ESTIMATION OF THERMODYNAMIC ISOTHERMS FOR MN ADSORPTION IN SOME CALCAREOUS SOILS AT SULAIMANI GOVERNORATE.

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ABSTRACT

This study was conducted to determine the description of Mn adsorption phenomena through adsorption isotherms in some calcareous soils at Sulaimani governorate. Soil samples were taken at 0-30 cm depth from five different agricultural locations. Duplicate 1 gm of soil samples were equilibrated at 298 and 318°K with 50 ml of 0.01M $CaCl_2$ containing (0, 2.5, 5, 10, 20, and 40) mg Mn L^{-1} as ($MnSO_4$. H_2O). The concentration of Mn determined in solution by using ICP-OES. The amount of Mn adsorbed by each soil samples was calculated. The thermodynamic parameters ΔH°, ΔG°, ΔS° were determined using adsorption data and concentration of Mn in equilibrium solution at two different temperatures. The results indicated that the Freundlich equation is the best model to describe Mn adsorption in studied soils due to the result the higher (R^2), with lower (RMSE) and (AIC). The results of (ΔH°) indicated that the Mn adsorption processes in the Sharazor, Qaradagh and Mawat soils were exothermic reactions. While, the Mn adsorption processes in both Bazian and Surdash locations were endothermic reactions. The (ΔS°) values of these soils were as follows: Surdash > Bazian> Sharazor > Qaradagh > Mawat. The results of (ΔG°) indicated that the reaction in all studied soil locations at temperature 298 °K is spontaneous, also the reaction stay spontaneous with increase temperature to 318°K only in both Bazian and Surdash locations.

Key words: Manganese, adsorption models, Thermodynamic parameters, Batch equilibrium

تقدير طاقة الحراري لأمتزاز المنغنيز في بعض التربة الكلسية في محافظة السليمانية.

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المستخلص

اجريت هذه الدراسة لوصف ظاهرة امتزاز المنغنيز في بعض الترب الكلسية في محافظة السليمانية. اخذت نماذج التربة من العمق 0–30 سم من خمسة مناطق زراعية مختلفة. اخذ مكررين(1غم) من نماذج التربة ووزنت في درجة حرارة 298 و 318 كلفن مع 50 مللتر من 0.01 مولار من $CaCl_2$ يحتوي على التراكيز 0 و 2.5و 5و 10و 20 و 40 ملغم منغنيز لكل لتر على شكل $MnSO_4$. H_2O . قدر تركيز المنغنيز في المحلول باستخدام جهاز ICP–OES. وتم حساب كمية المنغنيز الممتزة من قبل التربة. واستعملت بعض المعايير الثرموديناميكية ΔH°, ΔG°, ΔS° لتحديد امتزاز تركيز المنغنيز من المحلول المتوازن في الدرجتين الحرارية المختلفتين. أشارت النتائج إلى أن معادلة Freundlichهي أفضل نموذج لوصف امتزاز المنغنيز في الترب المدروسة نتيجة الأعلى (R^2) ،مع انخفاض (RMSE) و (AIC). أشارت نتائج (ΔH°) إلى أن عمليات ادمصاص المنغنيز في تربة شهرزور، قرداغ و ماوت كانت تفاعلات طاردة للحرارة، بينما كانت عمليات ادمصاص المنغنيز في كل من مواقع بازيان و سورداش ردود فعل ماصة للحرارة. كان تقيم الإنتروبيا (SΔ°) لهذه التربة كمايلي: سورداش >بازيان >شهرزور >قرداغ >ماوت. أشارت نتائج (ΔG °) إلى أن التفاعل في جميع مواقع التربة المدروسة عند درجة حرارة 298 كلفن هو تلقائي ، كما أن التفاعل يبقى تلقائيًا مع زيادة درجة الحرارة إلى 318 كلفن في مواقع بازيان وسورداش.

كلمات مفتاحية: نماذج تربة، مناطق زراعية، الحرارة، الانتروبيا.

