



Comparison of Adsorption Models for Determining Potassium Behavior of Some Selected Soil Series

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Abstract

Potassium (K) availability to plants varies with the adsorption characteristics of soil, to evaluate the adsorption capacity, five soil series of different characteristics were used. K adsorption isotherms were performed by equilibrating 2.5 g soil samples with 10 levels of K (30-300 mg kg⁻¹) as KCl in 0.01 CaCl₂ solutions and shaken for 24 h at 25 °C. The amount of K adsorbed ranged from 33.2 to 94.9% of added K. Freundlich model explained K adsorption behavior better than the other two equations. Higher coefficient of regression values 0.99, 0.97 and 0.96 were recorded in Sultanpur (Silt loam), Naivela (Fine sandy loam) and Bhutesar (Clay loam), respectively. The highest 1/n value 1.54 kg mg⁻¹ and kf value 31.47 mg kg⁻¹ of Freundlich isotherm were observed in Sultanpur (silt loam) due to high pH, high OM and high clay contents, lowest values of constants were observed in Wajan (loamy sand) with 1/n value 0.44 kg mg⁻¹ and kf value 0.28 mg kg⁻¹ might be due to high EC, high CaCO₃ and sand contents. The K adsorption of soil varied with physico – chemical characteristics of soil, especially clay content, alkaline pH and organic matter content.

Keywords: Potassium, Adsorption, Freundlich, Langmuir and Temkin

Introduction

The dynamics of soil potassium (K) and its availability to plant is regulated by the chemical and physical processes and phenomenon's of adsorption and desorption [1]. The sorption and desorption of potassium depend on the distribution and retention of K by the soil minerals [2]. K deficiency in different soils of Pakistan is increasing at a rapid rate. It has been found that 35% in KPK, 28 % in Punjab and 8% in Sindh [3] had improper plant accessible potassium. Elimination of straw from the field and applying K fertilizer at a lower rate affect potassium depletion in soil [4].

The physical, chemical and biological processes also affect the availability of K [5].

Amongst the solution and solid phase, adsorption is the gathering of the chemical sort [6]. The movement and fortune of nutrients in the soil are affected due to adsorption. Adsorption of K in the soil is influenced by the kind and quantity of clay minerals [7]. In the soil system, the movement of soil potassium depends upon the dynamics equilibrium. Several types of factors such as the category of clay mineral, tillage techniques, cation exchange capacity (CEC), fertilizer application, soil moisture contents, soil pH, organic matter (SOM) contents and Al(OH)₃ [8] influence the dynamics equilibrium.

Adsorption reaction involves the attachment of solution ions onto the surface of the solid soil particles [9]. Specific adsorption refers to the structural bonding between the ions and the surface of the soil particles. In the reaction, the K may either adsorbed quickly or slowly by dispersing through the micropores within the intra-crystalline sites or distant surfaces [10]. Adsorption phenomenon may be non-specific, specific and complex involving the soil organic matter. The association between the concentration of K in the solution phase and extents of immovable K per unit soil weight has been studied through K- adsorption isotherm or numerous curves. The adsorption is satisfactorily described by employing adsorption models. According to [11] the Langmuir and Freundlich are the most widely used models. The Freundlich equation resembles to a model of adsorption due to the rise in the amount of adsorption where the affinity duration decreases exponentially. Freundlich isotherm communicates K adsorption magnificently [12] in a narrow range of K concentrations. On those surfaces where only one layer of molecules can be adsorbed, the Langmuir isotherm is imperfect. With the presence of several types of K sorption sites in the soils, the Langmuir model is incompatible [13], each with the different selectivity of K.

The relationship between K adsorption capacity and other soil properties can be clarified through the experiment of K adsorbing potential of soil [14]. The association between the sorption isotherm (K quantity adsorbed by the soil) and the capacity of soil solution K is accomplished by this resolution. This contribution aware and assume to increase crop yield and productivity through plant nutrients attachment, contest or create an association with the soil and aids to boost fertilizer [15]. In order to understand its insistent nature and capacity of soil to supply K to plant and exchangeable K can be

evaluated by using the K sorption isotherm [16]. Additionally, it also pronounces the interchange of K from the soils by other ions, especially calcium [17]. The current study was aimed to evaluate the K adsorption potential of soils having different characteristics and apply different adsorption models which better fit the adsorption isotherm.

