USING OF SOME THERMODYNAMIC PARAMETERS OF NANO AND ORDINARY ZINC ADSORPTION IN DESERT SOIL

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ABSTRACT

A laboratory experiment was carried out to study the ability of soil to adsorption of Zinc added from three sources: nano-Zinc oxide (Zn_nO), nano-chelated Zinc (Zn_n-DTPA), and nano-organic Zinc (Zn_n-HA), with several concentrations ranging from 0-160 mg Zn kg^{-1}. Zinc was added for each concentration at an amount of 20 ml per 1 gm of soil. As for the ordinary sources, Zinc was added from the ordinary sources, Zinc oxide, ZnO, chelated Zinc , Zn-DTPA, and ordinary organic Zinc , Zn-HA, in several concentrations, ranging from 0-500 mg Zn kg^{-1}. Each concentration was added at 20 ml per 1 gm of soil and two repetitions for each source. The adsorption capacity of the soil and the binding energy of the adsorbed Zinc , and to estimate the thermodynamic parameters for the adsorption of nano-Zinc in desert soils, and Freundlich equations were used to study and evaluate the adsorption process. The thermodynamic parameters K^o, ΔG^o, ΔH^o, and ΔS^o were calculated based on the results of the adsorption experiment. The results of the experiment indicate that both equations succeeded in describing the adsorption of nano and ordinary Zinc depending on the value of the determination coefficient of (R^2), which ranged between (0.959 - 0.971) and (0.884 - 0.985) for each of the Langmuir and Freundlich equations respectively. As for the thermodynamic equilibrium constant K^o, it decreased with the increase in the reaction temperature for three sources: Zn_n-DTPA, ZnO, and Zn-HA, while it increased with the other three sources. The negative ΔG^o values for all sources of nano and ordinary Zinc parameters spontaneity of the reaction at both temperatures 25°C - 45°C.

Keywords: nano-zinc, adsorption isotherm, langmuir equations, freundlich equations, thermodynamic parameters

استخدام بعض المؤشرات الثرموديناميكية لامتزاز الزنك النانوي والاعتيادي في تربة صحراوية

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المستخلص

نفذت تجربة مختبرية لدراسة قابلية التربة على امتزاز الزنك المضاف من ثلاث مصادر نانوية لاوكسيد الزنك النانوي Zn_nO والزنك المخلبي النانوي Zn_n-DTPA والزنك العضوي النانوي Zn_n-HA بعدة تراكيز مداها من 0- 160 ملغم Zn كغم$^{-1}$ تربة وبمقدار20 مل لكل 1 غم تربة, اما المصادرالاعتيادية فقد اضيف الزنك من المصادر الاعتيادية اوكسيد الزنك الاعتياديZnO و الزنك المخلبي الاعتيادي Zn-DTPA و الزنك العضوي الاعتياديZn-HAبعدة تراكيزمداها من 0-500 ملغم Zn كغم$^{-1}$ تربة وبمقدار 20 مل لكل 1 غم تربة وبمكررين لكل مصدر, ولمعرفة سعة التربة الامتزازية وطاقة الربط للزنك الممتز وتقدير المؤشرات الثرموديناميكية لامتزاز الزنك النانوي في التربة الصحراوية. استخدمت معادلتي Langmuir و Freundlich في دراسة وتقييم عملية امتزاز الزنك النانوي والاعتيادي في التربة الصحراوية وكذلك حسبت المؤشرات الديناميكية الحرارية ΔS^o , ΔH^o , ΔG^o , K^o بالاعتماد على نتائج تجربة الامتزاز. وتشير نتائج التجربة ان كلا المعادلتين نجحت في وصف امتزاز الزنك النانوي والاعتيادي اعتماداً على قيمة معامل التحديد R^2 التي تراوحت بين0.959 – 0.971 و 0.884- 0.985 لكل من معادلتي Langmuir و Freundlich بالتتابع. اما قيمة ثابت الاتزان الثرمو ديناميكي K^o فقد انخفضت مع زيادة حرارة التفاعل لثلاث مصادر هي Zn_n-DTPA , ZnO و Zn-HA فيما ارتفعت مع المصادر الثلاثة الاخرى وتشير قيم ΔG^o السالبة لجميع مصادر الزنك النانوي والاعتيادي الى تلقائية التفاعل عند كلا درجتي الحرارة 25م °- 45م°.

الكلمات المفتاحية: الزنك النانوي، الامتزاز المتماثل حراريا، معادلة لانكمير، معادلة فرندلخ، مؤشرات الديناميكا الحرارية.

