

POTASSIUM ADSORPTION IN CALCAREOUS SOILS OF KURDISTAN REGION OF IRAQ

Gh. A. Mam-Rasul
Assistant Prof.

Dept. Natu. Res., Coll. of Agric. Engin.Sci., University of Sulaimani, Kurdistan Region, Iraq.

ghafwr.mamrasul@univsul.edu.iq.

ABSTRACT

Sorption is one of the most chemical important processes, which determine nutrients availability in soil. Sorption isotherms provide sufficient information about soils sorption's capacity, and it's data can be used to determine thermodynamic sorption parameters. The aim of this study is to evaluate the sorption of potassium onto some soils. An experiment was conducted with four calcareous soils of the Sulaimani province Kurdistan Region of Iraq by using the batch methods. 5g soil samples were equilibrated at 298 ± 1 Kelvin with 50 ml of 0.01M CaCl₂ containing 0 to 250 mg L⁻¹ K as KCl. Suspensions were centrifuged, filtered, and concentration of K⁺ in the clear extract solution was determined. Amount of K⁺ sorbed by the soil was calculated from the difference between the initial and final concentration of K⁺ in the equilibrium solution. Sorption of K⁺ was evaluated using adsorption isotherms. The results showed that K⁺ sorption was described by linear, Langmuir, Freundlich, and Temkin equations. Langmuir equation gave a better fit of equilibrium K adsorption when it has a higher R² and lowers SE. The data indicated that the maximum monolayer coverage capacity (b) from the Langmuir isotherm model ranged between (-113.63 to 2500) mg kg⁻¹. The negative values of (b) for studied locations soils indicated to potassium release instead of adsorption. The Langmuir isotherm constant (K_L) ranged from (-0.01 to 0.01) L mg⁻¹. Maximum buffering capacity (MBC) is a capacity factor, which measures the ability of the soil to replenish K ion to soil solution that the ability of a soil to supply K to the soil solution. The value of MBC of the studied soils ranged from 0.453 to 23.75 mg kg⁻¹. The sorption processes for the fourth locations are favorable and spontaneous because the value of R_L was an equal one.

Key words: langmuir model, freundlich model, temkin model, monolayer coverage, equilibrium binding constant.

مام رسول

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امتزاز البوتاسيوم في بعض الترب الكلسية لإقليم كردستان العراق

غفور احمد مام رسول

استاذ مساعد

قسم الموارد الطبيعية. كلية هندسة العلوم الزراعية. جامعة السليمانية

إقليم كردستان العراق

المستخلص

الامتزاز هو احد العمليات الكيميائية المهمة الشائعة في التربة والتي من خلالها الحصول على معلومات كافية عن سعة التربة للامتزاز ومعايره الترموديناميكية بهدف تحديد جاهزية المغذيات في التربة تهدف هذه الدراسة الى وصف ظاهرة امتزاز البوتاسيوم لاربع ترب كلسية من اقليم كردستان العراق من محافظة السليمانية باستعمال طريقة الوجبة بعمل ايزان ديناميكي على درجة حرارة 298 ± 1 كلفن مستويات من البوتاسيوم (0-250) ملغم لتر⁻¹ مذابة في محلول 0.01 مولار من كلوريد الكالسيوم. قدرت ايونات البوتاسيوم في محاليل الاتزان. حسبت كمية البوتاسيوم الممتزة من الفرق بين التركيز البدائي والنهائي لمحلول الاتزان والتي وصفت بمعادلات لانكماير وفرندلخ وتمكن الخطية. وقد بينت النتائج صلاحية المعادلات الثلاث في الوصف الرياضي للامتزاز مع تفوق لمعادلة لانكماير لحصولها على اقل خطأ قياسي. اذ تراوحت قيم سعة الامتزاز الاعظم لطبقة واحدة لمعادلة لانكماير من -113.63 الى 2500 ملغم كغم⁻¹ وبطاقة امتزاز من -0.01 الى 0.01 لتر غم⁻¹ القيم السالبة تشير الى حدوث عملية عكس الامتزاز لاحتوائها على بوتاسيوم اكبر من التراكيز المضافة اما قيم السعة التنظيمية العظمى والتي تعبر عن مقياس لقدرة الترب لامداد محلول لتربة بالبوتاسيوم وقيمتها لترب المدروسة تراوحت من 0.45 الى 23.75 ملغم كغم⁻¹. اما معامل التجزئة فكانت قيمته (1) للترب الأربعة مما يشير الى تلقائية التفاعلات.

الكلمات المفتاحية: معادلة لانكماير، معادلة فرندلخ، معادلة تمكين، امتزاز لطبقة واحدة، ثابت طاقة الارتباط.

