Plant Archives Vol. 20, Supplement 2, 2020 pp. 2982-2988 **e-ISSN:2581-6063 (online), ISSN:0972-5210**

CADMIUM ADSORPTION IN SOME IRAQI CALCAREOUS SOILS ACCORDING TO THERMODYNAMIC EQUILIBRIUM CONCEPTS

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Abstract

To study mechanical of Cadmium adsorption in calcareous soils according to thermodynamic equilibrium concepts, ten agricultural soil samples with different properties were distributed in the governorates of Iraq from north to south. A laboratory experiment was conducted where Cadmium was added at levels 0, 25, 50, 100, 150, 200, 250, and 300 µg ml^{-1} using of $CaCl_2$ 0.01M and NaCl 0.01M in 25 ± 1 C° and 45 ± 1C° with three replications, to assess the effect of temperature on the adsorption process in these soils using the equation of the two scientists Dubinin and Radushkevich, and through the data of the adsorption process, the following thermodynamic parameters have been estimated : the dynamic equilibrium constant at a specific temperature $K_t°$, the change in free energy ΔG°, the change in thermal content ΔH° and the change in randomness of the reaction ΔS°. The results showed that the D-R equation was able to describe the process of Cadmium adsorption in this according to the values of the R^2 coefficient of 0.91 and 0.87 in $CaCl_2$ and NaCl solutions alternately at 25 C°, and 0.87 and 0.86 in $CaCl_2$ and NaCl solutions alternately at a temperature 45 C° and an average of 0.88. The values of the dynamic equilibrium constant $K°_T$ increased with increasing temperatures from 25 C° to 45 C° and ranged between 4.282 to 56.271, and the values of ΔG° were negative and increased with increasing temperature and ranged from -3.603 to -10.655 KJ mole^{-1} at two temperatures which means that the interaction of Cadmium in this soil is an automatic spontaneous reaction and that the increase in temperature led to an increase in its spontaneity, and that the values of ΔH° were positive and ranged between 1.297 to 16.750 KJ mole^{-1}. This means that the interaction of Cadmium adsorption in this soil is of an endothermic type, that the values of ΔS° were positive and low and their values ranged from 30.987 to 72.577 J mol^{-1}, which means an increase in the level of randomness accompanying the adsorption process.

Keywords **:** Cadmium adsorption, Iraqi calcareous soils, Thermodynamic equilibrium concepts

Introduction

The element Cadmium is considered one of the most important and most dangerous heavy and toxic elements polluting the soil and agricultural crops due to its high mobility and toxicity at low concentrations in relation to the plant and its ability to move through the food chain (Ogunkunle *et al.*, 2020), as the critical concentration of the Cadmium element varies according to the limits approved by the World Health Organization (WHO/FAO, 2007) Between 1-3 mg Cd kg^{-1} soil, Cadmium contamination leads to toxic symptoms on plant growth and production capacity, affects ionic equilibrium, absorption of essential elements of the plant, inhibits the action of enzymes, disrupts metabolic reactions and photosynthesis of plants. (Nazar *et al*., 2012). It also causes human disease, kidney failure, lung damage and high blood pressure, and Cadmium compounds are carcinogens (Satarug *et al.,* 2017). This increase in concentrations comes through the inputs of heavy metals into the agricultural environment, which include major sources including agricultural pesticides, phosphate fertilizers, animal fertilizers, sanitation protectors, and irrigation with wastewater (Isa, 2018).

The soil surface layer generally contains the highest amount of pollutant elements that mainly depend on the physiochemical properties of the soil (Addis and Abebaw, 2017). As adsorption is one of the most important chemical processes that occur in the soil, which controls the behavior and availability of heavy metals in soil, and adsorption is classified into the physical and chemical, where the physical adsorption is through the weak attraction forces (Van der Waals force), while the chemical is done through the formation of chemical bonds with the adsorbed particles or particles.

Analysis of the data on adsorption curves (Isotherms) can provide important information on the extent to which pollutants are adsorbed by soil colloids and their potential for desorption (Dandanmozd and Hossienpur, 2010). Several mathematical equations have been developed to describe and know the adsorption steps and mechanics can be described and known. Dubnin and Radushkevich proposed in 1947 a simple and useful experimental formula (Keller and Steller, 2005) and more comprehensive because they do not assume a homogeneous adsorption surface or a proven electrical voltage but rather gives meaning to electrical voltage by calculating Polanyi potential (Ersoz and Unlu, 2006), by which the dominant adsorption type can be identified.

