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Application of adsorption isotherms in evaluating the influence of humic acid and farmyard manure on phosphorous adsorption and desorption capacity of calcareous soil

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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 360 mg L⁻¹ (initially applied P, IPA) to 5 g soils with and without HA (10 mg kg⁻¹) and FYM (20 g kg⁻¹). The soils along with respective phosphorus solution were taken in duplicates, were shaken on horizontal shaker for 30 hr 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 24 hr 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 X_{ad} and K_d 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

1. 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 [1]. Pakistani soil lack (80-90%) in P [2] 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 [3]. Soils of Peshawar valley are low in organic matter (less than 1%) with low-medium access of P [4].

Phosphorous is found in two different forms in soil: inorganic and organic. The main inorganic form of phosphorous in soil is H_2PO_4^- and HPO_4^{2-} which are also the available forms to plants. However, these ions can also be adsorbing onto the surface of solid matrices in the soil which make them unavailable to plants. Adsorption is a process that occurs when gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate). Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements (be they ionic, covalent or metallic) of the constituent atoms of the material are filled. But atoms on the (clean) surface experience a bond deficiency, because they are not wholly surrounded by other atoms. Thus it is energetically favorable for them to bond with whatever happens to be available. The exact nature of bonding depends on the details of the species involved, but the adsorbed material is generally classified as exhibiting physisorption or chemisorption. The physisorption is a type of adsorption in which the adsorbate adheres to the surface only through Van der Waals (weak intermolecular) interactions while the chemisorption is a type of adsorption whereby a molecule adheres to a surface through the formation of a chemical bond [5]. The process of adsorption is usually described through isotherms, that is, functions which connect the amount of adsorbate on the adsorbent, with its pressure (if gas) or concentration (if liquid). The different isotherms models describing process of adsorption included Freundlich isotherm, Langmuir isotherm, BET isotherm, etc. [5].

Many of the researchers have successfully confirmed the use of different adsorption equation in relation to phosphate adsorption [6, 7]. The equation of Langmuir and Freundlich described the phenomena of adsorption in a much better way [8]. The Langmuir and Freundlich isotherms were fitted for P adsorption data often calcareous soils [9] and it was observed that the data of adsorption were closely correlated with Freundlich isotherms, while the equation of Langmuir was positively correlated with the clay content, pH, CEC and in multiple regression analysis and negatively correlated with the CaCO_3 . [6] Observed that all soils under study showed adsorption with different slopes of line and soil P adsorption relationships satisfactorily were illustrated by the equations for soils under study except for Kari soil, which was not statistically significant and fit for Langmuir equation. They also observed a spontaneous, highly disordered and endothermic adsorption, because of the high values of enthalpy changes. This suggested that for different soils under study the slope of line was different.

The adsorption isotherm models could be successfully used for estimation of P requirements for optimal crop yields in the field condition which vary greatly from soil to soil and with crop [10]. [11] estimated the maize P requirement through sorption isotherm model by fitting the data in Langmuir and modified Freundlich equations and concluded that P in the level of 22-67 mg kg^{-1} is required to keep the level of soil solution in different soil series upto

0.2 mg P L⁻¹. According to the scale of P sorption studies given by [12], Pakistani soil requires 50-100 kg P₂O₅ ha⁻¹ to keep a desired level of soil solution P for optimum growth production [13].

Reported the beneficial effect of farmyard manures and green manures in increasing the phosphate availability. However, the increase in P may also be attributed to the release of appreciable quantities of CO₂ during organic matter decomposition and complexing of cations like Ca²⁺, which is mainly responsible for fixation of phosphorus in alkaline, particularly calcareous soils. High concentration of organic matter and organic anions has also been found to increase the activity of dicalcium phosphate (a more soluble Ca-P) in soil solution [14]. It is therefore suggested that farmyard manures enhance the phosphatase activity in soil which in turn provide more P in soil solution through mineralization/ solubilization.