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INTRODUCTION

Manganese (Mn) is an important element in the earth crust, and is the eleventh element, its average content of total Mn in soils is estimated of 900 mg kg^{-1} (5). In agricultural area, adsorption of ionic form of elements from the soil solution by soil particle is an interest process for determine soil properties such as soil fertility (8). Adsorption of elements is processes of retention elements from the solution by the surface during a time and then reversible process will occur (28). There are many factors that affect Mn adsorption in soils which is: soil organic matter, pH of soil solution, and cation exchange capacity (20). Heavy metal adsorption and their distribution are mainly depending on many parameters which is soil type, metal speciation, metal concentration, and soil pH (10, 25 and 22). In general, soils with pH alkaline often have the higher ability to adsorptions metal, since these soils have lower solubility (6, 29, and 30). The bioavailability of Mn in soils significantly decreases with high pH value (16). Manganese is an essential element for the plant which needed in a small amount, the availability of this element chiefly depending on soil reaction. As we know Sulaimani Governorate soils is calcareous soil and have pH neutral to alkaline, so these cause to decrease the availability of this element in our agriculture soil, also the forms of the element changed in the soil, so we need to know the amount of Mn adsorbed in this area. Few studies have been carried out to identify the adsorption of Mn in the Sulaimani soils. For this reason this study was selected to evaluate: (i) the description of Mn adsorption phenomena through some adsorption isotherms and the individual adsorption behavior of Mn in calcareous soils. (ii)Using some isotherm models to assess which model will be fit with the Manganese adsorption. (iii)To determine the relation between soil properties and Mn adsorption in studied area.

MATERIALS and METHODS

Description of field sampling locations:

This study conducted on the five Agricultural soil samples around Sulaimani region, the sampling sites are located in Sharazor (N 35°15′ 27″; E 45° 42′ 21″), Qaradagh (N 35° 20′ 00″; E 45° 25′ 12″), Bazian (N 35° 37′ 01″; E 45° 05′ 38″), Mawat (N 35° 52′ 34″; E 45° 24′ 35″), and Surdash (N 35° 46′ 09″; E 45° 07′ 37″).

Sample collections

Soil samples were collected from 5 locations around Sulaimani, soil samples were taken from depth 0-30 cm to the Laboratory. Samples were air dried for a few days then sieved through sieve 2 mm and then storage in plastic bags to use for some chemical and physical analysis.

Laboratory analysis: Physico-chemical analysis

Several physical and chemical analyses were done for whole soil samples. The particle size distribution was determined using the pipette method described by (33). Soil reaction (pH) of the saturation extract was measured with pH-meter, and EC was determined according to (33). Total $CaCO_3$ equivalent was determined according to the method described by (19). Soil organic matter was determined using the Walkley-Black wet digestion method (32). Available Mn was extracted by using (0.005M DTPA + 0.01M $CaCl_2$ +0.1M TEA) method. Extractable Mn was measured by using ICP as described in (24).

Batch equilibrium for Mn adsorption

Adsorption process was studied by equilibrating a duplicate 1 gm of soil samples was placed in plastic bottles and equilibrated with 50 ml of 0.01 M $CaCl_2$ solution to keep the ionic strength almost constant, containing a series of Mn concentrations 0, 2.5, 5, 10, 20, and 40 µg Mn .gm^{-1} as ($MnSO_4$. H_2O), two drops of toluene were added to each suspension to inhibit microbial activity. The suspension was shaken for 30 min. and then kept it at two difference temperatures 298°K and 318°K. The soil suspensions were immediately filtered through whatman paper No.42, then the concentration of Mn determined in solution by using ICP-OES. The amount of Mn adsorbed by each soil samples was calculated from the difference between the initial and final concentration in the extract solution.

Adsorption isotherm

Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm were used to describe Mn adsorption in studied area.

Langmuir isotherm

The Langmuir adsorption isotherm Langmuir, I. (23) was used to interpret adsorption phenomena. The linear form of Langmuir isotherm given in equation 1:

$$\frac{1}{q_{eq}} = \frac{1}{q_{max}\, k_L\, C_e} + \frac{1}{q_{max}} \quad \text{--- (1)}$$

Where q_{eq} is the amount of Mn adsorbed (mg g^{-1}), q_{max} is the maximum capacity of adsorption (mg g^{-1}), kL is an equilibrium constant (L mg^{-1}) related to adsorption energy which reflects the affinity between the adsorbent and adsorbate, and C_e is the concentration of Mn at equilibrium in (mg L^{-1}). The Langmuir adsorption isotherms were drawn by plotting the ratio of one over the amount of Mn adsorbed against one over equilibrium Mn concentration.