Some concepts of thermodynamics can also be used to form a comprehensive perception of what is going on during the adsorption process such as the amount of change in Gibbs free ΔG°, the dynamic equilibrium constant at a certain temperature $K°_T$, the amount of change in heat content ΔH° (Enthalpy) and the change in the randomness of the interaction (Entropy) ΔS° (Al Othman *et al*., 2011). So the values of Gibbs free can be inferred from the spontaneous of the reaction, Whereas ΔH° values indicate the enthalpy of the chemical reaction as if it were endothermic or exothermic, and ΔS° values indicate the randomness and the level of its chemical reaction (Adhikari and Singh, 2003).

Materials and Methods

Soil samples were collected at a depth of 0-30 cm for the period from 1/11/2018 to 1/1/2019 from ten agricultural regions with different characteristics distributed in the governorates of Iraq from north to south are Duhok / Darstan, Erbil / Thurak, Sulaimaniyah / Dokan, Baghdad / Abi Gharib, Najaf / Al Mishkhab, Babel / Al Nakhila, Al Qadisiyah / Sumer, Wasit / Al Hayy, Dhi Qar / Al Shatrah, Maysan / Al Muzbaniya. Samples were dried, ground, sifted and passed through a 2 mm diameter sieve, to study the adsorption process and estimating some physical and chemical properties of the soil models shown in Table 1.

Adsorption process

To know the susceptibility of the soil to adsorption of cadmium, soil samples were taken from ten agricultural sites distributed in the governorates of Iraq from north to south and carried out the adsorption experiment using 2 gm of each soil of air dried soil and sifted with a 2 mm hole sift and placed in a centrifuge tube with a capacity of 50 ml and added to each soil eight levels of studied cadmium concentrations are 0, 25, 50, 100, 150, 200, 250, 300 µg Cd ml^{-1} in the form of Cadmium Sulfate ($8H_2O.3CdSO_4$) with a volume of 20 ml which contains two salt (separately) is $CaCl_2$ 0.01 M and NaCl 0.01M. The tubes are shaken with an electrical shaker for 6 hours, then left for a period of 24 hours, until our equilibrium condition with temperatures of 25±1 C° and 45±1 C° in a water bath. Then the suspensions were separated by using a centrifuge at a speed of 3000 rpm^{-1} for 10 minutes and the concentration of Cadmium equilibrium solution was estimated using the Atomic Absorption Spectrophotometer (AAS).

Table 1 : Some chemical and physical properties of the study soils.

Location	$EC_{1:1}$ dS m^{-1}	$pH_{1:1}$	CEC $Cmol+kg^{-1}$	OM	Carbonate minerals	Oxides	Total Cd^{+2}	Available Cd^{+2}	Soil Particles			Soil texture
									Clay	Silt	Clay	
				gm kg^{-1}								
Duhok /Darestan	1.25	7.99	27.33	14.00	250.3	8.19	2.005	0.224	320	244	436	Clay loam
Erbil / Thurak	0.81	8.07	16.05	12.80	225.9	5.35	2.089	0.185	100	379	521	Sandy loam
Sulaymaniyah / Dokan	0.68	7.08	15.40	10.50	189.2	6.16	1.653	0.179	80.0	380	540	Sandy loam
Baghdad / Abi Gharib	2.60	7.87	25.53	8.80	264.7	3.49	1.886	0.23	348	451	201	Clay loam Silty
Najaf / Al-Mishkhab	2.14	7.89	26.90	11.40	298.4	4.18	1.862	0.225	353	447	200	Clay loam Silty
Babylon / The Nakhila	2.18	7.63	20.10	8.00	225.1	2.90	1.551	0.154	180	420	400	loamy
Qadisiyah / Sumer	2.34	7.53	18.40	6.60	244.2	3.34	1.619	0.181	130	576	294	Silt loam
Wasit / Hayy	2.10	7.86	21.05	6.80	260.9	3.71	1.732	0.16	252	483	265	loamy
Dhi Qar / Al-Shatrah	2.17	7.73	20.56	7.10	258.1	3.21	1.525	0.179	212	484	304	loamy
Maysan / Al-Mazbaniyah	2.91	7.99	29.80	7.90	355.6	4.09	1.715	0.198	387	373	240	Clay loam

The number of experimental units (10*2*2*8*3) represented: soil * Cadmium concentration * salts * temperature * repeaters, respectively) = 960 experimental units the adsorbed amount of Cadmium to the soil surface was calculated in units of µg g^{-1} through the following relationship: Dandanmozd and Hossienpur (2010).

$$q = \frac{(c_i - c) * v}{w}$$

q: the adsorbed amount of Cadmium (µg g^{-1})

Ci: primary Cadmium concentration (µg ml^{-1}).

C: Cadmium concentration in equilibrium solution (µg ml^{-1}).

