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THE EFFECT OF TEMPERATURE ON CADMIUM ADSORPTION AND DESORPTION IN SOME IRAQI CALCAREOUS SOILS

Mohammed Malik Hamid* and Kadhim Makke Naser
Department of Soil Science Engineering Science College of Agriculture, University of Baghdad, Iraq
*Corresponding author Email: mmhhmalz1@yahoo.com

Abstract

To study the effect of temperature on Cadmium adsorption and desorption in soils, 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 salt under 25 ± 1 C° and 45± 1 C° with three replications, the thermodynamic equilibrium concepts of adsorption equations Langmuir and Freundlich were tested, from the slope values of the equation for both processes the desorption coefficient of the adsorbed Cadmium was calculated. The results showed that the adsorbed amount of Cadmium increased with increasing concentrations in added solutions, and that the Langmuir equation surpassed the Freundlich equation in giving the best description of adsorption and desorption of Cadmium according to the values of the determining factor (R^2), and from the binding energy values we find that the energy needed to desorption Cadmium is higher from the adsorption energy, the values of the desorption index (DI) indicate that the Cadmium adsorption reactions in these soils are irreversible, and that they suffer from the phenomenon of non-recovery of adsorbed quantities of Cadmium, which is called Hysteresis.
***Keywords*:** Temperature, Cadmium Adsorption, Desorptio.

Introduction

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 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), 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 related to isotherms can provide important information on the extent of pollutants' excellence in 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, the most widely used equations in describing adsorption processes in the soil are the Freundlich and Langmuir equations.

Based on the foregoing, it includes the objectives of studying the excellence and desorption of Cadmium using isothermic adsorption curves.

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/Dastan, 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.

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

Location	$EC_{1:1}$ dSm^{-1}	$pH_{1:1}$	CEC $Cmol+kg^{-1}$	OM	Carbonate minerals	oxide	total Cd^{+2}	available Cd^{+2}	soil Particles Clay	Silt	Clay	Soil texture
				gm kg^{-1}								
Duhok /Darestan	1.25	7.99	27.33	14.00	250.3	8.19	2.005	0.185	320	244	436	Clay loam
Erbil / Thurak	0.81	8.07	16.05	12.80	225.9	5.35	2.089	0.248	100	379	521	Sandy loam
Sulaymaniyah / Dokan	0.68	7.08	15.40	10.50	189.2	6.16	1.653	0.173	80.0	380	540	Sandy loam
Baghdad / Abi Gharib	2.60	7.87	25.53	8.80	264.7	3.49	1.886	0.250	348	451	201	Clay loam Silty
Najaf / Al-Mishkhab	2.14	7.89	26.90	11.40	298.4	4.18	1.862	0.235	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	0.188	130	576	294	Silt loam
Wasit / Hayy	2.10	7.86	21.05	6.80	260.9	3.71	1.732	0.160	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	0.181	387	373	240	Clay loam

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 was 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 in equilibrium solution was estimated using the Atomic Absorption Spectrophotometer. 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 equilibrium solution 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).

Langmuir Equation

Langmuir isotherm is applied to the data of Cadmium ions and uses the formula in the following linear mathematical form Langmuir (1918).

$$C / X = 1/k\, X_{max} + C / X_{max} \quad \text{….(linear equation)}$$

X: the amount of Cadmium adsorbed (µg gm^{-1}).

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

X_{max}: the maximum adsorption capacity (µg gm^{-1}).

k: binding energy coefficient in soil unit (ml µg^{-1}).

To obtain the values of the constants of this equation, it requires converting them into a straight line equation by taking the natural algorithm of both sides of the equation according to the following:-

Freundlich Equation

Freundlich equation is applied to the data of Cadmium ions and the linear equation is used as follows: Freundlich (1906).

c….(linear equation) Ln X=Ln a +1/n Ln

µg g^{-1} (X: adsorbed Cadmium concentration)

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

a,n : the equation constants represent adsorption capacity (µg g^{-1}) and adsorption energy (ml µg^{-1}).

The desorption index (DI) was calculated from the desorption slope to the adsorption slope according to Marazadori *et al*., (1991).

$$DI = K_d / K_a$$

DI: desorption index.

K_d: slope of desorption.

K_a: slope of adsorption.

Results and Discussion

To study and describe the process of adsorption and desorption of Cadmium in some of Iraqi calcareous soils, the equations Langmuir and Freundlich were tested, as the values of the coefficient of determination (R^2) were obtained to describe the nature of the adsorption of Cadmium in soils by calculating the parameters of these equations (tables 2) and this it means the success of the two equations in describing the adsorption of Cadmium , and it appears from the results of the table 2 can adopting the Langmuir equation to describe adsorption of Cadmium of the soils and its using in describing the desorption of Cadmium, as this equation got the highest values to determination coefficient in describing the nature of Cadmium adsorption was that the mean of the R^2 was 0.96 and 0.97 using NaCl and $CaCl_2$ at a temperature of 25 C°, and 0.97 and 0.95 using NaCl and $CaCl_2$ sequentially at a temperature of 45 C° at a rate of 0.96, compared to the Freundlich equation that gave an average of R^2 values 0.90 and 0.92 in the NaCl and $CaCl_2$ solution sequentially at a temperature 25 C° and 0.91 and 0.90 using NaCl and $CaCl_2$ solution sequentially at a temperature 45 C° and a general rate 0.91, which means the advantage of the Langmuir equation in describing the isothermic adsorption and this is consistent with Esfandbod *et al*., (2010) in their study of Cadmium adsorption in Iran northern soils**.**

Table 2 : values for the Langmuir equation for the Cadmium adsorption in the study soil at 25 C° and 45 C°.