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INTRODUCTION

Adsorption is defined as a physicochemical reaction resulting from the adhesion of molecules, atoms, or ions of the adsorbent material to the active sites on the solid surface of the adsorbent, forming one or several layers of molecules, atoms, or ions that are concentrated on the surface of the adsorbent material, depending on the size, nature, and size of the adsorbent and the surface area of the adsorbent material (12). This definition is consistent with the modern definition of adsorption in principle that (15) mentioned that adsorption is a process of accumulation of the adsorbent substance on the surface of the adsorbent material, and adsorption is classified into two types according to the forces of attraction, the first is chemical, resulting from the exchange of electrons, and the second is physical, resulting from physical forces of attraction such as polarity and the forces of (Vander Waals). The rate of adsorption is high and the second stage begins to decline sharply with time (8). The adsorption in the first stage is on the outer surface and is called physical or chemical adsorption, while the adsorption in the second stage, it is the result of the entry of the element and its diffusion on the inner surface of the metal and is called chemical adsorption (Chemisorptions) and then it is precipitated in the form of compounds of the element by increasing the solubility product (13). Thajeel, (21) mentioned that the study of adsorption and release reactions is an important introduction to clarifying the mechanism and direction of any chemical reaction for the adsorption and release processes. Among the equations that describe the adsorption of Zinc in the soil is the one-surface equation Langmuir equation that was developed by the scientist Langmuir in the year 1916 and it is specific to the adsorption process. Where this scientist considered that solid surfaces are primary sites that adsorb one molecule of gas, and the Freundlich equation, which was developed more than forty years after the Langmuir equation by the scientist Freundlich specifically in the year 1959, and it is an empirical equation that does not depend on the foundations of chemical dynamics. This equation was used by (9) in studying the adsorption of Zinc and boron by soil, and it is a very suitable equation to describe the adsorption of ions in the case of low concentrations and other equations. Arias and others, (5) stated that the adsorption equations, although they are important in identifying the amount of the element held by the soil and the binding energy, the nature and type of reactions that accompany the adsorption process are considered one of the most important things to know and this is done using the thermodynamic parameters that through it is possible to know the nature of the reactions accompanying the adsorption process and the state of the nutrients in the soil system during the initial stages of unbalance conditions (20). One of the most important thermodynamic parameters is ΔG^o the standard free energy of Gibbs, which represents the amount of energy needed to move the elements through the electric double layer region from the liquid phase to the solid soil phase, and its negative sign expresses the spontaneity of the adsorption reaction or not for the element on the solid soil phase. The nature of the thermal reaction represents whether the reaction is an exothermic reaction with a negative sign or an endothermic reaction with a positive sign (7). The other parameter is the entropy ΔS^o, which refers to the randomness of the system that accompanies the chemical reaction in the region of overlap between the liquid phase and the solid phase. Studies showed the positive impact of adding zinc on different crops (1, 3, 19). However; the behavior and chemical interactions of nano-fertilizers in soil are few or almost non-existent. As a result: this study aimed to know the behavior and adsorption of nano-Zn and the use of thermodynamic parameters to identify the nature of the interactions accompanying the adsorption of nano-Zn in desert soils.

MATERIALS AND METHODS

Al-Dawwar Research Station of the Agricultural Research / Ministry of Agriculture, which is 35 km west of Ramadi district, is a soil representative of the soil of the desert areas in western Iraq. It was adopted as a composite sample representing the field of study and transferred to the Soil and Water Research Laboratories - Desert Studies Center - University of Anbar to estimate the chemical properties shown in Table 1 and to carry out laboratory experiments for studying the adsorption of nano and ordinary Zinc in desert soil. The adsorption experiment was carried out at a temperature of 25 and 45C° to study the ability of soil to adsorption Zinc added from nano and ordinary sources, where Zinc was added from the nano scale sources Zinc oxide nano-metal Zn_nO and the Zinc chelated nano-source Zn_n-DTPA and the nano-organic Zinc source Zn_n-HA With eight concentrations: 0, 20, 40, 60, 80, 120, 140 and 160 mg Zn kg^{-1} soil. As for the ordinary sources, Zinc was added from the ordinary sources ZnO, and the usual chelated Zinc source, Zn-DTPA, and the usual organic Zinc source, Zn-HA, with eight concentrations 0, 40, 80, 100, 200 and 300, 400 and 500 mg Zn kg^{-1} of soil and at a rate of two repetitions for each of the six sources and for each concentration, where 20 ml of each of the usual and nano sources was added to 1 gm of dry soil and sieved with a 2 mm sieve. After adding the solutions, the soil was shaken for two hours. After filtration through a Whatman filter paper 42. Zinc was estimated in the extract using an atomic absorption device (GBC), and the adsorbed amount of Zinc was estimated through the difference between the amount of Zinc added in the original solution minus the amount of Zinc in the extract after shaking and filtration and using the Langmuir equation that describes the relationship between the adsorbed Zinc and its concentration In equilibrium solutions and Freundlich's equation describing the adsorption of ions on a solid surface. The adsorption of nano-Zn in desert soil was evaluated using two equations:-

