

POTASSIUM ADSORPTION CHARACTERISTICS OF FOUR DIFFERENT TEXTURED ALKALINE CALCAREOUS SOILS

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A laboratory study was conducted to determine the Potassium (K) adsorption characteristics of four soils under potato-maize cultivation system in Punjab. Potassium adsorption isotherms were constructed by equilibrating 2.5 g soil samples with 11 levels of K ($0-250 \text{ mg L}^{-1}$) as KH_2PO_4 in 25 ml of 0.01 M CaCl_2 solutions. Sorption time of the samples varied from 2 to 36 hours. Adsorption data were fitted to Freundlich, Langmuir and Temkin adsorption equations. Loam, sandy clay loam and silt loam soils arrived at equilibrium after 12 hours while clay loam soil reached in steady state after 18 hours of equilibrium period. On an average amount of K adsorbed ranged from 30.10 to 37.67 % of added K. Freundlich equation explained K adsorption behavior better than the other two equations as evidenced by higher correlation coefficient values ranging from 0.95 to 0.99. All the four soils with almost similar clay contents differed in their adsorption characteristics.

Keywords: Potassium adsorption, Freundlich, Langmuir, Temkin model

INTRODUCTION

Potassium is an essential element for all plants and a significant quantity of K is removed by potato and maize crops (Mengel *et al.*, 2001; White, 2003). Potassium deficiency has been reported in soils of Pakistan especially under intensive potato-maize cultivation system (Bajwa, 1994; Malik *et al.*, 1989). In alluvial soils of Pakistan where mixed mineralogy is common, the fate of added K as fertilizer differs between soils because the responses of crops to applied K are erratic and this unpredictability is due to different adsorption characteristics of K by various soils. Depending upon the amount and type of clay minerals up to 57 % of applied K can be adsorbed by the soil colloids (Pal *et al.*, 1999). This is particularly true in case of soils with high K adsorption specificity like Illite and vermiculite (Backett and Nafady, 1967; Goulding, 1987). Similarly, the rate of K adsorption on Illite and vermiculite was reported to be much slower than montmorillonite and kaolinite (Ogwada and Sparks, 1986; Mehta and Singh, 1986). Adsorption sites for K by organic matter are similar to planar surfaces like kaolinite clays (Ehlers *et al.*, 1968). Soil pH has also significant effect on K adsorption as CEC increases with increase in pH (Loannou *et al.*, 1994). Some of the clay minerals like smectite and kaolinite easily release all of their adsorbed K than do illite and vermiculite (Mengel and Uhlenbecker, 1993).

The concentration of K in soil solution depends upon the rate of removal by the plants and the rapidity at which K can be desorbed from the adsorbed phase, whereas initial adsorption equilibrium solution K levels serve as an index of K availability. Thus equilibrium K

concentration appears to provide a better index of soil fertility. (Singh and Jones, 1975). A knowledge about the variation in K adsorption among soils and the equilibration between intensity and quantity phases of soil K is necessary to predict the fate of added K fertilizers in soils and to make precise K fertilizer recommendations (Sparks and Haung, 1985). Therefore, K fertilization is important factor to meet the K requirements of the potato-maize cropping system.

There is little information available relating to potassium adsorption characteristics of alluvial and calcareous soils. This is especially true under potato-maize cultivation system where K fertilizer is very important to compensate the deficiency of K and increase yields of potato crops. This study was conducted to determine the effect of contact time on the equilibrium potassium concentration and the extent of potassium adsorption characteristics of the selected soils by comparing different adsorption models.

MATERIALS AND METHODS

The soils samples were taken from 0-30 cm depths from each of the sites. Samples were passed through a 2 mm sieve and air dried. Selected physical and chemical properties of soils are presented in Table 1. The pH and EC of soil was determined in saturate soil paste. Organic matter, available P, Extractable K, CEC, CaCO_3 and particle-size analysis were determined by using standard procedures.