Locations	NaCl (0.01 M)				$CaCl_2$ (0.01 M)			
	X_m µg g^{-1}	k ml $µg^{-1}$	MBC ml g^{-1}	R^2	x_m µg g^{-1}	k ml $µg^{-1}$	MBC ml g^{-1}	R^2
C°25								
Duhok /Darestan	1111.11	0.037	41.32	0.99	1250.00	0.036	44.44	0.97
Erbil / Thurak	909.09	0.011	10.28	0.92	1000.00	0.015	15.24	0.97
Sulaymaniyah / Dokan	588.24	0.011	6.18	0.95	666.67	0.011	7.58	0.98
Baghdad / Abi Gharib	1000.00	0.020	20.33	0.99	1000.00	0.032	31.95	0.99
Najaf / Al-Mishkhab	1000.00	0.035	35.21	0.99	1000.00	0.048	47.62	0.99
Babylon / Al-Nakhila	588.24	0.010	5.77	0.93	625.00	0.014	8.94	0.96
Qadisiyah / Sumer	769.23	0.006	4.72	0.94	833.33	0.009	7.13	0.89
Wasit / Hayy	909.09	0.013	11.75	0.96	1000.00	0.015	14.60	0.95
Dhi Qar / Al-Shatrah	666.67	0.011	7.36	0.94	769.23	0.014	10.81	0.98
Maysan / Al-Mazbaniyah	909.09	0.024	21.51	0.98	1111.11	0.027	30.12	0.98
C°45								
Duhok /Darestan	1250.00	0.038	47.39	0.99	1428.57	0.034	48.08	0.97
Erbil / Thurak	909.09	0.015	13.7	0.95	1000.00	0.020	20.49	0.96
Sulaymaniyah / Dokan	625.00	0.011	6.87	0.98	714.29	0.012	8.25	0.96
Baghdad / Abi Gharib	1000.00	0.026	25.71	0.99	1111.11	0.034	38.02	0.99
Najaf / Al-Mishkhab	1000.00	0.043	43.10	0.99	1111.11	0.048	53.48	0.99
Babylon / Al-Nakhila	625.00	0.010	6.41	0.99	666.66	0.019	12.08	0.93
Qadisiyah / Sumer	833.33	0.007	6.19	0.95	833.33	0.012	9.39	0.86
Wasit / Hayy	1111.11	0.012	13.09	0.97	1250.00	0.015	18.45	0.96
Dhi Qar / Al-Shatrah	769.23	0.013	9.91	0.99	833.33	0.018	14.60	0.92
Maysan / Al-Mazbaniyah	1111.11	0.023	25.13	0.99	1250.00	0.025	31.75	0.98

Langmuir Isotherm

The result in table 2 shows the values of the Langmuir equation for the adsorption and desorption of Cadmium equation, which are the maximum adsorption capacity (X_{max}), binding energy (k), and the Maximum Buffering Capacity (MBC), the results shows that the values of X_{max} Cadmium adsorption ranged at a temperature 25 C° between 588.24 µg g^{-1} in the Sulaymaniyah and Qadisiyah soils to 1111.11 µg g^{-1} in Duhok soil using NaCl salt and between 625.00 µg g^{-1} in the Qadisiyah soil to 1250.00 µg g^{-1} in Duhok soil using $CaCl_2$ salt, either at a temperature 45 C° values ranged between 625.00 µg g^{-1} in Sulaymaniyah and Qadisiyah soil to 1250.00 µg g^{-1} in Dohuk soil using NaCl salt and between 666.66 µg g^{-1} in the Qadisiyah soil to 1428.57 µg g^{-1} in the Dohuk soil using $CaCl_2$, which indicates that the highest values of X_m were observed in the Duhok soil and this may be due to the higher soil content of oxides 8.19 Cmole + kg^{-1} (Table 1), which gave a greater opportunity to adsorb a greater amount of Iron ions as impurities on the surfaces of Carbonate minerals (Calcite) This presence of adsorbed or precipitate iron on the surfaces of carbonate minerals may contribute to an increase in the number of active sites, which is consistent to Pokrovsky and Schott (2002) who notice that the adsorption of cations on the surface of carbonate minerals at neutral and alkaline reaction levels is in the form of > $MeOH_2^+$ which can be associated with adsorbed or precipitate Iron on the surfaces of Carbonate minerals, as for the effect of saline composition on the maximum adsorption capacity, it is noted that the values of X_m ranged using NaCl salt between 588.24 - 1111.11 µg g^{-1} and increase between 625.00-1250.00 µg g^{-1} using $CaCl_2$, and at a temperature of 45 C° it ranged using NaCl between 625.00 - 1250.00 µg g^{-1} and increased between 666.66 - 1428.57 µg g^{-1} using $CaCl_2$, the high X_m values using $CaCl_2$ salt may be attributed to the increase in the concentration of Sodium ions using NaCl solution will increase the thickness of the electric double layer compared to the conditions of Calcium Chloride (Bohn *et al*., 2001 ; Ali and Al-Qaisi, 2011), which reduce the adsorption capacity of Cadmium on the surface Colloids, and increasing the ionic concentration of Calcium in the equilibrium solution will reduce Calcite solubility by the effect of the combined ion on solubility (Mendham *et al*., 2000).