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INTRODUCTION

Potassium is an essential element for crop production and productivity (43). Potassium plays a vital role in activates of over sixty (60) enzymes involved in the formation of carbohydrates, translocation of sugars, various enzyme actions, yield, quality parameters, tolerance to certain diseases, mechanisms to overcome abiotic stress, cell permeability, controls stomata opening, Also, K influences the microbial population in the rhizosphere. (35). Soil properties (physical, chemical, and biological), affect the availability of K (44). K adsorption in soils that is, the transformation of available K forms into unavailable ones, influences the effectiveness of fertilization in the soil-plant regime. The mechanism of adsorption of K in the soil is important because soils may contain widely variable pools of K that are potentially mobilized by chemical weathering of soil minerals (37). The equilibrium among the potassium retained by the interlayer sites controls the process of potassium adsorption by the surface and edge sites of the mineral crystal lattice and the potassium in the soil solution. The dynamic equilibrium is mainly affected by clay minerals types, pH, soil organic matter (SOM), hydroxide aluminum, soil moisture status, cation exchange capacity (CEC), fertilization and tillage system (29). The K adsorption in the soil is quite complex and may not be explained by the simple and single reaction. The amount of K can be adsorbed on the soil colloids depending on the amount and type of clay minerals up to 67%., and the high capacity of soils affecting negatively on the availability of K to crops (28). There is little information available relating to K adsorption characteristics of calcareous soils (18). To visualize the quantities of K adsorbed per unit soil mass, several equations or adsorption isotherms have been developed. Between the isotherms, Langmuir, and Freundlich adsorption isotherms are mostly employed and described the phenomena of quantities K adsorption per unit soil mass satisfactorily (8). The Freundlich equation is an empirical equation, which corresponds to a model of adsorption where the affinity term decreases exponentially as the amount of adsorption increases. Potassium adsorption was described

well often by Freundlich equation over a limited range of concentration (7). The theory of Langmuir is restricted to cases where only one layer of the molecule can be adsorbed on the surface. Therefore, the non-conformity to the Langmuir model suggests the presence of several types of K sorption sites in the soils, each with different selectivity for K (18). According to the Freundlich equation, the energy of adsorption decreases as the amount of adsorption increases. The aim of this study was to determining K adsorption capacity, bonding energy and other adsorption parameters of Langmuir, Freundlich and Temkin isotherms of calcareous soils of the Sulaimani province Kurdistan Region of Iraq.

MATERIALS AND METHODS

Sample collection and physicochemical analysis

The soils samples were taken at 0 to 30 cm depths from four locations that contained calcareous soils representative of the major agricultural soils of the Iraqi Kurdistan Region, Halabja, Said Sadiq, Chwarta, and Gerdjan. The soil samples were air-dried, crushed, and passed through a (2) mm, sieve for soil analysis and sorption studies. Selected physical and chemical properties of soils are present in Table 1. The particle size distribution of the soil samples was determined by the pipette method, according to Gee and Bauder (15). The soil reaction (pH) and electrical conductivity (ECe) were measured for the soil saturation extract by a pH meter (HANA), model (HI 83141), and EC meter, model (HI 2314) respectively. Cation exchange capacity (CEC) of soil was obtained by saturating the soil sample with 1M ammonium acetate (NH₄OAc) at pH 8.1 as an extraction solution according to the method described by Suarez (39). Organic matter (O.M.) content was determined by the method described by Nelson and Sommer (27). The total carbonate minerals in soil expressed as the carbonate minerals equivalent were determined by a rapid titration method, according to the method of Rayment and Higginson (32). The active carbonates or active equivalent carbonates (AEC), which was a fine particle size calcite, was estimated by the 0.5 M NH₄ oxalate method as described by Drouimeau (12).

Table 1. Some physical and chemical properties of studied soils

Location	pH	EC (dS m ⁻¹)	PSD (g kg ⁻¹)			Text. ¹	CEC (cmol _c kg ⁻¹)	OM (g kg ⁻¹)	CCE (g kg ⁻¹)	
			Sand	Silt	Clay				Total	Active
Halabja	8.04	0.28	273	313	414	C	55.00	4.30	100	35.0
Said Sadiq	7.79	0.15	210	359	431	C	57.00	2.20	325	188.0
Chwarta	8.11	0.33	32	503	465	SiC	54.50	1.30	200	110.0
Gerdjan	7.20	0.40	52	534	414	SiC	55.00	3.00	250	135.0

¹C, clay; SiC, silty clay

Potassium adsorption experiment procedure

For the construction of potassium adsorption isotherm 5.0 g of each soil sample, in duplicate, were placed in 100-ml plastic bottles and equilibrated with 50 ml of 0.01 M CaCl₂ (soil/solution ratio of 5/50), with the solution containing different levels of K (0, 25, 50, 75, 100, 125, 150, 200, 225 and 250 mg L⁻¹ K as KCl at 298±1 kelvin. The suspensions were then shaken with a horizontal flask shaker for 2 hours (180 rpm and 298 K) and overnighted to equilibrate. Each solution was centrifuged at 250 rpm for 5 minutes then filtered through a Whitman filter paper no. 42, and the filtrates were analyzed for K concentration by the flame photometer JENWAY model PFP7. The amount of adsorbed K (mg kg⁻¹) was calculated following Vanderborght and Van Grieken (40) as:

$$q_e = \frac{(C_o - C_e)V}{w} \dots \dots \dots (1)$$

Where q_e is the amount of K adsorbed from the solution (mg kg⁻¹), C_o is the initial concentration of K (mg L⁻¹), C_e is the concentration of K (mg L⁻¹) at an equilibrium state, V is the volume of the solution (L), and W the weight of the soil sample (kg) used in the experiment. The data were computed using the linearized forms of the following equations: Langmuir, Freundlich, and Temkin

Langmuir adsorption isotherm

The Langmuir model supposes monolayer adsorption of solutes on homogenous sorption sites, the Langmuir equation has described the distribution of K between the solid solution interface equilibrium (25), Langmuir isotherm was the most commonly used linear expression to studied the relationships between the concentration of solute in the liquid phase and the solid phase at equilibrium conditions (21).

