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Phosphorous Adsorption and Desorption Capicitiy as Influenced By Phosphorous Concentrations, Humic Acid and Farm Yard Manure

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Abstract

The phosphorus adsorption capacity of soil in the presence and absence of HA and FYM was determined by adding 0, 10, 20, 40, 60, 120, 240 and 360mg L^{-1} (initially applied P, IPA) to 5g soils with and without HA (10mg kg^{-1}) and FYM (20g kg^{-1}) .The soils along with respective phosphorus solution were taken in duplicates, were shaken on horizontal shaker for 30hr continuously. The suspension were then filtered through whattman-42 and analyzed for P which represented the equilibrium P concentration (EPC). These soils were then applied another 45 mL distilled water and shaken for 24hr for desorption study. The study revealed that the soils treated with P+FYM and P+HA significantly decreased the adsorption of Phosphorous at each level of IPA as compared with soil treated with P alone. Furthermore in case of alone P the higher Xad and Kd values attributed towards more P adsorption, at any levels of IPA than the soil which received HA and FYM treatments. Soils treated with P+FYM and P+HA indicated higher desorption of P as well at any IPA than the soil treated with P alone, confirmed that FYM and HA not only reduced P adsorption but also played a vital role in the release of P from soil surfaces into soil solution. Langmuir and Freundlich isotherms models were used in the study, however Freundlich model was found best fit in the present study. Such type of studies should be encouraged at field levels.

Keywords: Adsorption; Isotherm; Humic Acid

Introduction

Phosphorus has a vital role in the metabolism and energy production reaction and can survive the unfavorable environmental effects so cause increase in yield Azink and Kajfez [1]. Pakistani soil lack (80-90%) in P and further P applications are required to sustain enough P levels in soil solutions to boost up maximum crop yield. Soil with high pH and calcium content reduce the P access to crop because of the sorption and fixation process that should be advised at the time of P fertilizer application. Peshawar soils bear the properties of high calcareousness (lime 5 to 26%), and having high pH from 7.2 to 9.1 (Soil Survey of Pakistan, 1973). Soils of Peshawar valley are low in organic matter (less than 1%) with low-medium access of P Ahmad et al. [2]. Many researchers successfully explained the adsorption of P by using various adsorption equations [3-8]. Adsorption phenomena best described by two equations i.e. Langmuir and Frendlich equations Boschetti et al. [6] and mostly best fitted for calcareous soils Ghanbari et al. [9]. P requirements for different crops and soils in field conditions could be estimated with the help of adsorption isotherms [8]. Chaudhry et al. [7] concluded that maize required P levels of 22-67 mg kg^{-1} to developed 0.2 mg PL^{-1} level in soil solution. There are enough evidence which supported the fact that FYM and HA decreased P adsorption. FYM and GM play a positive role in the availability of P [10]. This study was initiated to evaluate the effect of humic acid and farmyard manure on P adsorption and desorption capacity of calcareous soil.

Materials and Methods

Effect of FYM and HA on P adsorption of highly calcarious alkaline soil of peshawar soil series was investigated during a lab experiment performed at the Dept of soil and Environmental sciences university of Agriculture Peshawar on 24/8/2014. Soil samples were collected from the University farm. Three treatments were used i.e addition of alone P, addition of FYM and HA.

P Adsorption Study

P adsorption capacity as influenced by humic acid (HA) and farmyard manure (FYM) was determined in soil by treating 1 kg soil with 50 mg HA and 20 g FYM kg^{-1}. Five gram soil of respective treatment was then added with 50 ml solution of 0, 10, 20, 40, 60, 120, 240 and 360 mg P L^{-1} solution in duplicates in 250 mL conical flasks. The solution mixture was then shaked on horizontal shaker continuously for 30 hours. The mixture was then centrifuged at 2500 rpm for five minutes to collect the supernatant, was analyzed for P concentration and the disappearance/decrease from initially applied P was considered as P adsorbed. For adding the solution, 1000 mg P L^{-1} stock solution was prepared by dissolving 4.387 g KH2PO4 in 1000 mL of water. From the stock solution a series of P solution were prepared as 0, 10, 20, 40, 60, 120, 240 and 360 mg P L^{-1} by diluting 0, 0.5, 1, 2, 3, 6, 12 and 18 mL of stock solution in 50 mL water. The sample was 21 times diluted for P determination.