Freundlich isotherm model: The linear form of Freundlich adsorption isotherm Freundlich, H. (17) was used as shown in equation 2.

$$\log q_{eq} = \log K_F + 1/n \log C_e \quad (2)$$

Where, q_{eq} is amount of Mn adsorbed (mg g^{-1}), K_F is the Freundlich constant related to sorption capacity in (mg g^{-1}), n is related to the intensity of adsorption for the adsorbent, and C_e equilibrium constant of Mn (mg L^{-1}). The Freundlich constants were calculated from linear plot between log q_e against log C_e.

Temkin isotherm model: The Temkin isotherm was used to calculate the interactions between adsorbents and adsorbed elements in ionic form Das, B. et al.(12). The linear form of the Temkin isotherm shown in equation 3.

$$q_e = B \ln A + B \ln C_e \quad (3)$$

Where: qe is the amount of Mn adsorbed at equilibrium (mg g^{-1}), A & B are constant, B is the heat of adsorption and A is the binding of equilibrium constant (L min^{-1}) conforming to the maximum binding energy, and Ce is concentration of Mn at equilibrium (mg L^{-1})

Temkin isotherms were drawn by plotting the amount of Mn adsorbed (q_e) against nature log equilibrium solution of Mn concentration (ln C_e).

Dubinin-Radushkevich isotherm; The Dubinin– Radushkevich (D-R) isotherm model Dubinin, et al (14) and Dubinin (15) was used to interpret the adsorption technique in heterogeneous surface (11). The linear form can be written as following equation 4.

$$\ln q_e = \ln q_D - 2B_D RT \ln (1 + 1/C_e) \quad (4)$$

Where, qe is the amount of Mn adsorbed (mg g^{-1}), q_D is the maximum adsorption capacity (mg g^{-1}), B_D is Dubinin-Radushkevich isotherm constant, R is the gas constant (8.314 kJ mol), T is temperature, Ce is Mn concentration at equilibrium (mg L^{-1})

Standard free energy ($\Delta G°$) = -RT ln K°

The enthalpy $\Delta H°$ calculated from integrated form of the Vant Hoff equation:

$\ln K2/K1 = \Delta H°/R[1/T1 – 1/T2]$

The standard entropy ($\Delta S°$) = ($\Delta H°$ - $\Delta G°$)/T

RESULTS AND DISCUSSION

Soil properties: The soil properties of five agriculture soils shown in Table 1, the soils were difference in texture classes ranging from (loam to Silty clay) which it means that the texture of these soils ranged from fine to moderately textured soils, (pH) value of soil samples ranged between (7.48 -7.9), and the soil were slightly to moderately alkaline. Electrical conductivity (EC) of the soil samples ranged between (0. 4-0.9 dS m^{-1}), this shows that the soil studied are non saline and this might be due to relatively higher precipitation and topography of these locations, which caused leaching of salts by natural drainage. Total Calcium carbonate (T.$CaCO_3$) ranged between (25 - 430 mg. kg^{-1}). This indicates that all soils are considered to be calcareous soils. Organic matter contents varied between the studied soils and ranged from (9-25 g kg^{-1}). The values of DTPA-extractable Mn ranged between 1.198-3.833 mg kg^{-1} in soil samples.

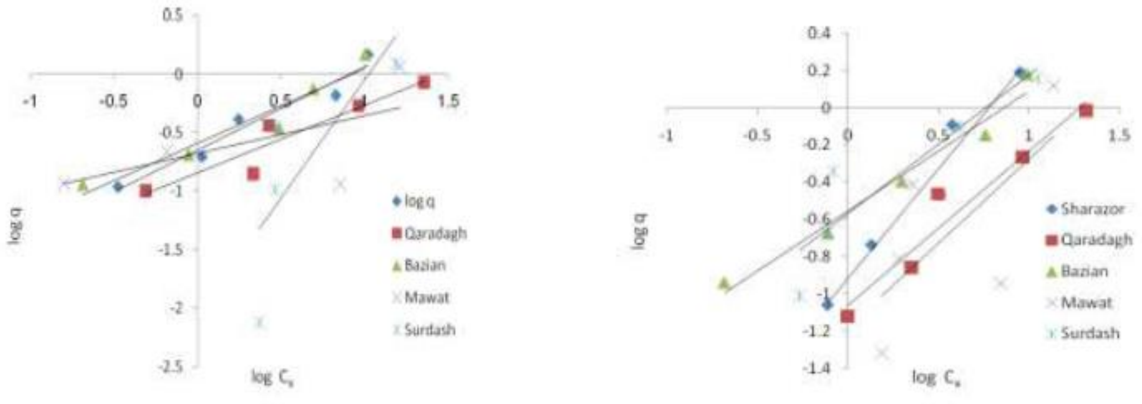
Table 1. Chemical and physical properties in studied soil samples

