

Full Length Research Paper

Potassium adsorption characteristics of soils under long term maize-legume cropping sequence

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Potassium adsorption isotherms of rainfed maize growing soils of North Kashmir were studied to visualize the adsorption behavior and factors affecting adsorption. The soils vary widely in their physico-chemical properties having lacustrine origin. Potassium adsorption isotherms were constructed by equilibrating 5 g soil samples with eight levels (0 to 200 mg K). At application rates of 1 and 200 mg of K contained in 10 ml of KCl solution per gram of soil, the adsorbed amounts of K varied from 13 to 15% and 9 to 12% of the added K with an average 13 and 11%, respectively. The adsorption data were fitted to Freundlich, Langmuir and Temkin equations. Freundlich equation explained K fixation behavior better than the either two equations as evidenced by higher coefficient of determination (0.90 to 0.99). The Freundlich parameter 'a' was significantly correlated with clay content (0.982), pH (0.919) and cation exchange capacity (CEC) (0.907) of soils.

Key words: Potassium adsorption, Freundlich, Langmuir, Temkin.

INTRODUCTION

Potassium is an essential element for all plants and a significant quantity of K is removed by maize crop (Mengel et al., 2001; White, 2003). The availability of K is affected by soil processes including physical, chemical and biological ones (HuiMin et al., 2009). K adsorption in soils, that is, transformation of available K forms into unavailable ones, influences the effectiveness of fertilization in soil-plant system. Understanding the mechanism that involves adsorption of K in soil is important because soils may contain widely variable pools of K that are potentially mobilized by chemical weathering of soil minerals (Simonsson et al., 2009). A rapid method for measuring K adsorption could help clarify relationship with other soil properties (Murashkina

et al., 2007).

The process of potassium adsorption is controlled by the equilibrium among the potassium retained by the interlayer sites, the surface and edge sites of mineral crystal lattice and the potassium in soil solution. The clay minerals types, pH, soil organic matter (SOM), hydroxide aluminum, soil moisture status, cation exchange capacity (CEC), fertilization and tillage system are the major factors affecting the equilibrium (Pannu et al., 2003). The K adsorption in soil is quite complex and may not be explained by simple and single reaction. To visualize the K adsorption in soil several equations or adsorption isotherms have been developed. Langmuir and Freundlich adsorption isotherms are mostly employed for understanding the relationship between the quantities of K fixed per unit soil weight and the concentration of K in solution. The Freundlich equation is the oldest adsorption equation in the literature on soils, first used by Russell

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and Prescott in 1916. It is an empirical equation and corresponds to a model of adsorption in which the affinity term decreases exponentially as the amount of adsorption increases. Over a limited range of concentration, Freundlich equation often described K adsorption well (Barrow, 1978). According to the Freundlich equation, energy of adsorption decreases as the amount of adsorption increases.

The K adsorption in North Kashmir soils specifically in rainfed soils is not well documented as intensive investigations in this regard has not been undertaken so far. This present study was therefore conducted to elucidate the K adsorption in rainfed soils.

MATERIAL AND METHODS

Soil sampling and experimental site

The study area is in the North of Kashmir valley, India. The cultivated area falls in the rainfed zone dominated by maize-legume cropping system followed from last 8 years. Four surface soil samples (0 to 30 cm) of Babaweyil (S1) clay loam, Satran (S2) silty loam, Doon (S3) silty clay loam and Mamar (S4) loam were collected. The samples inherit wider range of soil characteristics like texture, pH, clay contents, CaCO₃ and organic matter. The soil samples were air-dried and ground to pass through 2 mm sieve before use.

Measurement

Soil analysis

The pH was determined by 1:2.5 soil-water suspension by a glass electrode, EC with the help of solu bridge conductivity meter at 25°C (Jackson, 1967) and CEC by ammonium acetate (Lu, 1999). Particle size distribution was determined by the sedimentation procedure using the pipette method after dispersing the soil with sodium hexametaphosphate (Gee and Bauder, 1986). The total CaCO₃ in soil expressed as the calcium carbonate equivalent was determined by a rapid titration method (Rayment and Higginson, 1992). Organic matter was determined by wet digestion (Nelson and Sommers, 1996).

Potassium adsorption

Surface samples (5 g) were taken and equilibrated in 50 ml plastic bottles for 72 h after adding 0, 1, 5, 10, 20, 60, 100 and 200 mg K contained in a 10 ml KCl solution and then analyzed for K in 1mol/L NH₄OAc (pH 7) extract with a flame photometer. The assessment of K adsorption capacity is rather a complex procedure and was calculated as follows (Huang and Jin, 1996):

K adsorption capacity (mg/kg) = added K - (NH₄OAc extractable K - original soil K)

K adsorption rate (%) = (K adsorption capacity × 100)/ added K

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 slope (b), respectively. The necessary statistical analysis of the data were done using MS Excel software program.

