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A Study of potassium adsorption in some soils north of Dhi-Qar province in Iraq

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Abstract. To study the phenomenon of potassium adsorption to some soils in northern Dhi-Qar Governorate / southern Iraq with different characteristics, which included agricultural and non-agricultural sites such as Al-Shatrah, Al-Nasr, Al-Dawaya, Al-Rifai, Qalat Sukar, and Al-Fajr, 1 g of soil was taken and potassium was added to it at levels (0, 20, 40, 60, 80). 100, 120, 140) mg L⁻¹, prepared from potassium chloride KCl, and complete the volume to 50 ml with a solution of 0.01 M CaCl₂. The concepts of thermal symmetry of adsorption equations were tested (Langmuir, Freundlich). The results of the study showed that the adsorption equations succeeded in describing the adsorption of potassium by soil samples, but these equations differed in their efficiency depending on the soil properties of agricultural and non-agricultural sites. The Langmuir equation was the most efficient in describing the adsorption of potassium by soil samples of non-agricultural sites because it obtained the highest values of the coefficient of determination R² compared to the Freundlich equation. The results of the study also showed that the amount of potassium absorbed by the soil increased with the increase in the amount of potassium added to the balance solution, and the amount absorbed differed according to the characteristics of the soil and the sites studied. The values of the diffusion coefficient (K_d) decreased with an increase in the concentration of potassium added to the soil, and its value increased in the soil of non-agricultural sites compared to agricultural sites, where the value of (K_d) for the soil of non-agricultural sites ranged between (2.60 - 11.75) L kg⁻¹ and for agricultural sites between (2.70 - 11.25) L kg⁻¹.

Keywords: potassium, adsorption, Langmuir, K_d, K_f

1. Introduction

Potassium is one of the main nutrients necessary for plant growth due to its important role in many vital physiological processes in plants, such as photosynthesis and increasing the plant's tolerance to various environmental stresses such as heat, drought, and salinity, in addition to its role as an enzyme



activator, as it activates more than 70 enzymes, in addition to other functions important for plants [1]. The lack of potassium in the soil affects the productivity of economic crops, so many studies were conducted on the state of potassium in Iraqi soils [2, 3].

The results of these studies showed that Iraqi soils possess relatively large stores of potassium, as is the case for most soils in arid and semi-arid regions, but the speed of potassium release is relatively slow and may not be sufficient to meet the needs of many crops, especially in conditions of intensive agriculture [4]. In addition, the images of potassium are in a state of constant change, so traditional measurement methods in the soil are no longer a sufficient measure to detect the readiness of potassium and the ability of the soil to release it, as the results of the studies indicated the necessity of using thermodynamic and kinetic standards as more accurate and realistic to detect the behavior of potassium in the soil [5]. Adsorption process is one of the basic chemical reactions that take place in the soil, through which ions are attached to the surfaces of soil colloids with electrostatic bonds. The adsorption process limits the movement of nutrients, heavy elements, pesticides, and other organic compounds in the soil [6]. The adsorption process is linked to many soil characteristics, such as pH, surface charge, time, type of adsorbent, ionic strength, clay, organic matter, carbonate minerals, and iron and manganese oxides, and the interaction of these factors may increase or decrease the movement of ions between the colloidal surfaces and the soil solution [7].

The phenomenon of adsorption and release of nutrients in the soil and their importance to plants has been described using many equations, including the Frenndlich and Langmuir equation and other equations [8]. And the study of the kinetics of adsorption and release reactions is considered an important preface for clarifying the direction and mechanics of the chemical reaction of adsorption and release processes [9]. And it is also possible to predict the final state of the element in the soil system in the early stages of imbalance [10]. It is necessary to know the rate at which the element is absorbed or released to predict the conditions that lead to its adsorption on the solid phase or its descent into the equilibrium solution of the soil and the extent of its readiness for the plant. Also, researching the amount of the element that is predicted to be absorbed over time is considered useful for knowing the extent of the element's readiness in the soil [11].