V: volume of equilibrium solution (ml)

W: soil weight (gm).

Desorption Process

20 ml of electrolyte solution $CaCl_2$ 0.01M and NaCl 0.01M were added separately to the previous adsorption tube for each added concentration of Cadmium and Shaker for 6 hours at 25 C° and 45 C°. After finishing the shaking period, the solution equilibrium with the soil was separated using a centrifuge at a speed of 3000 rpm^{-1} at a period of 10 minutes, then the concentration of Cadmium in the equilibrium solution was estimated using the Atomic Absorption spectrophotometer (AAS).

D-R isotherm equation

Adsorption data is also applied to the D-R isotherm equation to estimate the adsorption type and its general formula (Dubinin and Radushkevich, 1947)

$$\ln q = \ln q_m - k\varepsilon^2$$

q: The adsorbed quantity (µg g^{-1})

q_m: Maximum adsorption capacity (µg g^{-1})

k: adsorption constant ($mole^2$ kJ^{-2})

represents a Polanyi potential, and is defined by the following formula:

$$\varepsilon = RT\,Ln\left(1 + \frac{1}{Ce}\right)$$

R: General constant gases (8.314 K^{-1} J mol^{-1}).

T: Absolute temperature.

The rate of adsorption free energy (E) is calculated from the calculated (K) values that are useful in estimating the type of adsorption process according to the following equation (Ünlü and Ersoz, 2006)

$$E = (-2K)^{-0.5}$$

To apply the concepts of adsorption thermodynamics requires knowledge of the thermodynamic equilibrium constant (K) as in the equation (Jain and Sharma, 2002):

$$K^o_T = Cs / Ce$$

K^o_T = thermodynamic equilibrium constant.

C_S = adsorbed amount of the element on the solid phase (µg g^{-1})

C_e = element ion concentration in equilibrium solution (mg L^{-1})

By the intersection of C_s / C_e values and Cs, K^o_T is calculated when Cs reaches zero.

then, the change in standard free energy (ΔG^o) is calculated according to the equation below (Ramesh *et al.*, 2005 and Atkins *et al.*, 2018).

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

As for the change in the standard enthalpy (ΔH^o), it is calculated from the integral of van 't Hoff equation (Atkins *et al.,* 2018).

$$\ln K_2/K_1 = - \Delta H^o / R\ [1/T_2 - 1/T_1]$$

The change in randomness or entropy (ΔS^o) is calculated from the equation below (Atkins *et al.*, 2018):

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

Results and Discussion

Dubinin-Radushkevich adsorption isotherm

The result in table 2 that the mean value of R^2 was 0.91 and 0.87 in NaCl and $CaCl_2$ solutions successively at 25 C°, 0.87 and 0.86 in NaCl and $CaCl_2$ solutions alternately at 45 C° and in a general rate of 0.88, which means that the D-R equation have been able to describe the process of adsorption of Cadmium in these soils by obtaining these values and this is consistent with the study of Al-Obaidi and Al- Hayani (2018) that this equation can describe the adsorption of Lead in some calcareous soils in northern Iraq.

Table 2 shows the values of the constant equations of D-R for the study soils and at temperatures 25 C° and 45 C°, as the Polanyi potential was calculated and from that the values of the maximum adsorption capacity (q_m) for the Cadmium element in the studied soil were calculated and ranged between 341.24 µg gm^{-1} in the soil of Qadisiyah to 802.96 µg g^{-1} in Najaf soil under conditions of NaCl salt and between 341.31 µg g^{-1} in Wasit soil to 851.59 µg g^{-1} in Dahuk soil in $CaCl_2$ solution at a temperature of 25 C°, but at a temperature of 45 C° it ranged between 367.86 µg g^{-1} in Sulaymaniyah soil to 842.69 µg g^{-1} in Najaf soil under conditions of NaCl salt and 413.89 µg g^{-1} in soil of Sulaymaniyah to 897.22 µg g^{-1} soil in Dohuk under the $CaCl_2$ solution conditions, as observed superiority of soil Dohuk and Najaf to achieve maximum capacity adsorption compared to the rest of soils, which may be due to soil Dohuk characterized by higher content of oxides 8.19 Cmole+ kg $^{-1}$ (Table 1) As for the Najaf soil, it may be attributed to the fact that it contains the highest content of organic matter 11.40 g kg^{-1} compared to the central and southern regions, and this is consistent with Mclean and Bledsone (2009), as they showed that Cadmium is directly related to the humic parts, in addition to the content of the two soils of clay particles 320 and 353 g kg^{-1}, as Karak *et al.* (2014) mentioned that the correlation of Cadmium is higher in soils with high content of clay, as the content and type of clay minerals play an active role in determining the adsorbed quantities of the element (Dahiya *et al.,* 2005).

