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Soil Phosphate Sorption Characteristics of Selected Calcareous Soil Series of Southern Punjab, Pakistan

ABSTRACT

To estimate the sorption and desorption capacity of some selected calcareous soils Jhatpat, Miani Pacca and Hadhwar from southern Punjab in Pakistan were analyzed. The sorption isotherms of the three soils yielded different curves. The maximum sorption was recorded in the Miani pacca soil series with value of sorption 201. 23 mg kg^{-1} which was followed by the Hadhwar series with peak sorption value of 190.04 mg kg^{-1}. The lowest value for sorption was determined in the Jhatpat soil series. Comparing the different models (Langmuir, Freundlich and Temkin), Freundlich model showed good fit to the sorption isotherms with regression coefficient (R^2) having value of 0.99, 0.99 and 0. 98 for Jhatpat, Miani pacca and Hadhwar soil series respectively, which was higher than the other two models used. The study on the effect of equilibration time (1, 10, 30 and 60 days) of applied inorganic Phosphatic fertilizers i.e. Single super phosphate (SSP) and diammonium phosphate (DAP) @ 60 and 120 kg ha^{-1} on two soil series with highest P sorption. The P sorption increased with increase in the time of equilibration, with higher value of extractable P was found 22.246 mg P kg^{-1} after 1 day of incubation, and it gradually decreased with the lowest value of 8.271 mg kg^{-1} after 60 days of incubation.

Key words: *Soil Phosphate, sorption, desorption, Langmuir, Freundlich, Temkin*

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INTRODUCTION

Phosphorus (P) is an essential macronutrient required by the plants in large amount. Phosphate has a central role in many physiological and biological processes of plant. It exists in soil as organic or inorganic forms. The organic source of P are slow releasing while the inorganic P sources are instantly available to plants. Availability of added phosphorus to plants is partly as it is sorbed to certain extent by various soil components (*Fink et al. 2016*). The soils of Pakistan are mostly alkaline calcareous having variable amount of lime content which limits the availability of phosphorus (*Memon et al. 2011*).

Phosphate sorption is defined as "a term used to describe the passage of orthophosphate-P from the soil solution to the solid phase"(*Frossard et al. 2000*). The sorbed phosphate is released from its sorbed state to the soil solution is termed as P desorption. The process of desorption is a very slow process and once the P is sorbed, it takes hours and days to release back. Due to the lack of intensive investigations in the different areas of Pakistan, P sorption is not well documented yet. However, some scientists documented that the rate of P sorption increased with the increase of clay contents in the soil but as the organic matter increases in the soil it decreases (*Waheed et al. 2004*). It is observed that fixation between clay components and sources of phosphate are very complex. It is also seen that clay contents has a very wide effect on phosphate retention in the soil. Lime content of the soil has also a great effect on phosphate fixation in the soil.

Phosphate sorption isotherms are one of the most useful methods of measuring the intensity and capacity factor of P in soil. There are difference linear and nonlinear isotherms commonly used to understand the sorption mechanism between sorbent soil solids and solute (*Jeppu and Clement 2012*). The P sorption curves are illustrated by using different models or equations. The different equations are used to describe the sorption of soil P. Among these equations, Langmuir, Freundlich and Temkin are the most common. In these equations, the amount of P adsorbed under certain sorption conditions is plotted against the actual concentration of phosphate-P in solution. These equations vary in their properties and

usefulness (*Horta and Torrent 2007*). Keeping in view of the above points, a study has been designed to test the sorption and desorption capacity of three different soil series of southern Punjab.

MATERIALS AND METHODS

To investigate the phosphorus sorption and desorption of some selected soil series of District Dera Ghazi Khan, a study was carried out by collection of samples from three different soil series from different locations (*Soil Survey Staff 1976*) (**Table 1**).

Analytical methods

After collection of sample soil analysis was carried out to determine the physico-chemical characteristics that include soil texture (*Bouyoucos 1951*), soil pH (*Jackson 1973*), Electrical conductivity (ECe) (*Jackson 1973*), Organic Matter (*Nelson and Sommer 1982*), Lime content (*Puri 1930*) and Carbonates and Bicarbonates (*Richard 1954*). Extractable Phosphorous (*Olsen et al. 1954*) (**Table 2**).

