zinc deficiency are estimated at 10-30% of the total soil in the world, and that 83% of Iraq’s soil because (adsorption, precipitation, and fixation), and there is zinc in the soil in many forms, some of which are in the form of free ions in the soil solution, in the form of complexes, or fixed within the mineral composition of carbonate minerals, silicate clays, or oxides in the soil, or they may be adsorbed on the solid surfaces of the soil particles [1]; [2]. Several processes control the behavior of Zn availability parameters in soils, including adsorption-desorption and precipitation-dissolution [3]; [4]; [5]. Some physical and chemical properties of the soil affect the Zn adsorption process, such as the amount of clay, O.M content, the total, active carbonate content, and increases soil pH; [6], suffering from Zn deficiency due to adsorption and precipitation under these conditions. which means that Zn will be unavailable to plants. Adsorption of Zn increased with the increasing level of Zn and also increased with an increase in clay and CaCO₃ contents. The availability of Zn in the soil is mostly regulated by the adsorption-desorption process and its partitioning between the solutions. Most studies on the nature of sorption of zinc ions in soil indicate the importance of application of adsorption curves for the purpose of estimating the zinc fertilizer requirements of the soil to raise the level of dissolved zinc to a certain level suitable for the growth of crops and account intensity and capacity factors, which are important for predicting the amount of soil nutrient required for maximum plant growth. [3]; [7] Maximum buffering capacity (MBC) measures the ability of soil to supply zinc in the soil solution when it tends to be depleted also can be used for estimating the required doses of zinc fertilizer as well as for assessing the soil power to replenish this element [8]; [9]. Adsorption is one of the most
important chemical processes in the soil, from which it is possible to determine the amount of retention of plant nutrients, minerals, and other organic chemicals on the soil surface. Therefore, this process is one of the primary processes that affect the transport of nutrients and pollutants in the soil [10]; [11]; [12]. Which are affected by the electrostatic properties of the gluten shipments which affect the adsorption of ions in the soil and thereby reduce their presence in the soil solution [13]. It also provides useful information on the soil's ability to retain metals and their resistance to loss through important adsorption metals [14]. The objectives of this research were to study the Zn sorption characteristics in some calcareous soil of Erbil province north of Iraq.

2. Materials and Methods

Four soil samples were collected from surface soils (0-0.3 m depth) from different agriculture fields at Erbil Kurdistan region-Iraq classified Calciorthed. The soil samples were air-dried and passed through a 2 mm sieve for some chemical and physical analysis (Table 1), including particle size distribution, calcium carbonate equivalent, soil pH, organic matter (OM), Electrical conductivity (EC), and cation exchange capacity (CEC) were determined using the standard method [13].

| Location  | Partial size mg Kg⁻¹ | pH  | EC dSm⁻¹ | CEC Cmol/Cg⁻¹ soil | OM  | CaCO₃ Active | Total CaCO₃ g Kg⁻¹ | Active/Total |
|-----------|----------------------|-----|----------|-------------------|-----|-------------|-------------------|--------------|
| Choman    | 73.7 405.3 521 7.35 1.76 28.6 21.1 35 2 0.057 |
| Herir     | 124.8 298.1 577.1 7.50 2.95 30.2 17.0 240 47 0.195 |
| Soran     | 102.2 476.9 403.3 7.55 1.30 26.3 20.0 113 25 0.221 |
| Qoshtepe  | 193.8 513.6 293 7.30 1.85 22.9 10.0 254 35 0.137 |

Isotherm adsorption studied by using Batch technique, 2 gm soil was shaken with 40 ml 0.01M CaCl₂ containing Zn concentrations of 0, 1, 2, 4, 8, 16, 32, 64, 128, and 256 mg Zn l⁻¹ for 24 hours at 298K. This process has proceeded for each soil. After shaking, soil solution was filtered through Whatman No.42 filter paper. After filtration Zn concentration was determined by atomic absorption spectrophotometer (Perkin Elmer A Analyst 100 U.S.A) according to Reed and Martens [19]. Adsorption isotherms were constructed following the methods described by [15]. Zn adsorption capacity was determined by the following equation [16]:

\[ Z_{\text{nad}} = (Z_{\text{ni}} - Z_{\text{nf}}) \frac{V}{W} \] (1)

where:- Znad is the amount of adsorbed metal (mg kg⁻¹), Zni is the initial concentration of Zn in solution (mg L⁻¹), Znf is the concentration of Zn in solution after equilibrium (mg L⁻¹), V is the solution volume, and W is the weight of air dried soil.