Materials and Methods

Soil Sampling and Experimental Sites

A laboratory experiment was carried out at the Department of Soil Science, Faculty of Agriculture, Gomal University, Dera Ismail Khan, KPK, Pakistan (Fig. 1). For this purpose, five different soil series of Dera Ismail Khan, i.e., Sultanpur (silt loam), Bhutesar (clay loam), Saggu (silty clay loam), Naivela (fine sandy loam) and Wajan (loam sandy) were collected from the Farm sites at a depth of 0-30 cm (Table. 1). At least one composite soil sample made from 5 cores was collected randomly from each sampling area with the help of augur. All composite soil samples were air dried and ground to pass through a 2mm sieve. Each sampling site was classified according to USDA-classification and marked with a GPS (Table. 1) for accurate soil location.

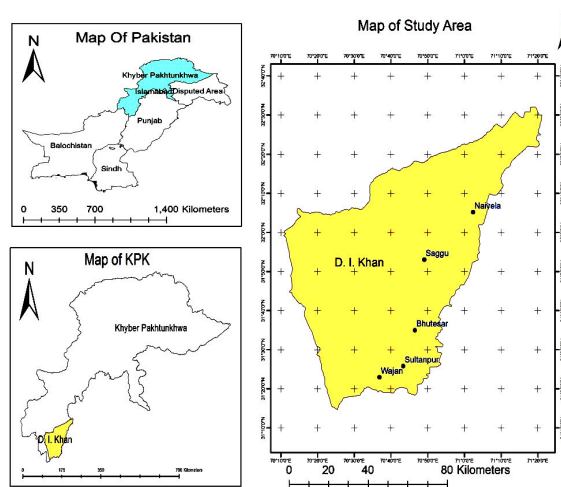


Figure 1. Location map of Dera Ismail Khan in Khyber Pakhtunkhwa (Pakistan), and map of study area

Table 1. Classification and location of Sultanpur, Bhutesar, Naivela, Saggu and Wajan soil series.

Soil Series	Texture Class	Classification	Location	GPS Readings
Sultanpur	Silt loam	Fluventic Haplocambids	D. G. Khan Road 48km southwest of D. I. Khan	N (31.430227) E (70.722437)
Bhutesar	Clay loam	Typic Haplocambids	D. I. Khan- D.G. Khan road near Hazara village	N (31.583788) E (70.775267)
Naivela	Fine sandy loam	Typic Torrifluvents	32 km north of D.I. Khan along with the Kot Hafiz Distributary	N (32.086266) E (71.039136)
Saggu	Silty clay loam	Vertic Haplocambids	11 km north-west of D. I. Khan on D.I. Khan-Tank road	N (31.884382) E (70.818103)
Wajan	Loam sandy	Typic Torrifluvents	1 km south-west of village Sarah Garah along the Ramak-Kiri Shamoza road	N (31.383002) E (70.614076)

Soil Analysis

Prior to the adsorption study, soil physicochemical characteristics were determined (Table. 2). The soil properties determined included soil texture, Soil pH and electrical conductivity were determined by the procedure given by Ryan *et al.*, [18]. While soil organic matter content [19], Calcium Carbonate [20] were determined titrimetrically. Soil nutrients, i.e., Extractable phosphorus [21] and Extractable K [22], were determined using the Spectrophotometer and Flame photometer, respectively.

Table 2. Physico-chemical properties of Sultanpur (Silt loam), Bhutesar (Clay loam), Naivela (Fine sandy loam), Saggu (Silty clay loam) and Wajan (Loam sandy) soil series.