Table 2 : D-R equation constant value for the adsorption of Cadmium in study soils at 25 C° or 45 C°.

C° 25								
Locations	**NaCl (0.01 M)**				**$CaCl_2$ (0.01 M)**			
	q_m µg g^{-1}	**K mol^2 KJ^{-2}**	**E KJ mol^{-1}**	**R^2**	**q_m µg g^{-1}**	**K mol^2 KJ^{-2}**	**E KJ mol^{-1}**	**R^2**
Duhok /Darestan	788.08	-100x10^{-6}	70.71	0.88	851.59	-67 x10^{-6}	86.39	0.84
Erbil / Thurak	555.41	-757 x10^{-6}	25.82	0.92	626.78	-452 x10^{-6}	33.33	0.89
Sulaymaniyah / Dokan	348.73	-1089x10^{-6}	21.52	0.89	404.12	-1020x10^{-6}	22.14	0.95
Baghdad / Abi Gharib	677.09	-286 x10^{-5}	42.26	0.84	769.31	-226 x10^{-6}	47.67	0.95
Najaf / Al-Mishkhab	802.96	-229 x10^{-5}	46.62	0.98	830.73	-114 x10^{-6}	66.23	0.95
Babylon / The Nakhila	459.14	-104 x10^{-6}	21.93	0.98	403.87	-464 x10^{-6}	32.83	0.72
Qadisiyah / Sumer	341.24	-795 x10^{-6}	25.16	0.90	396.95	-473 x10^{-6}	32.62	0.88
Wasit / Hayy	575.53	-600 x10^{-6}	28.86	0.92	341.31	-543 x10^{-6}	30.43	0.93
Dhi Qar / Al-Shatrah	425.39	-898 x10^{-6}	23.70	0.96	472.20	-440 x10^{-6}	33.43	0.82
Maysan / Al-Mazbaniyah	629.29	-227 x10^{-6}	47.67	0.85	782.04	-189 x10^{-6}	51.43	0.81
45 C°								
Duhok /Darestan	818.69	-71 x10^{-6}	83.92	0.86	897.22	-54 x10^{-6}	95.34	0.81
Erbil / Thurak	606.92	-656 x10^{-6}	27.73	0.95	714.44	-438 x10^{-6}	33.79	0.96
Sulaymaniyah / Dokan	367.86	-663 x10^{-6}	27.52	0.88	413.89	-566 x10^{-6}	29.88	0.84
Baghdad / Abi Gharib	706.48	-228 x10^{-6}	47.67	0.84	821.97	-186 x10^{-6}	51.85	0.95
Najaf / Al-Mishkhab	842.69	-181 x10^{-6}	52.70	0.99	859.89	-105 x10^{-6}	69.01	0.96
Babylon / The Nakhila	391.82	-460 x10^{-6}	27.12	0.76	440.85	-297 x10^{-6}	40.96	0.64
Qadisiyah / Sumer	375.29	-814 x10^{-6}	24.84	0.93	431.86	-298 x10^{-6}	41.52	0.87
Wasit / Hayy	628.79	-546 x10^{-6}	30.43	0.92	763.11	-415 x10^{-6}	34.67	0.92
Dhi Qar / Al-Shatrah	449.57	-442 x10^{-6}	33.71	0.80	557.30	-344 x10^{-6}	38.13	0.87
Maysan / Al-Mazbaniyah	707.54	-190 x10^{-6}	51.30	0.78	817.38	-190 x10^{-6}	51.30	0.83

As for the effect of salt composition on the maximum adsorption capacity, it is noted that the values of q_m ranged under NaCl salt conditions between 341.24 - 802.96 µg g^{-1} and increased to between 341.31 - 851.59 µg g^{-1} under $CaCl_2$ salt conditions in temperature from 25 C°, but at a temperature of 45 C° it ranged under salt conditions NaCl between 367.86 – 842.69 g^{-1} and increased to 413.89-897.22 µg g^{-1} under $CaCl_2$ salt conditions, the increase of q_m values under $CaCl_2$ salt conditions may be attributed to the increase in the concentration of Sodium ions under the conditions of the Sodium Chloride solution will increase the thickness of the electic double layer compared to the conditions of Calcium Chloride (Bohn *et al*., 2001, Ali and Al- Kaysi, 2011) which reduce the adsorption capacity of Cadmium on the surfaces of colloids, and increasing the ionic concentration of Calcium in the equilibrium solution will reduce calcite solubility by the influence of the common ion in solubility (Mendham *et al*., 2000) this is consistent with Sharif (2018) who showed the effect of Calcium Chloride salt in increasing the formation of Calcium Carbonate that increases from adsorption of heavy metals onto their surfaces.