The results of table 2 indicate a rise in the values of the maximum adsorption capacity when the temperature increase from 25 C° to 45 C°, it ranged using NaCl between 588.24 - 1111.11 µg g^{-1} at a temperature of 25 C° and increase between 625.00-1250.00 µg g^{-1} at a temperature of 45 C°, and using $CaCl_2$ salt ranged between 625.00 - 1250.00 µg g^{-1} at a temperature of 25 C ° and increase between 714.29 - 1428.57 µg g^{-1} at a temperature of 45 C°, and this may be due the increase in temperature to an increase the kinetic energy of the ions and increasing their diffusion speed and their ability to enter solid phase pores in addition to activating of sites a interchangeable on the surfaces of adsorption and thus increasing the quantity adsorbent of Cadmium increasing the temperature, and this is consistent with Li and others (2015) in their study of thermodynamic adsorption Copper in China northeast soils, who found increase X_{max} value with increasing temperature. the results in table 2 shows that values of the constant k which is a measure of the binding energy, at a temperature of 25 C° ranged between 0.006 µg g^{-1} in Babel soil to 0.037 µg g^{-1} in Duhok soil using NaCl solution and between 0.009 µg g^{-1} in Babel soil to 0.048 µg g^{-1} in Najaf soil using $CaCl_2$ solution, at a temperature of 45 C° the values ranged between 0.007 in Babel soil to 0.043 µg g^{-1} in Najaf soil in NaCl solution and between 0.012 µg g^{-1} in soil Babil and Sulaymaniyah to 0.048 µg g^{-1} in Najaf soil in $CaCl_2$ solution, the superiority of Duhok soil in giving the highest value of the binding energy may be attributed to know the content of organic matter and oxides with carbonate minerals, which is characterized by a high surface area and contributes to adsorption of a greater amount of ions and a high binding energy. as for the Najaf soil its superiority may be attributed to the high content of organic matter compared to the soil of other central and southern regions which amounted to 11.40 g kg $^{-1}$ (Table 1).

The results in table 2 show the effect of saline composition on the values of k, as the values of the constant at a temperature of 25 C° ranged between 0.006 - 0.037 ml µg^{-1} in Babel and Duhok soils sequentially using NaCl solution and increased between 0.009 - 0.048 ml µg^{-1} in the soils of Babel and Najaf using $CaCl_2$ solution, at a temperature of 45 C°, the values ranged between 0.007-0.043 ml µg^{-1} in Babel and Najaf soil using NaCl solution and increased to 0.048 ml µg^{-1} in the Najaf soil. The increase in k values using $CaCl_2$ solution may be due to an additional precipitation of more Carbonate (calcite) minerals due to the increase in the co-ion effect and consequently an increase in bonding energy compared to Sodium ions using NaCl solution, which can reduce the stability of this mineral in equilibrium conditions according to the principle of hetero-ion effect (Christian, 2004). as for the effect of temperature, the results of table 2 that the values of k using NaCl solution ranged between 0.006-0.037 ml µg^{-1} in Babel and Duhok soil sequentially and increased to 0.007-0.043 ml µg^{-1} in Babel and Najaf soil sequentially, either using $CaCl_2$ solution values ranged between 0.009-0.048 ml µg^{-1} in the soil of Babel and Najaf consequently and increase to 0.012-0.048 ml µg^{-1} in Babel and Sulaymaniyah soil and Najaf soil consequently, that this rise in the values of k in the adsorption conditions at a temperature of 45 C° may be attributed to increase the kinetic energy of the adsorbed ions and ability to enter phase pores to activate a solid addition to active of exchange sites.