Phosphate sorption and desorption was carried out using the procedure given by *Graetz and Nair* (*2009*), Soil sample was accurately weighed 1 g in a 50 mL polyethylene bottle, 25 mL of 0.01 M $CaCl_2$ solution containing 0, 1, 2, 5, 10, 20, 50 and 100 mg P L^{-1} as potassium di-hydrogen phosphate (KH_2PO_4). The soil suspension was shaken at 25°C for 24 h on a reciprocating shaker. After equilibration, the suspension was filtered using Whattman filter paper No. 2. Phosphorus concentration in the filtrate was determined by spectrophotometer.

Desorption of P was also determined simultaneously with the adsorption study. In the desorption study 0.5 g of soil samples was taken in polythene bottles and separately labeled. A 25 ml of 100 mg P L^{-1} was taken from the stock solution and added to each bottle with respective pipettes to have 1:50 soil solution rates. The bottles were shaken with the adsorption samples for 24 hr and diluted using distilled water as 0, 3, 5, 10, 15, 25, 50 ml. The solutions were set aside again for another 24-hour shaking.

Table 2. Physico-chemical characteristics of three soil series.

Parameters	Miani pacca	Jhatpat	Hadhwar
ECe (μSm^{-1})	571	576	440
pH	7.89	7.57	7.96
O.M (%)	0.890	0.54	0.81
Olsen P (mg kg^{-1})	5.167	6.464	7.830
CaCO3 (%)	25	20	27.5
CO_3 meq L^{-1}	14.4	8.4	12.8
HCO_3 meq L^{-1}	2.6	6.8	6.0
Sand (%)	17	42	39
Silt (%)	42	21	26
Clay (%)	41	37	35
Textural class	Silty clay	Loam	Clay loam

After 48 hours, the filtrate was obtained using Whattman filter No.2. The filtrate was used to determine the P by measuring the absorbance on spectrophotometer.

Equations describing P sorption Isotherm

a. Langmuir Equation (*Langmuir 1918*) $\frac{C}{X} = \frac{1}{K_L b} + \frac{C}{b}$

b. Freundlich Equation (*Freundlich 1926*) $X = K_f C^{1/n}$

c. Temkin Sorption Equation (*Temkin and Pyzhev 1940*)
$X = a + b \ln C$

Where C is the equilibrium concentration of phosphorus in solution (mg P L^{-1}), X is the phosphate adsorbed mg kg-1 of soil, b is the sorption maximum (mg P kg^{-1} soil), K_L is the bonding energy constant of Langmuir model (L $(mg P)^{-1}$), K_f is the proportionality constant for Freundlich model (mg kg^{-1}), n is the empirical constant related to bonding energy of soil for phosphate, a is the amount of P adsorbed of Temkin model (mg P kg^{-1}) and b is the buffer capacity of Temkin model (mL g^{-1}).

Equilibration Study of Phosphate adsorption

The two soils having the higher sorption capacity such as Miani pacca and Hadhwar were used for further study of incubation period. Two fertilizers viz. Single Super phosphate and Diammonium phosphate were applied @ 60 and 120 kg ha^{-1}. The extractable P was determined after 1 , 10, 30 and 60 days incubation period.

Table 1. Soil series with their location and GPS coordinates.