There is enough evidence that humic acid (HA) helps to enhance crops yield by promoting certain physical, chemical and biological activities in soil-plant system. Indigenously produced coal derived HA was added to saline-sodic clay soil and improvements in activities of alkaline phosphatase, urease, microbial activities, cation exchange capacity and moisture retention of soil were reported [15]. It was concluded from field experiments that HA can supplement the chemical fertilizers to reduce the input cost of agricultural production [16]. It is believed that the application of HA can reduce the bonding energy and thus the adsorption P could be decreased. This study was initiated to evaluate the effect of humic acid and farmyard manure on P adsorption and desorption capacity of calcareous soil.

2. MATERIALS AND METHODS

Effect of FYM and HA on P adsorption of highly calcareous 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 shaken 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.

$$Adsorption = S = \frac{C_0V_0 - CV}{M}$$

where: C_0 = initial concentration of P spike ($\mu\text{g mL}^{-1}$), C is the equilibrium concentration measured in the supernatant after shaking ($\mu\text{g mL}^{-1}$), V and V_0 are the volumes of the supernatant solution and the spike (mL), respectively, and M is the dry weight of the soil (g). So adsorption has a unit of $\mu\text{g P g}^{-1}$ dry soil.

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. The percentage of desorbed related to the quantity of P previously adsorbed was estimated as follows.

$$\% P \text{ desorbed} = \frac{S - S_{des}}{S}$$

where: S is the adsorbed P concentration as estimated in the sorption step ($\mu\text{g g}^{-1}$), S_{des} is the desorbed P concentration in the desorption step ($\mu\text{g g}^{-1}$), estimated as follows:

$$S_{des} = \frac{(CV_{in_soil} + S_m) - C_1V_1}{m}$$

where: V_{in_soil} and V_1 are the volumes of the soil solutions remaining in the sorption step and volume of the supernatant in the desorption step. C_1 the equilibrium P concentration in the desorption step and S_m is the estimated adsorbed 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.

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

$$\frac{EPC}{x/m} = \frac{1}{K_L} + \frac{1}{b} \quad (\text{EPC}) \quad (\text{Linear for of Langmuir Isotherm})$$

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

K_L = bonding energy constant

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

$K_L b$ = maximum buffering capacity of the soil system.

A linear graph was produced by plotting x/m against EPC, in which $1/K_L b$ 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 [5] was used as per the following formula:

$$\frac{x}{m} = b_1 - \frac{m_1}{K_1 EPC} + b_2 - \frac{m_2}{K_2 EPC}$$

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 [17]. [18] 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 [19, 20].

The Freundlich equation stated that on a uniform surface the energy of adsorption is independent of surface coverage [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 [5] and several other reviewers.

The equation is expressed was also applied to form its fitness in the given conditions.

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

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:

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

3. 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 by the procedure of [21] which has been used by the several researchers including [22, 23]. In this study, 50 mL solution containing 0, 10, 20, 40, 60, 120, 240 and 360 mg L⁻¹ (initially applied P, IPA) were applied to 5 g soils with and without HA (10 mg kg⁻¹) and FYM (20 g kg⁻¹) in 250 mL open mounted conical flasks. The soil along with respective phosphorus solution were taken in duplicates were shaken on horizontal shaker for 30 hr continuously. The suspension were then filtered through whattman-42 and analyzed for P which represented the equilibrium P concentration (EPC). The difference between the IPA and EPC was assumed to be the absorbed P mg kg⁻¹ denoted by x/m . The adsorption isotherm model of Langmuir and Freundlich were applied to investigate P adsorption capacity as influenced by HA and FYM application by comparing the

bonding strength, maximum P adsorption and buffering capacity. These soil were then applied another 45 mL distilled water and shaken for 24 hr. The EPC was again measured and this was EPC assumed to be equal to desorption from the soil into the solution.