1- Langmuir equation

$C/X/m = 1/Kb + 1/b.c$

Where X/m= the amount of the adsorbed element (µg g^{-1}). C= the concentration of the element at equilibrium (µg ml^{-1}), K = constant represents binding energy (ml^{-1} µg). b = constant represents maximum adsorption (µg g^{-1}).

2- Freundlich equation

$X = KC^b$

Where X = the amount of the adsorbed element at equilibrium. C = the concentration of the element at equilibrium. K = constant represents Adsorbent amount (µg g^{-1}), b = constant represents binding energy (ml^{-1} µg).

Table 1. Some chemical properties of the desert soil were used in the experiment

Saturated soil paste (pH)		**7.51**	
Saturated soil paste (EC)		**7.56**	**dS m^{-1}**
Organic matter		**3.3**	**gm kg^{-1}**
($CaCO_3$)		**330**	**gm kg^{-1}**
($CaSO_4.2H_2O$)		**5.20**	**gm kg^{-1}**
Cations	**(Ca^{+2})**	**21.7**	
	(Mg^{+2})	**5.9**	
	(Na^{+})	**22.9**	**Mmole l^{-1}**
Anions	**(Cl^{-})**	**26.2**	
	($SO_4^{=}$)	**22.5**	
	(HCO_3^{-})	**4.6**	
	(CO_3^{-})	**Nill**	
	(P)	**15.68**	**mg kg^{-1}**
	(K)	**152.5**	
	(Zn-DTPA)	**1.25**	
Soil Separators	**(Sand)**	**502**	
	(Silt)	**178**	**gm kg^{-1}**
	(Clay)	**320**	
soil texture			**Sandy Clay Loam**

Calculation of the thermodynamic parameters **ΔGº, ΔHº and ΔSº as follows:** Calculating the thermodynamic parameters of adsorption requires knowing the value of the thermodynamic equilibrium constant K, which is estimated through the relationship between (Cs/Ce) with Cs (K=Cs/Ce) as stated in (11),

Where:

Cs = the amount of the adsorbed element (mg g^{-1})

Ce = the conc. of element at equilibrium (mg l^{-1}).

After extracting the value of K, the following thermodynamic parameters are calculated

a- Standard free energy ΔGº

$\Delta G^o = -RT \ln K$

R = ($8.314*10^{-3}$) KJ K^{-1} mol^{-1} general gas constant

K = equilibrium constant

T = absolute temperature

b- Standard enthalpy from the integral of the Vant's Hoff. Equation

$\Delta H^o = (R\ T1\ T2 / T2 – T1) \ln(K2/K1)$

c. Standard entropy ΔSº

$\Delta S^o = (\Delta H^o - \Delta G^o) / T$

RESULTS AND DISCUSSION

Adsorption Isotherm of nano and ordinary Zinc: The adsorption process is very important in determining the fate of the nutrients in the soil and its vital readiness, and the study of the adsorption isotherm of Zinc by adding different concentrations of nano and ordinary Zinc from different sources to the desert soil will explain to us the nature of the behavior and interaction of Zinc in such soil. (Fig. 1-A, B, C for the sources of nano-Zinc and the forms Fig. 1- D, E, F, sources of ordinary Zinc). The relationship between the concentrations of Zinc in the equilibrium solution (µg ml^{-1}) added from the nano- and ordinary sources and the amount adsorbed (µg Zn g^{-1}). Adsorption isotherm curves (20). It is noted from Figure 1- A that the adsorption curve of nano-Zn added in the form of Zn_nO is of the type L according to the classification adsorption isotherm curves (20), which indicates the relatively high affinity of soil particles towards nano-Zn ions in the solution. The beginning of adding nano-Zinc with low concentrations and the increase in the amount of adsorbed Zinc continues with an increase in the concentration of added Zinc , and this is consistent with what was found by (2) when studying the adsorption of chelated and organic iron in calcareous soils. As for the Figure 1-B, it is noted that the adsorption isotherm curve is similar to the S-shaped isotherm, according to the classification of adsorption curves (20). This type refers to the splitting of nano-Zn ions between the equilibrium solution at low concentrations and adsorption on the surface of soil particles. The nano Zinc ions start with a small slope that increases with the increase in the concentration of Zinc in the solution. This slope indicates that the affinity of the adsorbing surface (soil particles) for Zinc ions in the case of low concentrations is less than the affinity of the solution to them. The affinity is greater and stronger than that of the solution, and this is consistent with what was found (18) when studying the adsorption of phosphorous on some soils. From Figure 1-C, it is noted that the adsorption curve is similar to the L-shaped isotherm, according to the classification of adsorption curves (20), and it is almost similar to the thermally homogeneous adsorption curve when adding Zinc in the form of Zn_nO, which indicates the high affinity of soil particles for adsorption of nano-Zn ions at low concentrations. The amount of Zinc adsorbed increases with increasing concentration in the solution. As for the ordinary sources of Zinc, it is noticed from the figures 1-D, E, and F that the adsorption curves of the ordinary Zinc sources are almost similar to the adsorption curves of the nano Zinc sources, except that they differ in the amount of Zinc adsorbed on the surfaces of soil particles as well as the amount of ready Zinc in the soil solution