S.No.	Soil Series	Location	GPS Coordinates
1.	Jhatpat	500 m east of Manka Road, Dera Ghazi Khan	30o 04' 55.55" N 70o 39' 58.25 E
2.	Miani Pacca	100 m on Talpur Road, Jampur, Dera Ghazi Khan	29o 52' 58.96" N 70o 38' 30.97" E
3.	Hadhwar	Makwal Kalan road, Taunsa Sharif Dera Ghazi Khan	30o 34' 56.52" N 70o 41' 23.08" E

RESULTS AND DISCUSSION

Phosphate sorption and desorption Isotherms

The phosphate sorption and desorption isotherms of the three soils series of Jhatpat, Miani Pacca and Hadhwar were determined by plotting the equilibrium concentration of phosphate against the amount of phosphate adsorbed. The sorption and desorption isotherms of the three soil series showed that these soil series covered in the analysis have exhibited different curves. Comparing the highest amount of P adsorbed in the soil series, it was evident that each series have different capacities to adsorb P present in the soil (**Table 3**). The results of the study showed that Miani Pacca soil showed the highest value of maximum sorption of 201.23 mg kg^{-1} and followed by Hadhwar soil that gave the maximum sorption of 190.04 mg kg^{-1}. While Jhatpat soil series had the maximum P adsorbed 105.04. The highest value of sorption in the Miani Pacca soil series may be due to more organic matter content and clay lattice. *Khan et al.* (*2010*) reported after comparing the three soil series that greater P sorption is noted in the soil having greater organic matter content and fine texture. Also, *Bai et al.* (*2017*) have reported increase in P sorption with increase in pH of the soil.

The sorption isotherms showed a smooth straight pattern, while the desorption isotherm in all the soil series appeared scattered especially at the initial low concentrations. Comparing the two curves, it was evident that with increase in equilibrium concentration, the rate of Phosphorus sorption increased gradually for all the three series (**Figure 1**). In Jhatpat soil series, the rate of sorption at lower concentration was more gradual, but at the higher concentration the points appeared more condensed until it reach the maximum, where it plateaud. However, the desorption isotherm were more linear and narrow to the sorption isotherm at higher concentration, but the gap widened at the lower concentrations.

The Miani pacca soil series showed more plateau on sorption and desorption curves, with sharp increase in the initial concentration, until it reaches the peak and then it horizontally straightened. The Hadhwar series on the hand

Table 3. Physico-chemical characteristics of three soil series.

S.No.	Name of Soil Series	Maximum P adsorbed (mg kg^{-1})
1.	Jhatpat	105.04
2.	Miani Pacca	201.23
3.	Hadhwar	190.04