P Desorption Study

One step desorption procedure was followed. After centrifugation, as much as possible the aqueous phase was removed. The volume of the solution removed was replaced by the same volume of water (reconstituted soil solution) i.e. 45 mL of water. The tubes were shaken for 20 hr and subsequently centrifuged. The supernatant was analyzed for P concentration. EPC was measured again and this time it was considered as desorbed P.

Adsorption Isotherm Models

Langmuir and Freundlich adsorption isotherm models were applied to examine P adsorption in the soil by relating the bonding strength, maximum P adsorption and buffering capacity of the soil. The classical Langmuir adsorption equation and its linear model, expressed by the following formulas were used.

$$\frac{X}{m}=\frac{K_L b(EPC)}{1+K_L(EPC)}$$ (Classical Langmuir Adsorption isotherm equation)

$$\frac{EPC}{\frac{X}{m}}=\frac{1}{k}+\frac{1}{b}$$ (EPC) (Linear for of Langmuir Isotherm)

x/m= amount of P adsorbed (mg P kg^{-1})

KL = bonding energy constant

EPC = concentration of P in soil solution at equilibrium (mg L^{-1})

KLb = maximum buffering capacity of the soil system.

A linear graph was produced by plotting EPC /(x/m) against EPC, in which 1/KLb represented the intercept and 1/b as slope of the linear scatter graph. For the said soil such types of plots were developed which showed curvilinear shape instead of straight line, and for such curvilinear shape Modified Langmuir Adsorption Isotherm Model Bohn et al. [5] was used as per the following formula:

$$\frac{x}{m}=b_1\frac{\frac{x}{m^1}}{k^1 EPC}+b^2-\frac{\frac{x}{m^2}}{k^2 EPC}$$

Where the subscripts 1 and 2 refer to the regions (mechanisms) I and II, respectively

The first straight portion (region I) may be associated to P adsorption while at high EPC precipitation may be responsible for the second straight line in region II (Lin) Barrow [3] also reported that when EPC is low P is adsorbed on lime surface in calcareous soil while at higher EPC precipitation of P takes place as a Ca-P compound. Phosphorus buffering capacity changes by addition or removal of P from soil.

The Freundlich equation stated that on a uniform surface the energy of adsorption is independent of surface coverage Bohn et al. [5] and decreased logarithmically with the increase in the fraction of the covered surface and it is due to surface heterogeneity. It is usually applied in a condition where the Langmuir equation fails as reported by Bohn et al. [5] and several other reviewers. The equation is expressed was also applied to form its fitness in the given conditions.

Where K and n are empirical constants, x/m is the adsorption and EPC is the equilibrium concentration of P. the linear model if the equation is:

Results and Discussion

The phosphorus adsorption and desorption capacity as influenced by P concentrations, HA and FYM was evaluated in calcareous alkaline soils collected from the NDF Farm of The University of Agriculture, Peshawar. The phosphorus adsorption capacity of soil in the presences and absences of HA and FYM was determined with the following results.