Maximum Buffering Capacity (MBC) values were calculated through the equation constants of Langmuir X_m and k, as their value in the study soils ranged between 4.72 ml g^{-1} in Babel soil to 41.32 ml g^{-1} in Duhok soil using NaCl solution, and between 7.13 ml g^{-1} in Babel soil to 47.62 ml g^{-1} in Najaf soil using $CaCl_2$ at a temperature 25 C°, while at a temperature 45 C° it ranged between 6.19 ml g^{-1} in Babel soil to 47.39 ml g^{-1} in Dohuk soil using NaCl solution, and between 8.25 ml g^{-1} in Sulaymaniyah soil to 53.48 ml g^{-1} in Najaf soil using $CaCl_2$ solution, this may be due to the superiority of the Dohuk and Najaf soil in the content of clay content and CEC comparison to the soil of Babel and Sulaymaniyah soil.

Table 3 shows effect of salt composition and temperature on MBC values ,which ranged in NaCl solution in both temperatures 25 C° and 45 C° between 4.72 - 47.39 ml g^{-1} and using $CaCl_2$ salt ranged between 7.13-53.48 ml g^{-1} , The superiority of $CaCl_2$ salt is due to the high values of X_m obtained in the presence of $CaCl_2$ salt compared to the NaCl salt and with different temperatures, also MBC value in both salts at a temperature of 25 C° ranged between 4.72 - 47.62 ml g^{-1} and at a temperature of 45 C° between 6.19 - 53.48 ml g^{-1}, and this indicates the superiority of the temperature of 45 C° in the values of MBC, which follows the general direction of the values of X_m and k because the values of the MBC of cadmium are the Outcome of these constants values. in general, the values of the MBC may be somewhat low, and the decrease in the values of the MBC of the cadmium may indicate that the movement of the Cadmium is less restrictive.

Table 3 : values of the constants of the freundlich equation for the adsorption of Cadmium in study soils at 25 C° and 45 C°.

Location	NaCl (0.01 M)			$CaCl_2$ (0.01 M)		
	a (µg g^{-1})	N (ml µg^{-1})	R^2	a (µg g^{-1})	n (ml µg^{-1})	R^2
25 C°						
Duhok -Darestan	115.90	2.371	0.90	128.43	2.339	0.94
Erbil - Thurak	21.370	1.505	0.89	37.23	1.696	0.90
Sulaymaniyah-Dokan	22.469	1.403	0.96	23.80	1.751	0.95
Baghdad- Abi Gharib	53.50	1.433	0.91	60.06	2.269	0.85
Najaf - Al-Mishkhab	92.55	2.206	0.81	126.18	2.455	0.85
Babylon – Al-Nikhela	10.820	1.492	0.95	25.28	1.752	0.98
Qadisiyah - Sumer	18.650	1.727	0.93	35.77	2.054	0.94
Wasit- Al-Haye	29.020	1.631	0.90	33.22	1.616	0.89
Dhi Qar - Al-Shatrah	18.570	1.603	0.89	32.65	1.813	0.95
Maysan-Mazbaniyah	65.96	2.087	0.91	68.80	1.866	0.90
45 C°						
Duhok -Darestan	129.89	2.429	0.92	130.60	2.243	0.95
Erbil - Thurak	31.34	1.656	0.83	49.00	1.798	0.84
Sulaymaniyah-Dokan	22.69	1.787	0.95	25.89	1.775	0.95
Baghdad- Abi Gharib	63.67	1.926	0.90	58.43	2.121	0.86
Najaf - Al-Mishkhab	113.18	2.379	0.79	129.27	2.425	0.86
Babylon – Al-Nikhela	17.41	1.571	0.97	36.29	1.909	0.94
Qadisiyah - Sumer	20.22	1.723	0.91	24.42	1.732	0.94
Wasit- Al-Haye	31.05	1.605	0.92	42.55	1.635	0.89
Dhi Qar - Al-Shatrah	28.78	1.745	0.97	48.40	1.970	0.92
Maysan-Mazbaniyah	64.23	1.908	0.93	70.50	1.844	0.89

Table 3 shows the values of the constants of the equation a and n, the values of the constant a, which indicates to Cadmium adsorption capacity, ranged in the soil study at a temperature of 25 C° between 10.82 g kg^{-1} in Babel soil to 115.90 g kg^{-1} in Dahuk soil using NaCl salt, while using $CaCl_2$ salt reached 23.80 g kg^{-1} in Sulaymaniyah soil to 128.43 g kg^{-1} in Dahuk soil, either at a temperature of 45 C° ranged from 17.41 g kg^{-1} in Babel soil to 129.89 g kg^{-1} in Dahuk soil using NaCl salt, and ranged between 25.89 g kg^{-1} in Sulaymaniyah soil to 130.60 g kg^{-1} in Duhok soil using $CaCl_2$ salt, this results indicate that the highest adsorption capacity values were observed in Duhok soil and this may be due to the high soil content of oxides 8.19 g kg^{-1} and also the clay content, organic matter and CEC, as they are Important parts responsible for adsorption (Dahiya *et al.*, 2005).