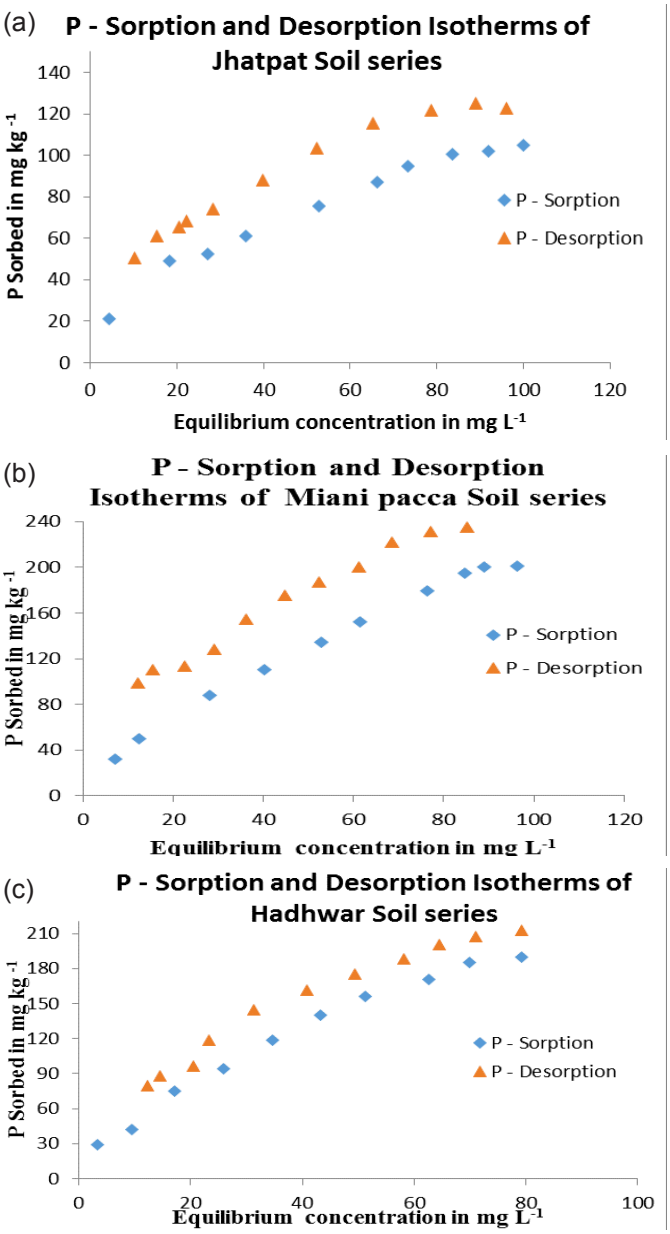

Figure 1. Phosphate sorption and desorption isotherm of Jhatpat, Miani pacca and Hadhwar soil series.

showed that the isotherm were smoothly constructed for P sorption, a narrow gap existed between the sorption and desorption isotherms. The difference in the two isotherms may be due to variation in the Physico-chemical characteristics of soil. *Khan et al.* (*2012*) reported that the difference between the phosphate sorption and desorption isotherm is due to various factors as more absorption or penetration of phosphate into the clay particles, immobilization by the microorganisms, soil organic matter , presence of soluble and exchangeable salts and soil alkalinity. *Xiaoyang et al.* (*2018*) reported that the rate of P- sorption in soil increases with the decrease of soil pH. The amount of phosphorus sorbed increased rapidly with rise in pH under acid conditions (*Gustafsson et al. 2012*).

Application of various equations to the P sorption data:

To comprehend the sorption process and quantify the sorption maximum, the data of P sorption was fitted to different equations. The most common equation used are Langmuir, Freundlich and Temkin. The Langmuir equation has the advantage that it computes the sorption maximum and bonding energy for P sorption (*Hussain et al. 2006*).

Khan et al. (*2010*) compared the three equations and reported that Freundlich equation was better fitted to the P sorption data of salt inherent in soils. *Hafiz et al.* (*2016*) reported that Freundlich equation best fitted the equilibrium P sorption data as compared with the Langmuir and Temkin equation for soil other than those treated with manures.

The comparison of the equation in the current study showed that Freundlich equation fitted better than the other two equations in the three soil series with the R^2 value of 0.993, 0.998 and 0.985 for Jhatpat, Miani pacca and Hadhwar respectively (**Figure 2**). Determination of Langmuir sorption maximum (b) for the soil series was 113.63, 400.00 and 303.03 mg kg^{-1} for Mianai pacca, Hadhwar and Jhatpat soils, respectively (**Table 4**).

Comparing the values of Langmuir sorption maximum with the actual calculated, it was observed that Langmuir sorption maximum calculated through the equation was greater than the actual determined (**Table 5**). The bonding energy calculated from the Langmuir equation was 0.035, 0.018 and 0.008 (L (mg P)$^{-1}$) for Jhatpat, Hadhwar and Miani pacca soil series respectively. The lowest value of the bonding energy constant might be due to the greater soil pH. *Olsen and Watanabe* (*1957*) reported 0.92 and 4.39 ml μg^{-1} in alkaline and acidic soil, respectively. Binding energy constant with similar