The well-known expression of the Langmuir model was used:

$$\frac{1}{q_e} = \frac{1}{b} + \frac{1}{bK_L C_e} \dots \dots \dots (2)$$

Where q_e = the amounts of adsorbed K per unit weight of soil (mg kg⁻¹), and C_e is the K concentration in solution at equilibrium (mg L⁻¹), K_L is a constant related to bonding energy or affinity constant of potassium to the soil (L mg⁻¹), and b is the soil's maximum monolayer coverage capacity during K adsorption(mg kg⁻¹). A plot of 1/q_e vs. 1/C_e gives a straight line with a slope of 1/bK_L and intercept of 1/b R_L the dimensionless constant called equilibrium parameter for Langmuir isotherm (22).

$$R_L = \frac{1}{(1 + K_L C_o)} \dots \dots \dots (3)$$

where K_L = a constant related to bonding energy (L mg⁻¹) and C_o is the initial K concentration (mg L⁻¹), R_L values indicate the type of isotherm (20). R_L value indicates the adsorption nature to be either unfavorable (R_L> 1), linear (R_L = 1), favorable (0 <R_L< 1) or irreversible (R_L = 0).

The maximum buffering capacity (MBC) was calculated as the product of K_L and b following Reyhanitabar et al. (34).

$$MBC = K_L \times b \dots \dots \dots (4)$$

Freundlich adsorption isotherm

Freundlich isotherm the earliest concepts the equation for adsorption isotherm (13). Freundlich isotherm is an empirical model, which can be applied to non-ideal adsorption on dissimilar surfaces along with adsorption multilayer, with the nonuniform distribution of adsorption heat and affinities over the heterogeneous surface (1). The empirical Freundlich equation based on sorption onto a heterogeneous surface is given as:

$$q_e = K_F C_e^{1/n} \dots \dots \dots (5)$$

Eq.(6) can be rearranged to obtain a linear form by taking logarithms Eq.(5):

$$\text{Log } q_e = \text{log } K_F + 1/n \text{ log } C_e \dots \dots \dots (6)$$

Where K_F = the energy of sorption or distribution coefficient (mg kg^{-1}), $1/n$ is the heterogeneity factor. n is the dimensionless constant, while $1/n$ represents the strength of adsorption in the adsorption process (41). If the Freundlich affinity value n is equal to 1, then the partition between the two phases is independent of the concentration. If $1/n$ is less than 1, the parameter indicates normal adsorption. Above 1, however, the parameter indicates cooperative adsorption (38). The Freundlich affinity value, n , is important for understanding sorption processes and the heterogeneity of the system. If the n value falls between 1 and 10, the sorption process is favorable (10 and 30). A more homogeneous system will have a $1/n$ value approaching unity, and a more heterogeneous system will have a $1/n$ value approaching zero (17).

Temkin isotherm

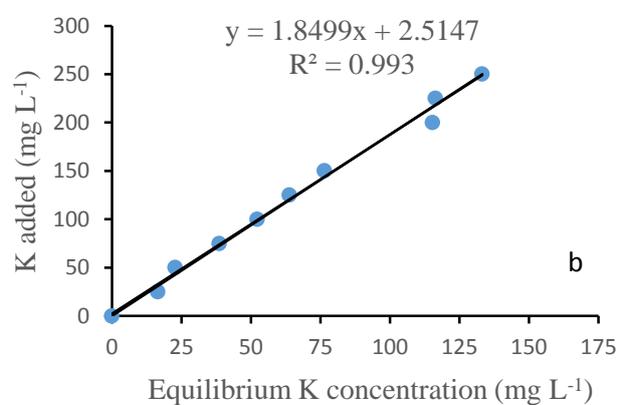
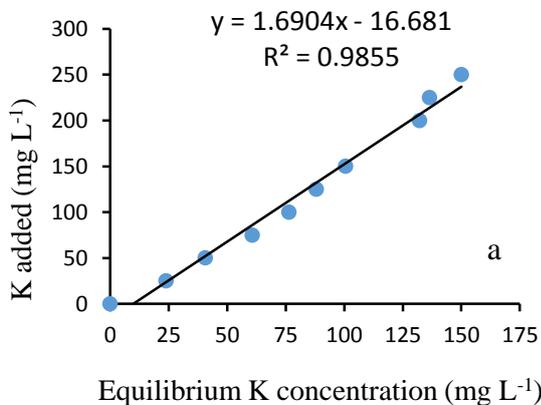
The Temkin isotherm contains a factor that taking into the account of adsorbent–adsorbate interactions and is simply a function of surface coverage (9). The Temkin isotherm is usually used for heterogeneous surface energy systems (nonuniform distribution of sorption heat) (5). The equation is stated as follows:

$$q_e = \frac{RT}{b_T} \ln(A_T C_e) \dots \dots \dots (7)$$

$$q_e = \frac{RT}{b_T} \ln A_T + \left(\frac{RT}{b_T}\right) \ln C_e \dots \dots \dots (8)$$