To obtain an economic return on the hand and solving the problems facing the management of this element in the soil before they occur on the other hand [12]. In addition to developing plans to evaluate the condition and behavior of the potassium element in the soil, and based on this modern vision, our study was conducted to use Thermodynamic criteria in studying potassium adsorption by soil colloids within the soil of northern Dhi-Qar Governorate.

2. Materials and methods

Soil samples were collected from twelve agricultural and non-agricultural sites north of Dhi Qar Governorate, southern Iraq, with different characteristics and from the surface layer of the soil 0-30 cm. The soil samples were dried, ground, and passed through a sieve with a holes diameter of 2 mm. Some chemical and physical properties of the soil were estimated according to the standard analysis methods mentioned in Page et al. [13]. And Black [14], tables (1 and 2).

Table 1. Selected physical and chemical properties in the agricultural soils.

Soil No.	Location	EC	pH	Cmol	gm . Kg ⁻¹				Texture	
		dS.m ⁻¹		Kg ⁻¹	CEC	O.M	CaCO ₃	Sand		Silt
1	Qalat Sukar	58.75	7.53	24.7	11.50	520	241	405	354	CL
2	Al-Nasr	41.50	7.23	26.0	6.19	460	191	292	517	C
3	Al-Shatrah	6.50	7.22	24.4	8.08	470	378	130	492	C
4	Al-Fajr	22.18	7.60	20.0	16.56	490	318	382	300	CL
5	Al-Dawaya	62.50	7.11	25.0	6.11	750	451	175	374	SC
6	Al-Rifai	18.25	7.18	26.5	8.08	450	443	267	290	SCL

Table 2. Selected physical and chemical properties in the non-agricultural.

Soil No.	Location	EC	pH	Cmol	gm . Kg ⁻¹				Texture	
		dS.m ⁻¹		Kg ⁻¹	CEC	O.M	CaCO ₃	Sand		Silt
1	Qalat Sukar	38.80	7.80	20.1	15.60	550	379	321	300	CL
2	Al-Nasr	22.01	7.13	23.1	8.25	650	191	330	479	C
3	Al-Shatrah	5.40	7.20	23.3	9.77	490	253	355	392	CL
4	Al-Fajr	2.60	7.40	20.0	21.80	490	313	417	270	CL
5	Al-Dawaya	7.30	7.3	23.1	8.57	400	250	393	357	CL
6	Al-Rifai	19.30	7.21	24.0	19.25	540	379	358	263	L

The potassium K⁺ adsorption experiment was carried out by taking 1 g of soil and placed in plastic tubes, to which a series of potassium concentrations (0, 20, 40, 60, 80, 100, 120, 140) mg L⁻¹, prepared from potassium chloride KCl, were added, the volume was completed to 50 ml with a 0.01 M CaCl₂ solution. The tubes were closed and the suspensions were shaken for one hour and left for 24 hours to reach a state of quiescent equilibrium at a temperature of 25 ± 1°C. The suspensions were filtered and

dissolved potassium was estimated using a flame photometer. The adsorbed amount of potassium was calculated using the following equation:

$$X = (C_0 - C)V / W \quad (1)$$

Where:

X = amount of potassium ion adsorbed (mg K kg⁻¹ soil)

C₀ = initial potassium concentration (mg L⁻¹)

C = concentration of potassium in the equilibrium solution (mg L⁻¹)

V = total volume of extraction solution (ml)

W = weight of soil (g).