Locations	pH	Ec (ds m^{-1})	T.$CaCO_3$ (g kg^{-1})	O.M (g kg^{-1})	Sand	Silt (g kg^{-1})	Clay	Texture	CEC $Cmol_c$ kg^{-1}	DTPA-Mn (mg kg^{-1})
Sharazor	7.49	0.6	180	25	37.2	475.1	487.7	SC	41.15	2.40
Qaradagh	7.65	0.7	25	17	383.5	370.3	246.2	L	26.93	3.46
Bazian	7.78	0.6	100	15	55.8	430.5	513.7	SC	41.57	7.67
Mawat	7.48	0.9	25	16	161.9	434.2	403.9	SC	39.42	5.42
Surdash	7.9	0.4	430	9	91.6	490.4	418.0	SC	36.39	2.91

SC, Silty Clay; L, Loam

Manganese adsorption in the studied soil

The simplest way of characterizing adsorption is in terms of size of the adsorbing surface (or the maximum adsorption) and the affinity of the surface for the adsorbate (binding energy of sorption). For the adsorption equation to be helpful in the interpretation of the experimental results it should not only give a satisfactory fit to the adsorption isotherm data, but also it should yield equation parameters with values meaningful in physicochemical sense (18). The results in Figure 1 (a and b) shows the Freundlich constants for Mn adsorptions were calculated from the fitting straight line between log q and log Ce at both temperature (298 & 318) °K in studied soils.



(a) **(b)**

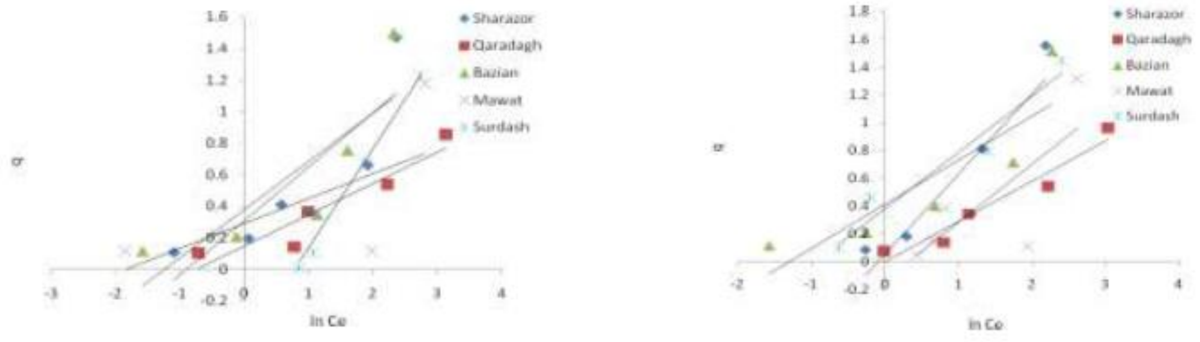
Figure 1. Linear form of Mn sorption in studied soil samples according to the Freundlich equation at 298 °K (a) and 318 °K (b).

Table 2 shows that higher value of (K_f) in Freundlich equation ranged between 3.900-117.22 at 298 °K, the highest value was in Surdash location, whereas lower value of (K_f) shown in Bazian location. These results also indicated that the Surdash location had a high capability to Mn adsorption when compared with other locations. This may be due to the high values of soil reaction in Surdash soil; high value of pH in soil solution cause to increase adsorption process of Mn. Mattias, et al. (26). The highest value of pH means low amount of H^+ in soil solution and the competition process will be decrease between H^+ and cations on the binding site, and then cause to adsorption of cations in the solution. (1). Further, the increase of adsorption process in Surdash might refer to the high amount of total $CaCO_3$ in the soil, high amount of $CaCO_3$ cause to increase adsorption process due to the hold of cations on the surface $CaCO_3$ site (physical adsorption). Moharami & Jalali (27) mentioned that the high value of Carbonate cause to increase Mn adsorption in the soil. Al-Janabi (4) and Al-Hassoon (3) observed that calcium carbonate cause to increase Cu adsorption process.

