

Potassium Adsorption Phenomenon in Calcareous Soils of Shahrzur Plain

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ABSTRACT

A laboratory study for adsorption of potassium (K) determination was conducted on six soils located in Sharazur plain from the Kurdistan Region of Iraq in 2021 using the batch technique method. Potassium (K) adsorption isotherms were achieved by equilibrating 5.0 g of soil samples with eight grades of K (0 to 300 mg L⁻¹) as KCl in 50 ml of 0.01M CaCl₂ solution. To match the data of adsorption, Freundlich, Langmuir, and Temkin adsorption isotherms were used. The results show that the amount of adsorbed K ranged between (45.78 to 52.49) % added K. The Freundlich model fit the equilibrium K adsorption data better for the Serwan location of soil (silty loam), as demonstrated by a greater coefficient of determination (R² = 0.90). The value of heterogeneity factor 1/n for the Freundlich model ranged from (0.34 to 0.47) kg mg⁻¹, which was less than one. The sorption processes for all of the studied soils were normal adsorption. The constant of the Langmuir isotherm (K_L) aligned from (0.107 to 0.425) L mg⁻¹. Smaller K_L values mean that more adsorbed K would be transformed to a non-exchangeable form, either through the creation of crystalline K or through ion occultation. The R_L values indicate the type of isotherm, the values of R_L > 1 that means the adsorption nature to be unfavorable. The Temkin equilibrium binding constant (A_T) was high for all studied soils except the soils of Bestan Sur and Grdigo locations, the high value of A_T indicates high binding energy. The Temkin constant (b_T) ranged from (10.46 to 13.47) J mole⁻¹ that was related to the nature of the adsorption energy, a positive value indicates that the adsorption process is exothermic.

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1. INTRODUCTION

One of the fundamental nutrients for the growth of the plant is potassium (K), and when it exists at an insufficient level in soils, plant growth is seriously hampered. Potassium is available to plants in the form of inorganic cations (K⁺) [1]. Over sixty (60) enzymes involved in carbohydrate production, sugar translocation, numerous enzyme actions, yield, efficiency parameters, disease tolerance, processes to resolve abiotic tension, cell permeability, and

stomata opening are stimulated by potassium. It also affects the microbial population in the rhizosphere [2]. Various soil processes, such as the physical, chemical, and biological properties, influence K availability [3]. The release of potassium influences by the interaction of soil mineralogy, soil texture, and biological processes [4].

Potassium is present in the soil in four different types. Soil minerals like feldspar and mica make up (90 to 98) percent of the total potassium in the soil. Plants can only use a small portion of this potassium supply. The second type of soil potassium is non-exchangeable potassium, it is related to the 2:1 clay mineral and ranges from 1% to 10% of total soil K. In the soil, the non-exchangeable potassium source functions as a potassium reserve. Non-exchangeable K release has a major impact on soil K fertility. The exchangeable or readily available potassium, which makes up 1 to 2 percent of the soil potassium, is found in the soil solution or on cation exchangeable sites [5]. The root system of the plant readily absorbs potassium from the soil solution, which is then replaced by potassium from the exchangeable sites. Since crops respond to applied potassium earlier, the rate of K^+ adsorption after fertilizer addition differs among soils, and thus its unpredictability is since different soils have varying potassium adsorption properties. Clay colloids can adsorb up to 57 % of the applied potassium, depending on the amount and form of clay minerals [6]. Kinetic and thermodynamic variables influence the amount of potassium adsorbed on clay particles [7].

According to Jalali [8], calcareous soils with enough exchangeable K and K-bearing minerals are capable of releasing enough K for optimal plant production. However, the exchangeable K in calcareous soils is not always reliable as a source of potassium for plants. The phenomenon of K adsorption in soils has altered the soil-plant system fertilization efficacy by converting available K into an unavailable form for plants. Due to the availability of different compelling potassium pools in the soil which could be mobilized by the chemical resistance of the mineral in the soil, understanding the process of K adsorption in the soil is essential [9]. A simple approach for determination K adsorption may aid in understanding the relationship among the adsorption of the alternative K soil characteristics [10]. The balance between K in the interlayer, the exterior, and K in the edge sites of the mineral crystal lattice is maintained by the solubilized K in soil solution which controls the potassium adsorption mechanism. The key elements impacting the equilibrium include clay mineral forms, soil (pH), soil organic matter (SOM, Al (OH)₃, moisture state of soil, cation exchange capacity (CEC), fertilizer rate, and the process of tillage [11]. Due to the complexity of the adsorption of potassium by the soil, it is difficult to explain it by the occurrence of a single reaction. Many equations have been advanced for the calculation of soil potassium. The Freundlich, Langmuir, and Temkin adsorption isotherms are often utilized to illustrate the relationship between the potassium quantity fixed per weight unit in the soil and the potassium concentration in the solution. The Freundlich equation was initially used by Russell and Prescott in 1961, and it is the earliest adsorption equation in the soil literature. It's a mathematical statement for an adsorption model that the sympathy term declined rapidly with increasing adsorption. The Freundlich equation effectively predicted K adsorption for a limited range of conditions [12]. The energy of adsorption decreases as the sum of adsorption increases, according to the Freundlich equation. The Temkin isotherm includes a component that accounts for adsorbent-adsorbate interactions and it is based solely on the exterior analysis [13]. The Temkin isotherm is intensely used for an exterior energy system that is heterogeneous [14].