It is noted from Table 2 that the rise in temperature from 25 C° to 45 C° has led to an increase in q_m values for all soils, and this rise may be due to the increase in temperature that will increase and activate the number of effective interchangeable sites on the adsorption surfaces which is consistent with Yavuz *et al.* (2003) mentioned, in addition to that the temperature increases the kinetic energy of the adsorbed ions and thus increases its ability to enter the solid phases pores of the solid phase and increases the speed of its diffusion or exchange with the exchange surfaces in the soil. Therefore, the amount of adsorption increases with increasing temperature, and this is consistent with the study of Al-Jumaili (2015)who showed that q_m increasing with temperature in studying Zinc adsorption using D-R equation in some soils in northern Iraq.

The results of table 2 indicate that the constant values of k, which express the binding energy, ranged at a temperature of 25 C° between -100x10^{-6} mol^2 kJ^{-2} in Duhok soil to -1089x10^{-6} mol^2 kJ^{-2} in Sulaymaniyah soil under conditions of NaCl solution and between -67 x10^{-6} mol ^{2} kJ^{-2} in the soil of Dohuk to -1020x10^{-6} mol^2 kJ^{-2} in Sulaymaniyah soil under the conditions of $CaCl_2$ solution, either at a temperature of 45 C°, the values ranged between -71 x10^{-6} mol^2 kJ^{-2} in the soil of Dohuk to 814 x10^{-6} mol^2 kJ^{-2} in Qadisiyah soil in NaCl solution and between -54 x 106 mol ^{2} kJ^{-2} in Dahuk soil to -566 x 10-6 mol ^{2} kJ^{-2} in Sulaymaniyah soil in $CaCl_2$ solution, that the Dahuk soil exceeds in giving the highest values of energy binding may be attributed to the high content of oxides and organic matter, which is characterized by a high surface area and contributes to adsorption of a greater amount of ions and a high binding energy.

The results in table 2 show the effect of the salt composition on the values of k, as the values of the constant at a temperature of 25 °C ranged between -100x10^{-6} to -1089x10^{-6} mol^2 kJ^{-2} in the Dohuk and Sulaymaniyah soils sequentially under NaCl solution conditions and rose between -67 x10^{-6} to -1020x10^{-6} mol^2 kJ^{-2} in Dohuk and Sulaymaniyah soil under conditions of $CaCl_2$ solution, while at a temperature of 45 C° the values ranged between -71 x10-6 to -814x10^{-6} mol^2 kJ^{-2} in the Dohuk and Qadisiyah in NaCl solution increased between -54 x 6-6 to -566 x 10^{-6} mol^2 kJ^{-2} in Duhok and Sulaymaniyah soil alternately under $CaCl_2$ salt conditions. This rise in k values under $CaCl_2$ solution conditions may be due to the effect of the solutions containing sodium ions which increase the solubility of the products of decomposition of organic matter (Bohn *et al*., 2001) and carbonate minerals which is consistent with what Yassin and Fakhir (2016) found in a study of adsorption of Copper. The adsorption energy ranged from -200 x 10^{-5} to -650 x 10^{-5} under $CaCl_2$ salt conditions and from -300 x 10^{-5} to -780 x 10^{-5} under NaCl salt conditions.

As for the effect of temperature, it is observed from the results of Table 2 that the values of k under the conditions of NaCl solution ranged between -100x10^{-6} to -1089x10^{-6} mol^2 kJ^{2-} in Duhok and Sulaymaniyah soil alternately at a temperature of 25 C° and increase to -71 x10^{-6} to -814 x 10^{-6} mol^2 kJ^{2-} in the Dohuk and Qadisiyah soil sequentially at a temperature of 45 C°, but under the conditions of $CaCl_2$ solution the values ranged between -67 x 10^{-6} to -1020 x 10^{-6} mol^2 kJ^{2-} in the Soil of Duhok and Sulaymaniyah sequentially and increase from -54 x10^{-6} to -566 x10^{-6} mol^2 kJ^{2-} in the Duhok and Sulaymaniyah soil alternately at a temperature of 45 C°, this rise in the values of k under adsorption conditions at a temperature of 45 C° it may be attributed to the increase in the kinetic energy of the adsorbed particles, which leads to its further spread and its ability to enter the solid phase pores in addition to activating the number of effective interchangeable sites

The value of E expresses the rate of activation energy or the free energy of the reaction, that is, the amount of force needed to overcome the adsorption force, as it ranged at a temperature of 25 C° between 21.52 to 70.71 kJ mol^{-1} in the Sulaymaniyah and Dohuk soils alternately under NaCl salt conditions and between 22.14 to 86.39 kJ mol^{-1} in the Sulaymaniyah and Dohuk soil sequentially under the conditions of $CaCl_2$ solution, while at a temperature of 45 C° it ranged between 27.12 to 83.92 kJ mol^{-1} in the Babylon and Dohuk soil sequentially under NaCl salt conditions and between 29.88 to 95.34 kJ mol^{-1} in the Sulaymaniyah and Duhok soils, alternately, the high activation energy values in the Duhok soils confirm what was obtained energy and maximum adsorption capacity of high adsorption of these soils (Table 2).