Table 2. Parameters of Mn adsorption for Freundlich, Temkin, Langmuir and Dubinin-Radushkevich equations in studied area at temperature 298 °K

Locations	Freundlich		Temkin		Langmuir		Dubinin-Radushkevich		
	K_f	n	B	A_T	q_{max}	K_L	q_D	B_D	E
Sharazor	4.464	1.407	0.343	2.451	0.904	0.390	1.027	0.364	1.173
Qaradagh	6.990	1.730	0.198	2.101	0.481	0.512	1.643	0.365	1.170
Bazian	3.900	1.574	0.306	3.453	0.592	1.120	1.165	0.257	1.396
Mawat	4.747	3.106	0.158	6.251	0.259	5.339	2.420	0.132	1.943
Surdash	117.22	0.496	0.626	2.167	0.028	0.145	4.702	2.857	0.418

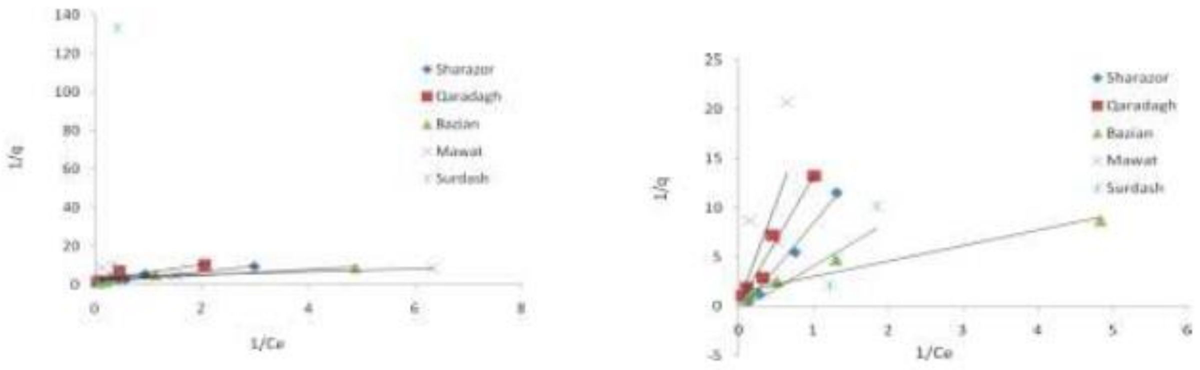
In Freundlich equation, (n) values interpret the strength of held cations by the soil, and the stability of formation complexes between cations and soil constituent. (9). The results in Table 2 shows that the Freundlich affinity values (n) for Mn in studied soils were ranged between (0.496-3.106), the highest value was in Mawat soil and the lowest value shown in Surdash soil. The value of (n) is less than one in Surdash soil. Temkin isotherm was drawn by plotting q against ln Ce at both temperature (298 & 318) °K in studied soils, as shown in Figure 2 (a & b). Also the Temkin constants for Mn adsorption were calculated in Table 2. The values of the heat of adsorption (constant B) ranged between (0.158-0.626), the highest value shows in Surdash location, while the lowest value shows in Mawat location. But the values of the maximum binding energy (At) ranged between (2.101 to 6.251), the highest value shows in Mawat, while the lowest value shows in Qaradagh locations.



(a) **(b)**

Figure 2. Linear form of Mn sorption in studied soil samples according to the Temkin equation at 298 °K (a) and 318 °K (b).

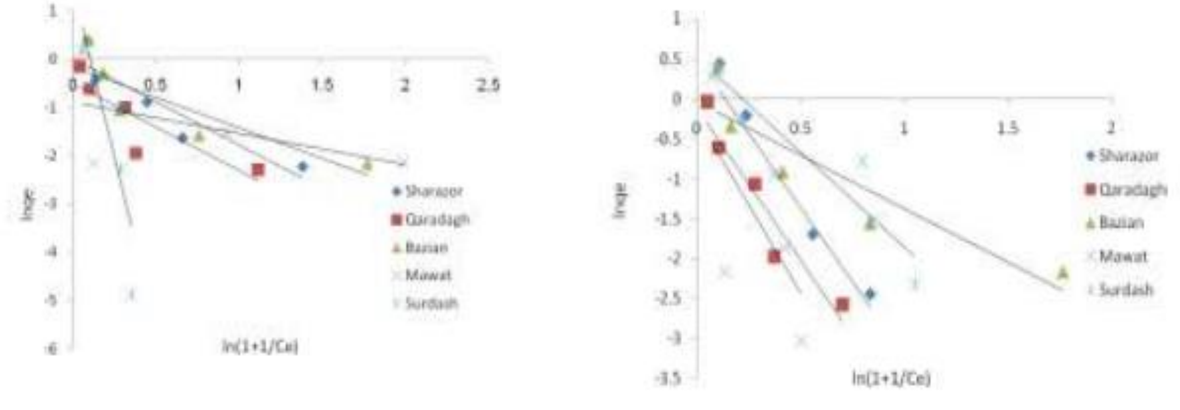
The results of Langmuir constants for Mn adsorption shows in Table 2, these constants were calculated from the fitting straight line between 1/q and 1/C_e at both temperature (298 & 318) °K in studied soils, as shown in Figure 3 (a & b). One of the benefits of the Langmuir equation is the ability of calculating the adsorption maximum and the binding energy from the regression line of equation.