2-METHODS AND MATERIALS

2.1 Study area and soil sampling

A study was conducted on the soil of Sharazur plain, which was located between the provinces of Suleimania and Halabja, situated in the southeastern part of Kurdistan Region, Iraq (Figure 1). The soil samples were randomly taken at 0 to 30 cm depths of the six major agricultural locations of the plain of Shahrazur during the spring season of 2021. For soil analysis and sorption experiments, the soil samples were air-

dried then it was grounded and screened through a (2) mm screen. According to Gee and Bauder [15], the pipette method was applied to obtaining the soil Particle Size Distribution (PSD) of the soil samples. A pH meter Professional Benchtop, model (BP3001), and EC meter HERMAN PAULSEN, model (D-2000 HAMBURG) was used for measuring the soil reaction (pH) and electrical conductivity (ECe) for the soil suspension 1:2 respectively. The soil samples Cation Exchange Capacity (CEC) was determined by saturating the soil with 1M ammonium acetate (NH₄OAc) at pH 8.1 as an extraction solution according to the method described by Suarez [16]. The content of Organic Matter (O.M.) was determined using Nelson and Sommer [17] technique. A quick titration method, based on the approach technique of Rayment and Higginson [18] approach, was used to quantify the total carbonate minerals in soil expressed as carbonate minerals equivalent. The Active Equivalent Carbonates (AEC), were estimated by the 0.5 M NH₄-oxalate method as described by Drouineau [19].

2.2 Potassium adsorption experiment procedure

For the construction of the potassium adsorption isotherm, each soil sample of 5.0 g was placed into a plastic bottle of 100-ml and then equilibrated with so ml of 0.01 M CaCl₂ with (soil/solution ratio of 5/50), using various concentration of potassium (K) which were (0, 25, 50, 100, 150, 200, 250, and 300 mg L⁻¹ K as KCl). The suspensions were then shaken for 2 hours at 180 rpm and 298 K in a horizontal flask shaker before being allowed to equilibrate overnight. Every solution was centrifuged at 250 rpm for 5 minutes after that, it was filtered through Whitman filter paper No. 42 and tested for K concentration using a Flame Photometer JENWAY model PFP7. By subtracting the quantity measured in the solution which was supernatant from the original amount of added K, the amount of K adsorbed was estimated, as shown below:

$$adsorbed\ K = C_o - C_e \dots\dots\dots (1)$$

Where C_o = the initial concentration of added K (mg L⁻¹) and C_e= concentration of K (mg L⁻¹) in the equilibrium supernatant solution.

The removal efficiency was determined by computing the percentage adsorption using the formulae in Mandal et al. [20].

$$K\ adsorbed(\%) = \frac{(con.\ of\ adsorbed\ K\ (mg\ L^{-1}) \times 100)}{C_o\ (mg\ L^{-1})} \dots\dots (2)$$

According to Vanderborght and Van Grieken [21], the amount of adsorbed Kat equilibrium (mg kg⁻¹) was determined as follows:

$$q_e = \frac{(C_o - C_e)V}{W} \dots\dots\dots (3)$$

Where q_e represents the quantity of K adsorbed from the solution (mg kg⁻¹),

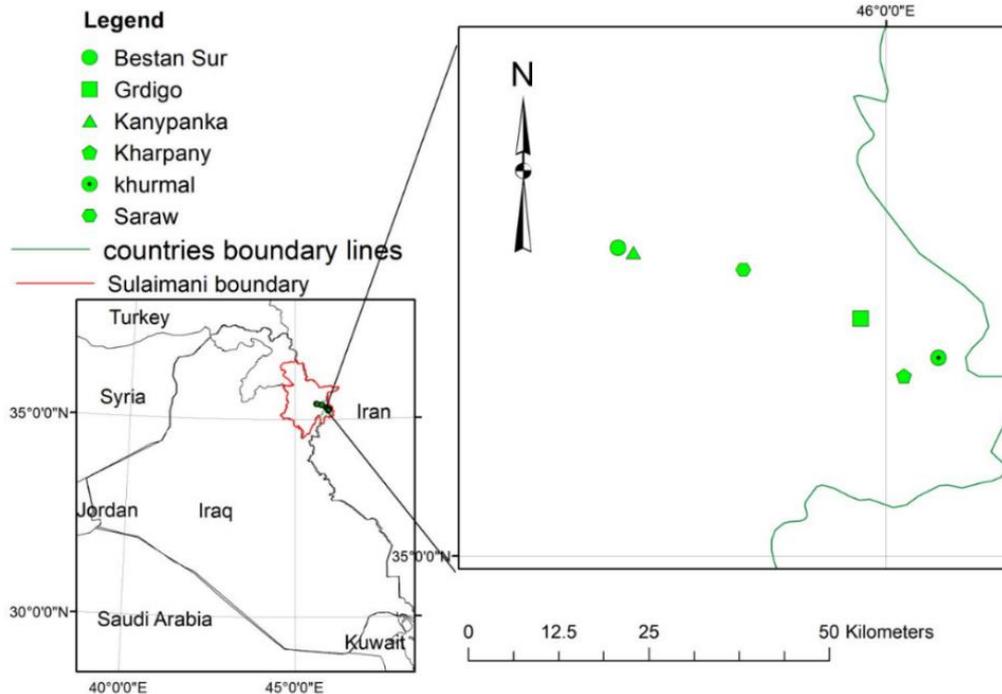


Figure 1: Geographical location of studied sites.