For the construction of potassium adsorption isotherm 2.50 g soil samples were equilibrated with different K concentration levels (0, 25, 50, 75, 100, 125, 150, 175, 200, 225 and $250 \text{ } \mu\text{g ml}^{-1}$) in 25 ml solution of 0.01 M

Table 1. Some basic physical and chemical properties of the selected soils

Soil characteristics	0-30 cm			
	Ustochrepts	Torrifluvents	Camborthid	Haplargid
EC (dS m ⁻¹)	0.75	0.89	1.92	1.51
pH	7.81	8.43	7.83	8.17
O.M (%)	0.72	0.52	0.43	0.91
Available P (ppm)	5.80	8.40	6.63	6.70
Available K (ppm)	71	87	92	140
CEC (cmol _c kg ⁻¹)	9.26	12.87	9.94	10.01
CaCO ₃ (%)	8.71	4.37	9.14	3.31
Sand (%)	43	36	55	52
Silt (%)	35	37	20	25
Clay (%)	22	27	25	23
Textural Class	Loam	Clay Loam	Sandy clay Loam	Silt loam

CaCl₂ at 25±1 C°. Samples were sorbed for study at 2, 6, 12, 18, 24, and 36 hours to determine time necessary to reach steady state. The amount of K adsorbed was determined as given below:

$$\Delta K = (CK_i - CK_f) / (V/W)$$

Where ΔK is the change of K in soil solution. CK_i and CK_f are the initial (K concentration added) and final equilibrium concentrations of K in solution. V and W are the solution volume and soil mass, respectively. Positive ΔK values indicate adsorption by the soil solid phase whereas negative values indicate desorption by the soil. The K adsorption data were fitted into following adsorption equations:

Langmuir adsorption equation:

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

Where C is the equilibrium solution K concentration (mg L⁻¹), x/m is the mass of K adsorbed per unit mass of soil (mg Kg⁻¹), k is a constant related to bonding energy of K to the soil, and b is the maximum K adsorption capacity of the soil.

Freundlich adsorption equation:

$$x/m = a C^b$$

By rearranging $\log (x/m) = \log a + b \log c$

Where x/m is the mass of K adsorbed per unit mass of soil (mg Kg⁻¹), C is the equilibrium solution K concentration (mg L⁻¹), a and b are constants. The values of a and b are obtained from the intercept and slope, respectively.

Temkin adsorption equation:

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

Where x/m is the mass of K adsorbed per unit mass of soil (mg Kg⁻¹), C is equilibrium solution K concentration

(mg L⁻¹), a and b are constants. The values of a and b are obtained from the intercept (a) and the slop (b), respectively. The necessary statistical analysis of the data were done using MS Excel software program.

RESULTS AND DISCUSSION

Effect of contact time and extent of adsorption

Potassium concentration in the equilibrium solution decreased upto 12 hours in loam, sandy clay loam and silt loam soils while it took 18 hours to reach equilibrium condition for clay loam soil and beyond that there was no detectable change (Fig. 1). However, quantity of K adsorbed at particular interval varied from soil to soil. Slow rate of adsorption of clay loam soil may be due to the of presence vermiculite in addition to illite clay minerals (Mehdi, 1993) because on these minerals planar, edge, and interlayer/wedge sites are available which require more sorption time to reach in equilibrium condition. The results are in line with the findings of Malcom and Kennedy, (1969) and Sparks *et al.* (1980 b). They have also ascribed slower reaction time to vermiculitic clay sites which promoted surface diffusion. These results indicated that so far as adsorption kinetics is concerned 24 hours is enough time to reach a satisfactory equilibrium condition. Our findings agree with the results of Du *et al.* (2004) who have reported 24 hours time for achieving steady state condition in two clay soils.