The linear form of the Temkin equation is:

$$q_e = B \ln A_T + B \ln C_e \dots \dots \dots (9)$$



where q_e = the mass of K adsorbed per unit mass of soil (mg kg^{-1}), C_e is equilibrium solution K concentration (mg L^{-1}), A_T = the Temkin isotherm equilibrium binding constant (L kg^{-1}), and B is a constant related to the heat of sorption (J mol^{-1}) calculated as:

$$B = \frac{RT}{b_T} \dots \dots \dots (10)$$

where b_T = Temkin constant related to the nature of the adsorption energy (J mol^{-1}) a positive value of b_T indicates that the adsorption process is exothermic while a negative value of b_T is an indication of the endothermic process (26), R is the universal gas constant ($8.314 \text{ J mol}^{-1}\text{K}^{-1}$), T is the absolute temperature 298 kelvin. A plot of q_e versus $\ln C_e$ enables the determination of the isotherm constants A_T and b_T .

RESULTS AND DISCUSSION

Soil potassium adsorption characteristics

Potassium adsorption isotherms for the studied soils samples are presented in Figure 1. The soils varied K adsorption behavior. The amount of K adsorbed increased with the increasing K additions irrespective of soil type (Figure 2). For the initially added solution concentration of K (25 mg L^{-1}), K adsorbed ranged from 11.64 to $169.36 \text{ mg kg}^{-1}$ and for the highest added solution concentration of K (250 mg L^{-1}) 999.95 to $1441.54 \text{ mg kg}^{-1}$. The equilibrium K concentration in soil solution (that is, not net release or adsorption) ranged from 8.06 to 23.84 mg L^{-1} for 25 mg L^{-1} of added K and from 105.85 to 150.01 mg L^{-1} for 250 mg L^{-1} of added K.

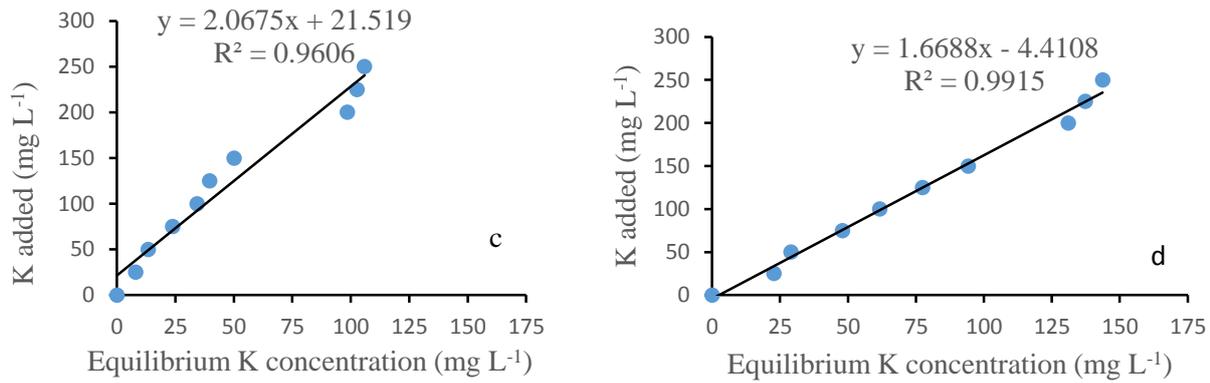


Figure 1. Potassium adsorption characteristics of (a) Halabja, (b) Said Sadiq, (c) Chwarta and (d) Gerdjan soils of Kurdistan Region of Iraq.