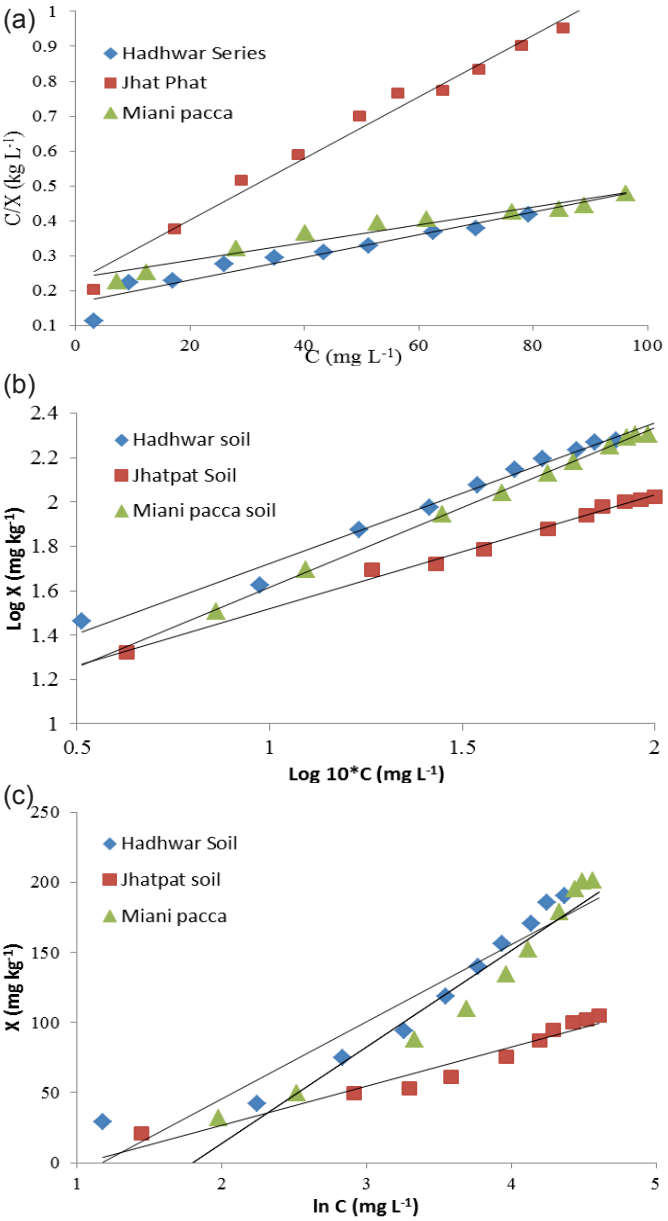

Figure 2. Fitting the P sorption data to (A) Langmuir, (B) Freundlich and (C)Temkin equations for three soil series.

Table 4. Regression equations with R^2 value for three soil series.

Soil Series	Model	Equation	R^2
Jhatpat	Langmuir	y = 0.0088x + 0.225	0.9832
	Freundlich	y = 0.5115x + 1.0074	0.9936
	Temkin	y = 27.879x - 28.957	0.9355
Miani Pacca	Langmuir	y = 0.0025x + 0.2349	0.9486
	Freundlich	y = 0.7173x + 0.8978	0.9989
	Temkin	y = 68.854x - 123.69	0.9448
Hadhwar	Langmuir	y = 0.0033x + 0.1635	0.9152
	Freundlich	y = 0.6342x + 1.0889	0.9857
	Temkin	y = 55.001x - 64.431	0.9181

results have been reported by *Khan et al.* (*2010*) for the saline-sodic soil. The better fit of the Freundlich equation over the Langmuir equation, for various soils have already been observed by different workers (*Khan et al. 2010*). *Rehman et al.* (*2005*) have also reported high value of $R^2 = 0.95$, which indicated that high conformity of the sorption data with the modified Freundlich model.

It was found that the Temkin equation did not show a good fit to the data of the three soil series. In the Temkin equation, the exponent (b) was greater in all the three series, as compared with the other equation with maximum value of 68.85 found in the Miani Pacca series where the sorption was greater. The sorption energy

Table 5. Comparison of Langmuir Sorption maximum and bonding energy constant.

S.No.	Soil Series	Sorption Maximum (b) (mg kg^{-1})	Bonding Energy Constant (K) (L (mg P)$^{-1}$)
1.	Jhatpat	113.63	0.0355
2.	Miani Pacca	400.00	0.0085
3.	Hadhwar	303.03	0.0184

decreases linearly with increasing surface coverage in the Temkin equation. The P sorbed and logarithmic P should yield a straight line which was found in the current study. These results agree with *Khan et al.* (*2012*). The Temkin equation thus has limited value, despite its potential usefulness over large concentration ranges.