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. Fig. 1 and Fig. 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 (xx/m) expressed in percent of IPA (X_{ad}) and the ratio of x/m to EPC denoted as distribution co-efficient (K_d) 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 X_{ad} and K_d 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 a factual criteria that high X_{ad} and K_d values indicate more efficient removal of P from the soil solutions by soils [23].

The higher X_{ad} and K_d 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 [23]. Furthermore from the lower X_{ad} and K_d in initial lower IPA levels 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 [20] also confirmed that HA could decrease P adsorption in the same soil.

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		X _{ad}	K _d	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
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

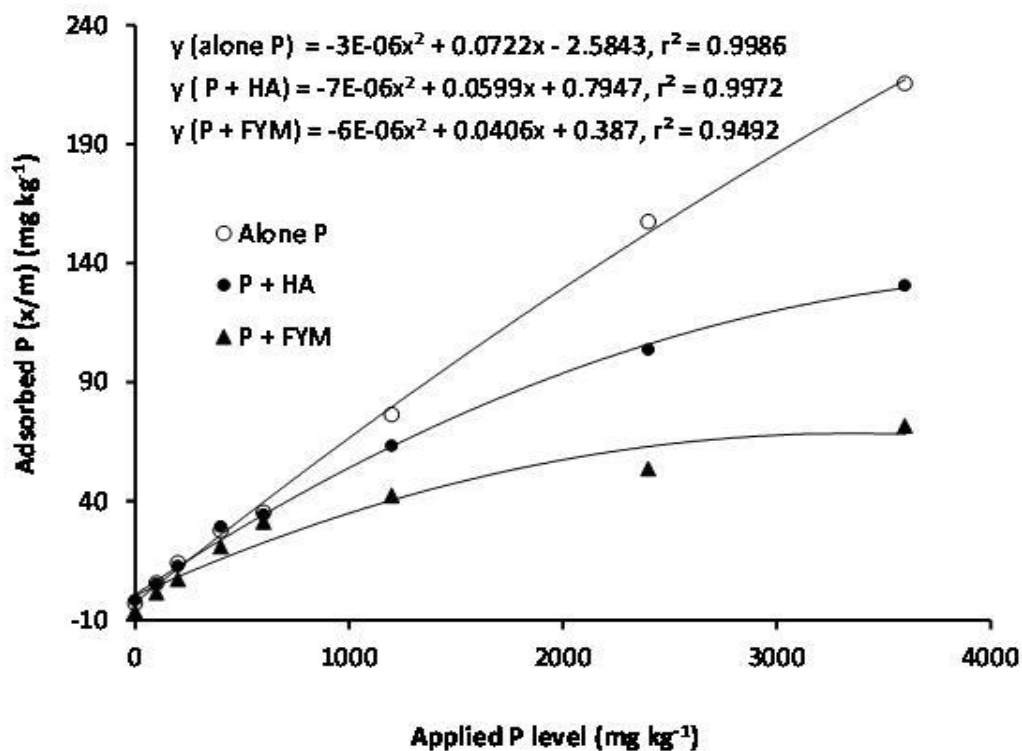


Fig. 1. Adsorption of isotherm showing relationship of applied P solution concentrations (IPA) with incremental P adsorption as influenced by HA and FYM application in calcareous soils