The results in table 3 show the effect of the salt composition on a constant values, as the constant values at a temperature 25 C° ranged between 10.820-115.90 µg g^{-1} in Babel and Duhok soil sequentially using NaCl solution and the values for freundlich equation increase between 23.80 - 128.43 µg g^{-1} in Wasit and Najaf soil using $CaCl_2$ solution at a temperature of 45C°, the values ranged between 17.41-129.89 µg g^{-1} in Wasit and Duhok soil sequentially using NaCl solution and the values increased to 24.42 - 130.60 µg g^{-1} in the Qadisiyah soil and Duhok using $CaCl_2$ solution, and this shows the high adsorption capacity values using $CaCl_2$ salt compared to NaCl salt and this may be attributed to the role of $CaCl_2$ salt in the precipitation of carbonate metals and thus increase the adsorption capacity on their surfaces, the results indicate an increase in the adsorption capacity values when the temperature increase from 25 C° to 45 C°. it ranged between 10.82 - 115.90 µg g^{-1} and 23.80 - 128.43 µg g^{-1}using of the NaCl and $CaCl_2$ sequentially at a temperature 25 C°, and the values increased when rose the temperature to 45 C°and ranged between17.41-129.89 µg g^{-1} and 24.42-130.60 µg g^{-1} using NaCl and $CaCl_2$ sequentially, this may be attributed to the increased activation of the number of effective interchangeable sites on surfaces adsorption and thus the adsorbed amount of Cadmium increases with increasing temperature, and this is consistent with Hlihor *et al.*(2010) who found in their study of thermodynamic Cadmium adsorption, increase of adsorption capacity from 1.271 µg g^{-1} to 1.979 µg g^{-1} with increase temperature from 21C°to 41C°.

The results in table 3 show the values of the constant n, which indicates adsorption intensity, which ranged from 1.403 to 2.371 ml µg^{-1} in Sulaymaniyah soil and Duhok sequentially using NaCl, and between 1.616 to 2.455 ml µg^{-1} in Sulaymaniyah soil and Najaf sequentially using $CaCl_2$ at a temperature of 25 C°, between 1.571 to 2.429 ml µg^{-1} in Sulaymaniyah soil and Duhok sequentially using NaCl, and between 1.635 to 2.425 ml µg^{-1} in Wasit soil and Najaf sequentially using $CaCl_2$ at a temperature of 45 C°, and this variation between regions may be due to the difference in the soil content of the clay, as well as the variation in the CEC, as Dohuk and Najaf soils have higher adsorption capacity values compared to the Sulaymaniyah and Wasit soils with low adsorption amplitude values in their content of clay, organic matter and CEC, which amounted to 320 g kg^{-1} 14.00 g kg^{-1} and 27.33 Cmol+ kg^{-1} sequentially in the Dohuk soil, 353 g kg^{-1}, 11.40 g kg^{-1} and 26.90 Cmol+kg^{-1} sequentially in Najaf soil, 80 g kg^{-1}, 10.50 g kg^{-1} and 15.40 Cmol+kg^{-1} sequentially In Sulaymaniyah soil, 252 gm kg^{-1}, 6.80 gm kg^{-1} and 21.05 Cmol+kg^{-1}, in Wasit soil. The results in table 3 show the effect of the salt composition on the adsorption density values, as the constant values at a temperature 25 C° ranged between 1.403-2.371 ml µg^{-1} in Sulaymaniyah and Duhok soil sequentially using NaCl solution and the values increased between 1.616 - 2.455 ml µg^{-1} in Wasit and Najaf soil using $CaCl_2$ solution. At a temperature of 45 C°, the values ranged between 1.571- 2.429 ml µg^{-1} in Sulaymaniyah and Duhok soil sequentially using NaCl solution and the values increased to 1.635 - 2.425 ml µg^{-1} in Wasit and Najaf soil using $CaCl_2$ solution, this indicates an increase in the adsorption density values using $CaCl_2$ salt compared to NaCl salt. This may be due to the effect of Calcium Chloride salt on the precipitation of carbonate minerals (Calcite) by the effect of the common ion, as the highest values were found in $CaCl_2$ salt conditions in Najaf soil containing a higher amount of carbonate minerals compared to the Duhok soil 298.4 and 250.3 gm kg^{-1} sequentially. as the effect of temperature, observed from the results that n values at the temperature of 25C° and using both salt ranged between 1.403 - 2.455 ml µg^{-1} in the Sulaymaniyah and Najaf soil sequentially and increased at a temperature of 45 C ° between 1.571 - 2.429 ml µg^{-1} in Sulaymaniyah and Najaf soil, and this may be due to the increased activation of the number of effective sites by increasing the temperature, which is consistent with Hlihor *et al.* (2010) in their study of Cadmium adsorption thermodynamics, as they reached a high adsorption density from 1.00 to 1.21 ml µg^{-1} with the temperature rise from 31C^o to 41C^o, and with Villanueva and others (2014) who found the constant values increased from 2.76 to 3.90 ml µg^{-1} with temperature increase from 25 C° to 50 C°. The results of table 3 show that the values of the constant n ranged between 1.403 - 2.455 ml µg^{-1} for all regions and under both conditions of the salt and at temperatures of 25 and 45 C°, so it is noted that all the values of this constant in general and under all conditions greater than one ($n > 1$) and this indicates, according to the hypothesis of adsorption states, that this type of reaction is favorable according to Dada *et al.*,(2012) and these values are consistent with Hlihor *et al.*, (2010) who found adsorption density values ranged between 1.00 to 1.20 ml µg^{-1} in their study of Cadmium thermodynamics under different temperature conditions using the Freundlich equation.