V represents the volume of the solution (L), and W represents the weight of the soil sample used in the experiment (kg). The linearized forms of the Freundlich, Langmuir, and Temkin isotherms were used to calculate the results.

2.3 Freundlich adsorption isotherm

Freundlich isotherm was one of the first to propose an adsorption isotherm equation [22]. The Freundlich isotherm is an empirical model for non-ideal adsorption on homogeneous surfaces, as well as multilayer adsorption with an uneven distribution of heat of adsorption and sympathies all over the surface that was heterogeneous [23]. Based on sorption onto a heterogeneous surface, the empirical Freundlich equation is:

$$q_e = K_F C_e^{(1/n)} \dots \dots \dots (4)$$

By taking logarithms, Eq.(4) can be rearranged to obtain a linear form. Equation (5):

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \dots \dots \dots (5)$$

Where K_f is the energy of sorption or distribution coefficient (mg kg^{-1}). In the adsorption process, n is the dimensionless constant, and $1/n$ is a function of the strength of adsorption in the adsorption process [24]. The partition between the two phases is concentration-independent if the Freundlich affinity value n equals 1. If $1/n$ is smaller than 1, the value shows normal adsorption. However, if the value is more than 1, it suggests cooperative adsorption [25]. The Freundlich sympathy value, n is important for consideration sorption processes and heterogeneity of the system. The process of sorption is favorable when the value of n is between 1 and 10, [26, 27]. A $1/n$ value approaching unity denotes a more homogenous system, while a $1/n$ value near zero denotes a more heterogeneous system [28].

2.4 Langmuir adsorption isotherm

The Langmuir model assumes monolayer adsorption of solutes on homogenous sorption sites, and the Langmuir equation defines the distribution of K between the solid-liquid interface equilibrium.

The Langmuir isotherm was the most extensively used linear expression for studying the interactions between solute concentrations in the liquid and solid phases at equilibrium conditions [29, 30]. Equation (6) describes the Langmuir isotherm model.

$$\frac{1}{q_e} = \frac{1}{b} + \frac{1}{bK_L C_e} \dots\dots\dots (6)$$

Where q_e represents the amount of adsorbed potassium per unit of soil weight (mg kg^{-1}), C_e represents the concentration potassium in the solution at equilibrium (mg L^{-1}) point, K_L represents the bonding energy or affinity constant of potassium to the soil (L mg^{-1}), and b represents the soil's highest monolayer coverage ability while K is adsorbed (mg kg^{-1}). A consecutive line with a slope of $1/bK_L$ and an intercept of $1/b$ when plotted against $1/C_e$. R_L is the dimensionless constant called the equilibrium parameter for Langmuir isotherm [31].

$$R_L = \frac{1}{(1 + K_L C_o)} \dots\dots\dots (7)$$

where K_L is a constant relative to bonding energy (L mg^{-1}) and C_o is the initial K concentration (mg L^{-1}), R_L values indicate the shape of isotherm [32]. The R_L value indicates whether the adsorption is favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$), or irreversible ($R_L = 0$).

According to Reyhanitabar et al. [33], the buffering capacity (MBC) which was at its highest value was estimated as the product of K_L and b .

$$MBC = K_L * b \dots\dots\dots (8)$$

2.5 The Temkin isotherm

The Temkin isotherm was estimated that the heat of adsorption decreases in a linear rather than logarithmic manner. Furthermore, it is restricted to chemical adsorption and has homogeneous binding energy [34].

Equation (9) can be used to describe the Temkin isotherm.

$$q_e = \frac{RT}{b_T} \ln(A_T C_e) \dots\dots\dots (9)$$

$$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e \dots\dots\dots (10)$$

The linear form of the Temkin isotherm model is given by the following [35]:

$$q_e = B \ln A_T + B \ln C_e \dots\dots\dots (11).$$

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

$$B = \frac{RT}{b_T} \dots\dots\dots (12)$$

where b_T is the Temkin constant linked 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 [36] R is the universal gas constant ($8.314 \text{ J mol}^{-1}\text{K}^{-1}$), T stands for the temperature with an absolute value of 298 kelvin. A plot of q_e versus $\ln C_e$ (equation 10) results in a straight line of slope RT/b_T and intercept $\frac{RT}{b_T} \ln A_T$

enables the determination of the isotherm constants A_T and b_T .