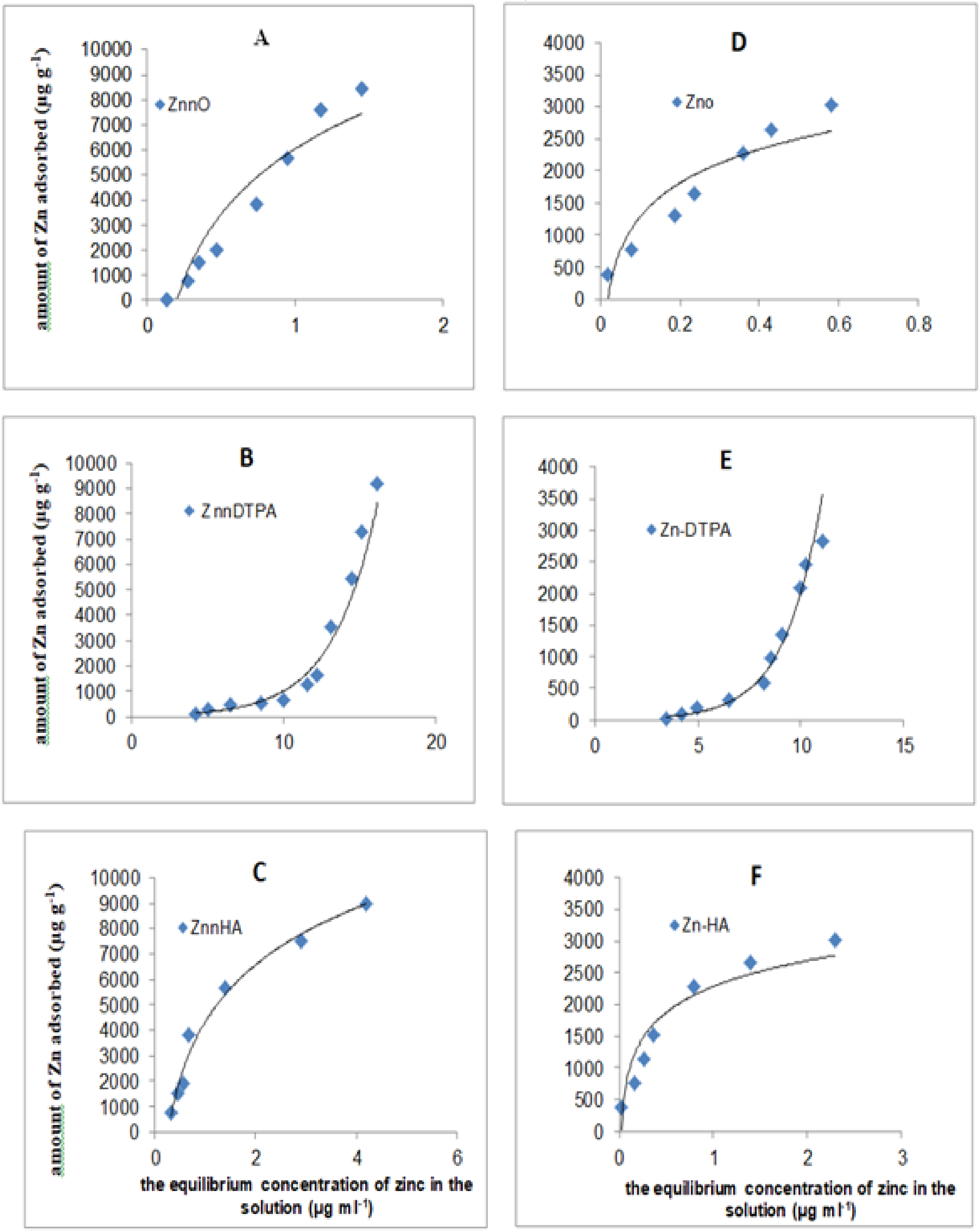

Figure 1. The relationship between equilibrium concentration of Zinc in the solution (µg ml^{-1}) and the amount of Zn adsorbed (µg g^{-1})
Nanosources A: Zn_nO, B: Zn_nDTPA, C: Zn_nHA
Ordinary sources D: ZnO , E: ZnDTPA , F: ZnHA

Using Langmuir and Freundlich Equations to Describe the Adsorption of Nano and Ordinary Zinc: The Langmuir equation was used to describe the adsorption process of nano and ordinary Zinc added with different concentrations by plotting the relationship between (C/X/m) and (C) µg ml^{-1} the equilibrium concentration of Zinc in a solution. Figure 2 showed the adsorption of Zn at a temperature of 25 C° . The Freundlich equation was also used to describe and evaluate the adsorption of nano and ordinary Zinc in desert soil conditions at a temperature of 25 C°. Figure 3 showed the relationship between the values of log X/m and the values of log C to obtain the values of the constants of the Freundlech equation, which is K, which represents the intercept, which expresses the adsorbed quantity in units µg g^{-1} and the slope of the line is b, which represents the binding energy in ml^{-1} µg, and Table 2 shows the parameters of nano and ordinary Zinc adsorption according to the Langmuir and Freundlich equations at a temperature of 25 C°. It is noted that both equations succeeded in describing adsorption of nano and ordinary Zn depending on the value of the determination coefficient(R^2) which ranged between 0.959 - 0.971 and 0.884 - 0.985 