It is noted from the results of Table 2 that the activation energy values in both temperatures ranged between 21.52 to 83.92 kJ mol^{-1} in NaCl solution and increased between 22.14 to 95.34 kJ mol $^{-1}$ under the conditions of $CaCl_2$ solution, and this may be due to additional precipitation of Carbonate minerals (Calcite) because of the increase in the influence of the common ion (Ali and Al- Kaysi, 2011), this sedimentation probably worked to increase the binding energy, this is consistent with Yassin and Fakher (2016) in their study of Copper adsorption in some calcareous soils.

The results indicate that the rise in temperature had an effect in increasing the values of activation energy, as it ranged at a temperature of 25 C° and by using both salt between 21.52 to 86.39 kJ mol^{-1} and increased between 27.52 to 95.34 kJ mol^{-1} at a temperature of 45 C°. increased adsorption efficiency with increasing temperature from 25 C° to 45 C° which may be due to an increase in the adsorption velocity coefficient due to the increased kinetic energy of the adsorbed particles and consequently an increase in their diffusion speed and their ability to enter solid phase pores, this results consistent with the study of Roth *et al.,* (2012), who shows increase in activation energy values with higher temperature in their study of effect the temperature (10 C°, 20 C° and 30 C°) the adsorption of Cadmium in different soils.

Knowing the range of activation energy values is useful in determining the mechanisms of the adsorption process, as Tran *et al*., (2016) mentioned that the activation energy values if they are less than 8 kJ mol^{-1} then the physical adsorption in its nature and if it is within the range of ion exchange energy 8-16 kJ mol^{-1}, it is subject to the concept of ion exchange, but if the values are higher than 16 kJ mol $^{-1}$, it indicates that the adsorption process is of the chemical type (chemical adsorption), and since the results of the study in Table 2 ranged between 21.52 - 95.34 KJ^{-1} in the two temperatures and under the conditions of the salt, this indicates that the adsorption process may be subject to the mechanism of chemical adsorption (chemisorption).

Thermodynamic process

In order to study the effect of temperature on Cadmium adsorption, it is necessary to adopt some basic concepts in thermodynamic to understand the behavior of Cadmium and to know the properties and direction of the chemical reaction. The value of Gibbs free energy expresses the amount of change in free energy resulting from the transport of the element from the solution to the double electrode region (Karak *et al*., 2011).

The results of tables 3 and 4 show that the free energy values for the thermodynamic equilibrium state at a temperature of 25 C° ranged between -3.577 to -9.245 kJ mol^{-1} in the presence of NaCl salt and -4.152 to -9.770 kJ mol^{-1} in the presence of $CaCl_2$ salt in sequentially, either at a high temperature to 45 C°. Values ranged from -4.771 to -10.342 kJ mol^{-1} in the presence of NaCl and -5.549 to -10.655 kJ mol^{-1} of the $CaCl_2$ salt sequentially.

Results of Tables 3 and 4 show the free energy values for the state of thermodynamic equilibrium, which ranged using NaCl salt between 3.603 - kJ mol $^{-1}$ in Sulaymaniyah soil to -9.245 kJ mol $^{-1}$ in Duhok soil at a temperature of 25 C° and between - 4.771 kJ mol^{-1} In Sulaymaniyah soil to -10.342 kJ mol $^{-1}$ in Duhok soil at a temperature of 45 C°, and using $CaCl_2$ salt the values ranged between-4.152 in Sulaymaniyah soil to -9.770 in the Duhok soil at a temperature of 25 C° and between 5,549 kJ $^{-1}$ in Sulaymaniyah soil to -10.655 kJ mol^{-1} in Duhok soil at a temperature of 45 C°, the rise of negative value of standard free energy in Dahuk soil compared to the Sulaymaniyah soil is due to the high values of its thermodynamic equilibrium constant , which depends on the amount of the adsorbed element S_e in soil, and since the Dahuk soil has a high adsorption capacity due to the high values of the CEC and the content of clay minutes and organic matter which reached 27.33 Cmole + kg^{-1} and 320 gm kg^{-1} and 14.00 gm kg^{-1} in sequentially compared to the Sulaymaniyah soil 15.40 Cmole+kg^{-1} and 80.0 gm kg^{-1} and 10.50 gm kg^{-1} sequentially (Table 1) which is consistent with what they found by Yousra *et al.* (2019) in their study of adsorption of Cadmium in different Pakistani soil, as they found that the highest negative value of ΔG° - 15.31 were in the soil of the city of Kotli which has high exchange capacity and high content of clay minutes and organic matter compared to the rest of the soils study.