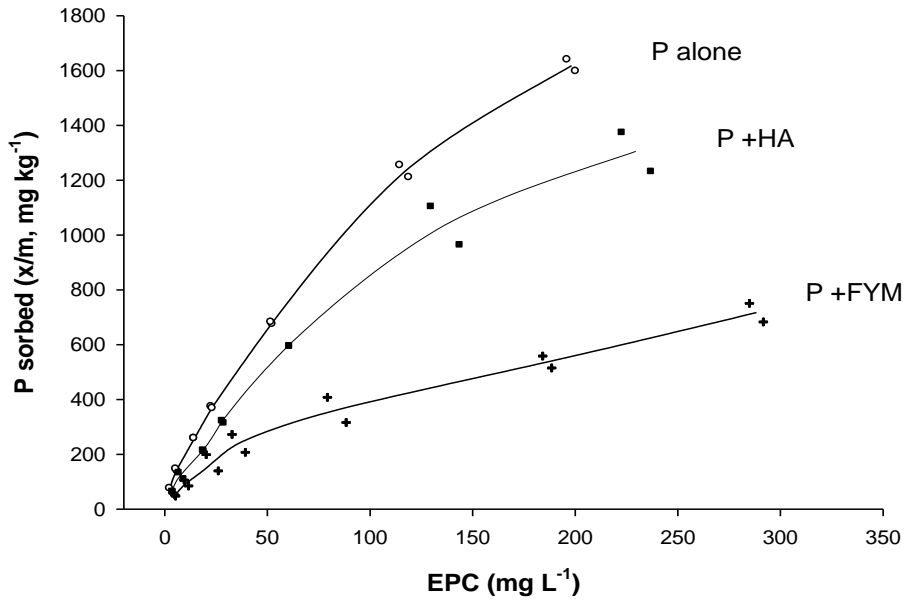


Fig. 2. Adsorption of isotherm showing relationship of Equilibrium P solution concentration (EPC) with incremental P adsorption as influenced by HA and FYM application in calcareous soils

Adsorption Isotherm

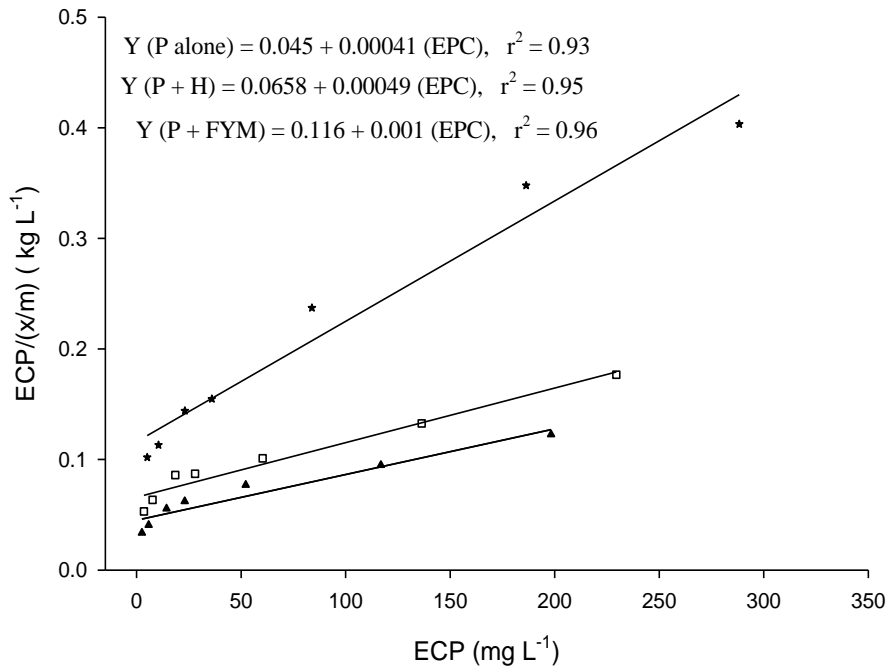


Fig. 3. Langmuir isotherm model for P adsorption at given treatments of P alone, P+HA and P+FYM under calcareous soils conditions

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 (Fig. 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).

The following Freundlich equation was also applied on the data.