3-RESULTS AND DISCUSSION

Table 1 demonstrates some of the soil characteristics (physical and chemical) that were studied previously. The concentration of equilibrium K in the soil solution ranged from 1.65 to 3.76 mg L⁻¹ for 25 mg L⁻¹ added K, and from 170.15 to 181.81 mg L⁻¹ for 300 mg L⁻¹ added K. The direct proportionality that existed was demonstrated by the linear relationship between additional K and equilibrium K (mg L⁻¹) (Figure 2). With increasing K concentrations, the percent of K adsorbed did not increase equally (Figure 3). The range (%) of the adsorbed potassium (K) was lined in a range between 84.953 to 93.421% for the added K concentration which was lowest (25 mg L⁻¹) and from 39.398 to 43.284% for the maximum added concentration of K (300 mg L⁻¹). All the studied soils indicated a decrease in percentage adsorption K after initially adding with different K levels for the three first K levels and the presence of adsorbed K for all studied soils at the latest three added K concentration levels, are close to each other and in parallel. These results are similar to the finding by Auge et al [37].

Table 1: Some physicochemical properties of the studied soils

Locations	pH (1:2)	EC dS m ⁻¹	Particle Size Distribution (PSD) (g kg ⁻¹)			Texture* (cmol _c kg ⁻¹)	CEC (cmol _c kg ⁻¹)	OM (g kg ⁻¹)	CCE** (g kg ⁻¹)	
			Sand	Silt	Clay					Total
Bestan Sur	7.73	0.241	190	620	190	SL	43.50	13.5	61.0	41.0
Serwan	7.91	0.472	140	640	220	SL	37.00	16.2	121.0	82.0
Grdigo	7.92	0.512	210	570	220	SL	38.00	17.4	106.0	61.0
Khurnal	7.74	0.392	180	280	540	C	35.00	15.3	146.0	99.0
Kharpany	7.85	0.494	190	270	540	C	40.00	16.6	186.0	120.0
Kanypanka	7.88	0.498	90	550	360	SCL	42.00	17.1	139.0	89.0

* SL, silty loam, C, clay, SCL, silty clay loam, ** CCE, calcium carbonate equivalent

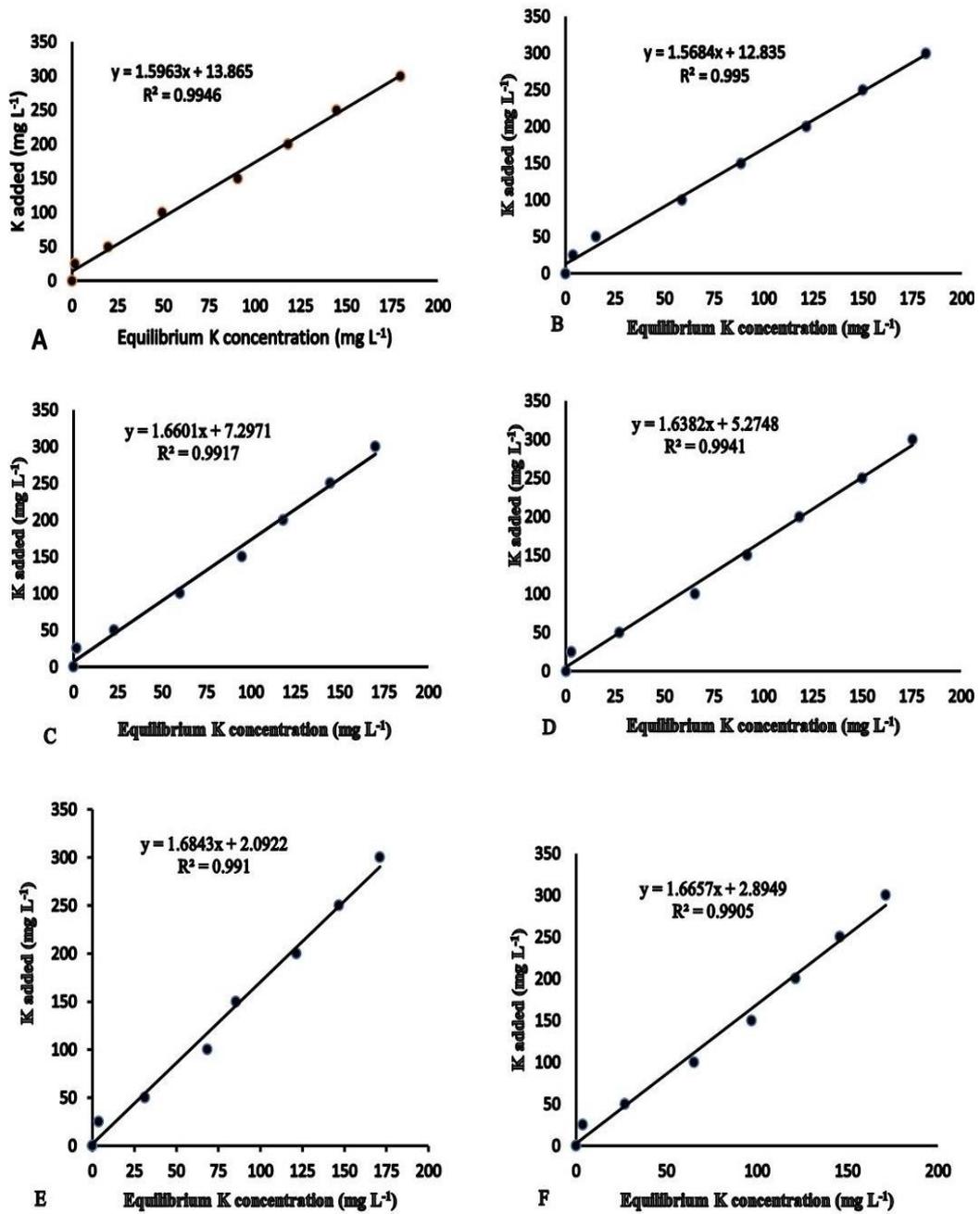


Figure 2: Potassium adsorption characteristics of (A) Bestan Sur, (B) Serwan, (C) Grdigo, (D) Khurmal, (E) Kharpany, and (F) Kanypanka locations.