Table 3 : Thermodynamic indicators of Cadmium adsorption in the presence of NaCl 0.01M solution.

N	Locations	K_t°		ΔG° KJ mol^{-1}		ΔH° KJ mol^{-1}	ΔS° J mol^{-1}	
		25 C°	45 C°	25 C°	45 C°		**25** C°	45 C°
1	Duhok /Darestan	41.735	49.982	-9.245	-10.342	7.139	54.979	54.971
2	Erbil / Thurak	8.307	10.222	-5.245	-6.146	8.212	45.158	45.150
3	Sulaymaniyah / Dokan	4.282	6.077	-3.603	-4.771	13.862	58.610	58.595
4	Baghdad / Abi Gharib	18.518	21.476	-7.231	-8.109	5.867	44.808	43.950
5	Najaf / Al-Mishkhab	28.907	36.337	-8.335	-9.499	9.056	58.360	58.350
6	Babylon / The Nakhila	4.605	6.300	-3.784	-4.866	12.404	54.322	54.309
7	Qadisiyah / Sumer	4.775	6.474	-4.344	-4.938	12.054	55.029	53.435
8	Wasit / Hayy	10.485	11.945	-5.822	-6.558	5.161	39.227	38.852
9	Dhi Qar / Al-Shatrah	6.533	10.070	-4.650	-6.106	8.366	43.678	45.510
10	Maysan / Al-Mazbaniyah	20.732	22.809	-7.511	-8.268	3.780	37.890	37.886

Table 4 : Thermodynamic indicators of Cadmium adsorption in the presence of $CaCl_2$ 0.01M solution.

N	Locations	K_t°		ΔG° KJ mol^{-1}		ΔH° KJ mol^{-1}	ΔS° J mol^{-1}	
		25 C°	45 **C°**	25 C°	45 C°		**25** C°	45 **C°**
1	Duhok /Darestan	51.593	56.271	-9.770	-10.655	3.436	44.316	44.313
2	Erbil / Thurak	13.125	15.152	-6.379	-7.186	5.686	40.484	40.478
3	Sulaymaniyah / Dokan	5.343	8.157	-4.152	-5.549	16.750	70.143	70.125
4	Baghdad / Abi Gharib	27.546	27.546	-8.479	-8.767	4.221	42.621	41.970
5	Najaf / Al-Mishkhab	44.226	47.690	-9.390	-10.218	2.950	41.410	41.407
6	Babylon / The Nakhila	7.918	10.507	-5.126	-6.218	11.199	54.786	54.774
7	Qadisiyah / Sumer	9.821	14.700	-5.660	-7.106	15.968	72.577	72.560
8	Wasit / Hayy	12.336	16.401	-6.225	-7.396	11.276	58.729	58.717
9	Dhi Qar / Al-Shatrah	10.528	14.478	-5.832	-7.066	12.613	61.898	61.884
10	Maysan / Al-Mazbaniyah	24.630	25.450	-7.938	-8.557	1.297	30.989	30.987

The results of tables 3 and 4 show the effect of the type of saline composition on the free energy values of the thermodynamic equilibrium state ΔG°, as the values ranged between -3.603 to -9.245 kJ^{-1} using NaCl and increased between -4.152 to -9.770 kJ^{-1} using salt $CaCl_2$ at a temperature of 25 C°, and at a temperature of 45 C° it ranged between -4.771 to -10.342 kJ mol^{-1} using NaCl salt and increased between -5.549 to -10.655 kJ^{-1} using $CaCl_2$ salt, and this may be due to the increasing of values Thermodynamic equilibrium as a result of higher adsorbed amount of Cadmium under $CaCl_2$ salt conditions compared to NaCl salt and this is consistent with Yassin and Fakhir (2016) in a study for adsorption of Copper in some Iraqi calcareous soils.