The soils having divergent texture indicated maximum adsorption behavior upto 100 ppm of added K and the relationship was nonlinear (Fig. 2) while from 100 to 200 ppm adsorption pattern remained more or less similar and from 200 to 250 ppm it showed decreasing

Potassium adsorption characteristics of soils

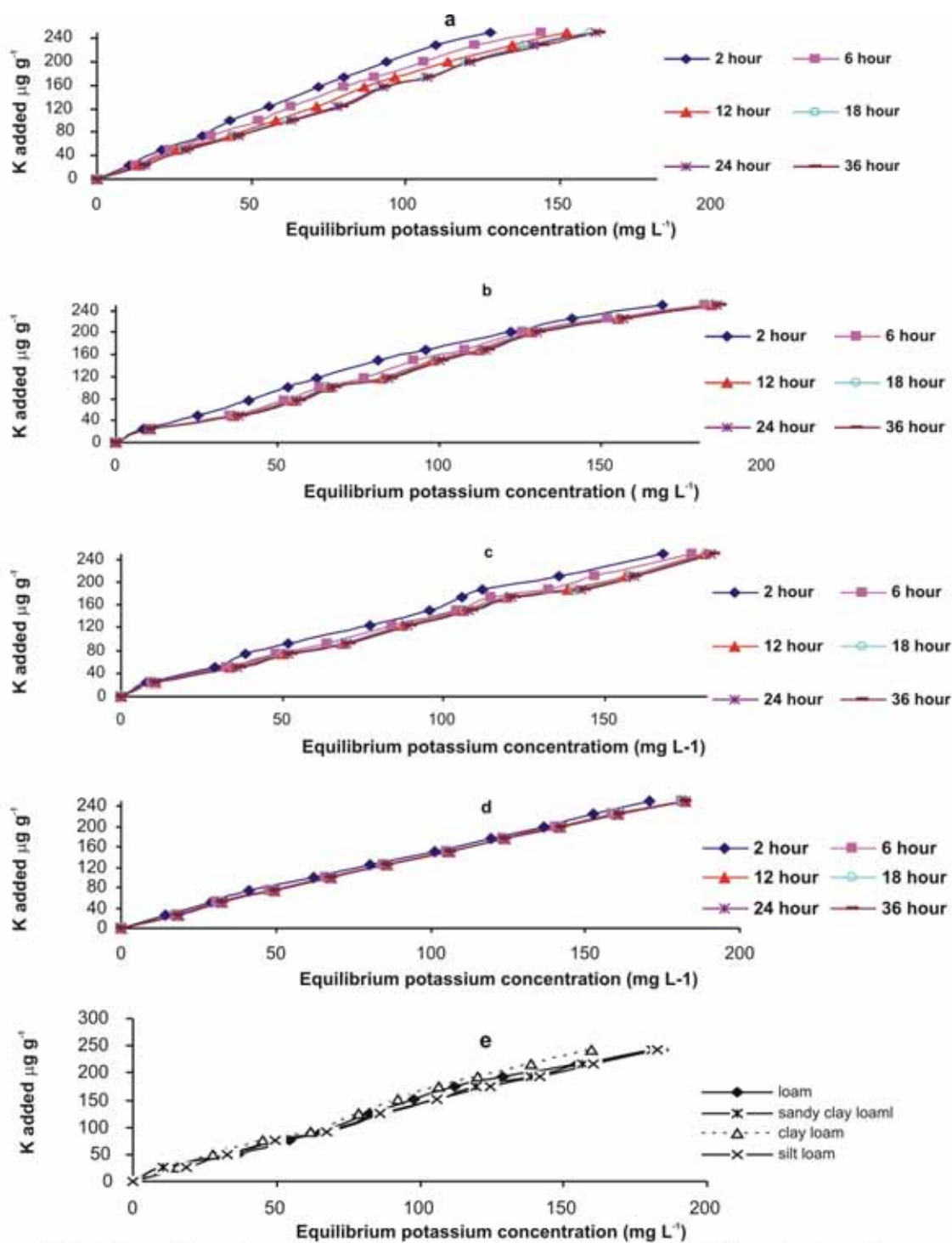


Fig. 1. Potassium adsorption characteristics of soils as a function of different adsorption times a) clay loam, b) loam, c) sandy clay loam, d) silt loam, e) Comparison of adsorption behavior of four soils after 24 hours of equilibrium time.

trend. The non linear relationship in the initial portion of the curve may be due to mass action exchange at sites on external surfaces. These results are supported by Sparks and Haung (1985). On an average highest adsorption was found in clay loam soil (37.67 %) followed by sandy clay loam (36.64 %), loam (34.49 %) and silt loam (30.10 %).