RESULTS AND DISCUSSION

The selected physical and chemical properties of the studied soils are shown in Table 1. K adsorption isotherms for the studied soils samples under continuous maize-legume cropping are presented in Figure 1. The soils varied in their K adsorption behavior. The amount of K adsorbed increased with the increasing K additions irrespective of soil type and texture (Figure 2). For the initial added solution concentration of K (1 µg ml⁻¹), K adsorbed ranged from 13 to 15% and for the highest added solution concentration of K (200 µg ml⁻¹) 9 to 12%. The equilibrium K concentration in soil solution (that is, not net release or adsorption) ranged from 0.25 to 0.60 µg ml⁻¹ for 1 µg ml⁻¹ of added K and from 166 to 180 µg ml⁻¹ for 200 µg ml⁻¹ of added K.

The soils of varying texture indicated maximum adsorption behavior up to 100 µg ml⁻¹ and the relationship was nonlinear while from 100 to 200 µg ml⁻¹ adsorption pattern remained more or less similar or showed a decreasing 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 Asterios et al. (2007). On an average highest adsorption was found in S3 Silty clay loam (13%) because of high clay content and CEC of the soil followed by S4 Loam (12%), S1 Clay loam (11%) and S2 Silty loam (9%) likely due to its coarse texture and low CEC. K

For these results, it could be concluded that adsorption of K was mainly governed by the clay content and CEC of the soil. Zhang et al. (2009) and Jafari and Baghernejad

Table 1. Physico-chemical properties of (a) Clay loam, (b) Silty loam, (C) Silty clay loam and (d) Loam soils of rainfed maize growing soils of North Kashmir.

Location	pH	EC(dSm ⁻¹)	Organic carbon	CaCO ₃	Clay	Sand	Silt	CEC	Available K
				(%)				(cmol _c Kg ⁻¹)	
S1 Clay loam	7.1	0.35	2.21	0.55	26	43	21	15.50	0.24
S2 Silty loam	7.1	0.38	2.45	0.45	14	47	32	15.01	0.21
S3 Silty clay loam	7.8	0.29	1.07	0.43	37	12	60	17.50	0.53
S4 Loam	7.7	0.44	1.52	0.52	31	40	18	16.20	0.13