(a) **(b)**

Figure 3. Linear form of Mn sorption in studied soil samples according to the Langmuir equation at 298 °K (a) and 318 °K (b).

As shown in Table 2 the constant value of Langmuir equation, maximum adsorption (q_{max}) which is measuring of soil adsorption capacity, ranged between (0.028-0.904) at temperature 298°K in all studied soil locations, the highest value was in Sharazor soil and the lowest value was shown in Surdash soil. The value of (q_{max})ranged between (0.709-4.016) at temperature 318°K in all studied soil locations, the highest value was in Qaradagh soil and the lowest value was shown in Bazian soil. The Dubinin-Radushkevich constants for Mn adsorptions were calculated from the plotting straight line between ln qe and ln (1+1/C_e) at both temperature (298 & 318) °K in studied soils, Figure 4 (a, b).



(a) (b)

Figure 4. Linear form of Mn sorption in studied soil samples according to the Dubinin-Radushkevich equation at 298 °K (a) and 318 °K (b).

According to Dubinin-Radushkevich equation shown in Table (2, 3) the highest value of adsorption capacity (q_D) in Surdash locations were (4.702 and 1.683) at temperatures (298 & 318) °K, respectively; this is may be due to the high amount of pH and calcium carbonate in Surdash location compared to other locations. The value of free energy (E) in Dubinin-Radushkevich equation helps us to determine the mechanism of Mn adsorption in the studied locations. The value of (E) ranged from 0.418-1.943 and 0.751-1.355 KJ mol^{-1} at temperatures (298 & 318) °K, respectively. All these values less than 16 KJ mol^{-1}, this means the mechanism of Mn adsorption in these five locations happening by ion exchange process according to Unlu & Ersoz (31).

Table 3. Parameters of Mn adsorption for Freundlich, Temkin, Langmuir and Dubinin-Radushkevich equations in studied area at temperature 318 °K

Locations	Freundlich		Temkin		Langmuir		Dubinin-Radushkevich		
	K_f	n	B	A_T	q_{max}	K_L	q_D	B_D	E
Sharazor	**8.224**	**0.847**	**0.580**	**1.091**	**1.666**	**0.066**	**1.646**	**0.752**	**0.815**
Qaradagh	**11.561**	**1.205**	**0.289**	**1.010**	**4.016**	**0.019**	**1.123**	**0.768**	**0.807**
Bazian	**3.588**	**1.553**	**0.317**	**3.648**	**0.709**	**0.890**	**1.029**	**0.272**	**1.355**
Mawat	**15.066**	**1.109**	**0.419**	**1.388**	**1.890**	**0.026**	**1.268**	**0.886**	**0.751**
Surdash	**3.703**	**1.342**	**0.407**	**2.546**	**2.269**	**0.098**	**1.683**	**0.481**	**1.020**

A comparison between different isotherms using for Mn adsorption

These figures were plotted according to the linear form of Freundlich, Langmuir, Timken, and Dubinin-Radushkevich equations. The fitness of these models is compared with the determination of coefficient (R^2) value of their regression lines, the standard error of estimate (RMSE) and Akaike information criterion (AIC). The results in (Figure 4 and Table 4, 5) indicate that the Dubinin-Radushkevich equation does not coincide very well with adsorption data of Mn as indicated by the R^2 with mean value of 0.674 and 0.793 at 298 and 318°K temperature respectively, in comparison to Freundlich, Temkin and Langmuir equations (Table 4, 5). The results in (Figure 3 and Table 4, 5) shows that the Langmuir equation does not fit well with adsorption data of Mn as indicated by the R^2 with mean value of 0.669 and 0.807 at 298 and 318°K temperature respectively, in comparison to Freundlich and Temkin equations (Table 4 , 5). The Temkin equation gave a better fit of the equilibrium Mn adsorption data than the Langmuir and Dubinin-Radushkevich equations. (Figure 2 and Table 4, 5). The mean R^2 value for the Temkin equation was higher than the Langmuir and Dubinin-Radushkevich equations these values were 0.749 and 0.807 at 298 and 318°K temperatures respectively.