Comparison of different adsorption models

A comparison of adsorption isotherms of the four soils is given in Fig.3. As depicted from the data shown in

the mixed mineralogy of soils. The Temkin adsorption isotherm similarly agreed with the trend of potassium adsorption behavior as was evident from Freundlich equation but somewhat lower values of R^2 i.e. 0.84, 0.91, 0.89 and 0.88 of loam, clay loam, sandy clay loam and silt loam soils, respectively. The results are supported by Goulding and Talibudeen (1980), and Dufey and Delvaux, (1989). Understandably, the distributions of different sites for adsorption depend on quantity and quality of clay minerals, their degree of depletion and complementary ions. As Langmuir model

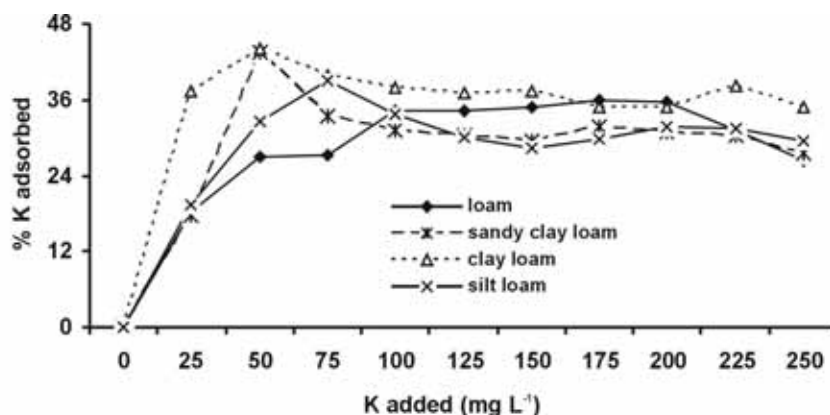


Fig. 2. Percent K adsorbed as a function of different K concentration levels of four soils

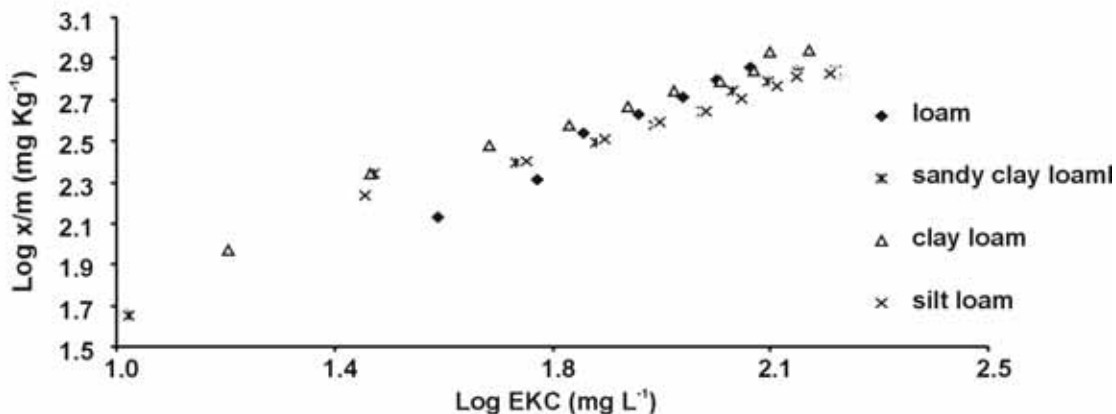


Fig. 3. A comparison of Freundlich adsorption isotherms of the selected soils

Table 2 Freundlich equation described sorption isotherm with a higher degree of accuracy followed by Langmuir and Temkin. The coefficient of determination values of 0.96, 0.98, 0.95 and 0.99 for loam, clay loam, sandy clay loam and silt loam soils, respectively indicated that Freundlich equation gave a better fit of equilibrium K adsorption data for these soils as the model assumes unlimited adsorption sites having heterogeneous surfaces which correlated better with