The ability of soils to retain cadmium can be determined through the desorption index (DI) , which is calculated from the ratio of the desorption slope the to the adsorption slope according to the Langmuir equation due to the high value of the determining coefficient R^2 compared to other equations if the value of this index is greater than one ($DI > 1$) then this means that the adsorption reactions are irreversible, and if the values of this index are less than one ($DI < 1$) this means that the adsorption reactions are reversible (Marzadori *et al.*, 1991 and Al-Mousili, 2018).

Figures 1, 2, 3, and 4 show that the value of this index ranged from 1.00 in Al-Qadisiyah and Sulaymaniyah soil to 1.44 in Duhok soil using NaCl salt and between 1.06 in Al-Qadisiyah soil to 1.63 in Duhok soil in $CaCl_2$ solution at a temperature of 25 C°, and between 1.06 In Qadisiyah and Sulaymaniyah soils to 1.5 in the Duhok soil using NaCl salt and between 1.07 in the Sulaymaniyah soil to 1.86 in the Duhok soil using $CaCl_2$ solution at a temperature of 45 C°, as it is clear from these results that the soil that is less capable of retaining Cadmium is the Qadisiyah soil and Sulaymaniyah, where the average value of the desorption index was 1.05 and 1.08 sequentially, and it has the highest capacity for storage it is the soil Cadmium Dohuk reached as evidence value rate of DI 1.60 due of clay content and CEC which had an impact on the DI values for those soils.

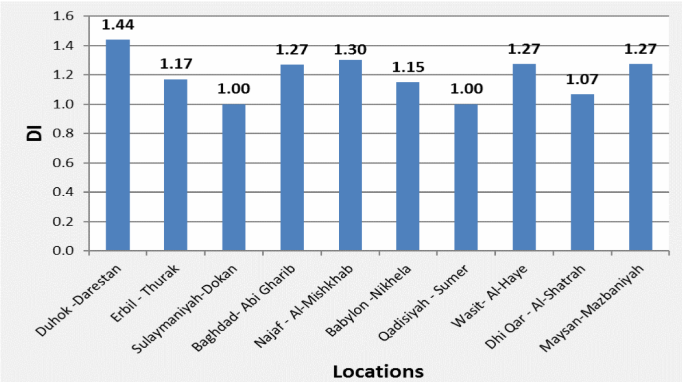

Fig. 1 : The desorption index (DI) values for the study soil in NaCl solution were at 25 ºC.

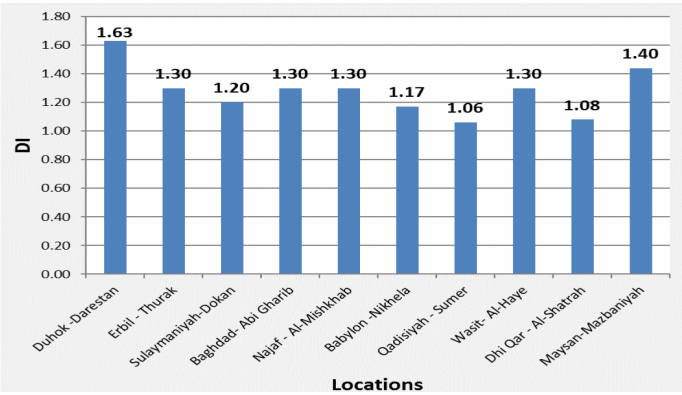

Fig. 2 : The desorption index (DI) values for the study soil in $CaCl_2$ solution were at 25 ºC.

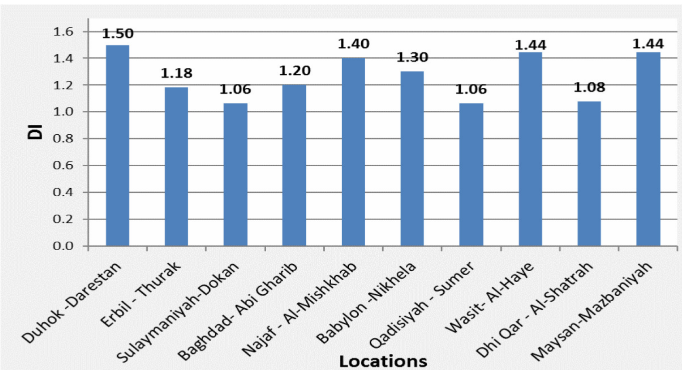

Fig. 3 : The desorption index (DI) values for the study soil in NaCl solution were at 45 C°.