Location	Sultanpur	Bhutesar	Naivela	Saggu	Wajan
pH	8.58	8.19	7.31	7.35	7.01
EC (dsm ⁻¹)	0.68	1.98	0.75	2.25	0.66
O.M %	0.75	0.61	0.39	0.33	0.41
CaCO ₃ %	7.6	8.3	12.21	15.5	13.4
CEC (cmol. kg ⁻¹)	17.51	11.32	12.32	9.01	9.21
Available K (mgkg ⁻¹)	141	175	131	153	126
Clay %	19	35	18	35	07
Silt %	56	38	22	47	10
Sand %	25	27	40	18	83
Texture class	Silt Loam	Clay Loam	Fine Sandy loam	Silty clay loam	Loam sandy

Adsorption Study

For the construction of potassium adsorption isotherm ten potassium

concentrations as KCl (30, 60, 90, 120, 150, 180, 210, 240, 270 and 300 mg kg⁻¹) with 0.01 M CaCl₂ were made by adding 25 mL solution in 2.50 g of soil samples. Soil samples with K concentrations were shaken up to 24 h at 25 °C to enhance adsorption equilibrium.

The experimental data of K adsorption were subjected to adsorption equations given below:

Langmuir adsorption equation

$$C/(x/m) = 1/kb + C/b$$

Potassium concentration (mg L⁻¹) in the equilibrium solution represented by C and potassium adsorbed per unit mass of soil (mg Kg⁻¹) presented by x/m.

Freundlich adsorption equation

$$x/m = a C^b \text{ By rearranging } \log (x/m) = \log a + b \log c$$

x/m and C represent the mass of potassium adsorbed per unit mass of soil (mg kg⁻¹) and the equilibrium solution potassium concentration (mg L⁻¹), respectively.

1/n and kf are constants obtained from the slope intercept, respectively.

Temkin adsorption equation

$$x/m = a + b \ln C$$

Where C and x/m determine the equilibrium solution K concentration (mg L⁻¹) and mass of

potassium adsorbed per unit mass of soil (mg kg^{-1}), respectively.

Linear regression equations were applied to the adsorption data using the procedure given by Kunter *et al.*, [23].

Results and Discussion

Adsorption Isotherm

The curve formed in Sultanpur (silt loam) showed a linear trend from 30 to 150 mg kg^{-1} K, but at highest concentrations, 210 to 300 mg kg^{-1} showed a curvilinear trend. Maximum adsorption (69.04 %) was recorded at 210 mg kg^{-1} K. The K adsorption slightly decreased at higher K concentrations (Fig. 2). Maximum adsorption was observed in Sultanpur (silt loam) among other soil series due to maximum pH (8.58), high cation exchange capacity EC 17.51 $\text{cmol}_c \text{ kg}^{-1}$ and high OM content 0.75% (Table. 2). As compared to soil mineral components the fast rate of K adsorption, which enhanced the adsorption of K was due to the existence of high organic matter. Presence of organic matter in soil release organic anions in the rhizosphere, which enhances the K adsorption capacity [24] due to the greater total negative surface charge of the soils.

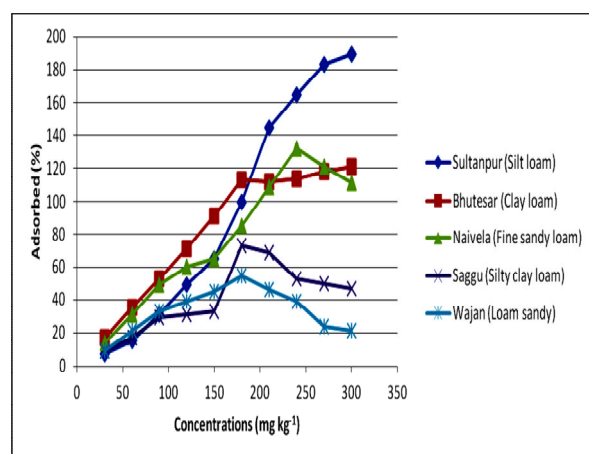


Figure 2. Different K concentration influenced K adsorption percentage on Silt loam, Clay loam, Fine sandy loam, Silty clay loam and Loam sandy of Dera Ismail Khan (Pakistan)

In Bhutesar (clay loam) soil series, the adsorption curve showed a linear trend initially, at higher potassium concentration curvilinear trend was observed. In Bhutesar (clay loam) soil series, maximum adsorption was recorded (62.77%) at 180 mg kg^{-1} , which revealed that adsorption was comparable with Sultanpur (silt loam) among others (Fig. 2), influenced by the same physico-chemical properties with higher pH 8.19, Higher clay contents 35%, OM 0.61% and lower CaCO_3 contents 8.3% (Table. 2). At a higher concentration of K the clay loam soil texture showed an enhanced K adsorption rate initially but the rate reduced after some time [25]. Furthermore, it was found from the study that loam, silty clay loam and sandy clay loam textures showed a reduction in K adsorption in the start as the rate increase, it enhanced. In clay soils, maximum adsorption of K was observed as compared with the other textures.