The results shown in Tables 3 and 4 indicate that all the free energy values of the equilibrium solution were negative, which indicates that the adsorption of Cadmium on adsorption sites is an Spontaneous reaction by nature, that is, it does not require energy from outside the system, a high degree Heat up to 45 C° to a decrease in free energy (an increase in negativity) for Cadmium adsorption, that is, there is an increase in the spontaneous of the reaction with the rise in temperature, this my be due to the high equilibrium temperature which lead to soil proportion by thermal energy lowers free energy remaining in the solution, and this is consistent with Al- Jumaili (2015) The study of indicators thermodynamic adsorption of Zinc in some soils of northern Iraq, and what they have reached Yousra *et al.* (2019) in their study of the adsorption of Cadmium in some Pakistani soil. The enthalpy is an indication of the amount of heat released or absorbed during the Cadmium adsorption process that occurs in the soil system.

The change in the heat capacity of the adsorption process is a measure of the reaction temperature. It is noted from the results in tables 3 and 4 that the values of ΔH° was positive for all study soils, indicating that the interaction of Cadmium adsorption on the adsorption surface is of a endothermic nature. The thermal content ranged between 3.780 kJ mol^{-1} in Maysan soil to 13.862 kJ mol^{-1} in the Sulaymaniyah soil in solution. NaCl and between 1.297 kJ mol^{-1} in Maysan soil to 16.750 kJ mol^{-1} in Sulaymaniyah soil in $CaCl_2$ solution, these values of enthalpy content may indicate that the adsorption mechanism did not change with the temperature change but the amount of adsorption changed with the change of thermal energy, and that heat absorbing nature shows that adsorption processes are highly unstable, according to Hosseinpur and Dandanmozd (2010). These results are consistent with Hlihor *et al*. (2010) found of a reaction with an endothermic nature. The heat content values ranged between 23.95 - 41.65 kJ mol $^{-1}$ in their study of thermodynamic parameters of Cadmium in the soils of the Roman city of Iasi, and Wang *et al* (2013) who found of endothermic reaction with values ranging between 13.18 to 40.16 kJ mol^{-1} in their study of adsorption of Cadmium in some soils in southeastern China, and the findings of Al-Jumaili (2015) of values ranged from 12.776 kJ mol $^{-1}$ to 20.1662 kJ mol^{-1} and that the reaction is endothermic in his study of Zinc adsorption in some soils in northern Iraq.

It is noted from Tables 3 and 4 that the entropy values of ranged between 30.987 and 72.577 J mol^{-1}, and these results indicate that all values were positive, which indicates an increase in the randomness of the surface interference of the solid and liquid phase during the adsorption process, and also the surface reflectance of the adsorption the Cadmium ion (Abo Mesalam, 2003) and that the positive values for the entropy ranged using NaCl solution between 37.890 J mol^{-1} in Maysan soil to 58.10 J mol^{-1} in the Sulaymaniyah soil at a temperature of 25 C° and between 37.886 J mol^{-1} in Maysan soil to 58.595 J mol^{-1} in the Sulaymaniyah soil at a temperature of 45 C°, and ranged using $CaCl_2$ solution between 30.989 J mol^{-1} in Maysan soil to 72.577 J mol^{-1} in Al Qadisiyah soil at a temperature of 25 C° and between 30.987 J mol^{-1} in Maysan soil to 72.560 J mol^{-1} in Al Qadisiyah soil at a temperature of 45 C^{o}, the low values of ΔS° in Maysan soil may be due to an increase in the value of the reciprocal capacity that amounted to 29.80 Cmole+kg^{-1} compared to the Sulaymaniyah and Qadisiyah soil 15.40 and 18.40 Cmole+kg^{-1} consecutively , as randomness decreases with increasing adsorption and the bonding of ions with surfaces.

It is noted from tables 3 and 4 that the entropy values for all soils at a temperature of 45 C° are lower compared to the values at a temperature of 25 C°. As the values using NaCl solution ranged between 37.890 J mol^{-1} in the Sulaymaniyah soil to 58.10 J mol^{-1} in soil of Maysan at a temperature of 25 C° and decreased between 37.886 J mol^{-1} in Sulaymaniyah soil to 58.595 J mol^{-1} in Maysan soil at a temperature of 45 C°, and ranged using $CaCl_2$ solution between 30,989 J mol^{-1} in Maysan soil to 72.577 J mol^{-1} in Qadisiyah soil at a temperature of 25 C° and between 30.987 J mol^{-1} in Maysan soil to 72.560 J mol^{-1} in Qadisiyah soil at a temperature of 45 C°, which may be due to Adsorption ions become constrained by their association with the surface and the randomness of the system decreases, these results for randomness values came similar to results of Yassin and Fakhir (2017) in their study of thermodynamic parameters for Copper adsorption in some calcareous Iraqi soil, who found that randomness values were positive, that indicates Until the adsorption reaction is a non-reverse reaction as mentioned by (Roth *et al.,* 2012).

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