The results of adsorption reactions for potassium were tested by applying the Langmuir equation in its single-plane linear form for isotherm equilibrium.

$$C/X = 1 / kb + C / b \quad (2)$$

Where:

X = amount of potassium ion adsorbed (mg K kg⁻¹ soil)

C = concentration of potassium in the equilibrium solution (mg L⁻¹)

k = binding energy factor constant (ml.μg⁻¹)

b = maximum adsorption limit constant (mg.kg⁻¹)

The value of the constants was calculated by drawing the relationship between the values of C/X and C and obtaining a straight line the slope of the line represents a value of 1/b, while the intercept represents a value of 1/kb. Adsorption reactions were also tested using the Freundlich equation in its linear form.

$$\text{Log } X = \text{Log } K + 1/n \text{ Log } C \quad (3)$$

Where:

X = amount of potassium ion adsorbed (mg K kg⁻¹ soil)

C = concentration of potassium in the equilibrium solution (mg L⁻¹)

(k, 1/n) = Freundlich equation constants

k = maximum adsorption limit (mg.kg⁻¹)

1/n = binding energy factor (ml.μg⁻¹)

These constants were calculated by drawing the relationship between the values of Log X and Log C, where the value of Log K represents the intercept, while the value of 1/n is the slope of the straight line.

The distribution coefficient (K_d) for the adsorption process of potassium was calculated according to the equation given in [15].

$$K_d = S/C \quad (4)$$

Where:

K_d = diffusion coefficient ($L \text{ kg}^{-1}$)

S = amount of potassium adsorbed (mg.kg^{-1})

C = concentration of potassium ion in the equilibrium solution (mg L^{-1})

3. Results and discussion

3.1. Evaluation of the constants of adsorption equations

The results of the study, tables (3 and 4), showed the values of the constants of the adsorption equations for the one-plane Langmuir equation and the Freundlich equation, as studying these values gives us useful and important information about the ready and adsorbed amount of potassium in addition to the strength of its connection to the adsorption sites [6], it is noted from the results of the study that the values of the constants of the adsorption equations for potassium differed according to the properties of the soil, where the constant (b) of the Langmuir equation, which represents the maximum adsorption capacity, recorded values ranging between (333.333 - 555.315) mg kg^{-1} and (334.321 - 370.376) mg kg^{-1} for soils of non-agricultural and agricultural sites, respectively. While the value of the binding energy factor constant (K_L) for the soil of non-agricultural sites reached (0.0021 - 0.0561) $\text{ml } \mu\text{g}^{-1}$, while for agricultural sites, values ranged between (0.0380 - 0.0767) $\text{ml } \mu\text{g}^{-1}$.

As for the values of constants for the Freundlich equation, the record constant (K_f), which represents the greatest adsorption, ranged between (23.120 - 52.808) mg kg^{-1} and (42.305 - 45.789) mg kg^{-1} for non-agricultural and agricultural soils, respectively, while the constant (n), which represents the value of the binding energy between the adsorbed element and the solid phase of the soil, recorded values ranging between (1.617 - 2.647) $\text{ml } \mu\text{g}^{-1}$ for non-agricultural soils, while for agricultural soils it recorded values ranging between (2.315 - 2.657) $\text{ml } \mu\text{g}^{-1}$.

It is noted from the results of the study that the value of the maximum adsorption capacity in the Freundlich equation was lower than that of the one-plane Langmuir equation for agricultural and non-agricultural soils, in contrast to the value of the binding energy coefficient, which recorded a higher value for the Freundlich equation compared to the one-plane Langmuir equation.

Table 3. Constants of the Langmuir and Freundlich equation for potassium adsorption in study soils for non-agricultural sites.

Soil No.	Langmuir eq.			Freundlich eq.		
	K_L $\text{ml.}\mu\text{g}^{-1}$	b mg.kg^{-1}	R^2	K_f mg.kg^{-1}	n $\text{ml.}\mu\text{g}^{-1}$	R^2
1	0.0021	476.190	0.987	26.369	1.814	0.979
2	0.0206	526.315	0.984	24.490	1.662	0.968

3	0.0194	555.555	0.988	23.120	1.617	0.975
4	0.0251	416.666	0.989	28.674	1.916	0.981
5	0.0236	434.782	0.990	28.503	1.908	0.985
6	0.0561	333.333	0.997	52.808	2.647	0.909

Table 4. Constants of the Langmuir and Freundlich equation for potassium adsorption in study soils for agricultural sites.