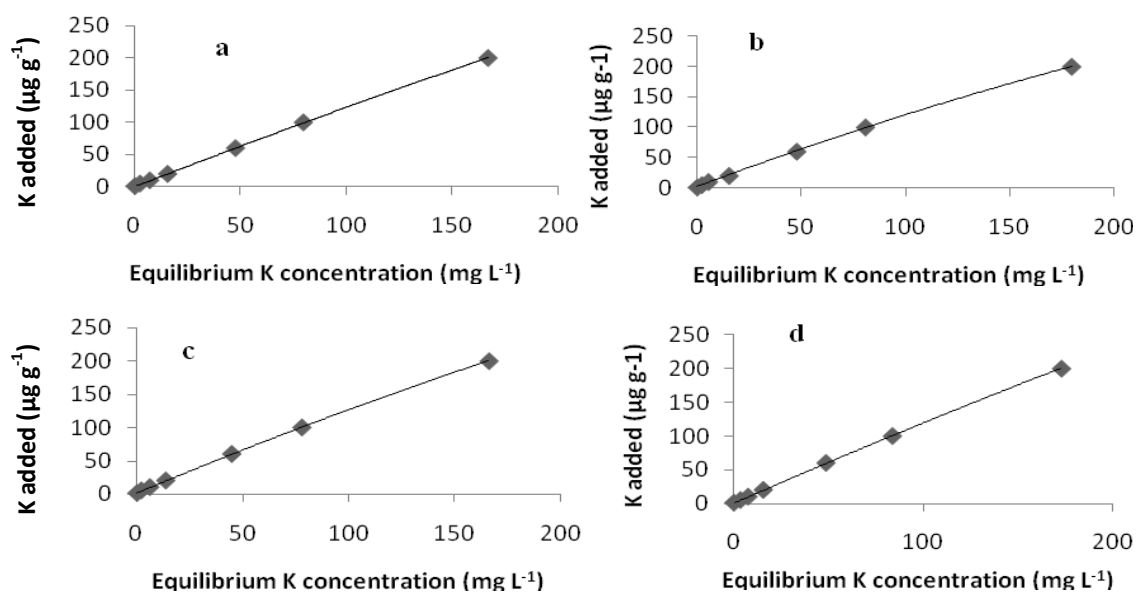
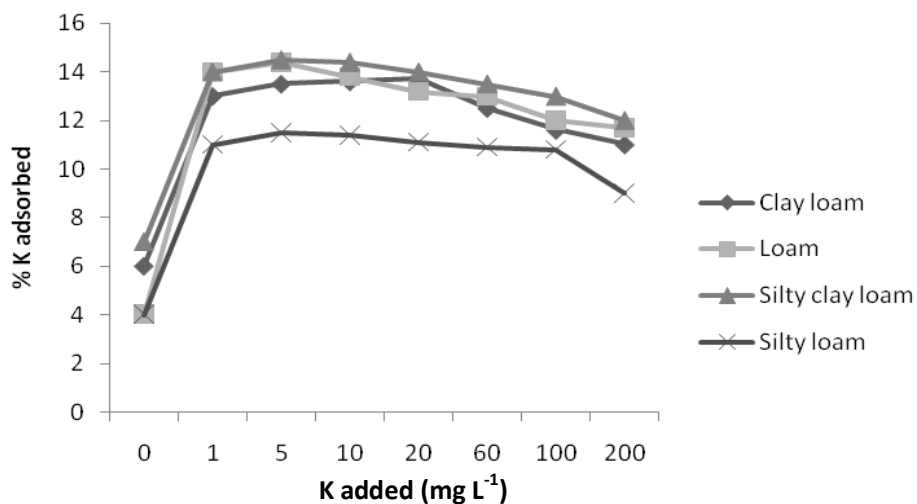
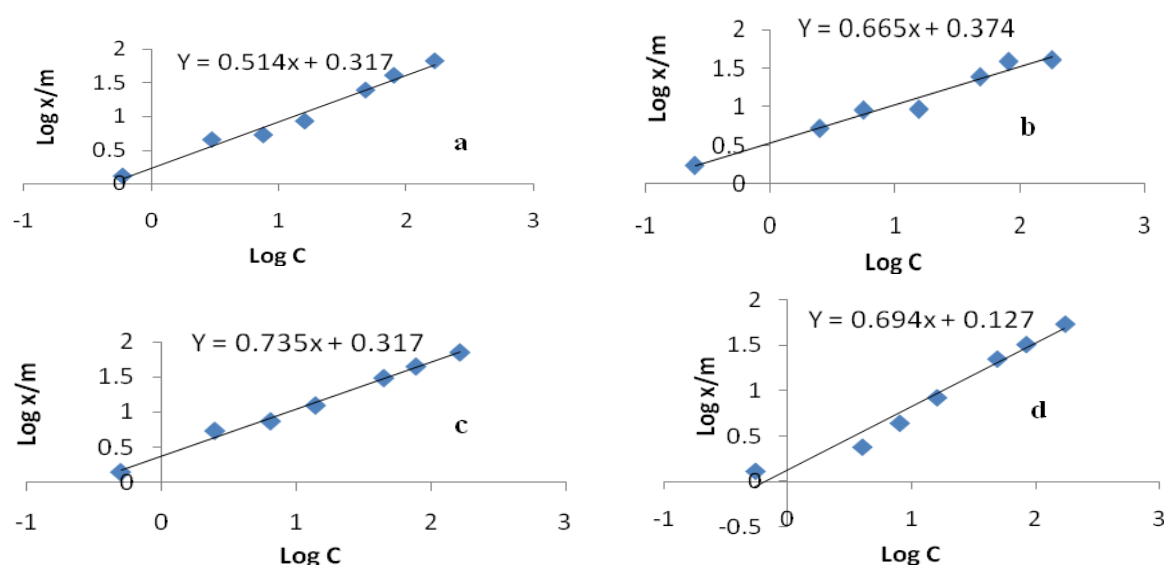
**Figure 1.** Potassium adsorption characteristics of (a) Clay loam, (b) Silty loam, (c) Silty clay loam and (d) Loam soils of rainfed maize growing soils of North Kashmir.**Figure 2.** Percent of K adsorbed under different K concentration levels of (a) Clay loam, (b) Silty loam, (c) Silty clay loam and (d) Loam soils of rainfed maize growing soils of North Kashmir.

Table 2. Comparison of coefficients of determination (R^2) for the Freundlich, Langmuir and Temkin equations to the adsorption data of the soils of North Kashmir.

Location	Equation	R^2	K adsorption parameters of the Freundlich equation	
			Adsorption capacity 'a' ($\mu\text{g g}^{-1}$)	Intensity of adsorption 'b'
S1 Clay loam	Freundlich	0.978*	1.67	1.44
	Langmuir	0.713 ^{ns}		
	Temkin	0.836**		
S2 Silty loam	Freundlich	0.972*	1.14	2.02
	Langmuir	0.724 ^{ns}		
	Temkin	0.804**		
S3 Silty clay Loam	Freundlich	0.993*	2.35	1.50
	Langmuir	0.760 ^{ns}		
	Temkin	0.893**		
S4 Loam	Freundlich	0.965*	2.19	1.45
	Langmuir	0.790 ^{ns}		
	Temkin	0.846**		

*Significant at $P = 0.01$, **Significant at $P = 0.05$; ns = non-significant.