Naivela (fine sandy loam) soil showed a nonlinear trend initially and remain linear at mid concentrations of K. At maximum concentrations ranging from 240 to 300 mg kg^{-1} the downward plateau in the curve was observed in the Naivela soils. Maximum adsorption was observed 51.90% at 210 mg kg^{-1} (Fig. 2), this adsorption remains lower than Sultanpur (silt loam) and Bhutesar (clay loam) series. The texture class was fine sandy loam, pH 7.31 and low OM 0.39% (Table 2). Through three different soils texture, the maximum K adsorption was due to factors including soil pH, organic matter accumulation and clay mineral constituents [26]. The rate of K adsorption was increased by the change in pH value, while the capacity of K adsorption has been increased in the soils with pH range from 6 to 7.5.

The fourth soil series, namely Saggu (silty clay loam) showed a linear pattern initially, but a downward trend was observed from 180 mg kg^{-1} . In applied concentration, the highest adsorption 40.55 % was recorded

at 180 mg kg^{-1} (Fig. 2). As compared to Sultanpur (silt loam), Bhutesar (clay loam) and Naivela (fine sandy loam), Saggi isotherm has lowest adsorption because of the lowest OM 0.33 %, high EC $2.25 \text{ (dsm}^{-1}\text{)}$ and high CaCO_3 contents 15.5 % (Table. 2). Another characteristic, such as higher CaCO_3 contents (lime) liable for the reduction in adsorption of K in soil. Due to the monovalent K ion, it can easily dislocate through the presence of lime containing divalent cations like calcium, which prefers calcium attachment on binding sites due to the greater cation exchange capacity of Ca^{2+} . Thus K reduction in soil was observed due to the presence and accumulation of maximum Ca or Mg contents [27].

The K adsorption curve of Wajan (loam sandy) soil series showed a linear trend

initially and bent from concentration 180 mg kg^{-1} (Fig. 2). The highest adsorption rate was 36.66 % at 90 mg kg^{-1} . In Wajan (loam sandy), soil adsorption percentage was decreased gradually from 90 mg kg^{-1} . The properties of Wajan (loam sandy) soil series have neutral pH, high CaCO_3 13.4% and sand contents 83 % (Table. 2).

Comparison of different sorption models

The different model was used to explain the complex process of adsorption. In terms of sorption isotherm coefficient of determination was more favorable in the Freundlich equation as compared to Langmuir and Temkin equation (Fig. 3-5). Sultanpur series (silt loam) showed better in all three isotherm equations.