Generally, the Freundlich equation have good coincide with adsorption data of Mn in comparison to Temkin, Langmuir and Dubinin-Radushkevich equations equations, depending on the R^2 and RMSE. The results in Table 4, 5 indicated that the mean values of the R^2, RMSE and AIC were 0.751, 0.283 and -13.515 respectively at 298°K temperature and means 0.829, 0.205 and -16.318 respectively at 318°K temperature Fig. 1& 2. Jar Allah (21) indicated that Freundlich equation have the best fit to Iron adsorption. The above equation describes Mn adsorption well over the range of equilibrium Mn concentrations used in this study. The effectiveness of these equations in accordance to these results can be arranged as follows:Freundlich > Temkin> Langmuir > Dubinin-Radushkevich. These results are in agreement with earlier reportes by Willett and Bond (34) which indicated that both Langmuir and Freundlich equations gives best fit to the Mn adsorption data.

Effect of temperature on Mn adsorption:

Generally, the Freundlich constant (K_f) values of Mn adsorption increased with increasing temperature from 298 to 318°K in Sharazor, Qaradagh and Mawat locations as shown in Table 4 and 5. The higher value of constant (K_f) found in Surdash soil at 298°K temperatures. This was also clear in the higher Mn adsorption capacity of this soil in comparison with other soils.

Table 4. Determination of coefficient (R^2), standard error of estimate (RMSE) and Akaike information criterion (AIC) at 298 ◦K for linear Freundlich, Temkin, Langmuir and Dubinin-Radushkevich equations

Locations	Freundlich			Temkin			Langmuir			Dubinin-Radushkevich		
	R^2	RMSE	AIC	R^2	RMSE	AIC	R^2	RMSE	AIC	R^2	RMSE	AIC
Sharazor	0.953	0.110	-20.599	0.771	0.302	-10.511	0.950	0.899	28.804	0.857	0.445	-6.655
Qaradagh	0.893	0.148	-17.664	0.883	0.123	-19.539	0.787	2.015	8.451	0.745	0.524	-5.014
Bazian	0.922	0.143	-18.004	0.695	0.360	-8.767	0.891	1.232	3.530	0.749	0.590	-3.833
Mawat	0.384	0.380	-8.219	0.433	0.388	-8.010	0.303	3.372	13.600	0.299	0.934	0.767
Surdash	0.605	0.635	-3.088	0.967	0.104	-21.213	0.412	51.433	40.849	0.721	1.231	3.525
Means	0.751	0.283	-13.515	0.749	0.255	-13.608	0.669	11.790	19.047	0.674	0.745	-2.242

Table 5. Determination of coefficient (R^2), standard error of estimate (RMSE) and Akaike information criterion (AIC) at 318 ◦K for linear Freundlich, Temkin, Langmuir and Dubinin-Radushkevich equations

Locations	Freundlich			Temkin			Langmuir			Dubinin-Radushkevich		
	R^2	RMSE	AIC	R^2	RMSE	AIC	R^2	RMSE	AIC	R^2	RMSE	AIC
Sharazor	0.954	0.123	-19.480	0.833	0.285	-11.109	0.981	0.705	-2.052	0.903	0.413	-7.409
Qaradagh	0.940	0.126	-19.282	0.936	0.105	-21.094	0.964	1.101	2.407	0.921	0.333	-9.561
Bazian	0.971	0.086	-23.036	0.753	0.324	-9.813	0.936	0.951	0.939	0.836	0.473	-6.041
Mawat	0.456	0.467	-6.176	0.568	0.398	-7.759	0.400	7.025	20.941	0.424	1.105	2.448
Surdash	0.827	0.222	-13.616	0.947	0.144	-17.941	0.753	2.236	9.491	0.881	0.424	-7.134
Means	0.829	0.205	-16.318	0.807	0.251	-13.543	0.807	2.404	6.345	0.793	0.550	-5.539