P adsorption as Influenced by Application of HA and FYM

The adsorption (x/m) and equilibrium P (EPC) increased with increase in applied P levels (IPA) in alone P, P+HA, and P+FYM treated soils but with different pattern. Treating the soil with HA the P adsorption ranged from -17.46 to 1305.02 mg kg^{-1} , treating the soil with FYM the P adsorption ranged from -63.16 to 719.94 mg kg^{-1} at IPA from 0 to 360 mg L^{-1} which was significantly lower than the range of -21.00 to 1617.60 mg kg^{-1} recorded in case of P alone (Table 1). This lower adsorption of P in HA and FYM treated soils resulted in significantly higher EPC mg L^{-1} at each IPA level than soil received alone P. Figures 1 & 2 both revealed that P adsorption at any IPA or EPC levels were lower for P+HA and P+ FYM treated soils than alone P. The P adsorbed (x/m) expressed in percent of IPA (Xad) and the ratio of x/m to EPC denoted as distribution co-efficient (Kd) simply decreased from 74.8 to 44.9 and from 29.68 to 8.16 respectively with increase in IPA from 10 to 360 mg P L^{-1} in alone P treated soils. While on other hand HA and FYM treated soils, these Xad and Kd decreased from 36.3 to 5.69 and 19.9 to 2.49 respectively, representing comparatively lower P adsorption in HA and FYM treated soils. It is afactual criteria that high Xad and Kd values indicate more efficient removal of P from the soil solutions by soils Hussain et al. [11]. The higher Xad and Kd in case of alone P indicated its comparatively higher affinity and more adsorption of P, at any levels of IPA than the soil which received HA and FYM treatments. Up to significant level P adsorption could be decreased by the addition of organic matter Hussain et al. [11]. Furthermore from the lower Xad and Kd in initial lower IPA levels

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it was cleared that HA and FYM reduced more P adsorption at lower P concentration as compared with EPC. Our results was also in lined with khan et al. (2016) also confirmed that HA could decreased P adsorption in the same soil.

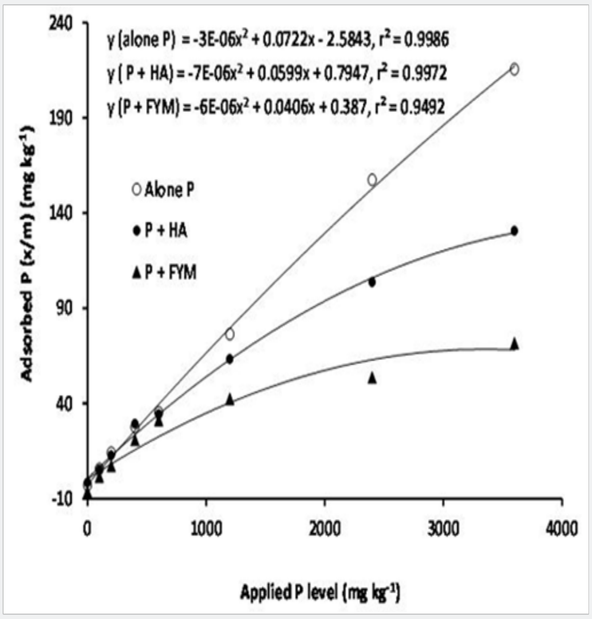

Figure 1: Adsorption of isotherm showing relationship of applied P solution concentrations (IPA) with incremental P adsorption as influenced by HA and FYM application in calcareous soils.