for each of the Langmuir and Freundlich equations sequentially and this agrees with what was found (4). As for the other adsorption parameters, only the Langmuir equation, it is noted that the Zn_nHA source gave the highest maximum adsorption value of 12500 µg g^{-1} among the nano and ordinary Zinc sources, the reason may be due to the role of organic humic acid, which contains active organic groups that behave as an adsorbent surface, and this is consistent with what was found (4). According to Freundlich's equation, it is noted that the Zn_nO source gave the highest adsorbent amount of 5727 µg g^{-1} among all the nano and ordinary Zinc sources, while Zn-HA gave the highest binding energy among the other Zinc sources, with a value of 2,160 ml^{-1} µg

Table 2. Adsorption parameters of nano and ordinary Zinc according to Langmuir and Freundlich equations at a temperature of 25 C

Sources Of Zinc	Langmuir 25C°			Freundlich 25C			Freundlich 45C°		
	Binding Energy(K) (ml^{-1} µg)	Maximum Adsorption (µg g^{-1}) (b)	R^2	Binding Energy(b) (ml^{-1} µg)	Adsorbent Amount (K) (µg g^{-1})	R^2	Binding Energy(b) (ml^{-1} µg)	Adsorbent Amount (µg (K) g^{-1})	R^2
Zn_nO	0.667	5000	0.965	0.701	5727	0.981	1.041	4211	0.885
Zn_nDTPA	0.063	434.78	0.962	0.332	1.329	0.903	0.205	3.723	0.971
Zn_nHA	0.800	12500	0.959	1.127	3187	0.884	1.610	2816	0.979
Zno	2.222	5000	0.971	1.618	4101	0.985	0.708	17194	0.995
Zn-DTPA	0.097	70.42	0.960	0.266	2.981	0.973	0.134	337.9	0.982
Zn-HA	3.000	3334	0.971	2.160	2202	0.974	1.139	2846	0.986