Soil No.	Langmuir eq.			Freundlich eq.		
	K_L ml. μgm^{-1}	b mg. kg^{-1}	R^2	K_f mg. kg^{-1}	n ml. μgm^{-1}	R^2
1	0.0475	334.827	0.996	47.588	2.483	0.960
2	0.0380	370.376	0.989	42.305	2.315	0.944
3	0.0438	357.142	0.990	48.139	2.481	0.950
4	0.0767	333.333	0.998	54.087	2.594	0.882
5	0.0563	344.827	0.994	54.789	2.646	0.900
6	0.0571	334.321	0.992	54.062	2.657	0.894

In general, the adsorption capacity exceeded the binding energy, which gives us clear indications that there is a high surface area for the adsorption of nutrients, including potassium. To determine the best mathematical description of the adsorption process, researchers resort to adopting some statistical criteria, including the statistical coefficient of determination (R^2), as the results of the study (tables 3 and 4) show that the values of (R^2) for the Langmuir equation ranged between (0.984 - 0.997) and (0.989 - 0.998) for non-agricultural and agricultural soils, respectively.

As for the values of (R^2) for the Freundlich equation, they ranged between (0.975 - 0.985) and (0.882 - 0.960) for non-agricultural and agricultural soils, respectively. It is clear from the results of the study that the values of (R^2) were high for both equations, which indicates that both equations have succeeded in describing the adsorption process for potassium, but the one-plane Langmuir equation was more efficient in describing the adsorption process because it had a higher value for the statistical coefficient of determination (R^2) compared to the Freundlich equation.

The results of the study (see table 5) showed that the values of the constants for the Langmuir equation differed in the soils of agricultural sites compared to non-agricultural sites, as the value of the constant (b) increased in the soils of non-agricultural sites compared to agricultural sites, while the value of the constant (K_L) decreased, on the contrary.

It is clear from the above that there is a difference in the values of adsorbed potassium between the soil of agricultural and non-agricultural sites, and this may be attributed to many factors, including the mineral composition, soil clay content, wetting, drying, and organic matter, and the exposure of potassium to loss through washing and absorption by plants, which led to a decrease in its content in the agricultural soil sites compared to non-agricultural soil sites.

Table 5. Constants of the Langmuir equation for potassium adsorption in the study soils for agricultural and non-agricultural sites.

Soil No.	Non- agricultural			Agricultural		
	K_L ml μgm^{-1}	b mg Kg^{-1}	R^2	K_L ml μgm^{-1}	b mg Kg^{-1}	R^2

1	0.0021	476.190	0.987	0.0475	334.827	0.996
2	0.0206	526.315	0.984	0.0380	370.376	0.989
3	0.0194	555.555	0.988	0.0438	357.142	0.990
4	0.0251	416.666	0.989	0.0767	333.333	0.998
5	0.0236	434.782	0.990	0.0563	344.827	0.994
6	0.0561	333.333	0.997	0.0571	334.321	0.992

The results of the study (figures 1 and 2) indicate, through the potassium adsorption curves and using the one-plane linear Langmuir equation, that the amount of potassium adsorbed by the soil varied according to the initial concentration of the added potassium and the characteristics of the soil under study. In general, the amount of potassium adsorbed increased with the increase in the amount of added potassium, and this is agreed with what was found by [12] and the variation in chemical and physical properties of the soil (soil texture, its content of calcium carbonate, available potassium, organic matter, and soil salinity) had a clear impact in determining the amount of potassium adsorbed on the exchange surfaces of soil colloids and the amount of potassium remaining in the equilibrium solution.

