PHOSPHORUS ADSORPTION AS DESCRIBED BY FREUNDLICH ADSORPTION ISOTHERMS UNDER RAINFED CONDITIONS OF PAKISTAN

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Soil phosphorus availability is the limiting factor for crop production in Pakistan. The objective of the study was to investigate the phosphorus adsorption as described by Freundlich adsorption isotherm under rainfed conditions. Ten soil series of Pothwar Plateau were taken for study. These soils are treated with three different P fertilizers i.e DAP, SSP and NP at equilibrium solution concentration of 10, 20, 40, 60, and 80 μ g ml^{-1}. A decrease in P-adsorption with successive increase in equilibrium phosphorus solution concentration was recorded in all the soils under study. Maximum Freundlich adsorption parameters i.e maximum adsorption (μg g^{-1}) and buffer capacity (ml g^{-1}) were observed in Chakwal soil followed by Balkassar soil. The minimum values of these two Freundlich parameters were observed in Kahuta soil. Maximum value of K_{OC} was observed in Chakwal soil with DAP, SSP and NP while minimum value of K_{OC} was observed in Bather soil with all fertilizers under investigation. The minimum ΔG -20.19 KJ mol^{-1}, -20.55 KJ mol^{-1} and -20.28 KJ mol^{-1} with DAP. SSP and NP, respectively was observed in Chakwal soil, while maximum values of ΔG was observed in Bather soil. The SSP showed maximum adsorption on the whole and DAP resulted in minimum adsorption of P fertilizer calculated by Freundlich adsorption isotherm. Buffer capacity was highest with SSP treatment and minimum with DAP fertilizer treatment in all ten soils under study. Further studies on P release pattern are suggested under rainfed conditions of Pakistan which would be important for plant nutrition.
Keywords: P adsorption, soils, Freundlich, isotherms, rainfed conditions

INTRODUCTION

The soils in Pakistan are mostly alkaline, having variable amounts of calcium carbonate and are generally deficient in organic matter (less than 0.86g100g^{-1}), that limit availability of phosphorus (Memon *et al*., 1992). The use of fertilizers in rainfed areas is, however, considerably less (P) than the crop requirements. It has been observed that phosphorus availability to plants is dependent upon many factors like texture, pH, calcium carbonate, organic matter, source of phosphatic fertilizers, nutrient balance, organic matter and crop husbandry practices (Dibb *et al.*, 1990). Soils with higher clay tend to fix more P than sandy soils. The P Fixation increases with increase in clay, so large amounts of P must be applied to arid land soils that contain more clay in order to optimize P availability to plants. The recovery of phosphorus is reported only 15-25% of the amount applied in irrigated areas (Nisar, 1985), and recovery in arid areas is not well documented but is quite low than the irrigated areas. The P adsorption in soil is quite complex and may not be explained by simple and single reaction. To visualize the phosphorus adsorption in soil several equations or adsorption isotherms had been developed. Langmuir and Freundlich adsorption isotherms are mostly employed for understanding the relationship between the quantity of phosphorus adsorbed per unit soil weight and the concentration of phosphorus in solution. The Freundlich equation is the oldest adsorption equation in the literature on soil phosphate, first used by Russell 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 P adsorption well (Barrow, 1978). According to the Freundlich equation, energy of adsorption decreases as the amount of adsorption increases.

In Pakistan Langmuir and Freundlich equations had been modified by scientists to describe the adsorption data keeping in view the soil characteristics and the fertilizer applied. The P adsorption in Pakistani soils specifically in rainfed soils is not well documented as intensive investigations in this regard had not been undertaken so far. Only few researchers documented that P adsorption increased with increase in clay contents in the soil and decrease with increase in organic matter in the soil (Mehmood *et al*. 2000, Waheed *et al.* 2004, Yousaf, 2004).

The present study was therefore, conducted to elucidate the phosphorus adsorption in rainfed soils.