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

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:

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

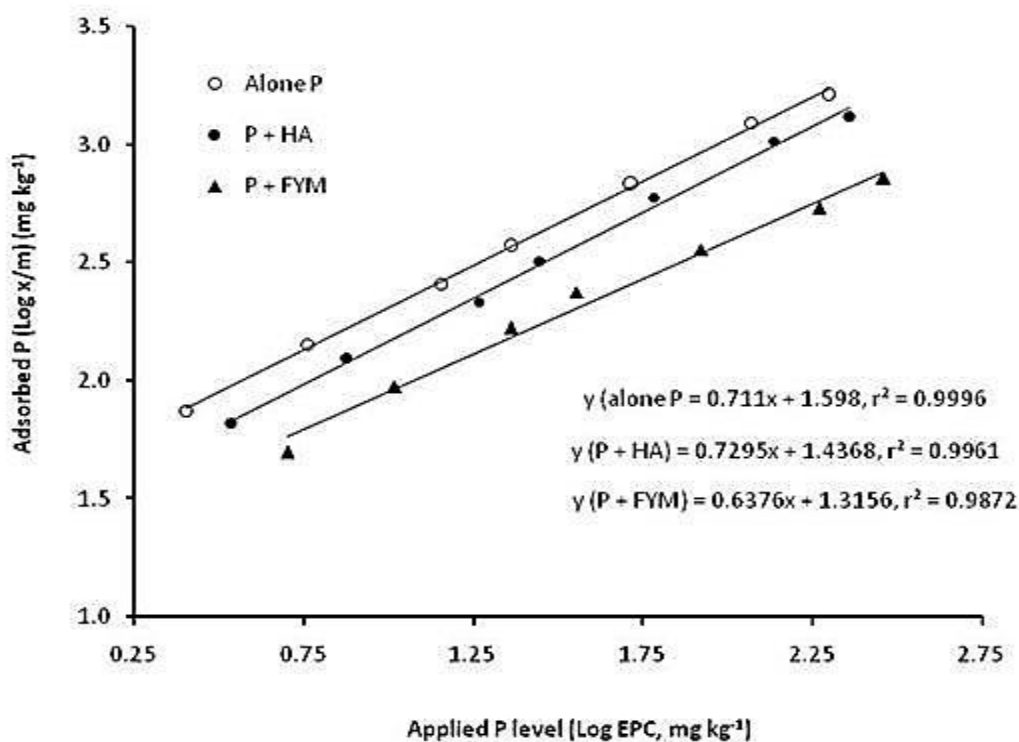


Fig. 4. Freundlich isotherm model for P adsorption at given treatments of P alone, P+HA and P+FYM under calcareous soils conditions

The data were plotted according to the above linear model in Fig. 4, which produced linear relationships with r^2 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 [20] proposed that heterogeneity of soil increased with FYM. [23] 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. [24, 25] suggested that at low [P] adsorption is expressed while at higher P the dominant mechanism is precipitation. [26] Suggested that P may replace an adsorbed water molecule, bicarbonates or hydroxyl ion when it is adsorbed by calcite.

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
r ²	0.994	0.996	0.987
K adsorption maximum	39.63	27.34	20.65
N value	0.880	0.696	0.760

[26] Reported that andisols usually fix large amounts of phosphorous on surface-reactive sites but with addition of water-soluble organic matter (WSOM) reduced the binding strength of phosphate and possibly induced subsequent phosphate desorption and recommended the combine use of manure and inorganic phosphate fertilizer. [27] While studying the influence and mechanism of soil-derived humic acid (SHA) on adsorption of P onto particles in soils and by synthetic goethite (FeOOH), they reported that addition of SHA can significantly reduce the amount of PO₄ adsorption as much as 27.8%. It was concluded that both generated electrostatic field and competition for adsorption sites were responsible for the mechanism by which SHA inhibited adsorption of PO₄ goethite.

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. Due to chelating effect of HA and FYM they increased desorption of P from soil into solution. Our results was also supported by the work of Khattek and Muhammad (2008) and Haroon et al. (2010) verified that HA reduced the P fertilizers requirements of maize, wheat and sugar beet by 50%.