assumes homogeneity of sorption sites with complete monolayer adsorption of solutes it could not fit well to the K sorption data of the soils under study. The Freundlich constant a and b (Table 3) may be taken as a measure of the extent of adsorption and rate of adsorption or energy of adsorption. The constant a is the intercept at zero equilibrium K concentration and represents the labile pool of K. Loam soil has less intensity (3.57 L Kg^{-1}) of adsorption as its available K

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

Site	Equations		R^2
Okara (Loam)	Freundlich	$Y = 1.0489x + 0.55732$	0.96**
	Langmuir	$Y = 0.0002x + 0.137$	0.43 ^{ns}
	Temkin	$Y = 0.0031x + 2.9225$	0.84*
Kasur (Clay loam)	Freundlich	$Y = 0.9038x + 0.9584$	0.98**
	Langmuir	$Y = 0.0003x + 0.1441$	0.47 ^{ns}
	Temkin	$Y = 0.0028x + 2.8568$	0.91**
Sahiwal (Sandy clay loam)	Freundlich	$Y = 0.9092x + 0.8358$	0.95**
	Langmuir	$Y = 0.0004x + 0.1852$	0.31 ^{ns}
	Temkin	$Y = 0.0038x + 2.6831$	0.89**
Faisalabad (Silt loam)	Freundlich	$Y = 0.7957x + 1.0449$	0.99**
	Langmuir	$Y = 0.0006x + 0.1613$	0.79 ^{ns}
	Temkin	$Y = 0.0042x + 2.5982$	0.88**

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

ns = Non-significant

status is low with higher percentage of CaCO_3 (Table 1) consequently a fraction of applied K might had adsorbed by specific sites (fixation sites) and caused a decrease in soil solution but its high adsorption capacity may be attributed to the dominance of illite (hydrous mica) type of clay minerals controlling mainly the buffering capacities of soils (Mengel and Busch, 1982). Relatively higher intensity of adsorption in silt loam soil may be due to highest organic matter (0.91 %), lowest CaCO_3 (3.11 %) and a high degree of sand percentage on which adsorption is similar to planar sites as on kaolinite clays desorbing most of the adsorbed K (Ehlers *et al.*, 1968; Mengel and Uhlenbecker, 1993). Xu *et al.* (2004) have also postulated that the release of organic anions in the rhizosphere due to organic matter which may increase the net negative surface charge of the soils and consequently enhance the adsorption of potassium ions. On the whole a comparatively high adsorption capacity (8.01 mg kg^{-1}) and intensity (9.09 L kg^{-1}) of clay loam soil may be due to high pH (8.43), greater CEC ($12.87 \text{ cmol}_c \text{ kg}^{-1}$) and less percentage of CaCO_3 and highest fraction of clay contents as compared to other soils. The results are in line with the findings of Loannou *et al.* (1994) who reported that with increase in pH greater amounts of potassium being adsorbed as a result of formation of new sites, together with a decrease of competition between H^+ and K^+ for the same sites. Similarly Khodabakhsh (2006) found a high negative correlation coefficient ($r = -97\%$) between amount of K adsorbed and CaCO_3 contents of soils. Our results also agree with the data described by Pal *et al.* (1999). The distributions of K between exchange and solution phases depend upon the amount and type of clay minerals. This quantity intensity relationship is a useful parameter in formulating precise fertilizer

recommendations according to the adsorption capacity of the soils (Samadi, 2003).

Table 3. Potassium adsorption parameters of the Freundlich equations

Site	Adsorption capacity 'a' mg kg^{-1}	Intensity of adsorption 'b' L kg^{-1}
Okara	11.19	3.57
Kasur	8.01	9.09
Sahiwal	8.11	6.85
Faisalabad	6.25	11.09

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