Langmuir Model\[ \frac{1}{Z_{\text{ni}}} = \frac{1}{K_{L}C_{e}} + \frac{1}{K_{L}} \] (2)

The data plotted as \( \frac{1}{Z_{\text{ni}}} \) vs. \( \frac{1}{C_{e}} \) and the plot gives a straight line of the equation with an intercept \( \frac{1}{b} \) and slope \( \frac{1}{bK_{L}} \). Also the

Where, \( \frac{x}{m} \) = Amount of Zn adsorbed per unit weight of soil (mg kg⁻¹) \( C = \) Equilibrium Zn concentration in soil solution (mg L⁻¹) \( K = \) It is a constant related to bonding energy of Zn to the soil. \( b = \) It is the maximum adsorption capacity of soil.

\[ MBC = K_{1} \times KL \] (3)

\[ RL = \frac{1}{1+(1+KL)} \] (4)

The modified Freundlich model used to describe the soils in this work is as follows:

\[ X = aC^{b} \] (5)

Where \( X = \) quantity of Zn adsorbed per unit mass of soil (mg kg⁻¹), \( a = \) Equilibrium concentration of Zn in soil solution (mg L⁻¹) and \( b = \) constants that represent the intercept and slope of the sorption isotherms respectively.

Dubinin-Radushkevich (D-R) isotherm describes sorption on a single type of uniform pores. In this respect, the D-R is analogous to the Langmuir type but it is more general because it does not assume a homogeneous surface or constant sorption potential [17]. To understand the adsorption type, D-R isotherms were determined.
The D-R isotherm has the form: $\ln q = \ln q_m - k \varepsilon^2$ and $\varepsilon = [RT \ln (1 + (1/C_e)]$ where $\varepsilon$ is Polanyi potential, $q$ is the amount of Zn sorbed by the soil (mol g$^{-1}$), $k$ is a constant related to the adsorption energy (mol$^2$ kJ$^{-2}$) and $q_m$ is the adsorption capacity (mol g$^{-1}$). The mean free energy of adsorption ($E$) was calculated from the $k$ values using the equation: $E = (-2k)^{-0.5}$.

The magnitude of $E$ is useful for estimating the type of adsorption process. If this value is between 8 and 16 kJ mol$^{-1}$, the adsorption process can be explained by ion exchange [17].

3. Result and Discussion

The adsorption of Zn increased when Zn concentrations increased in the contact solution in all the soils. Similar results were also reported by Rasul [2] and maximum adsorption of Zn of 3357 mg kg$^{-1}$ was seen on Herir soil and the minimum of 1813 mg kg$^{-1}$ was observed in Choman soil at the highest level of added Zn. The maximum adsorption of Zn in the Herir soil might be due to the highest contents of total and active CaCO$_3$ (240 and 125 gm kg$^{-1}$) respectively, the maximum amount of clay (32 %), and relatively high pH (8.2). Soil carbonates are important sites for the absorption of added Zn [2], Dandammoed and [7]; [18]. The higher pH increased the adsorption of Zn as a result of the complexation of Zn by OH ions and a higher net negative charge (1). Also, the clays have high sorption sites that allow the non-exchangeable (specific) sorption of Zn. The majority of the soil samples had higher pH values (Table 1). Figure (1) shows clearly the magnitude of calcium carbonate on Zn adsorption as active masterly in the adsorption. And also active CaCO$_3$ was more effective than total CaCO$_3$ on Zn adsorption this may be due to the high surface area of active CaCO$_3$ compare with total CaCO$_3$.

![Figure 1](image.png)

Figure 1. Effect of total and active CaCO3 on Zn adsorption in study soils.

3.1. Langmuir adsorption isotherms of soils.

For proper evolution of the environmental threat posed by zinc on its availability, it is necessary to evaluate the zinc individual sorption characteristics-Langmuir equation was fitted to sorption data to predict the behavior of zinc sorption by the soils (Table 3). The experimental data fit the Langmuir model as $R^2$ values ranged from 0.75 to 0.95 for the linear plot (table 2), and SE values raged from 0.003 to 0.074 The Langmuir equation describes a formation of a monolayer of adsorbed on the adsorbent surface which prevents further adsorption [15] Isotherm study was carried out using Langmuir equilibrium isotherm data for Zn$^2+$ adsorption on the study soils, was achieved by plotted $1/C_e$ against $1/Zn_{ads}$ (Figure 2).
Table 2. Langmuir equations of Zn adsorption.