MATERIALS AND METHODS

In order to conduct phosphorus adsorption study ten prominent soil series of Potohar region were selected. The soil series were Bather, Balkassar, Khaur, Chakwal, Guliana, Missa, Kahuta, Rawalpindi, Basal and Rajar that inherit wider range of soil characteristics like texture, pH, clay contents, $CaCO_3$ and organic matter. These soils were treated with three commonly used P fertilizer sources i.e Single Super phosphate (SSP), Diammonium phosphate (DAP) and Nitrophos (NP). A 25g of soil was placed in 100 ml polyethylene bottles and 25ml solution each having concentrations equivalent to 10, 20, 40, 60 and 80 µg ml^{-1} P from each source of fertilizer were added to each bottle. Final soil suspension ratio of 1:3 was achieved by adding 50ml of distilled water. The suspension was shaken for four hours on a reciprocating shaker and filtered through Whatman's No. 42 filter paper. The filtrate was analyzed for phosphorus using the procedure of (Olsen and Sommers, 1982). The difference between the amount of P added initially and that recovered after equilibration was considered as the amount of P adsorbed by various soils. The data so obtained were fitted to the following linear form of Freundlich adsorption equations.

Log x/m = 1/n log C + log k

Where

k and n Empirical constants

x/m Amount of adsorbate per gram soil (µg Pg^{-1} soil)

C The equilibrium solution concentration of P (µg Pg^{-1} soil)

Organic carbon sorption partition coefficients of the soils used under investigation were calculated (Raturi *et al*., 2004) by the following formula:

K_{OC} = (a x 100) / (Soil Organic C)

The change in free energy for phosphorus adsorption was calculated (Kim and Feagley 1998) as follows:

$\Delta G = -RT \ln K_{OC}$

Where G is the Gibbs free energy (KJ mol^{-1}).

All the soil data in results and discussion section is presented on oven dry basis.

RESULTS

According to the Freundlich equation, energy of adsorption decreases as the amount of adsorption increases. The parameters of equation are presented in Tables 1–3. Two main parameters were calculated by this equation. First is the amount of P adsorbed (a) µg g^{-1} when concentration C is 1µg ml^{-1} and other is buffer power (b) ml g^{-1} defined by slope of the adsorption curve. The main advantage of the equation is that both amount (a) and buffer power (b) is at the same point on the curve. These parameters were estimated by regression of logarithmic form of the data obtained from the adsorption isotherm. The combined linear form of Freundlich equation for each soil with three fertilizers is presented in Figs. 1–10.

The data in tables revealed that maximum P adsorption (a) 13.95 µg g^{-1} that correspond to Log k and buffer capacity of the soil (b) 4.43 ml g^{-1} that represent x/m, was observed in Chakwal soil followed by Balkassar 7.54 µg g^{-1} and 4.38 ml g^{-1} soil when treated with DAP fertilizer. Adsorption (a) was maximum, 16.32 µg g^{-1} again in Chakwal with SSP and also maximum with 14.63 µg g^{-1} NP fertilizers but (b) was maximum in Balkassar 6.34 ml g^{-1} and 5.85 ml g^{-1} in SSP and DAP fertilizer treatments, respectively. The minimum values of these two (a & b) Freundlich parameters were observed in Kahuta and Vather soils. This is also obvious from the date that SSP showed maximum adsorption on the whole and DAP resulted in minimum adsorption of P fertilizer. Buffer capacity was highest with SSP treatment in all soils and minimum with DAP fertilizer in all soils under study.

Gibbs Free Energy (ΔG)