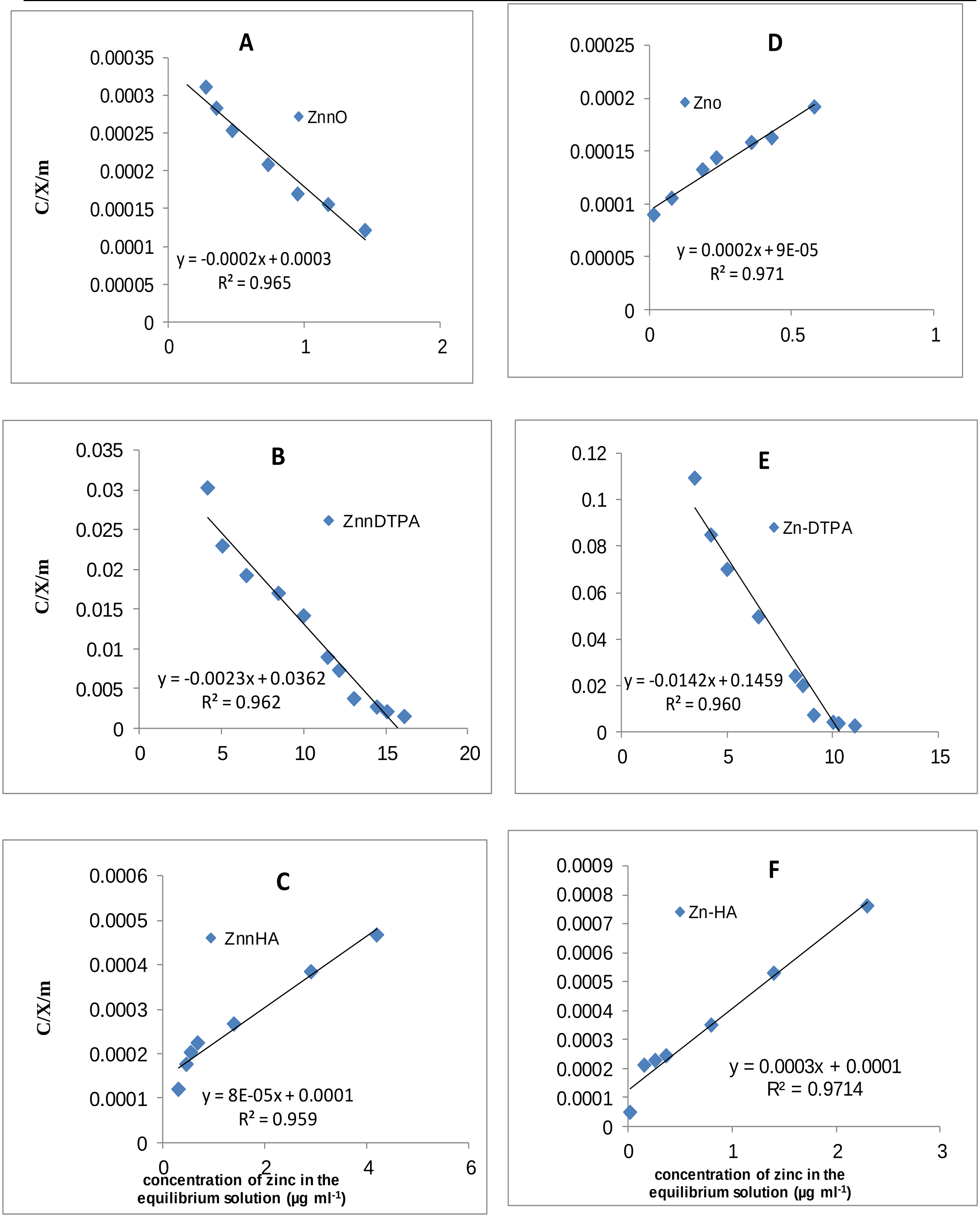

Figure 2. The linear relationship between concentration of Zinc in equilibrium solution (µg ml^{-1}) and C/x/m according to the Langmuir equation at a temperature of 25°C
Nanosources A: Zn_nO, B: Zn_nDTPA, C: Zn_nHA
Ordinary sources D: ZnO , E: ZnDTPA , F: ZnHA