3.2. Distribution Coefficient (K_d)

The results of the study in tables (6 and 7) show the values of the diffusion coefficient (K_d) for the adsorption process of potassium to the soils of non-agricultural and agricultural sites, respectively. The values of the diffusion coefficient (K_d) for the soils of non-agricultural sites ranged between (2.60 - 11.75) L kg⁻¹, while its values of agricultural sites ranged from (2.70 - 11.25) L kg⁻¹.

It is clear from the results of the study that the value of the diffusion coefficient (K_d) decreased with the increase in the concentration of potassium added to the soil, and its value increased in the soil of non-agricultural sites compared to agricultural sites. High values of the diffusion coefficient (K_d) indicate greater retention of the element on soil particles, while lower values of it indicate an increase in the concentration of the element in the soil solution and the ability of the element to participate in the chemical processes of the soil [16]. High values of the diffusion coefficient (K_d) are related to the high adsorption capacity and high binding energy of the element on the adsorption sites for organic and mineral soil colloids, especially calcium carbonate and iron oxides, to precipitate these elements within the soil colloids [17]. Many researchers also reported that soils containing carbonate and gypsum minerals are characterized by a high adsorption capacity compared to other soils [18. 19].

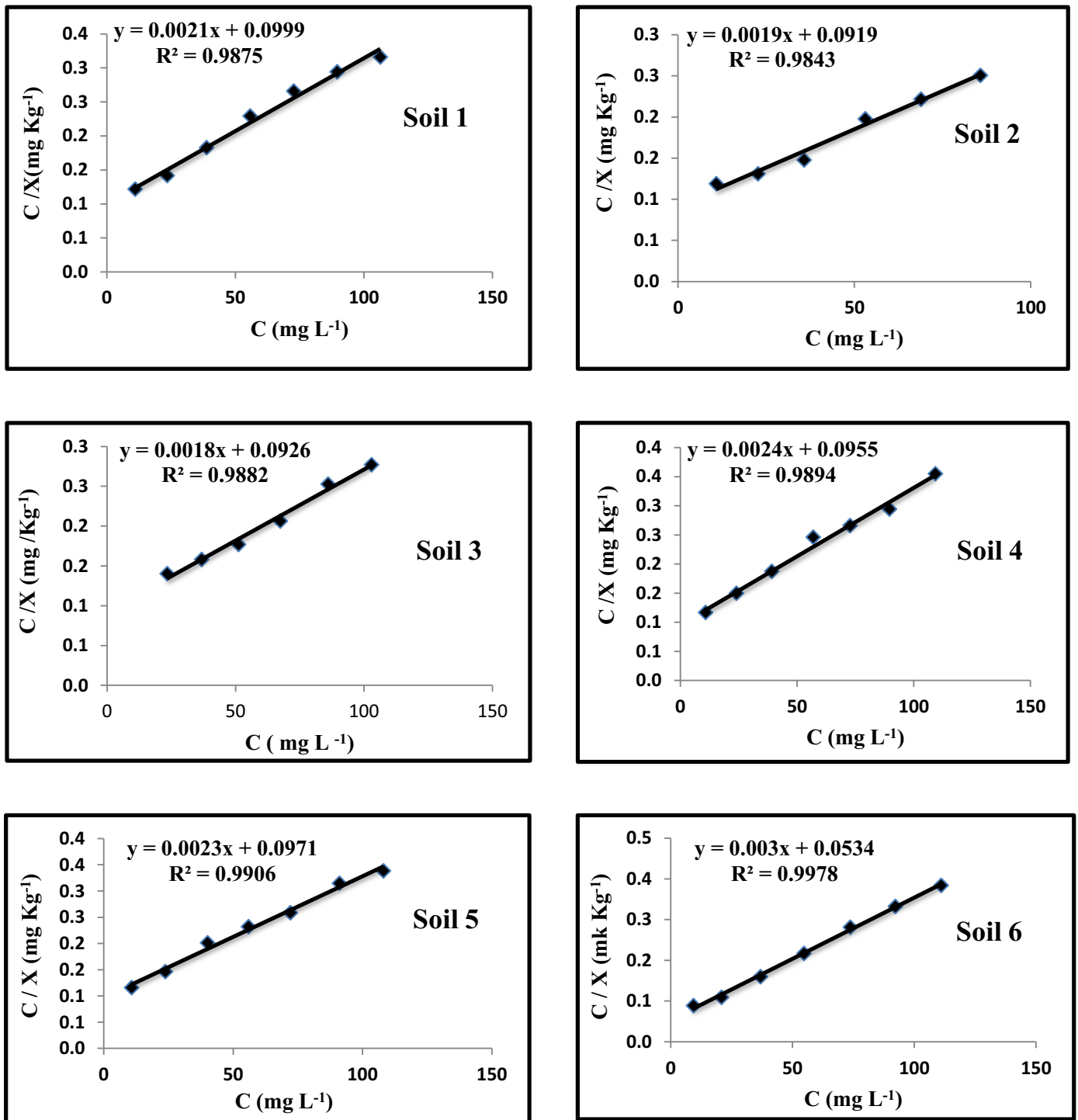


Figure 1. Potassium adsorption curves to describe the relationship between adsorbed (X) and dissolved (C) potassium in the soil of non-agricultural sites (soil1-6), according to the linear Langmuir equation.