Effect of incubation period on extractable phosphorus of two inorganic fertilizers used in soil with high sorption capacity. In the incubation study it was found that the rate of extractable P was decreased with the days of incubation. The Miani pacca soil showed that DAP applied at 120 kg ha^{-1} gave the maximum value of 22.246 mg P kg^{-1} determined after 1 day of incubation, after 10, 30 and 60 days the extractable P was 14.621, 11.796 and 8.271 mg kg^{-1}, respectively (**Figure 3**).

The similar decreasing pattern was observed for the SSP at 120, 60 kg ha^{-1} and DAP 60 kg ha^{-1}. Similarly for the Hadhwar soil series, the rate of extractable P was reduced as the period for incubation increased (**Figure 4**).

Similar results have been reported for the applied organic (DCD) and inorganic (SSP) fertilizers and found that by increasing the incubation period, the extractable

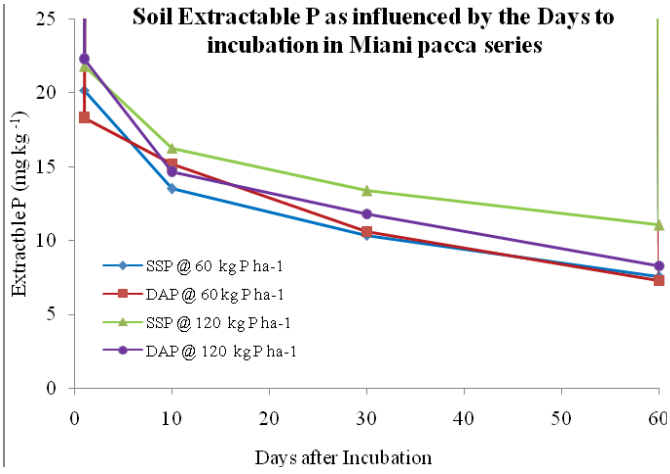

Figure 3. Effect of Incubation period on extractable P of Miani Pacca soil series.

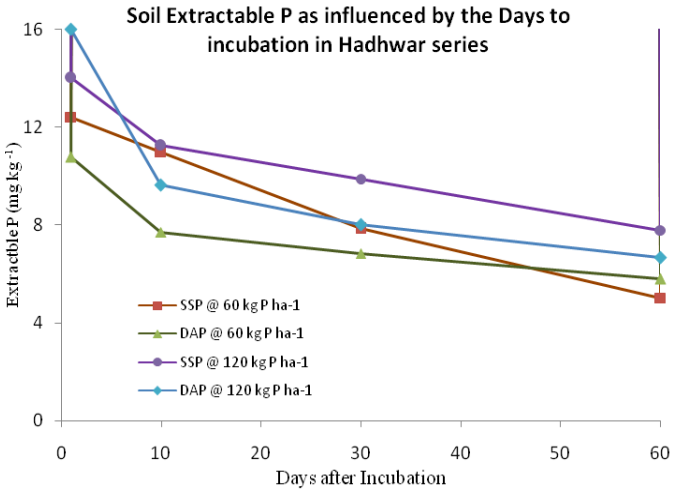

Figure 4. Effect of Incubation period on extractable P of Hadhwar soil series.

phosphorus was decreased (*Akhtar and Alam 2001*). *Karimian et al.* (*2012*) reported that with increase in incubation period Olsen P was reduced. Availability of phosphorus applied (recovery by NaHCO extractant) showed decreased with the time in three soils (*Samadi 2003*). The finding of the current study coincide with the studies of *Horta* (*2017*).

CONCLUSION

Phosphorus sorption and desorption data of three soil series exhibited different curves. Comparing sorption isotherm by using the three equations it was found that Freundlich equations gave a better fit to the data of three soil series with R^2 values of greater than 0.98. The Temkin equation showed comparatively lower value for Coefficient of regression. In the incubation study it was recorded that SSP and DAP applied @ 60 and 120 kg ha^{-1} showed decrease in P concentration with the increase in days to incubation.

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