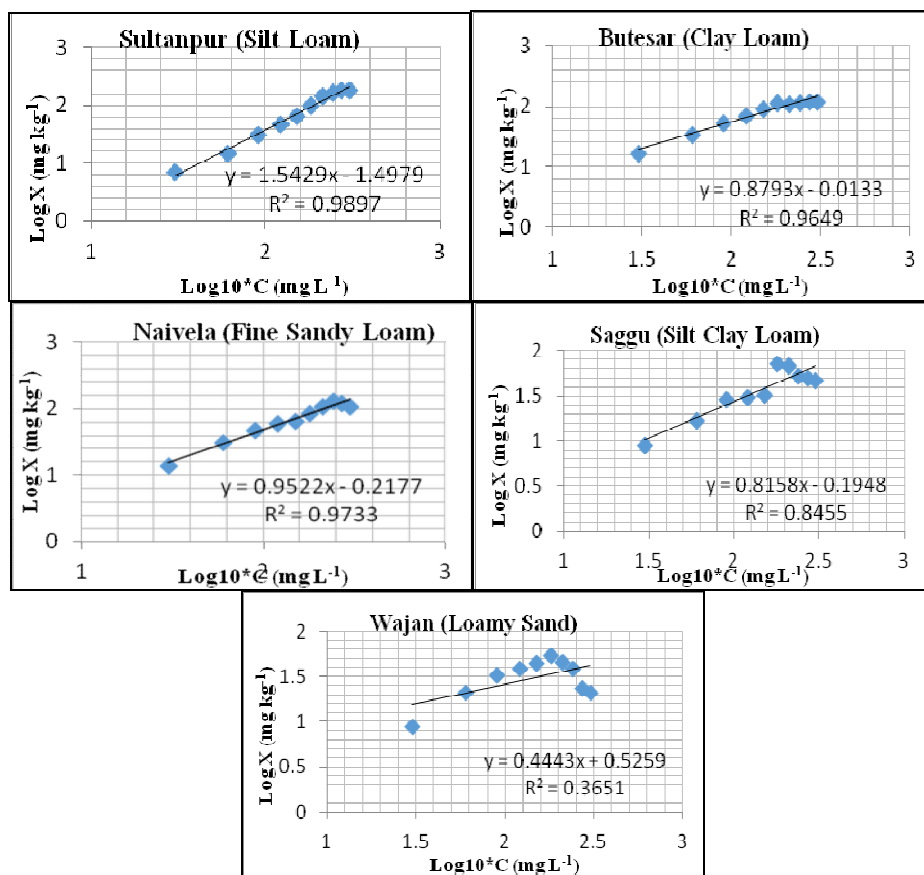


Figure 3. Freundlich adsorption isotherm of potassium adsorption for five soil series

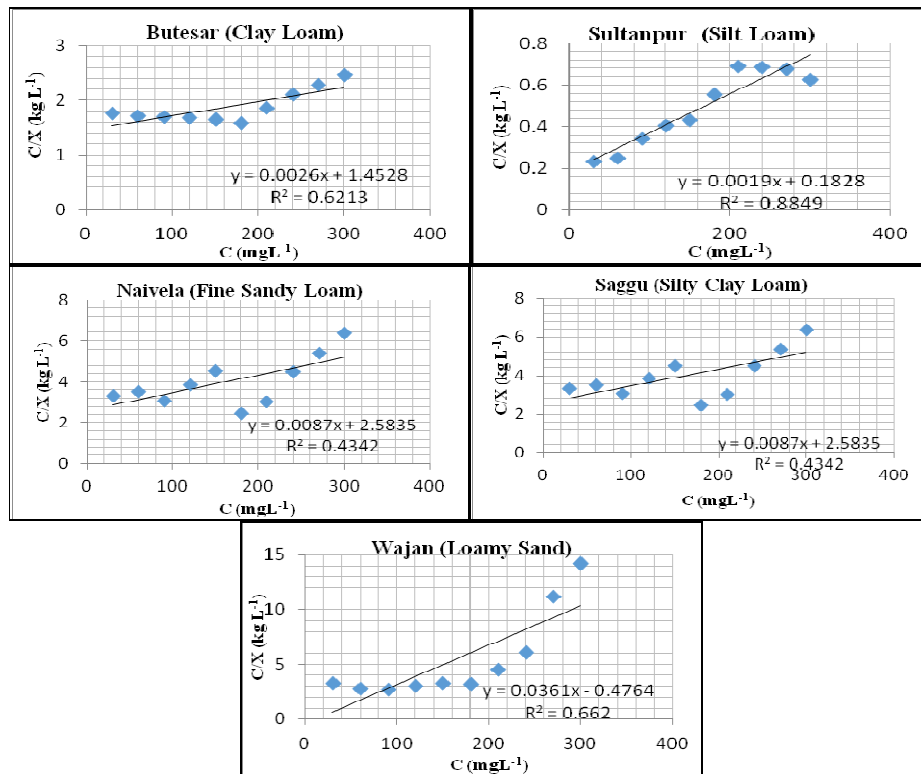


Figure 4. Langmuir adsorption isotherm of potassium adsorption for five soil series