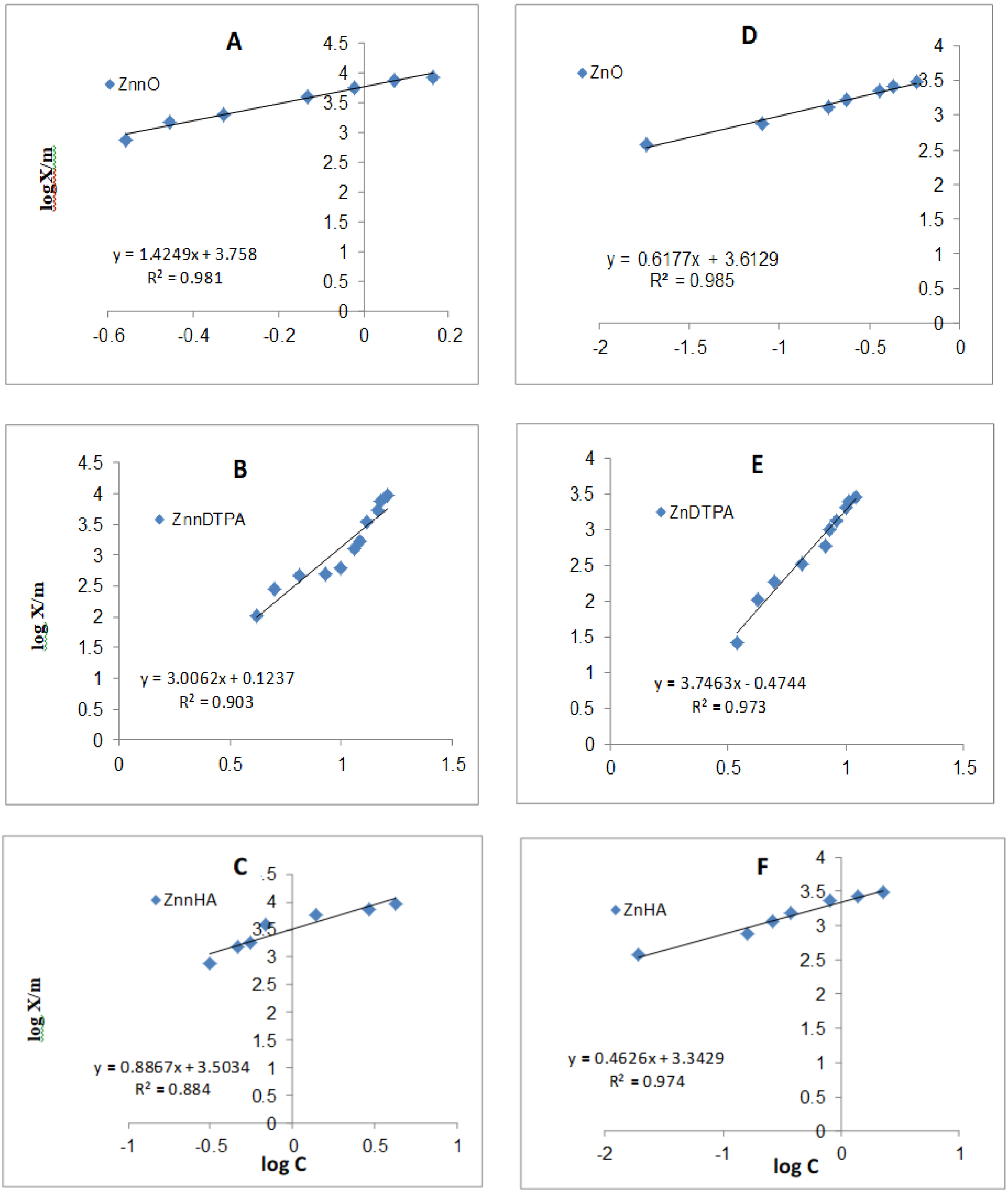

Figure 3. The linear relationship between log X/m and log C according to Freundlech's equation at a degree of 25 C°
Nanosources A: Zn_nO, B: Zn_nDTPA, C: Zn_nHA
Ordinary sources D: ZnO , E: ZnDTPA , F: ZnHA

Thermodynamic parameters of Nano and Ordinary Zinc Adsorption: Table 3 shows the value of the thermodynamic parameters for the adsorption of nano and ordinary Zinc added from different sources. The value of the thermodynamic equilibrium constant (K°) increases with the increases of the reaction temperature from 25 C° to 45 C°. It increased when using the Zn_nO source from 8.125 to 8.408 as well as the Zn_nHA source where the value of K° increased from 8.187 to 9.033 in the increase in temperature and reason.

Increasing the value of the equilibrium constant with an increase in the reaction temperature may be due to the fact that raising the temperature may lead to the breaking of the bonding bonds of some adsorbed ions other than Zinc , which causes an increase in soil adsorption through an increase in the adsorption surface activity and an increase in the number of active sites (12) in contrast to the Zn_nDTPA source, the value of K° decreased from 4.029 to 3.679, and the reason may be due to the return of Zinc ions adsorbed on the adsorbent surface to the equilibrium solution as a result of high temperatures. This is consistent with his (16) stating that the nature of the exothermic reaction in which the value of the equilibrium constant decreases with the increase in temperature.When using ordinary Zinc sources, its behavior is opposite to that of nano sources in terms of changing the value of the equilibrium constant with the increase in temperature. It is noted that the value of K° increased from 3.254 to 4.420 with the increase in temperature when using the ZnDTPA source, and in contrast it decreased when using ZnO and Zn-HA and this is consistent with With what he found (10).