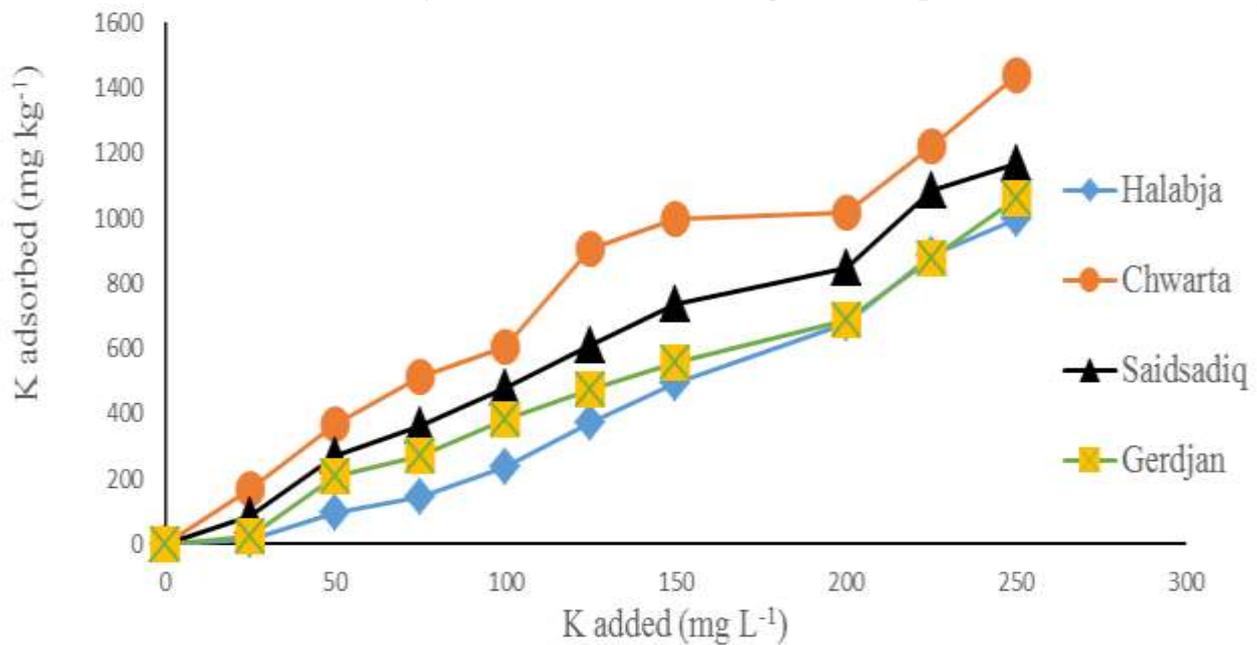


Figure 2. Amount of K adsorbed as a function of different K concentration levels of studied soils

Potassium adsorption study from graphical analysis of Langmuir, Freundlich and Temkin equation plots

The degree of accuracy of the sorption isotherms varied from soil to soil. The coefficient of determination (R^2) values in Table 2 indicate that the Langmuir equation

has a better fit (Figure 3c) of equilibrium K adsorption data for Chwarta location than the other studied locations. This may be due to the high of clay content which had unlimited adsorption sited having a heterogeneous surface (19).

Table 2. Langmuir isotherm constants for the adsorption of potassium on the studied soils

Locations	Langmuir equation	R^2	SE	b (mg kg^{-1})	K_L (L mg^{-1})	MBC (mg kg^{-1})	R_L
Halabja	$Y = 2.2228X - 0.0214$	0.850	0.0114	-46.729	-0.01	0.453	1
Said Sadiq	$Y = 0.1794X - 0.0011$	0.861	0.0014	-909.09	-0.006	5.545	1
Chwarta	$Y = 0.0422X + 0.0004$	0.954	0.0004	2500	0.01	23.75	1
Gerdjan	$Y = 0.887X - 0.0088$	0.657	0.0089	-113.63	-0.01	1.125	1
Mean		0.831	0.005	357.64	0.004	7.72	1