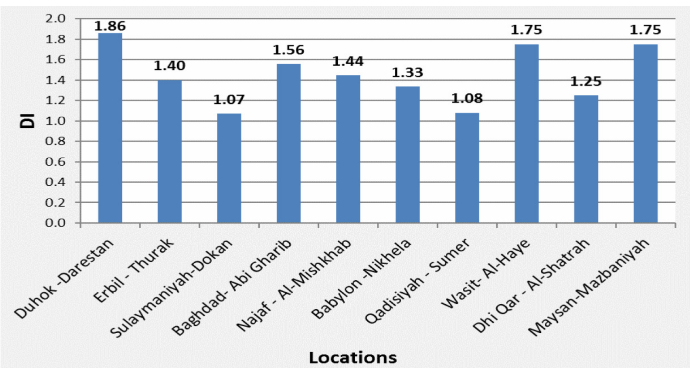

Fig. 4 : The desorption index (DI) values for the study soil in $CaCl_2$ solution were at 45 C°.

The figures 1, 2, 3 and 4, shows the effect of the salt composition on the values of the desorption index, that the values of the desorption index at the temperature of 25 C° ranged between 1.00 to 1.44 using NaCl salt, and the values increased between 1.06 to 1.63 using $CaCl_2$, as well as in the temperature of 45 C° ranged between 1.06 to 1.50 using NaCl and the values increased between 1.07 to 1.86 using $CaCl_2$. the higher values of desorption index and the higher ability of the soil to retain the added Cadmium in $CaCl_2$ solution compared to its decrease in NaCl solution may be due to the high content of carbonate minerals in the study soils is considered as calcareous soils, as the Sodium ions can disturb this stability of a metal according to the principle of the effect of a different ion in the equilibrium solution (Christian, 2004), therefore the release of some adsorption Cadmium from there minerals can lead to the solution and lower its retention and increasing the concentration of Sodium ions increases the thickness of the double electic layer compared to with Calcium Chloride solution (Bohn *et al.*, 2001 ; Ali and Al-Qaisi, 2011) which reduces the chance of Cadmium adsorption on soil colloidal surfaces and increased reflectivity, as well as the effect of Sodium ions on dispersing soil colloids which can contribute to increasing contact surfaces between colloids and solution equilibrium which gives more opportunity for quantitative desorption greater from Cadmium to soil solution, and contrast in the case of Calcium ions because they are prone to precipitation in equilibrium solution within the installation of precipitation carbonate minerals (Shahwan *et al.,* 2005; Al-Mamooree and Al-Kaysi, 2011b). as for the effect of temperature, it is noticed through the results that the values of the rate of desorption evidence increase with the rise in temperature, as it is observed from figures 1 and 3 that the values of evidence ranged using NaCl salt between 1.00 to 1.44 at a temperature of 25 C° and increased between 1.06 to 1.50 at the temperature 45 C°, and in figures 2 and 4 using $CaCl_2$ salt ranged between 1.06 to 1.63 at a temperature of 25 C° and between 1.07 to 1.86 at a temperature of 45 C°, and this may be due to the increase in temperature increasing the adsorption, which is reflected in the values of the desorption index were evaluated, as both Ghayad (2012) and Karak *et al.* (2014) in their studies of adsorption of Cadmium at different temperatures found an increase in the adsorption quantity. Adsorbed when increasing the temperature, which reflects the role of environmental conditions, especially heat, on adsorption reactions. in general, the general average of the desorption index for all soils and under all conditions was 1.30, which means that the adsorption process for these soils is irreversible reactions, it means that it is characterized by Hystersis and this is consistent with Al-Awsi (2014) indicated in its study of some Iraqi calcareous soils, and with Tahervand and Jalali (2016) has attained is a decrease in the desorption of Cadmium at a soil reaction of more than 7, and with Esfandbo and others (2010) who found is that alkaline soils are highly adsorbed to Cadmium and may precipitate as $CdCO_3$, which may reduce the bioavailability of the element, As the toxicity of Cadmium is less in soil with high a degree of soil reaction (Karak *et al.*, 2014).

References

Addis, W. and Abebaw, A. (2017). Determination of heavy metal concentration in soils used for cultivation of *Allium sativum* L.(Garlic) in East Gojjam Zone, Amhara Region, Ethiopia. Cogent Chemistry, 3(1), 1419422.

Al-Awsi, W.S.A. (2014). The role of soil tissue in adsorption and desorption of Lead and Cadmium in calcareous soils treated with used motor oil. Master Thesis. Faculty of Agriculture. Baghdad University.

Ali, N.A.S and Al-Kaysi, S.J. (2011). Soil Chemistry (Interpreter). Ministry of Higher Education and Scientific Research, Department of Soil Science and Water Resources, College of Agriculture, University of Baghdad. Written by Carson Spoceto, 2008, second edition.

Al-Mamooree, A.D. and Al-Kaysi, S.C. (2011b). Role Ca/Mg ratio and precipitated pattern in mineral composition and weight of precipitated carbonate minerals in soil and this effected in Zinc sorption – desorption. II- Zinc sorption – desorption. Iraqi J. of Soil Sci., 11(1):91 - 102.