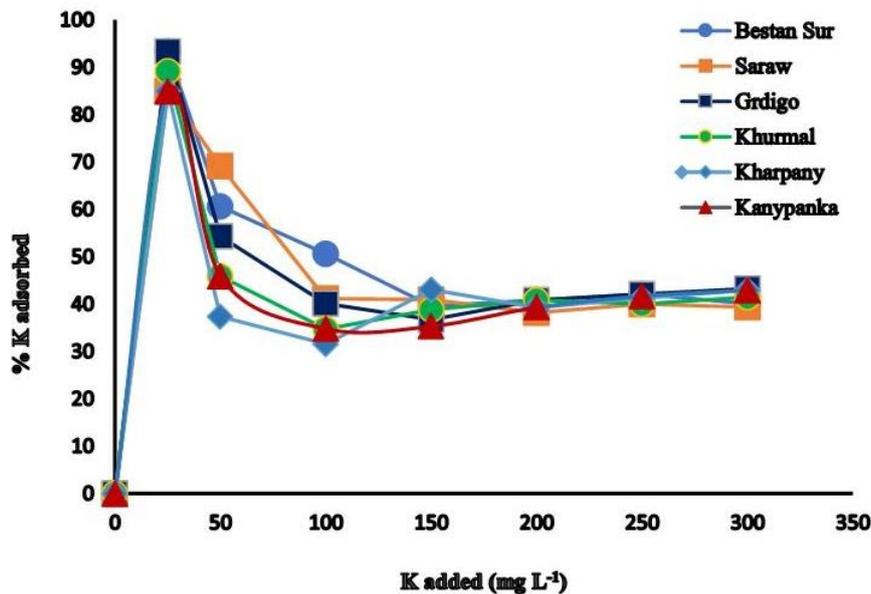


Figure 3: Percent K adsorbed as a function of different K concentration levels of studied soils.

3.1 Comparison of different adsorption isotherms

The sorption isotherms precision alters depending on the soil. In comparison to the Langmuir and Temkin models, the Freundlich model exhibited an advanced match (Figure 4) of equilibrium K adsorption for the soil of silty loam type at Srwan site, as demonstrated by the (R^2) values coefficient (Table 2). These findings are consistent with Kassa et al. [38], who indicated that the Freundlich model performed better than the other model in describing K adsorption. This was due to qualitative changes in the mineralogy and chemistry of the fractions that were separated [39].

Freundlich's isotherm assumes low adsorption energy, for the constant K_f , and $1/n$ (Table 2) as a measure of adsorption extent [24]. The buffering capacity of the soil is performed by the constant value of $1/n$. [40]. The $1/n$ value is a heterogeneity parameter, and it is a function of the strength of adsorption in the adsorption process, with less $1/n$ values indicating more heterogeneity [26]. As a result, the soils of the whole studied locations have a high heterogeneity, and a normal adsorption process [25] the n parameter values reflect even if the process of sorption is favorable or not [37]. For favorable sorption processes, the value of n lies between one and ten [37,27]. Depending on the values of n parameters in this study the sorption processes for the whole studied soils are favorable (Table 2). These findings are consistent with Mam Rasul [41] findings. The adsorption capacity (K_F) Freundlich constants describe the amount of potassium (K) held on non-specific sites they are ready to be released for uptake by plants during cropping season [24, 40]. It was 74.75 to 156.39 mg kg⁻¹ on average, with a mean value (112.41 mg kg⁻¹). The Langmuir isotherm assumes that all adsorption sites have the same affinity for the adsorbate molecules. As a result, the existence of adsorbed molecules at a nearby location is noteworthy [26]. From the intercept and slope of the straight equations of figure 5, depending on the Langmuir isotherm model's the maximum monolayer coverage capacity (b) ranged from 500.00 to 714.29 mg kg⁻¹ (Table 2), all the studied soils indicated high monolayer coverage capacity possessing the best fit to Langmuir model. These findings are consistent with those of Auge et al. [37].