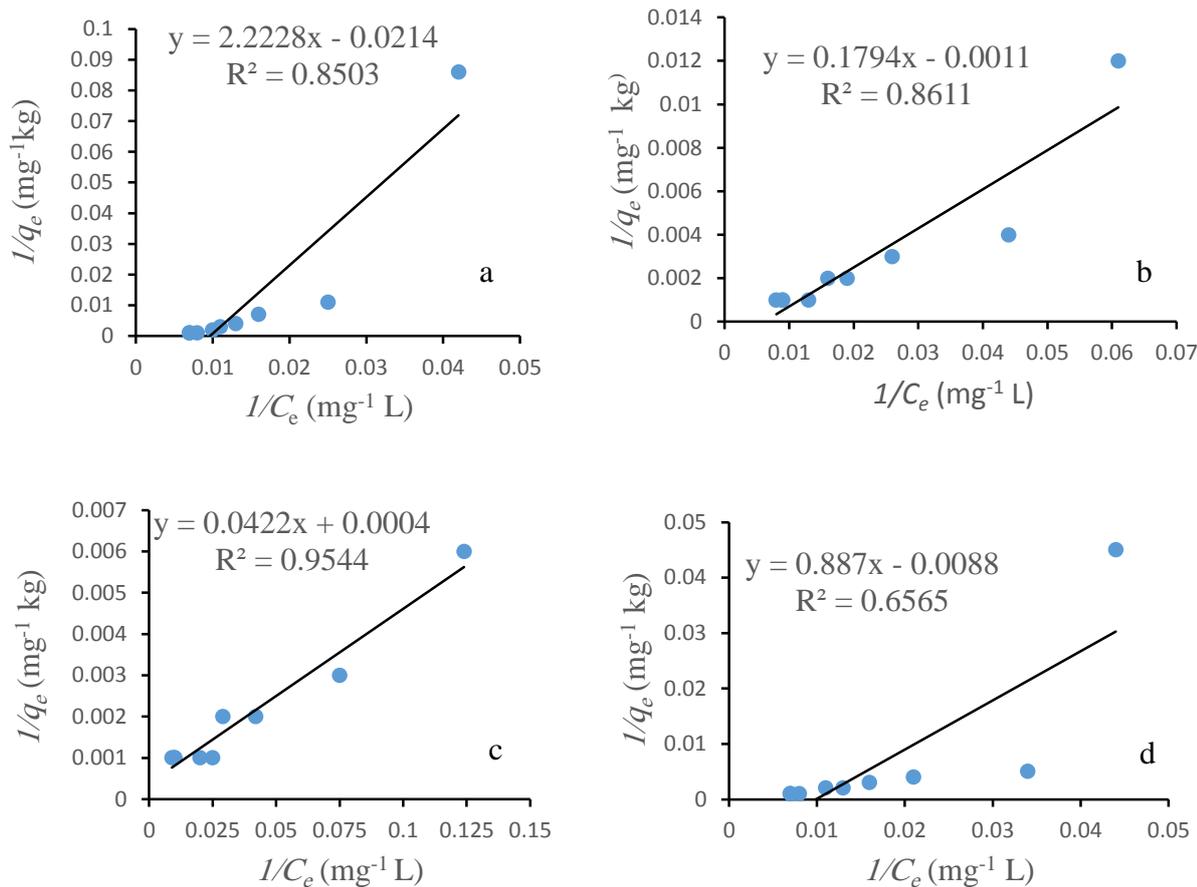


Figure 3. Langmuir adsorption isotherms for (a) Halabja, (b) Said Sadiq, (c) Chwarta and (d) Gerdjan soils of Kurdistan Region of Iraq.

Langmuir isotherm parameters

For Langmuir isotherm, it is assumed that the adsorption sites have equal affinities for molecules of the adsorbate. Therefore, the presence of adsorbed molecules at an adjacent site (10). The maximum monolayer coverage capacity (b) from Langmuir isotherm model ranged between -113.63 and 2500 mg kg⁻¹ (Table 2), the monolayer coverage capacity of the studied locations except for Chwarta were found to be below zero this may be due to the variation of organic matter content among the studied soils (Table 1). This result is harmonic with the result found by Ravikovitch et al. (31). Their result observed that the soils with a higher amount of OM per unit mass are likely to be covered by an extensive humic layer, sufficient to coat the core particle mineral surface, this indicated that the decline the value of monolayer coverage capacity of the soil. These negative intercepts suggest that the adsorption behavior of the tested systems does not follow the assumption of the Langmuir approach (6). The

maximum adsorption (b) can be used to estimate the amount of fertilizer to be added to unfertilized soil (33). The soil of these locations also had no best fit for the coefficient of determination (R^2) of the Langmuir model (Figures 3 a, b and d). On the other hand, soil possessing best fit to Langmuir model (Chwarta location) (Figure 3c) indicated high monolayer coverage. These results in agreement with the results of Auge et al. (6). The Langmuir isotherm constant (K_L) ranged from -0.01 to 0.01 Lmg⁻¹. According to Mehandi and Taylor (24), smaller the K_L values indicated that more amount of adsorbed K would be converted to non-exchangeable form either by the formation of crystalline K or by occultation through K ions. According to Del-Bubba et al. (11), K_L is a measure of the affinity of the adsorbate for the adsorbent. Anderson and Wu (4) stated that a high K_L value is an indication of the high clay contents of respective soil, and also shows the strength of bonding to clay minerals in the soil. The adsorption nature of K for all studied soils are

linear because the diffusion coefficient (R_L) values equal to one (Table 2). Al-Hassoon et al. (3) observed that diffusion coefficient (R_L) value of Cu adsorption in predominance soil orders (Entisols) Jadriya and Najaf of Iraq less than one which means that the reaction of the adsorbed copper is spontaneous. Maximum buffering capacity (MBC) of the studied soils ranged from 0.453 to 23.75 mg kg⁻¹, MBC is a capacity factor, which measures the ability of the soil to replenish K ion to soil solution as they tend to be decreased (33). Fried and Shapiro (14) stated that the ability of a soil to supply K to the soil solution an important factor in evaluating the K status of a soil.

Freundlich isotherm parameters

The coefficient of determination (R^2) value in Table 3 indicated that the Freundlich equation gave a better fit (Figure 4a) of equilibrium K adsorption data for Halabja location. This may be due to the high organic matter content in Halabja location, and soil organic matter may considerably favor a very fast initial adsorption of K (42)., for having sorption sites more accessible compared with the mineral components of the soil Sheikh-Abdulla et al.(36) found that the Freundlich isotherm is the best model to describe Mn adsorption in some calcareous soils at Sulaimani governorate.

Table 3. Freundlich isotherm constants for the adsorption of potassium on the studied soils

Locations	Freundlich equation	R^2	SE	1/n kg mg ⁻¹	n mg kg ⁻¹	K_f (mg kg ⁻¹)
Halabja	$Y = 2.2665X - 1.8881$	0.971	0.111	2.2665	0.441	0.013
Said Sadiq	$Y = 1.0682X + 0.8217$	0.9235	0.105	1.0682	0.936	6.633
Chwarta	$Y = 0.7096X + 1.7083$	0.9273	0.084	0.7096	1.409	51.086
Gerdjan	$Y = 1.1478X + 0.3799$	0.7121	0.289	1.1478	0.871	2.398
Mean		0.883	0.149	1.298	0.914	15.033