The data pertaining to organic carbon partition coefficient (K_{OC}) and Gibbs free energy is presented in Table 1–3. It is apparent from the data that maximum value of K_{OC} was observed in Chakwal soil with DAP, SSP and NP, while minimum value of K_{OC} was observed in Bather soil with all these fertilizers used under investigation. By comparing the effect of phosphatic source on K_{OC} values it is obvious from the data that SSP showed maximum K_{OC} values and minimum value was observed in DAP fertilizer. NP showed the intermediate results of organic carbon partition coefficient. The ΔG is the change in Gibbs free energy which showed that whether P in soil is adsorbed by weaker or stronger bonds, favourable or unfavorable formations, or spontaneous or nonspontaneous reactions. When $\Delta G > 0$ (positive) energy is absorbed in the reaction and it is some time defined as endogenic (energy absorbing) reactions. The change in Gibbs free energy (ΔG) calculated by putting the K_{OC} values in formula showed that minimum ΔG -20.19 KJ mol^{-1} with DAP, -20.55 KJ mol^{-1} with SSP and -20.28 KJ mol^{-1} with NP was observed in Chakwal soil. As far as maximum values of ΔG were concerned the Bather soil showed maximum values for Gibbs free energy with -13.55 KJ mol^{-1} with DAP, -14.65 KJ mol^{-1} and -14.13 KJ mol^{-1} with SSP and NP treatments, respectively. The positive and large values of ΔG suggest that instead of SOM, P may be chemically adsorbed or strongly inactivated by soil components like Ca and $CaCO_3$ and P will be less available to crops over time. When $\Delta G=0$, it means there is reversible equal reaction. When $\Delta G < 0$, negative, energy is evolved in the reaction and change can do useful work or favorable reaction. The negative and small values of ΔG as observed in the present study suggest a weak physical adsorption of P, which over time may maximize the reaction and availability of P in soil. This enhanced availability of P which is good for crop production.

Table 1. Amount of adsorbed P (a), buffer capacity (b), partition coefficient (K_{oc}) Giggbs free energy (Δ G) and r^2 by applying DAP in different soils obtained from Freundlich equation.

Soil	DAP				
	a (µg g^{-1})	b (ml g^{-1})	K_{oc}	Δ G KJ mol^{-1}	r^2
Basal	6.958	3.343	1690.19	-18.42	0.96
Balkassar	7.549	4.386	1480.93	-18.10	0.98
Bather	1.222	1.137	236.71	-13.55	0.98
Chakwal	13.954	4.431	3436.67	-20.19	0.80
Gulliana	5.515	2.888	1044.82	-17.23	0.96
Kahuta	2.038	1.166	328.36	-14.36	0.96
Khuar	1.759	1.425	315.88	-14.27	0.98
Missa	3.589	2.023	594.94	-15.84	0.98
Rajar	3.297	2.155	660.93	-16.10	0.98
Rawalpindi	3.412	1.853	646.40	-16.04	0.97

Table 2. Amount of adsorbed P (a), buffer capacity (b), partition coefficient (K_{oc}) Giggbs free energy (Δ G) and r^2 by applying SSP in different soils obtained from Freundlich equation.

Soil	SSP				
	a (µg g^{-1})	b (ml g^{-1})	K_{oc}	Δ G KJ mol^{-1}	r^2
Basal	14.154	4.327	3169.02	-19.98	0.87
Balkassar	10.06	6.343	2141.16	-18.99	0.97
Bather	1.907	1.765	369.40	-14.65	0.99
Chakwal	16.323	4.798	4020.12	-20.55	0.83
Gulliana	7.866	3.512	1490.21	-18.10	0.96
Kahuta	3.804	2.127	612.90	-15.89	0.95
Khuar	15.523	5.141	2787.67	-19.66	0.77
Missa	7.744	3.341	1283.71	-17.74	0.95
Rajar	14.862	3.013	2979.31	-19.81	0.97
Rawalpindi	6.832	3.282	1294.32	-17.76	0.95

Table 3. Amount of adsorbed P (a), buffer capacity (b), partition coefficient (K_{oc}) Giggbs free energy (Δ G) and r^2 by applying NP in different soils obtained from Freundlich equation