| Location | Langmuir equation | R²   | SE   |
|----------|-------------------|------|------|
| Choman   | $y = 0.1308 \frac{1}{ce} -0.0024$ | 0.95 | 0.004|
| Qoshtepe | $y = 0.0194 \frac{1}{ce} +0.0015$ | 0.91 | 0.074|
| Herir    | $y = 0.0181 \frac{1}{ce} +0.0015$ | 0.92 | 0.019|
| Soran    | $y = 0.0074 \frac{1}{ce} +0.003$ | 0.75 | 0.003|

In the beginning, the adsorption amount of Zn$^{2+}$ increased rapidly with the solution concentration and the adsorption rate was close to 100%. The adsorption amount of Zn$^{2+}$ in all soil samples was almost the same. This may be attributed to many adsorption sites at the surface of the soil when the solution concentration is low, and the adsorption rate is high since the adsorption amount is not saturated. Nonspecific adsorption and physical adsorption was the main process in this stage. And then the adsorption sites were gradually occupied by Zn$^{2+}$, so the increase speed of adsorption amount became slow and the adsorption-isotherm curve tended to be gentle and finally reached adsorption equilibrium. This process may due to specific adsorption and chemical adsorption [18]. The adsorption of Zn$^{2+}$ from aqueous solution on soil solid phase has been studied initially at the room temperature (298 K). The results showed an increase in adsorptive capacity of (four soils) as the concentration of Zn$^{2+}$ increased until reaching a limited value. Soil surface are heterogeneous surfaces heterogeneous is attributed to different properties of unsaturated adsorption sites leading to different energetic characters of these sites. Surface imperfection and the presence of impurities can play an important role in this respect. The adsorption on different forces leading to the formation of cultures or spaced lines of the adsorbed molecules on the surface [19]. Isotherm studies are necessary for insight into the adsorption mechanism pathways, adsorbent capacity, surface properties, and a degree of affinity to the adsorbent and an effective design of the adsorption system. The isotherm of mentioned system obeyed the Langmuir equation leading to the assumption of high adsorption affinity between the Zn$^{2+}$ and clay surface in addition to the formation of one adsorption layer of zinc on the soil surface. According to Giles’s interpretation for the adsorption isotherm shape the Zn$^{++}$ could be oriented parallel to surface clay. In other words, an excess of negative charge. The behavior of clay in a solution can be predicted by Gouy-Chapman’s theory according to the concept of a diffuse double layer. This fact means that, the clay particles in aqueous solution are charged [20], demonstrated that in clay minerals, an atom of lower position valence replaces one of the higher valances, resulting in deficit of positive charge, or Zn$^{2+}$ isotherm curves. Some adsorption isotherm may be interpreted as a combination of chemical and physical adsorption curves. The shape of adsorption isotherm can be used to diagnose the adsorption mechanism and the nature of adsorption. It is assumed that adsorption from solution is continuous function of the concentration of the solution. Molecular interaction of the solution components with the adsorbent and with each other in the surface and bulk solutions affect the shape of the adsorption from the solution.

![Figure 2. Adsorption isotherms of Zn according to Langmuir equation on some selected soils of Erbil](image-url)
3.2 Maximum Adsorption:
The maximum quantities of soil adsorbed of Zn $^{++}$ on the studied soils followed the order Soran, Choman, Qoshtepe, and Herir). The values for Langmuir parameter bonding energy (KL) and maximum adsorption (qmax) were obtained from the slope and the intercept of the graph (Figure 2). The maximum adsorption capacity and the adsorption energy coefficient are enlisted in (Table 3)

| Location | qmax mgkg$^{-1}$ | KL mg L$^{-1}$ | MBC | RL | $\Delta G$ kJmol$^{-1}$ |
|----------|-----------------|----------------|-----|----|-------------------------|
| Choman   | 416             | 0.018          | 7.65| 0.71| -2.16                   |
| Qoshtepe | 666             | 0.077          | 51.28| 0.52| -1.96                   |
| Herir    | 666             | 0.083          | 55.28| 0.51| -1.94                   |
| Soran    | 333             | 0.405          | 134.87| 0.32| -1.72                   |

The correlation of Zn with organic matter and clay content suggests that these two soil components were not responsible for the retention of native Zn in these calcareous soils. (1) inner-sphere complexion (2) outer–sphere complexion (3) diffuse ions warm. The inner sphere complexion (specific or selective adsorption influences by various factors. 1-properties of substances (ionic radius polarity, hydrated radius, equivalent conductivity hydration the enthalpy and entropy.) 2- The value of pH –dependent sorption sites. 3- steric factors. 4-formation of hydroxyl complexes. 5- the affinity of ions for organic mineral complex formation and their stability. 6-interaction with amorphous hydroxides, while outer sphere will contribute to nonspecific sorption. The third category of sorption is where a hydrated ion is merely attracted to the surface by electrostatic forces arising from charged surfaces.