Al-Mawsali, M.A.D. (2018). Complete fertilizer and fertilization (soil, plant and water analysis). Library science, Beirut. P. 190.

Bohn, H.L.; McNeal, B.L. and O'onnor, G.A. (2001). Soil chemistry. John Wiley and Sons, Inc.

Christian, D.G. (2004). Analytical Chemistry 6th John Wiley and Sons,Inc.

Dada, A.O.; Olalekan, A.P.; Olatunya, A.M. and Dada, O.J. (2012). Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of Zn^{+2} unto phosphoric acid modified rice husk. IOSR Journal of Applied Chemistry, 3(1): 38-45.

Dahiya, S.; Shanwal, A.V. and Hegde, A.G. (2005). Studies on the sorption and desorption characteristics of Zn (II) on the surface soils of nuclear power plant sites in India using a radiotracer technique. Chemosphere, 60(9): 1253-1261.

Dandanmozd, F. and Hosseinpur, A.R. (2010). Thermodynamic parameters of Zinc sorption in some Calcareous soils. Journal of American science, 6(7).

Esfandbod, M.; Forghanib, A.; Adhami, E. and Rashti, R. Cadmium adsorption behavior of some soils from northern of Iran. Proceedings of the 19th World Congress of Soil Science: Soil solutions for a changing world, Brisbane, Australia, 1-6 August 2010. Symposium 3.5. 1 Heavy metal contaminated soils. International Union of Soil Sciences (IUSS), Institut für Bodenforschung, Universität für Bodenkultur.

Freundlich, H.M.F. (1906). Over the adsorption in solution. J. Phys. Chem. 57: 385–471.

Ghiad, E.W. (2012). Thermodynamic study of adsorption of Cadmium on activated carbon prepared from nuclei of Iraqi dates. Anbar University Journal of Pure Sciences, 6(3): 109-114.

Hlihor, R.M.; Cozma, P.; Ghinea, C.; Pavel, V.L.; Robu, B.M. and Gavrilescu, M. (2010). Thermodynamic study of Cd (II) sorption on soil. Lucr Stiint, 53(2).

Isa, F.I. (2018). Environmental pollutants and their side effects. Scientific Books House. P. 156.

Karak, T.; Paul, R.K.; Das, D.K.; Boruah, R.K. and Sonar, I. (2014). Thermodynamics of Cadmium sorption on different soils of West Bengal, India. The Scientific World Journal.

Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, Mica and Platinum. Journal of the American Chemical Society, 40(9): 1361-1403.

Li, C.L.; Wang, S.; Ji, F.; Zhang, J.J. and Wang, L.C. (2015). Thermodynamics of Cu^{+2} adsorption on soil Humin. International Journal of Environmental Research, 9(1): 43-52.

Marzadori, C.; Antisari, L.V.; Ciavatta, C. and Sequi, P. (1991). Soil organic matter influence on adsorption and desorption of Boron. Soil Science Society of America Journal, 55(6): 1582-1585.

Mendham, J.; Denny, R.; Barnes, J.; Thomas, M. (2000). Vogel's Textbook of Quantitative Chemical Analysis. 6th ed. Addison Wesley Publisher, New York, 69-71.

Nazar, R.; Iqbal, N.; Masood, A.; Khan, M.I.R.; Syeed, S. and Khan, N.A. (2012). Cadmium toxicity in plants and role of mineral nutrients in its alleviation.

Ogunkunle, C.O.; Odulaja, D.A.; Akande, F.O.; Varun, M.; Vishwakarma, V. and Fatoba, P.O. (2020). Cadmium toxicity in cowpea plant: Effect of foliar intervention of nano-TiO_2 on tissue Cd bioaccumulation, stress enzymes and potential dietary health risk. Journal of Biotechnology.

Pokrovsky, O.S. and Schott, J. (2002). Surface chemistry and dissolution kinetics of divalent metal Carbonates. Environ. Sci. Technol., 36: 426-432.

Satarug, S.; Vesey, D.A. and Gobe, G.C. (2017). Current health risk assessment practice for dietary Cadmium: Data from different countries. Food and Chemical Toxicology, 106: 430-445.

Shahwan, T.; Zunbul, B.; Tunusoglu, O. and Eroglu, A. (2005). ASS, XRPD, SEM/EDS and FTIR characterization of Zn^{+2} retention by Calcite, Calcite-Kaolinite, and Calcite – Elinoptilolite minerals. J. colloid interface Sci., 286: 471-478.

Tahervand, S. and Jalali, M. (2016). Sorption, desorption, and speciation of Cd, Ni, and Fe by four calcareous soils as affected by pH. Environmental monitoring and assessment, 188(6): 322.

WHO/FAO (World Health Organization/Food and Agriculture Organization). 2007. Joint FAO/WHO Food Standard Programme Codex Alimentarius Commission 13th Session. Report of the Thirty Eight Session of the Codex Committee on Food Hygiene.