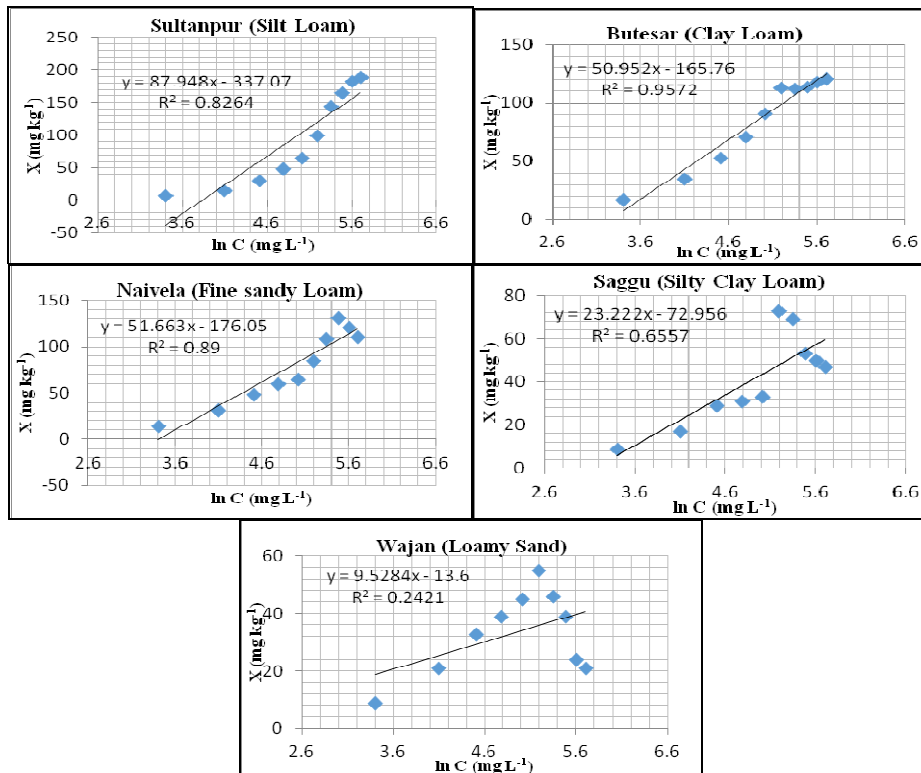


Figure 5. Temkin adsorption isotherm of potassium adsorption for five soil series

In the Sultanpur series (silt loam) coefficient of determination of Freundlich equation was observed highest 0.99. This is due to the fact that Sultanpur series (silt loam) have high organic matter content 0.75%, high clay contents and low CaCO_3 . Previous studies showed that for determining the heterogeneity, the Freundlich isotherm is considered as diver binding model and broadly valid for measuring and afford space for heterogeneity [28]. The Freundlich R^2 value of Naivela (fine sandy loam) and Bhutesar (clay loam) series was 0.97 and 0.96, which was better than Saggu (silty clay loam) and Wajan (loam sandy) (Table. 3).

The Freundlich constant $1/n$ indicates the buffering capacity of the soil. In this study $1/n$ value showed from 0.44 to 1.54 kg mg^{-1} [29]. Sultanpur (silt loam) has a greater $1/n$ value 1.54 kg mg^{-1} due to the low sand contents 25%. Similarly lowest $1/n$ value 0.44 kg mg^{-1} was recorded in Wajan (loam sandy) soil due to high sand contents 83% (Table. 4). $1/n$ value indicated heterogeneity; smaller $1/n$ value reveals greater heterogeneity according to [30]. Our result was in accordance with researchers who reported that loam texture soil and sandy clay loam texture soil have a low $1/n$ value due to the presence of maximum sand proportions [25].

Freundlich n value determines the degree of non-linearity between the applied concentration and adsorption [31]. For a suitable sorption process [32], the value present in the middle of one and ten. If n value equal, less and greater than 1 it indicates that adsorption is a linear, chemical and physical process, respectively. In this study, n value of all soil series lies between 1 and 10 except n value 0.65 was recorded in Sultanpur (silt loam) soil (Table. 4), for these sites sorption is favorable. They expect more than a single layer of adsorbed molecule.

The amount of K in the solid phase to the amount of K solution is the ratio of Freundlich constant k_f [33]. The soil with more adsorption capacity have higher value of Freundlich k_f constant and the soil having lower adsorption capacity have less value of Freundlich constant k_f [33]. In this study Sultanpur (silt loam) has a high k_f value 31.47 mg kg^{-1} due to high pH, O.M, CEC, with low CaCO_3 contents. The lowest k_f value 0.28 mg kg^{-1} was recorded in Wajan (loam sandy) due to high CaCO_3 and sand contents (Table. 4). High adsorption capacity (8.01 mg kg^{-1}) of clay loam soil might be due to minimum percentage of CaCO_3 , greater CEC ($12.87 \text{ cmol}_c \text{ kg}^{-1}$), high pH (8.43) and greater fraction of clay substances as compared to other soils [13]. The maximum concentration of K is adsorbed through higher pH due to the formation of new sites and decreased the antagonism behavior between K^+ and H^+ for similar sites [34].