3.3. The Bonding energy:
The value of the bonding energy is a real guide to the nature of the real interaction between the added ion and the adsorption surface and this is consistent with what was reached, varied in studied soil types and ion concentration. Also could be used to partially explain the widespread zinc deficiency in plants grown in calcareous soils. Table 3 shows these values for the zinc reaction bonding energy were (0.018-0.405) mg/L. This can be explained as one of the following, ionic deposition in the form of carbonate and the replacement of the added ion type replacing calcium in carbonate and ion adsorption on the carbonate surface. The ability of carbonate minerals to adsorption of ionic species to zinc is due to the presence of electrical charge on the surfaces of carbon metal resulting from the refraction of the calcite metal surfaces and the relatively small positive ion ions that are carried into the crystal while the large negative charge carbonate ions rush outward causing a negative charge Surface of crystalline or minute calcium carbonate The affinity coefficient (KL) indicated comparatively how easily the added zinc is adsorbed on or release from the adsorbing surface. According to Mehandi and Taylor [12], smaller KL values indicated that more amount of adsorbed zinc would be converted to non-exchangeable from either by the formation of crystalline zinc or by occultation through zinc ions, KL is a measure of the affinity of the adsorbate for the adsorbent. The value of zinc bonding energy (KL) for the surface layer was 0.01 L mg$^{-1}$ at 298oKelvin in they stated that high values of KL give an indication of a strong attraction between sorbed zinc and soil surface which is sorbent surface in the study of sorption [21]; [22]; [2] Soil pH, solution ionic strength, and solution ionic composition. also affect Zn sorption, increasing soil pH increases the total number of negative sites of clay minerals and (OM), and therefore increases the capacity of Zn sorption, stated that high KL value is a sign of high clay content in the soil and also it gives a hint on the strength of bonding to clay minerals in the soil. It was also found at the same location. The surface of the clay content in the soil hold negative charges and they encourage more Zn adsorption in the soil also made a strong bond between them [23] ; [24] argued that the Langmuir parameters (b) maximum adsorption and (KL) bonding energy constant are dependent on soil chemical and physical properties.
3.4. Maximum Buffering Capacity.

The Maximum Buffering Capacity of soil (MBC) are presented in Table (4), the value were ranged from 7.65 to 134.87 mg/Kg a higher equilibrium solution concentration is required for soils with a low adsorption capacity for maximum growth. And the soils with higher MBC value required less zinc saturation than those with lower MBC value. Maximum adsorption capacity are a real guide to the nature of the real interaction between the added ion and the adsorption surface and this is consistent with what was reached [23] proposed that value of MBC of zinc is affected by soil conservation measure, application of manure rather than solution zinc concentration, and reflected the strength and capacity factor of Zn$^{2+}$ adsorbed by soil. The maximum zinc adsorption on the studied soil indicating higher values of maximum adsorption capacity 134.87 mg kg$^{-1}$ [20], demonstrated that in clay minerals, an ion of lower position valence replaces one of the higher valences, resulting in a deficit of positive charge, some adsorption isotherm may be interpreted as a combination of chemical and physical adsorption curves. This may be attributed to many adsorption sites at the surface of the soil when the solution concentration is low, and the adsorption rate is high since the adsorption amount is not saturated. Non-specific adsorption and physical adsorption was the main process in this stage. And then the adsorption sites were gradually occupied by zinc, so the increased rate of adsorption amount became slow then the adsorption isotherm curve tended to be gentle and finally reached adsorption equilibrium. This process may due to specific adsorption and chemical adsorption. The increase in the number of ions and the decrease of the ion bonding energy in such soils clearly means the adsorption surfaces to the soil solution cause increased propagation rates of these ions and increase their availability for absorption by the plant [25]. The increase in the amount of ion adsorbed and the low binding energy of the ion in such soils means that it is easily released from the adsorption surfaces to the soil solution, thus increasing the propagation rates of this ion, which increases its absorption. The maximum adsorption (b) can be used to estimate the amount of fertilizer to be added to an unfertilized soil. Maximum adsorption and Zn adsorption energy varied with soil.