The effect of temperature on Mn adsorption can be expressed through some thermodynamic parameters of Mn adsorption like (ΔH°), (ΔG°) and (ΔS°) in these studied soils. The value of enthalpy (ΔH°) in these soils we can express the heat energy transferred into or out of a system during Mn adsorption process in these soils. Generally, the value of (ΔH°) of Mn adsorption in the Sharazor, Qaradagh and Mawat soils were negative as shown in Table (6) which indicated that the Mn adsorption processes in these soils were exothermic reactions (heat transfer in from the system to the surroundings). While, positive value recorded in Bazian and Surdash soils which indicated that the Mn adsorption processes in both locations were endothermic reactions (heat transfer from surroundings in to the system). As shown in the Table 6 the value of (ΔH°) for Sharazor, Qaradagh, Bazian, Mawat and Surdash were -23.869, -31.793, 4.442, -86.968

and 21.028 respectively. The lowest values for (ΔH°) were found in the Mawat soil. This would be expected due to the present of lower amount of T.$CaCO_3$ and pH value in Mawat soil in comparison with the other soils, while the Surdash soil has higher value of (ΔH°) due to the high amount of T.$CaCO_3$ in the Surdash soil with the higher value of soil pH. A lower value of ΔH° of Mn adsorption in Mawat may be attributed to more specific adsorption of Mn in this soil. Battacharyya and Tenuv (7), and Al-Hassoon, et al.(2) reported that the adsorption of cations in soils affected by soil properties as pH, calcium carbonate content, organic matter, …The values of (ΔS°) in studied soils were negative in the Sharazor, Qaradagh and Mawat soils. Whereas, positive in Bazian and Surdash soils. ΔS° used to measure of the order or disorder formed in a system during a given reaction. Apparently one would look for that the adsorption of ions from solution would form more order in a given system since the random movement of ionic species in solution has become subjected to prevent adsorption force of the surface. The (ΔS°) values of these soils were in the order of Surdash > Bazian> Sharazor > Qaradagh > Mawat. The higher (ΔS°) value present in Surdash soil is could be due to the high amount of T.$CaCO_3$ may be of the high activity of Ca^{+2} which is react rapidly with Mn in that system. These results indicated that Surdash soils adsorbed higher amounts of Mn as compared with the other soils. The values of free energy found (ΔG°) were negative at both temperatures and in all five locations except Sharazor, Qaradagh and Mawat locations which is positive at temperature 318°K as shown in Table (6), obviously there was a increase in (ΔG°) with increasing in temperature from 298 to 318°K in Sharazor, Qaradagh and Mawat locations. While, the value of (ΔG°) increase more negative value with increase temperature from 298 to 318 °K in Bazian and Surdash locations. The results indicated that the reaction in all studied soil locations at temperature 298 °K is spontaneous, also the reaction stay spontaneous with increase temperature to 318 °K in both Bazian and Surdash locations. The negative value of (ΔG°) indicated that the reaction is spontaneous (13).

Table 6. Calculated values of enthalpy (ΔH°), free energy (ΔG°) entropy (ΔS°) and (K) for the Mn adsorption in studied area:

Locations	Temperatures (°K)	ΔH° ($kJ\ mol^{-1}$)	ΔG° ($kJ\ mol^{-1}$)	ΔS° ($J\ mol^{-1}\ k^{-1}$)	K°
Sharazor	298	-23.869	-1.114	-76	1.568
	318		0.413	-76	0.855
Qaradagh	298	-31.793	-0.407	-105	1.178
	318		1.700	-105	0.526
Bazian	298	4.442	-1.347	19	1.723
	318		-1.736	19	1.928
Mawat	298	-86.968	-2.061	-285	2.297
	318		3.638	-285	0.253
Surdash	298	21.028	-0.198	71	1.083
	318		-1.623	71	1.847

The Mn adsorption data were better described by Freundlich isotherm than were described by Temkin, Langmuir and Dubinin-Radushkevich isotherms. The majot properties of soil affecting Mn adsorption in calcareous soil are Calcium carbonate content and pH of the soil. The adsorption of Mn increase with increases both pH and calcium carbonate content in the soil. Thermodynamic parameter shows that Mn adsorption in five studied soils was spontaneous at temperature 298°K. The adsorption of Mn in Sharazor, Qaradagh and Mawat soils were exothermic reactions. While the Mn adsorption processes in both Bazian and Surdash locations were endothermic reactions. This suggests that the adsorption capacity of Bazian and Surdash increased with an increase temperature. Further more research requires determining effect of the type of the mineral on the Mn adsorption in the studied locations.

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