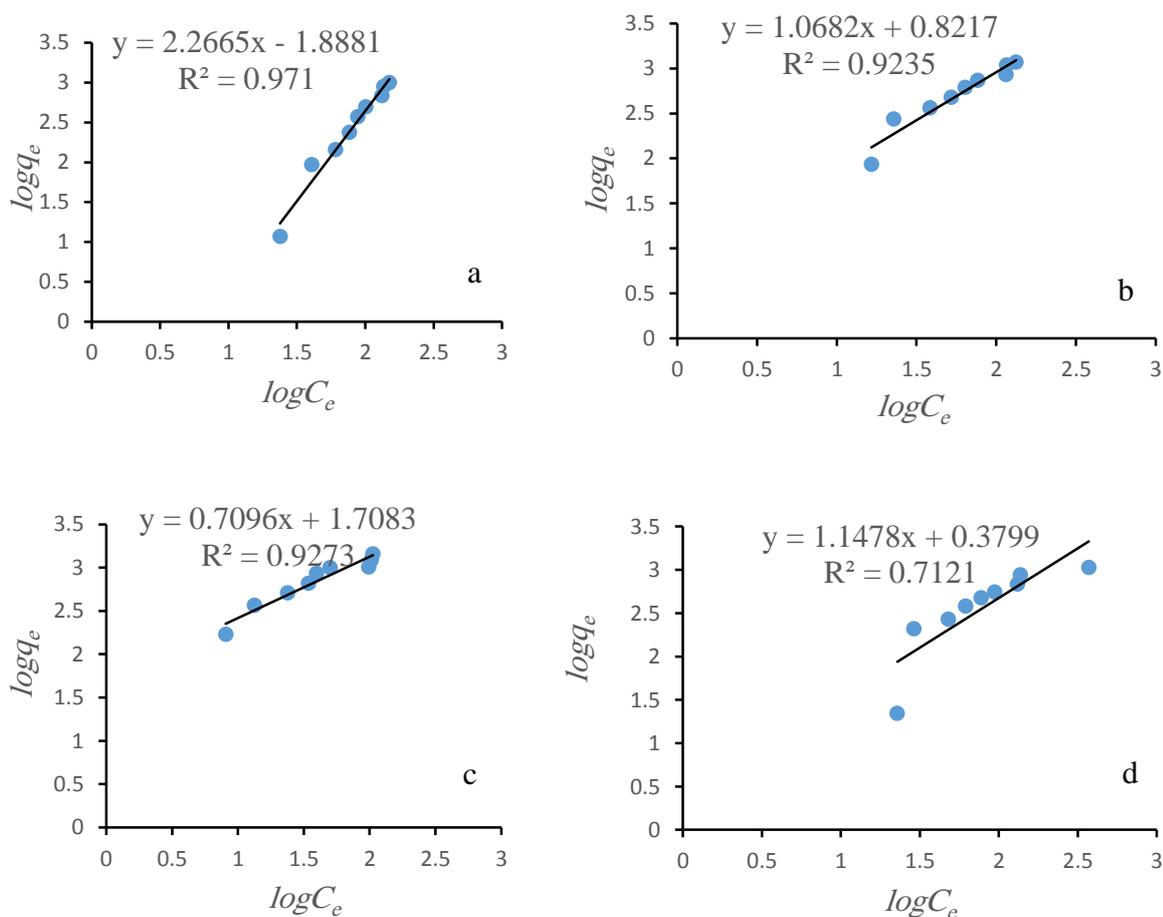


Figure 4. Freundlich adsorption isotherms for (a) Halabja, (b) Said Sadiq, (c) Chwarta and (d) Gerdjan soils of Kurdistan Region of Iraq.

For Freundlich, isotherm assumes low energy of adsorption, its constant K_f and $1/n$ (Table 3) may be taken as a measure of the extent of adsorption (41). Mburvi et al. (23) highlighted that the constant $1/n$ (Eq. 6) also represents the buffering capacities of soils. In this study, it ranged from 0.7096 to 2.665 mg kg^{-1} with a mean of 1.298 mg kg^{-1} . In the range, Chwarta soil had low $1/n$ values due to low sand proportion. The values of $1/n$ also indicate a heterogeneity parameter where smaller $1/n$ values reveal greater heterogeneity (10). Accordingly, Chwarta soil had high heterogeneity, and the parameter indicates normal adsorption for Chwarta location while for other locations, the adsorption process is cooperative (Table 3). The n values indicate whether the sorption favorable or not (16). For favorable sorption processes, it lies between one and ten (16). The adsorption capacity, K_f

(Eq 6) represents the amount of potassium held on non-specific sites that ready to be released for uptake by plants during cropping season (23). It ranged from (0.013 to 501.086) mg kg^{-1} and had a mean of 15.033 mg kg^{-1}

Temkin isotherm parameters

The coefficient of determination (R^2) value in Table 4 indicated that the Temkin isotherm has a better fit (Figure 5b) of equilibrium K adsorption data from Said Sadiq location compare to other studied locations. This could be due to the high cation exchange capacity (CEC) of the soil and high amount of active lime content of Said Sadiq location, which may be related to the soil mineralogical composition of the soil for this location (Table 1). Al- Janabi (2) observed that high calcium carbonate content causes an increase in cation adsorption on active sites of calcium carbonate like Cu.