3.5. Langmuir separation factor (RL).

Langmuir separation factor is a dimensionless constant. For the surface layer soil value of RL were (0.32) Soran, (0.51) Herir, (0.52) Qoshtepe, and (0.71) Choman at the value of RL was greater than zero but less than one (0<RL<1) thus indicating that the sorption process of P is favorable for studied location. The variation of a separation factor (RL) with initial concentration is shown in Figure 3. The RL values were in the range 0 < RL < 1 in studied soils which indicated Zn$^{2+}$ exchange with soil was favorable for solid-phase from the liquid phase. The RL value was decreasing with an increase in concentration which indicates Zn$^{2+}$ exchange is less favorable at a high initial concentration. Where Zn (mg L$^{-1}$) is the initial concentration of Zn$^{2+}$ and KL is the Langmuir constant (L mg$^{-1}$). There are four possible outcomes of RL value that is (i) 0 < RL < 1; favorable adsorption, (ii) RL > 1; unfavorable adsorption., (iii) RL = 1, linear adsorption and (iv) RL = 0, irreversible These results were in close agreement with those previously obtained by [21];[2]; [7]. The dimensionless constant known as a separation factor (RL) is used to express the essential features of Langmuir isotherm which is given in the equation assumes unlimited sorption sites which correlated better with a heterogeneous soil medium having different chemical/physical properties. These results are similar to those of [21]; [19]; [2]

![Figure 3. Variation of separation factor (RL) as a function of initial concentration of Zn$^{2+}$ ion.](image)
3.6. Freundlich isotherm

The adsorption isotherms were examined according to the linear form of the Freundlich equation (Ince vs. In Znads) which gave a linear fit (Figure 2 and Table 4). The Freundlich equation is an empirical equation and corresponds to a model of adsorption in which the affinity term decreases exponentially as the amount of adsorption increases. Stated that the advantage of the Freundlich isotherm is that it as far as the R² values in Freundlich equations were concerned these were highly significant (at P< 0.05), suggesting that the data were well fitted to the Freundlich adsorption isotherm equations. These results were comparable to the work reported by Aljumaily [21],[2], concerning the adsorption isotherms. In Freundlich isotherm, the dimensionless constant 1/n indicates whether the experimental conditions are favorable or unfavorable for the adsorption experiment. If n >1, experimental conditions are favorable for the experiment [13].

![Figure 4. Adsorption isotherms of Zn according to Freundlich equation on some selected soils of Erbil.](image)

| Location  | Freundlich equation             | R²  | SE  |
|-----------|---------------------------------|-----|-----|
| Choman    | Lnads= 1.1651lnce+2.0699        | 0.95| 0.410|
| Qoshtepe  | Lnads= 0.9037 lnce +3.648       | 0.97| 0.269|
| Herir     | Lnads= 0.9038 lnce + 3.678      | 0.96| 0.319|
| Soran     | Lnads= 0.6902 lnce +4.0546      | 0.88| 0.502|

3.7. Dubinin-Radushkevich (d-r) parameters

Figures (5) show the curves of the D-R equation for the four soils under study. The curves show that the determination factor R² ranged between 0.76 - 0.93, which means that the DR equation had a good fitness to describe the zinc adsorption process in these Soils by obtaining these values. While the values of the constants of the D-R equation for the four soils from this table it can be seen that the values of qm, the maximum adsorption for the four soils, ranged between 1.383-17.58 mg.gm⁻¹, where the soil outperformed by achieving maximum adsorption of mg.gm⁻¹ and Erbil soil came in the last location mg.gm⁻¹.
Figure 5. Curves of the DR equation for the four soils of Erbil

With reference to Table (4) for some of the chemical properties of soils, we note that the soil is characterized by its high content of clay compared to other soils since the clay minerals and their type have an effective role in determining the adsorbed quantities of the trace elements. As for the difference in the maximum adsorption between the soils, it may be due to the high content of lime CaCO₃, as the soil content of
lime effectively affects the adsorbed quantities of the elements [1]. As such the most important characteristic of the D-R equation from others is the possibility of obtaining E values for the mean of free energy adsorption. From Table (4) it can be seen that the E values and at temperatures 25°C ranged between 0.33-30.4 K.J. mole⁻¹. This indicates that the zinc adsorption process in these soils is an ion exchange process [26], stated that if the E values ranged between 8-16 K.J.mole⁻¹, then this means that the adsorption process expresses an ion exchange process. As for the values of K in the DR equation, which expresses a constant related to the adsorption energy, it ranged from (1E.06 to -7E.08).

Table 5. Dubinin-Radushkevich D-R parameters for studied Location Soil

| Location | lnqm | Qm mole⁻¹ | Kmole⁻² KJ | E KJ.mole⁻¹ |
|----------|------|-----------|-------------|-------------|
| Choman   | 2.8668 | 17.58 | 7E.08 | 30.4 |
| Herir    | 0.7285 | 2.066 | 1E.06 | 0.33 |
| Soran    | 0.3282 | 1.383 | 2E.06 | 0.65 |
| Qoshtepe | 0.7285 | 2.066 | 1E.06 | 0.33 |

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