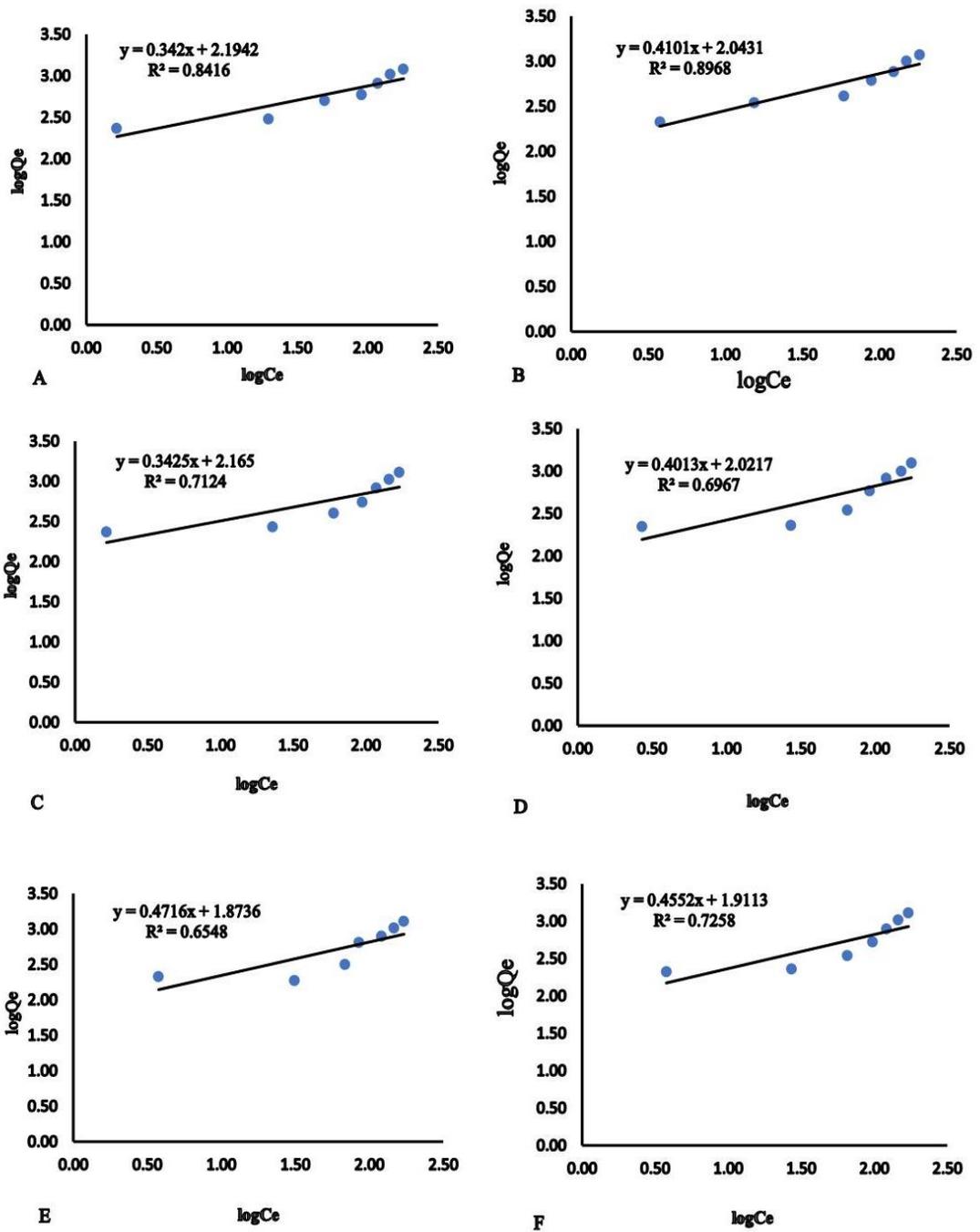


Figure 4: Freundlich adsorption isotherm for (A) Bestan Sur, (B) Serwan, (C) Grdigo, (D) Khurmal, (E) Kharpany, and (F) Kanypanka locations

Table 2: Freundlich, Langmuir and Temkin isotherms constants for the adsorption of potassium on the studied soil

Locations	Freundlich Isotherm				Langmuir Isotherm				Temkin Isotherm				
	R ²	1/n	n	K _F	R ²	b	K _L	MBC	R _L	R ²	A _T	b _t	B
		kg mg ⁻¹	mg kg ⁻¹	L kg ⁻¹									
Bestan Sur	0.84	0.34	2.92	156.39	0.65	666.67	0.319	212.67	1.11	0.68	0.003	13.47	186.93
Saraw	0.90	0.41	2.44	110.43	0.84	714.29	0.107	76.43	1.01	0.74	0.148	11.48	215.91
Grdigo	0.71	0.34	2.92	146.22	0.51	588.24	0.425	250.00	1.2	0.55	0.041	13.37	185.30
Khormal	0.70	0.40	2.49	105.12	0.43	526.32	0.247	130.00	1.07	0.58	0.346	11.89	208.31
Kharpany	0.66	0.47	2.12	74.75	0.33	500.00	0.177	88.50	1.03	0.60	0.464	10.46	236.76
Kanypanka	0.73	0.46	2.20	81.53	0.49	555.56	0.153	85.00	1.02	0.58	0.479	10.51	235.57
Mean	0.75	0.40	2.16	112.41	0.54	591.85	0.288	140.43	1.07	0.62	0.280	11.86	211.46