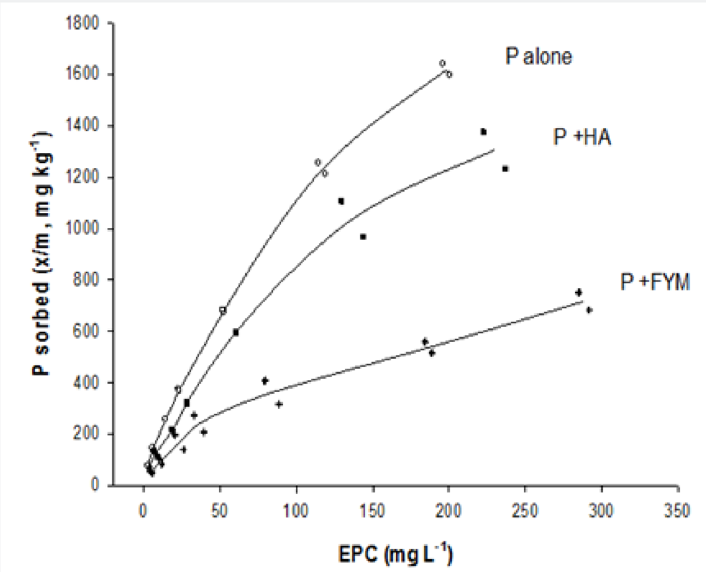

Figure 2: Adsorption of isotherm showing relationship of Equilibrium P solution concentration (EPC)with incremental P adsorption as influenced by HA and FYM application in calcareous soils.

Table 1: Effect of HA and FYM application on P adsorption characteristics in the given alkaline calcareous soil of Peshawar series.

Initial P applied		Equilibrium P	P adsorbed		Xad	Kd	EPC/X/m
mg/L	mg/kg	mg/L	mg/L	mg/kg	%	-	L kg-1
--- P alone ---							
0	0	2.10	-2.10	-21.00			
10	100	2.52	7.48	74.80	74.8	29.68	0.03
20	200	5.78	14.23	142.25	71.1	24.63	0.04
40	400	14.28	25.72	257.20	64.3	18.01	0.06

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60	600	23.00	37.01	370.05	61.7	16.09	0.06
120	1200	52.19	67.82	678.15	56.5	13.00	0.08
240	2400	116.87	123.14	1231.35	51.3	10.54	0.09
360	3600	198.24	161.76	1617.60	44.9	8.16	0.12
-- P+HA --							
0	0	1.75	-1.75	-17.46			
10	100	3.47	6.54	65.35	65.4	18.86	0.05
20	200	7.66	12.34	123.44	61.7	16.12	0.06
40	400	18.48	21.52	215.20	53.8	11.65	0.09
60	600	27.94	32.06	320.60	53.4	11.47	0.09
120	1200	60.30	59.70	596.99	49.7	9.90	0.10
240	2400	136.39	103.61	1036.14	43.2	7.60	0.13
360	3600	229.50	130.50	1305.02	36.3	5.69	0.18
--- P+FYM --							
0	0	6.32	-6.32	-63.16			
10	100	5.04	4.96	49.60	49.6	9.84	0.10
20	200	10.50	9.50	95.00	47.5	9.05	0.11
40	400	23.10	16.90	169.00	42.3	7.32	0.14
60	600	36.02	23.99	239.85	40.0	6.66	0.15
120	1200	83.82	36.18	361.76	30.1	4.32	0.24
240	2400	186.33	53.67	536.74	22.4	2.88	0.35
360	3600	288.31	71.69	716.94	19.9	2.49	0.40

Adsorption Isotherm

By plotting the EPC (x/m) against EPC gives Langmuir adsorption model which produced linear forms with r^2 from 0.93 to 0.96 (Figure 3). However, when plotted according to Freundlich model, the coefficient of regression was raised from 0.98 to 0.99 suggesting that P adsorption in the present study was more fitted to this model than Langmuir (Figure 4).

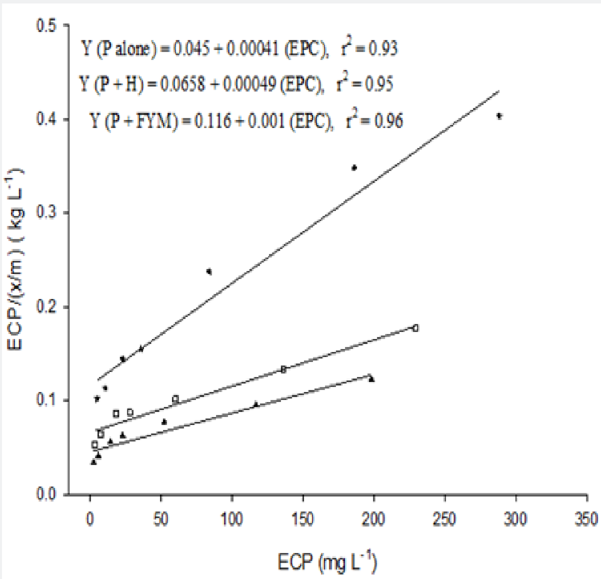

Figure 3: Langmuir isotherm model for P adsorption at given treatments of P alone, P+HA and P+FYM under calcareous soils conditions