Langmuir coefficient of determination was lowest in all series except Sultanpur with R^2 (0.88) (Table 3). In the Sultanpur soil the better fit of the data may be attributed to the percent organic matter and cation exchange capacity. In a similar study, a significant correlation was recorded between K adsorption and CEC and it was attributed to the availability of vacant sites for the adsorption of K [25]. The K adsorption data of the soils could not be suitable for the similar sites sorption with complete monolayer solute adsorption as assumes by Langmuir equation [35].

Temkin equation agrees with Freundlich coefficient of determination but has a lower R^2 value. Temkin coefficient of determination was highest 0.96 in Bhutesar series (clay loam) as compared to other series (Table 3), our results were similar with Desta [31] that adsorption data of K for clay loam soil texture showed better fit in Temkin isotherm as compared to others.

Table 3. Comparison of coefficients of determination R^2 for the fit of the Freundlich, Langmuir, and Temkin equations to the sorption data of five soils.

Site	Equations	R^2
Sultanpur	Freundlich $Y = 1.5429x - 1.4979$	0.99**
	Langmuir $Y = 0.0019x + 0.1828$	0.88**
	Temkin $Y = 87.948x - 337.07$	0.83**
Bhutesar	Freundlich $Y = 0.8793x - 0.0133$	0.96**
	Langmuir $Y = 0.0026x + 1.4528$	0.62**
	Temkin $Y = 50.952x - 165.76$	0.96**
Naivela	Freundlich $Y = 0.9522x - 0.2177$	0.97**
	Langmuir $Y = 0.0013x + 1.8817$	0.21 ^{Ns}
	Temkin $Y = 51.663x - 176.05$	0.89**
Saggu	Freundlich $Y = 0.8158x - 0.1948$	0.85**
	Langmuir $Y = 0.0087x + 2.5835$	0.43*
	Temkin $Y = 23.222x - 72.956$	0.66*
Wajan	Freundlich $Y = 0.4443x + 0.5259$	0.37 ^{Ns}
	Langmuir $Y = 0.0361x - 0.4764$	0.66**
	Temkin $Y = 9.5284x - 13.6$	0.24 ^{Ns}

** Significant at $P=0.01$ *Significant at $P=0.05$

Ns = Non-significant

Table 4. Potassium adsorption parameters of the Freundlich equation.

Sites	Freundlich Isotherm		
	$1/n$	N	k_f
Sultanpur	1.54	0.65	31.47
Bhutesar	0.88	1.14	1.03
Naivela	0.95	1.05	1.65
Saggu	0.82	1.23	1.57
Wajan	0.44	2.25	0.28

Conflicts of Interest

The authors declare that there is no conflict of interest.

Conclusion

The present investigation showed that soil properties influenced the K adsorption capacity of the soil. Increased soil EC exhibited maximum adsorption at lower concentrations due to the competition between K^+ and Na^+ ions on the clay surface. The soil series, i.e., Bhutesar and Saggu having high clay contents, which resulted in greater K

adsorption at lower concentration due to engagement of clay contents with Na^+ ion and provide less vacant site for K adsorption. Amongst the different models applied, Freundlich model gave a better fit to all soil series than Langmuir and Temkin models. Freundlich constant $1/n$ value 1.54 kg mg^{-1} and k_f value 31.47 mg kg^{-1} was highest in Sultanpur (silt loam) due to high pH, CEC, OM and clay contents, lower EC and $CaCO_3$ contents. The lowest value of constant was observed in Wajan (loam sandy) due to high EC, high $CaCO_3$ and sand contents. We conclude that clay textured soil with high pH and high OM contents have positive affect on K adsorption capacity while factor like high EC and high $CaCO_3$ contents have a negative effect on K adsorption capacity.

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