The maximum monolayer capacity (b) can be used to calculate how much fertilizer should be applied to unfertilized soil [25]. The Langmuir isotherm constant (K_L) ranged from 0.107 to 0.425 Lmg⁻¹. Smaller K_L values, according to Mehandi and Taylor [42], mean that the adsorbed K is more accessible to transform to non-exchangeable form, either through the production of crystalline K or through occlusion through K ions. K_L indicates the measurement of adsorbent

sympathy, according to Del-Bubba et al. [43], A high K_L value, according to Anderson and Wu [44] indicates the power of attaching to the minerals of the soil was clay. The adsorption nature of the potassium (K) for all studied soils is unfavorable because of the diffusion coefficient values ($R_L > 1$) (Table 2). These results not matching with the results of Mam Rasul [41], who found that the adsorption nature of potassium for calcareous soil in the Kurdistan Region of Iraq is linear because in his study the value of $R_L = 1$. The maximum buffering capacity (MBC) of the studied soil ranged between (85.00 to 250) $L\ kg^{-1}$ (Table 2). MBC is a capacity factor that assesses the soil's ability to release the restored K ions from adsorbed K to soil solution as mentioned by Rehman et al. [45]. The ability of a soil to give K to the soil solution, according to Fried and Shapiro [46], is an important component in determining a soil's K status.

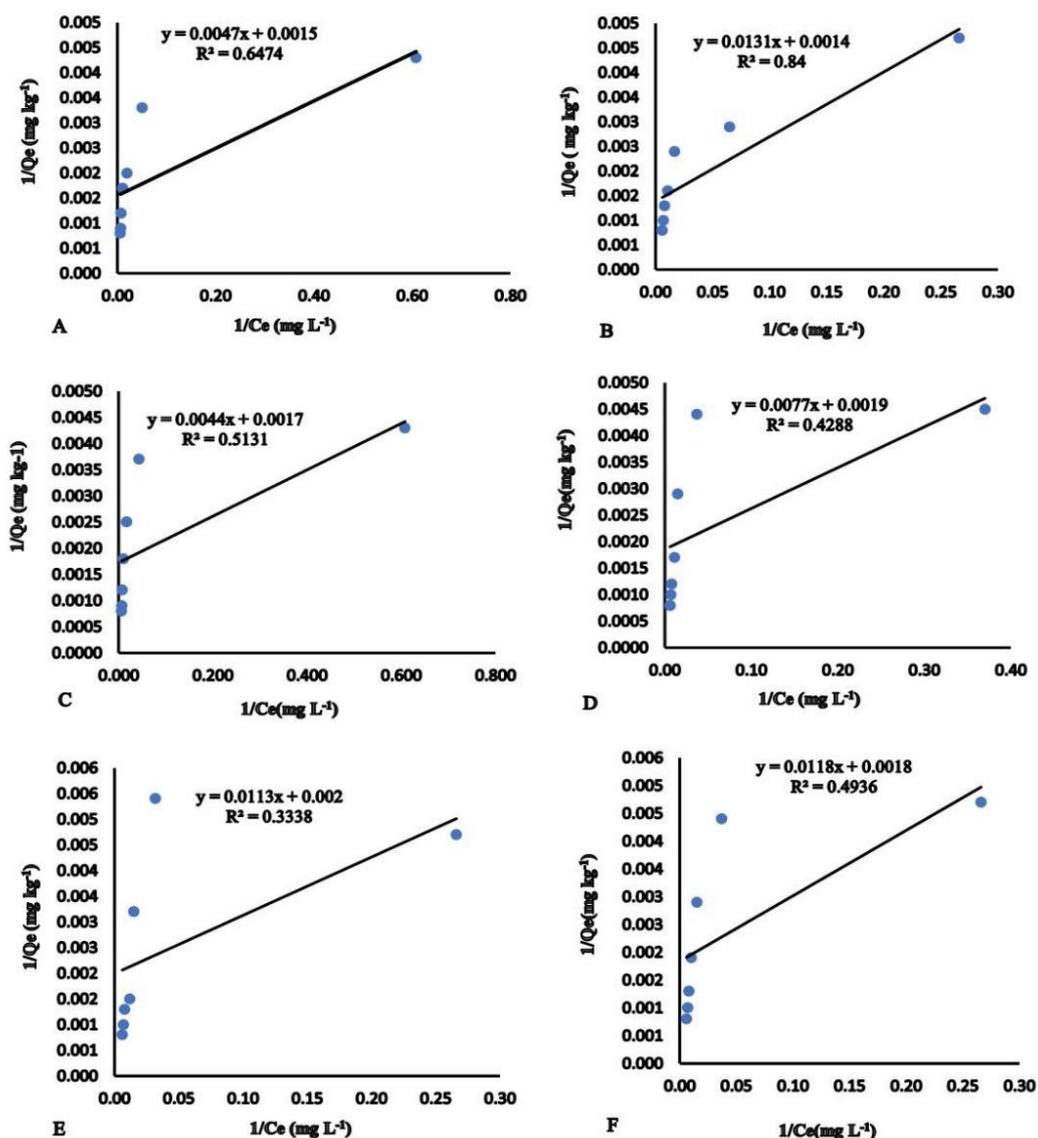


Figure 5: Langmuir adsorption isotherm for (A) Bestan Sur, (B) Serwan, (C) Grdigo, (D) Khurmāl, (E) Kharpany, and (F) Kanypanka locations.