Soil	NP				
	a (µg g^{-1})	b (ml g^{-1})	K_{oc}	Δ G KJ mol^{-1}	r^2
Basal	10.162	3.806	2274.78	-19.14	0.95
Balkassar	8.476	5.851	1802.75	-18.57	0.96
Bather	1.557	1.458	300.24	-14.13	0.99
Chakwal	14.638	4.595	3603.16	-20.28	0.85
Gulliana	5.806	3.033	1098.81	-17.35	0.98
Kahuta	2.459	1.548	394.74	-14.80	0.97
Khuar	6.806	3.706	1221.16	-17.60	0.93
Missa	4.809	2.460	795.69	-16.56	0.95
Rajar	4.435	2.540	888.05	-16.81	0.98
Rawalpindi	4.320	2.508	818.42	-16.61	0.97

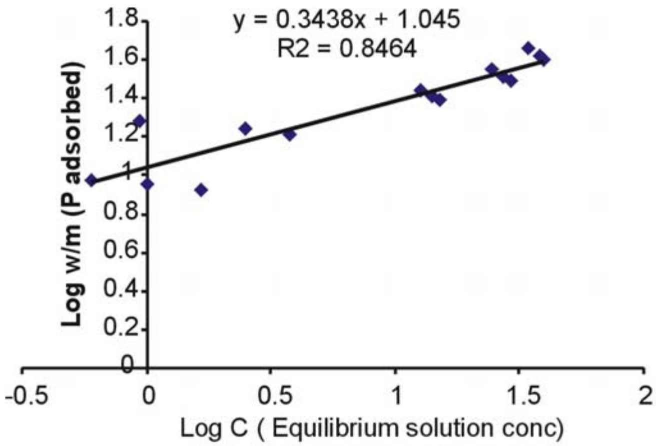

Fig. 1. Freundlich adsorption equation of Basal soil with DAP, SSP and NP fertilizers

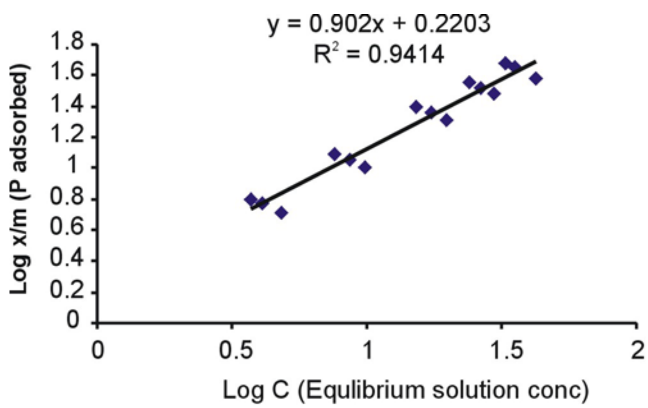

Fig. 2. Freundlich adsorption equation of Bather soil with DAP, SSP and NP fertilizers

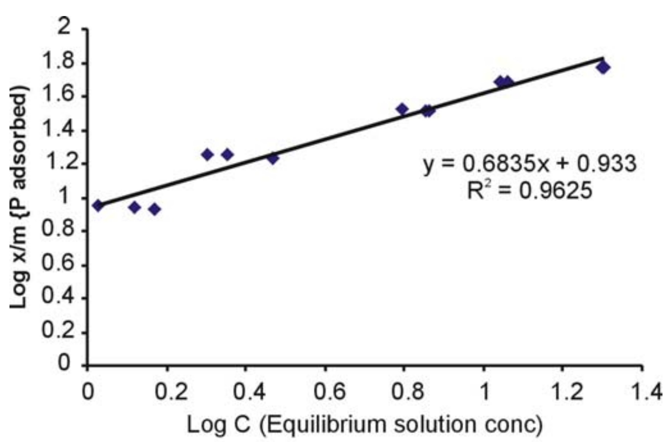

Fig. 3. Freundlich adsorption equation of Balkassar soil with DAP, SSP and NP fertilizers