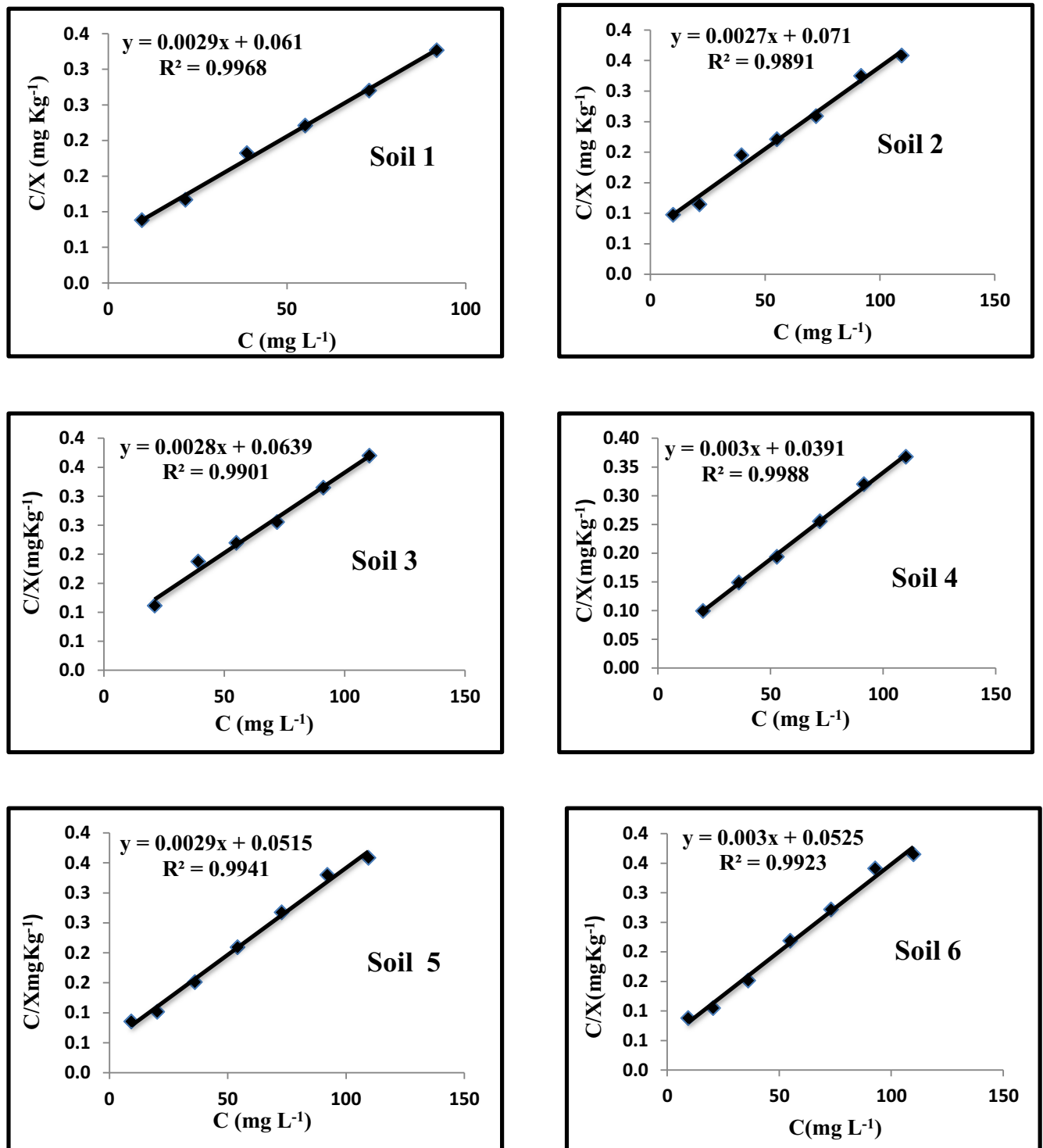


Figure 2. Potassium adsorption curves to describe the relationship between adsorbed (X) and dissolved (C) potassium in the soil of agricultural sites, according to the linear Langmuir equation.

Table 6. Values of the diffusion coefficient K_d ($L\ Kg^{-1}$) for the adsorbed amount of potassium in the soil of non-agricultural sites.

Soil No.	Addition Levels K(mgL^{-1})						
	20	40	60	80	100	120	140
1	11.32	8.45	5.48	4.52	3.76	3.40	3.17
2	10.26	8.74	5.13	4.52	4.51	3.99	3.62
3	11.75	8.97	5.33	4.55	4.85	3.96	3.61
4	11.46	10.04	6.71	5.16	3.76	3.40	2.82
5	11.72	9.85	6.63	4.78	3.86	3.18	2.95
6	11.39	9.55	6.61	4.61	3.55	3.01	2.60
Average	11.32	9.27	5.98	4.69	4.05	3.49	3.13
Max.	11.75	10.04	6.71	5.16	4.85	3.99	3.62
Min.	10.26	8.45	5.13	4.52	3.55	3.01	2.60

Table 7. Values of the diffusion coefficient K_d ($L\ Kg^{-1}$) for the adsorbed amount of potassium in the soil of agricultural sites.

Soil No.	Addition Levels K(mgL^{-1})						
	20	40	60	80	100	120	140
1	8.21	7.06	5.47	4.36	3.70	3.06	2.73
2	8.42	7.64	6.77	5.06	3.86	3.08	2.79
3	8.59	7.12	6.32	5.65	3.91	3.17	2.70
4	8.57	6.68	5.34	4.06	3.91	3.12	2.72
5	8.62	6.82	4.97	4.31	3.74	3.03	2.79
6	11.25	9.15	6.25	4.57	3.68	2.93	2.74
Average	8.94	7.41	5.85	4.67	3.80	3.07	2.75
Max.	11.25	9.15	6.77	5.65	3.91	3.17	2.79
Min.	8.21	6.68	4.97	4.06	3.68	2.93	2.70

4. Conclusions

The single-plane Langmuir equation, in its linear form, seems more appropriate in describing the adsorption of potassium by soil colloids compared to the Freundlich equation, as it obtains the highest value of the coefficient of determination R^2 . The properties of the soil played a role in the adsorption of potassium, and increasing the concentration of potassium added to the soil led to a decrease in the diffusion coefficient K_d .

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