The Temkin isotherm equilibrium parameters are calculated from the intercept and slope of the straight-line equation of figure 6. The binding constant, A_T ($L\ kg^{-1}$) value, ranged from (0.003

to $0.479) \text{ L kg}^{-1}$ (Table 2), the soil of Kanypanks location had a high binding constant. The values of b_T ranged from 10.46 to 13.47 J mole^{-1} with the mean of $11.86 \text{ J mole}^{-1}$. A positive value of b_T implies that the adsorption processes in the soil of the analyzed areas are exothermic. Furthermore, high constant values related to sorption heat, $B (\text{J mol}^{-1})$ demonstrate a high contact between the adsorbent and that of adsorbate, implying the mechanism of the exchange of ion [26]. These findings are consistent with the results of Mam Rasul [41].

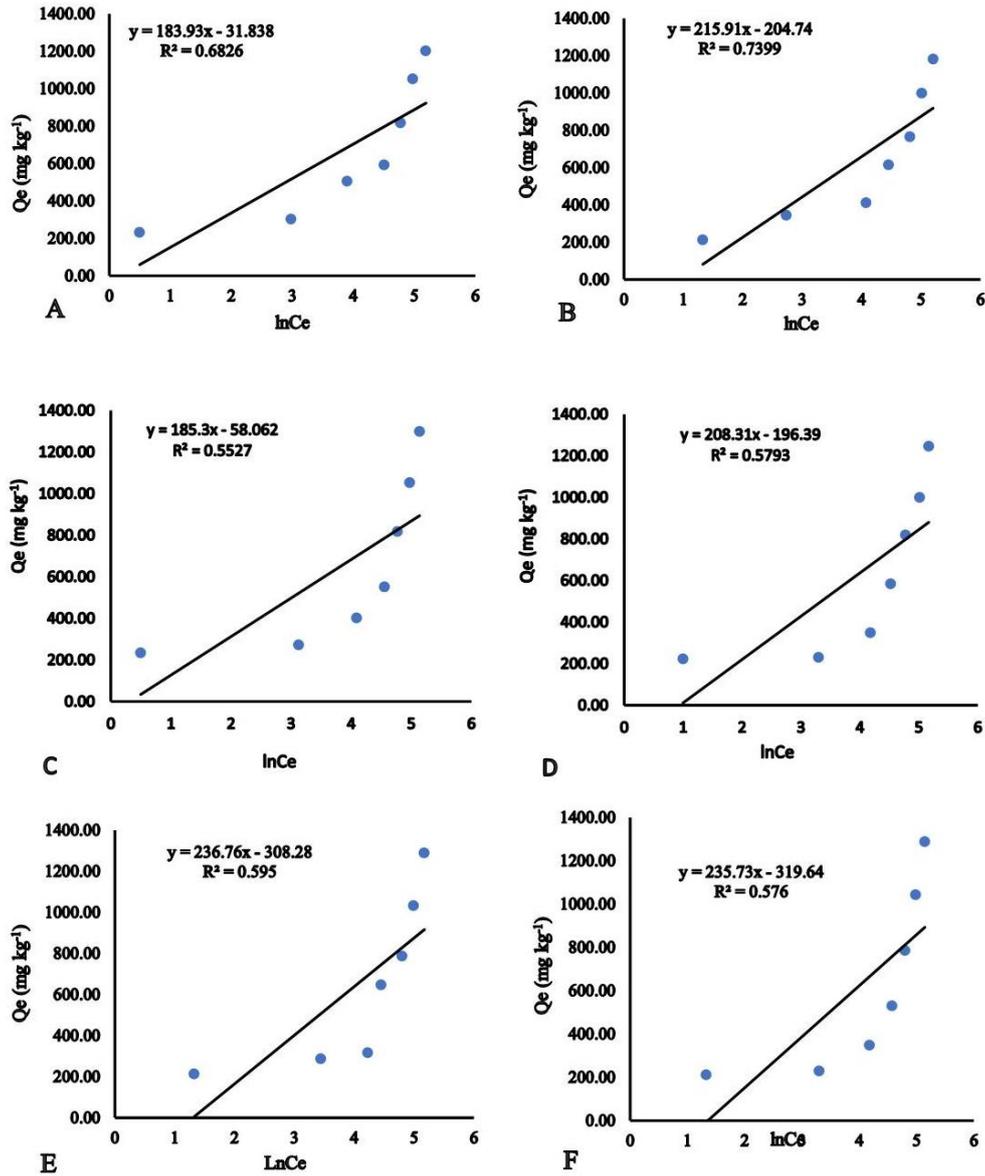


Figure 6: Temkin adsorption isotherm for (A) Bestan Sur, (B) Serwan, (C) Grdigo, (D) Khurmal, (E) Kharpany, and (F) Kanypanka locations.

4. CONCLUSION AND RECOMMENDATION

The importance of isotherms in assessing soil K adsorption characteristics was revealed by the outcomes of this study. The low $1/n$ values of the soils investigated suggest that the soil has a low buffering capacity. Exchangeable potassium has high binding energy on exchangeable sites. These showed that the crop in the examined soils had a limited supply of K. As a result, it can be observed that K fertilizer is required to restore the soil solution K in the examined soils. This suggested that crops in the examined soils were inadequate in K, proposing that K should be one of the soil management options.

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