The following Freundlich equation was also applied on the data.

$$\frac{x}{m} = K * EPC^{1/n}$$

Where K and n are empirical constants, x/m is the adsorption and the EPC equilibrium of P. The linear model of the equation is:

$$\frac{\log x}{m} = \log K + 1/n \log(EPC)$$

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The data were plotted according to the above linear model in Figure 4, which produced linear relationships with r2 values of 0.99, 0.99 and 0.98 in case of P alone, P+HA and P+FYM respectively. Values of K representing the adsorption coefficient of soil were 39.63 in case of alone P which ultimately decreased to 27.34 in case of P+HA and to 20.68 in case of P+FYM (Table 2). In the same way the value of N representing inverse of the slope of graph were 0.880 for alone P which decreased to 0.696 in case P+HA but increased to 0.760 in case of P+FYM. Since the lower in n or higher 1/n value designates more heterogeneity (Gregory) proposed that heterogeneity of soil increased with FYM. Javid also supported our statement that lower K of 27.34 and 20.68 in case of P+HA and P+FYM, respectively would have lower P adsorption capacity at low P concentration than in case of alone P.

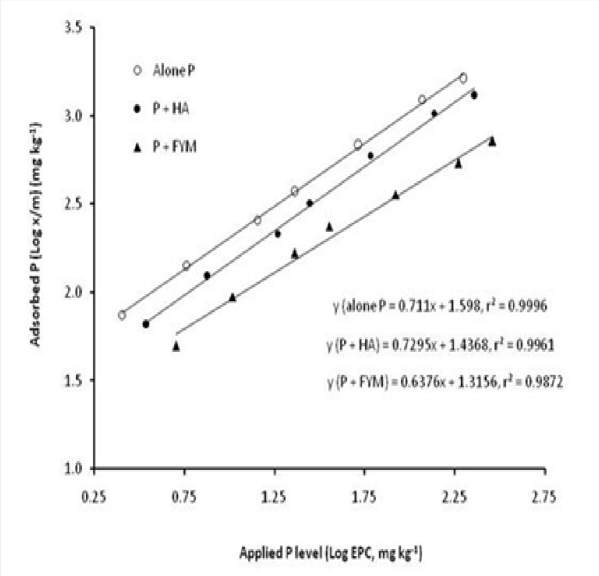

Figure 4: Freundlich isotherm model for P adsorption at given treatments of P alone, P+HA and P+FYM under calcareous soils conditions

Table 2: Comparative Equilibrium parameters of the Freundlich adsorption isotherm equation of the given treatments of alone P, P+HA and P+FYM.

Parameters	P alone	P+HA	P+FYM
Intercept	0.711	0.729	0.637
Slope	1.598	1.436	1.315
r2	0.994	0.996	0.987
K adsorption maximum	39.63	27.34	20.65
N value	0.880	0.696	0.760

Desorption of P

Higher desorption of P was recorded in the soils treated with HA and FYM than the soil treated with alone P. The desorbed P ranged from 62.71 to 426.55 and 35.24 to 301.14 mg L^{-1} at 0 to 360 mg IPA L^{-1} in P+HA and P+FYM treated soils that were higher than the desorbed P (7.73 to 439.85 mg P L^{-1}) detected in P alone treated soils (Figures 5 & 6). Due to chelating effect of HA and FYM they increased desorption of P from soil into solution. Our results were also supported by the work of Khattek and Muhammad; Haroon et al. verified that HA reduced the P fertilizers requirements of maize, wheat and sugar beet by 50% (Table 3).