**Figure 3.** Freundlich adsorption isotherms for (a) Clay loam, (b) Silty loam, (c) Silty clay loam and (d) Loam soils of rainfed maize growing soils of North Kashmir.

(2007) also found similar correlation that the black soils (high clay content and CEC) fixed more K as compared to the red soils (low clay content and CEC).

K adsorption study

As depicted from the data shown in Table 2, Freundlich equation described sorption isotherm with a higher degree of accuracy followed by Langmuir and Temkin. The coefficient of determination values in Table 2 indicated

that Freundlich equation gave a better fit (Figure 3) of equilibrium K adsorption data for these soils as the equation assumes unlimited adsorption sites having heterogeneous surfaces which correlate better with 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 . 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

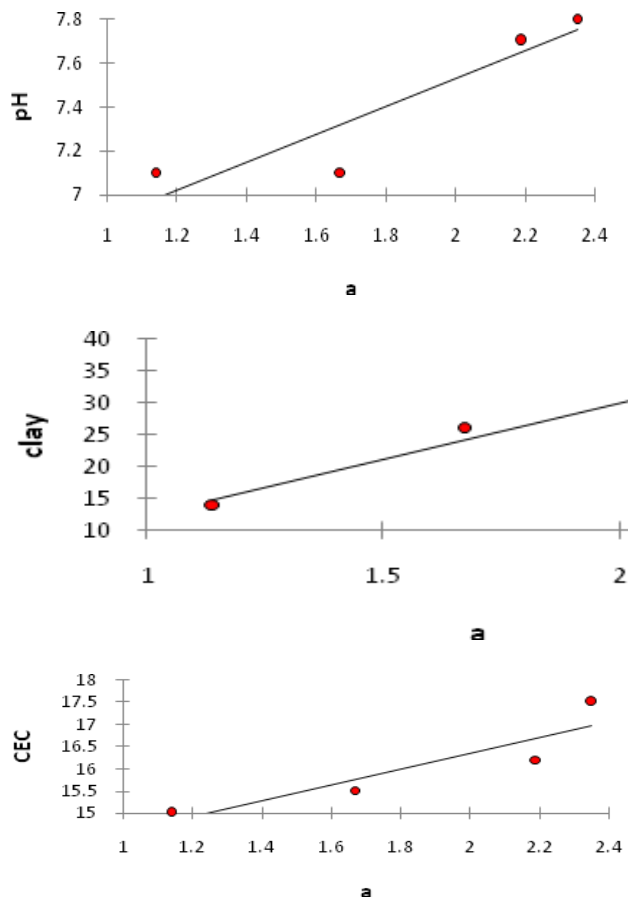


Figure 4. Correlation plots of adsorption capacity (a) with the pH (0.919*), clay (0.982**) and CEC (0.907*) respectively (**Significant at $P=0.01$ and *Significant at $P=0.05$)

and quality of clay minerals, their degree of depletion and complementary ions. As Langmuir equation 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 2) 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. S1 caly loam and S4 loam soil has less intensity (1.44 and 1.45%, respectively) of adsorption as their available K status is low with higher percentage of CaCO_3 (Table 1) consequently a fraction of applied K might had fixed by specific sites (adsorption sites) and caused a decrease in soil solution but its high adsorption capacity may be attributed to the dominance of illite (hydrrous mica) type of clay minerals controlling mainly the buffering capacities of soils (Mengel and Busch, 1982). Relatively higher intensity of adsorption in S2 silty loam soil may be due to highest organic carbon (2.45%), lowest CaCO_3 (0.45%) 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. (2005) 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 and intensity of S3 silty clay loam soil may be due to high pH (7.8), greater CEC ($17.50 \text{ cmol}_c \text{ kg}^{-1}$) and less percentage of CaCO_3 (0.43%), and highest fraction of clay (37%) contents as compared to other soils. There was a significant correlation between adsorption capacity with pH, clay content and CEC of soils (Figure 4). 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).

Conclusion

The four divergent soils show different K adsorption characteristics. There is a significant positive relationship between the amount of potassium adsorption and clay content. The adsorption of K in all soils increased with the increase in concentration of added K. The adsorption isotherm was best described by Freundlich equation followed by Langmuir and Temkin with Freundlich's constants significantly correlated with pH, clay content and CEC of soils.

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