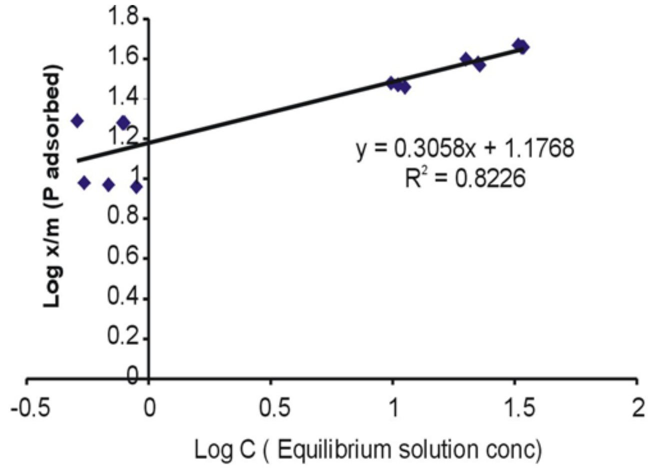

Fig. 4. Freundlich adsorption equation of Chakwal soil with DAP, SSP and NP

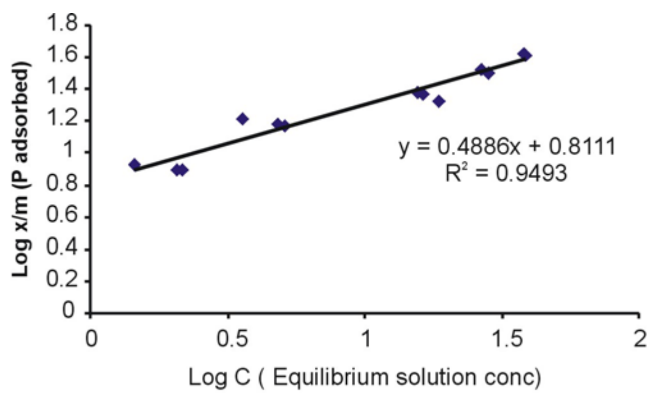

Fig. 5. Freundlich adsorption equation of Gulliana soil with DAP, SSP and NP fertilizers

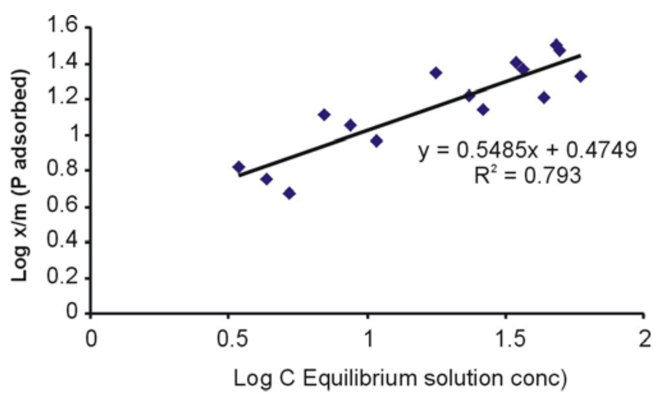

Fig. 6. Freundlich adsorption equation of Kahuta soil with DAP, SSP and NP

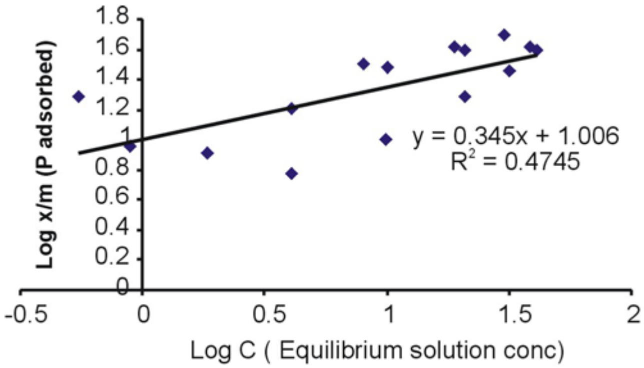

Fig. 7. Freundlich adsorption equation of Khaur soil with DAP, SSP and NP fertilizers