Table 3. Thermodynamic parameters of nano and ordinary Zinc adsorption in desert soils at different temperatures

Sources Of Zinc	K°		ΔG° kJ mol^{-1}		ΔH° kJ mol^{-1}	ΔS° J mol^{-1}	
	25K°$_1$C°	K°$_2$45C°	25C°	45C°		25C°	45C°
Zn_nO	8.125	8.408	-5.190	-5.275	1.349	21.945	20.831
Zn_nDTPA	4.029	3.679	-3.452	-3.227	-3.578	-0.422	-1.103
Zn_nHA	8.187	9.033	-5.209	-5.452	3.870	30.470	29.320
ZnO	9.669	8.899	-5.621	-5.415	-3.267	7.899	6.756
ZnDTPA	3.254	4.420	-2.923	-3.682	12.069	50.310	49.533
ZnHA	9.574	8.123	-5.596	-5.190	-6.470	-2.931	-4.026

As for the negative values of the standard free energy ΔG° for all nano and ordinary Zinc sources at both temperatures, they indicate spontaneous adsorption of nano and ordinary Zinc on the adsorption sites. All nano and ordinary Zinc sources, but they vary from one source to another in terms of increasing or decreasing the spontaneity of the reaction, as some nano Zinc sources such as Zn_nO and Zn_nHA showed a decrease in the standard free energy value of nano-Zn adsorption through (increasing negativity) by increasing the temperature, which indicates that increases in the spontaneity reaction. In contrast to Zn_nDTPA, an increase in the value of ΔG° is observed through the (negative decrease) of the reaction and thus a decrease in the spontaneity of the reaction with the continuity of its occurrence in the same direction. This is consistent with what was found by (14), when their study of the thermodynamic criteria for adsorption of leads and copper at different temperatures. And what I found by (19) when studying manganese adsorption in some soils of Sulaymaniyah Governorate. As for the enthalpy index, ΔH°, it is clear from the table that the interactions of nano- and ordinary Zinc sources differ between emitting and endothermic sources, as the positive value of Zn_nO and Zn_nHA sources, which amounted to 1.349 and 3.870 kJ mol^{-1}, respectively, indicates that the adsorption reactions of nano-Zn for these sources are of the absorbent (Endothermic) type. While the enthalpy value of the adsorption reaction of Zinc added in the form of Zn_nDTPA was -3.578 kJ mol^{-1}, the negative sign indicates that the adsorption reaction of this nano-source is of an (Exothermic) type. Yassin and Fakher, (22) mentioned that there is no certain measure of enthalpy index (ΔH°) that enables us to know the type of adsorption, but there is an assumption that the temperature is associated with chemical reactions ranges between 20.9 - 418.4 KJ mol^{-1}. Since the positive values of the enthalpy index for each of the nano and ordinary Zinc sources are less than the thermal range above, the adsorption of Zinc in the study soil may be ion-exchange or, as mentioned by (17) the possibility of Zinc ions forming different water pools and their movement from Soil solution to its solid phase, and this agrees with what was found (4). As for the negative values of the enthalpy index for some nano and ordinary sources, they may be due to the effect of the added Zinc sources on the soil content of calcium carbonate, as well as soil s reaction (pH), as the two properties are among the most important soil properties affecting the cations adsorption (6). The values of the randomness index (entropy) ΔSº also showed a difference between the nano sources as well as the ordinary sources in the increase and decrease of this dynamic index, where an increase in randomness is observed accompanying the adsorption process of nano Zinc added in the form of Zn_nO and Zn_nHA at both temperatures while the Zinc adsorption process was accompanied From Zn_nDTPA source, a decrease in randomness at the same temperature, while the adsorption process of Zinc from ordinary sources was accompanied by an increase in randomness with Zinc added in the form of ZnO and ZnDTPA. Where the value of ΔSº at the same temperature was 7.899 and 50.310 J mol^{-1}, while the value of ΔSº decreased using ZnHA, reaching -2.931 J mol^{-1}. The soil content of calcium carbonate and the effectiveness of the calcium ion Ca^{+2} in interactions with Zinc added to the soil system. Since the value of ΔSº reflects the randomness of the system in the region of the solid phase overlap with the liquid phase, the positive values of this parameter the influence of the Zinc source on the soil content of calcium carbonate, thus increasing the randomness of the system. In contrast to the negative values of other Zinc sources, which indicate the desorption ions from the adsorbent surface and the decrease in the randomness of the system within the overlap area between the solid and liquid phase, this in turn, explains the decrease in the value of the randomness index for all nano and ordinary sources by increasing the reaction temperature from 25-45 C°, and this is consistent with what he found (14).

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