Table 3: Effect of HA and FYM on P desorption characteristics in the given alkaline calcareous soil of Peshawar series.

Applied P Level	Solution P (mg L^{-1})			Desorbed P (mg kg^{-1})		
IPA mg L-1	P alone	P+HA	P+FYM	P alone	P+HA	P+FYM
0	0.04	0.30	0.17	7.73	62.71	35.24
10	0.05	0.32	0.20	10.02	66.34	41.64
20	0.09	0.42	0.26	19.36	87.23	54.33
40	0.17	0.63	0.42	35.99	132.55	87.42
60	0.31	0.75	0.57	65.84	158.21	118.94
120	0.74	0.83	1.25	155.80	173.54	262.71

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240	1.44	1.47	1.33	303.26	308.93	280.14
360	2.09	2.03	1.43	439.85	426.55	301.14

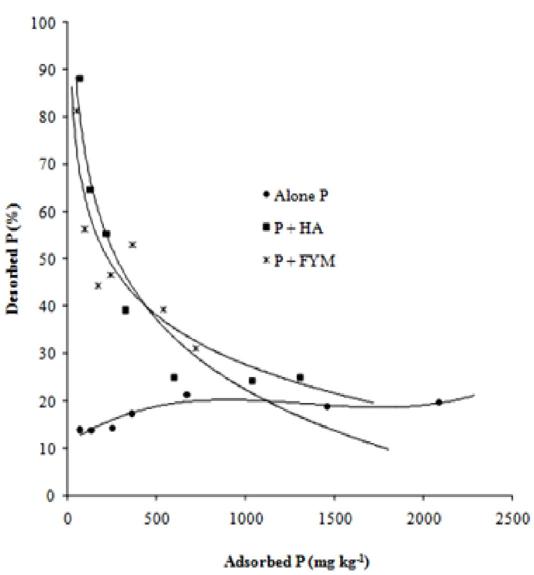

Figure 5: The pattern of desorption of P shows that desorption is higher at P + HA and P +FYM as compared to P alone indicating the binding of P with organic materials.

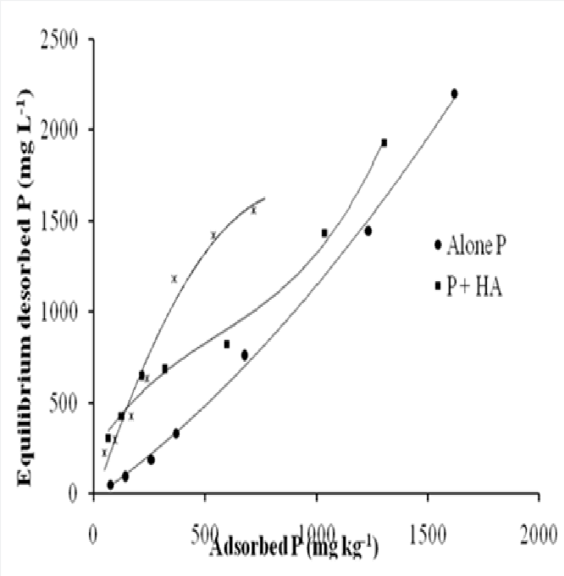

Figure 6: Desorption pattern of P at different treatments of P alone, P + HA, and P+FYM

Conclusion

a) The lower adsorption and higher EPC revealed that HA and FYM reduced the P adsorption over alone P application. However, the effect was more pronounced for FYM than humic acid in the present study.

b) The Freundlich model was more fit to adsorption isotherm for all treatments than Langmuir model in the present study.

c) HA and FYM increased desorption of P from soil into the solution that could be associated to the chelating effect of HA and FYM. The lower K values in case of P+HA and P+FYM suggested reduction in P adsorption with addition of humic acid and farmyard manure.

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