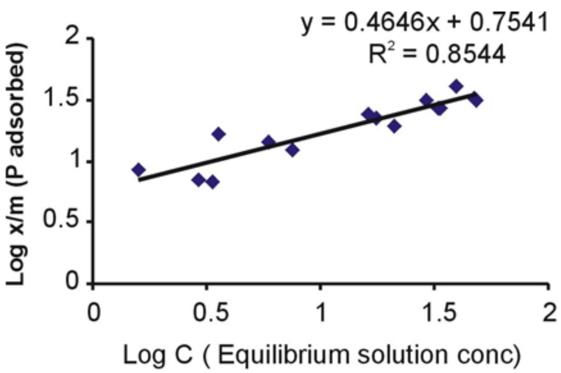

Fig. 8. Freundlich adsorption equation of Missa soil with DAP, SSP and NP fertilizers

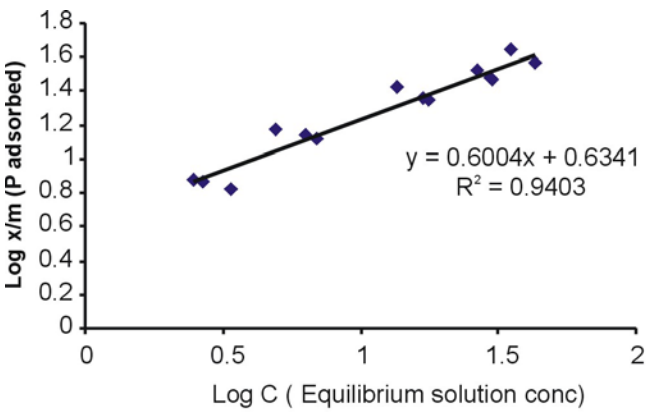

Fig. 9. Freundlich adsorption equation of Rajar soil with DAP, SSP and NP fertilizers

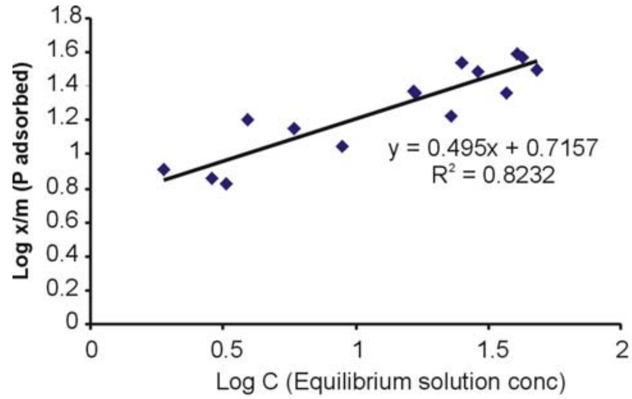

Fig. 10. Freundlich adsorption equation of Rawalpindi soil with DAP, SSP and NP

DISCUSSION

Phosphorus fertilizers are used to correct commonly occurring P deficiency in plants grown under alkaline and calcareous soils of arid and semi arid environments. The added P is involved in the several physical, chemical and biological reaction in the soil and its recovery is commonly low rather major part of it is retained by the constituent minerals of soil solid phase which are in equilibrium with soil solution phase bathing plant roots (Rahmatullah et al., 2003). It is obvious from the data (Table 1-3) that Chakwal soil showed maximum P adsorption, followed by Basal and Balkassar soil. This is due to the reason that these soil series are rich in clay contents and low in organic matter, which contributes to maximum P adsorption, while minimum values of P adsorption were found in Kahuta and khuar soil which are rich in organic matter (Waheed *et al.* 2004). In general,most of the compounds with which phosphorus react were in the finer soil fraction. Therefore, the soils with similar pH phosphorus fixation tend to be more pronounced and ease of phosphorus release tends to be the lowest in the soils with more clay contents (Brady and Weil, 2002). The relationship of soluble and adsorbed P was best described by the Freundlich isotherm. These results are in accordance with the finding of (Loux *et al*., 1989, Weber 1993, Kim and Feagly 1998). They reported that the negative ΔG values suggested a spontaneous nature of pesticide adsorption on both thatch materials and in the soils. The P adsorption studies are important to assess the P retention in soil that will be helpful in assessment of P availability to the crops over a period of time. More P adsorption studies are needed to have compressive data on P adsorption in soils of Pakistan.

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