Table 4. Temkin isotherm constants for the adsorption of potassium on the studied soils

Locations	Temkin equation	R^2	SE	A_T (L kg^{-1})	b_T (J mol^{-1})	B (J mol^{-1})
Halabja	$Y = 521.28X - 1836.4$	0.8046	169.163	0.029	4.753	521.28
Said Sadiq	$Y = 477.63X - 1305.4$	0.9269	103.811	0.173	5.928	417.94
Chwarta	$Y = 417.94X - 733$	0.9121	127.454	0.065	5.187	477.63
Gerdjan	$Y = 461.38X - 1450.9$	0.8864	119.345	0.043	5.37	461.38
Mean		0.883	130.17	0.0775	5.309	469.558

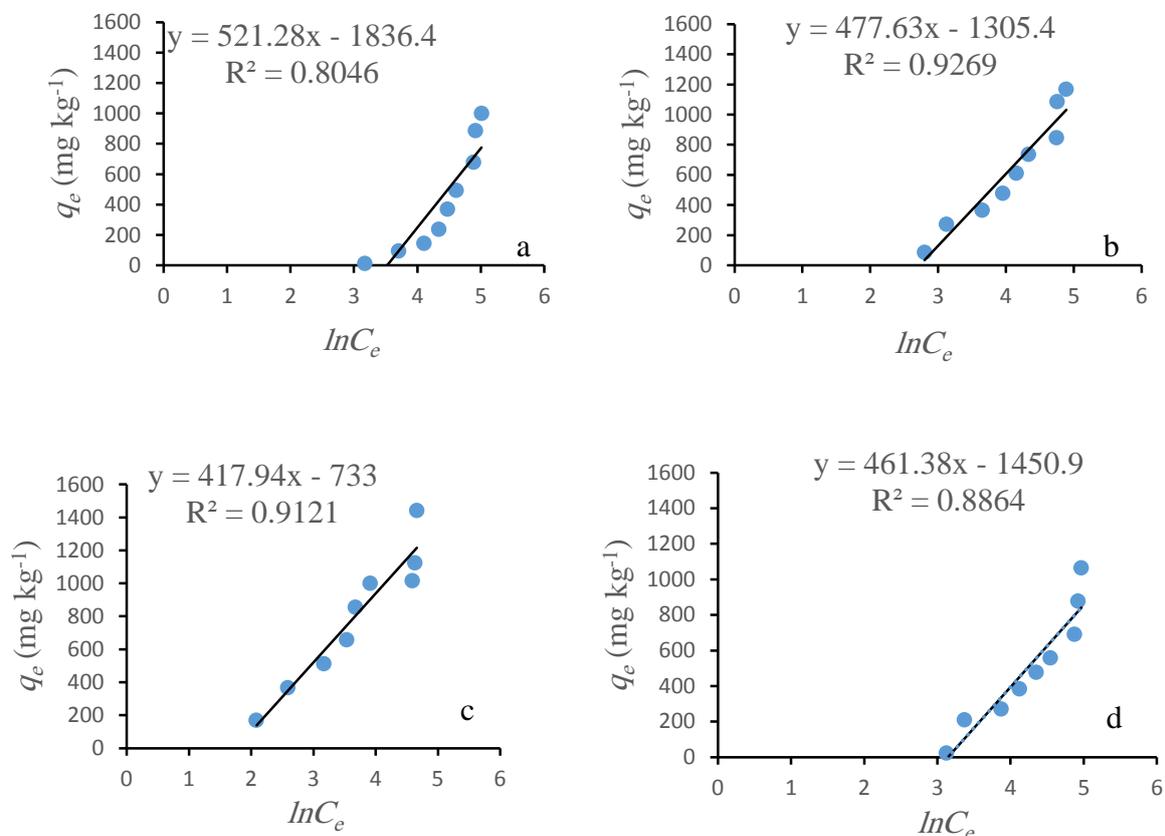


Figure 5. Temkin adsorption isotherms for (a) Halabja, (b) Said Sadiq, (c) Chwarta and (d) Gerdjan soils of Kurdistan Region of Iraq.

From the Temkin plot shown in Figure 5 and Table 4, values of Temkin isotherm equilibrium binding constant, A_T ($L\ kg^{-1}$) ranged between 0.029 and 0.173. In this range, the soil of Said Sadiq location had a high binding constant and high coefficient of determination (Figure 5b). The values of b_T ranged from 4.753 to 5.928 $J\ mol^{-1}$ with the mean of 5.309 $J\ mol^{-1}$ a positive value of b_T indicates that the adsorption process is exothermic for studied locations. Furthermore, high values of constant related to the heat of sorption, B ($J\ mol^{-1}$) indicate a strong interaction between adsorbent and adsorbate supporting a mechanism of ion exchange (10). The studied soils were varied from adsorption behaviors; all soils adsorbed the added K to a high degree. This indicated the high potential of studied soils to decrease crop availability of applied K. This indicated that crops in the studied soils were in K deficient condition and hence K recommendation should be one of the soil management choices.

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