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)		
	P alone	P+HA	P+FYM	P alone	P+HA	P+FYM
IPA mg L ⁻¹						
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
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

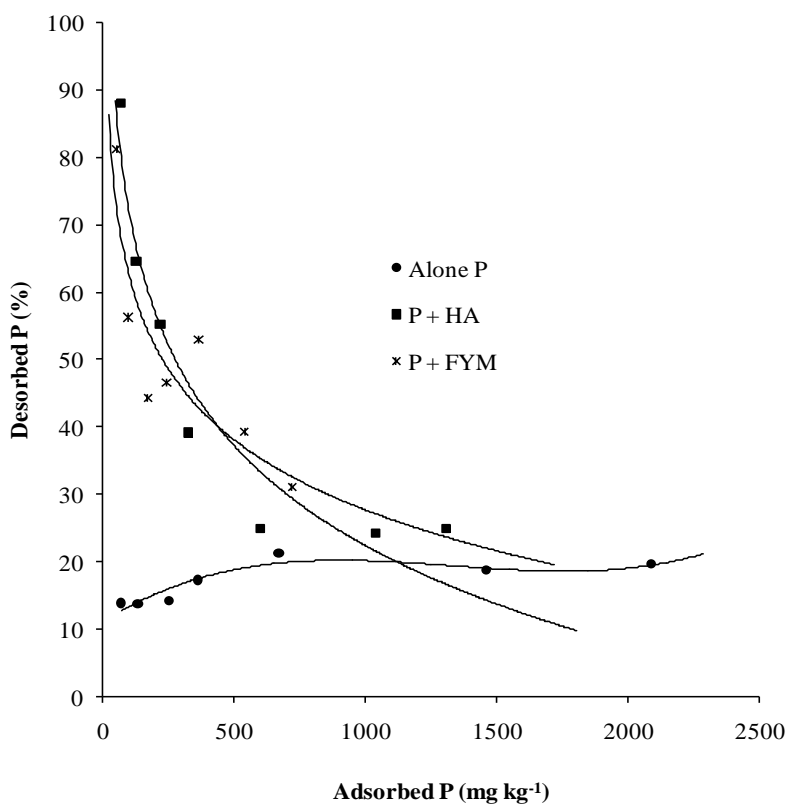


Fig. 5. The pattern of desorption of P shows that desorption is higher at P + HA and P +FYM as compared to P alone indicating the binding of P with organic materials

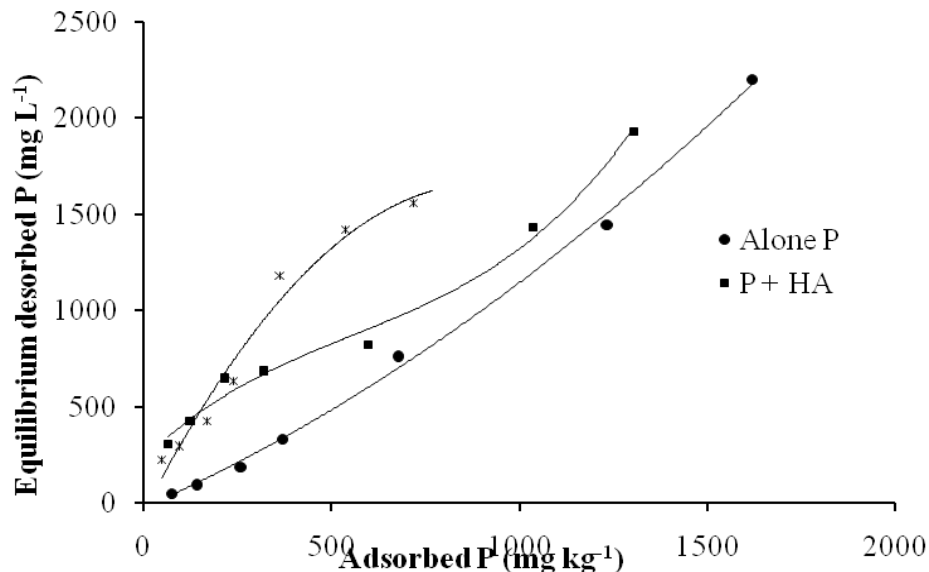


Fig. 6. Desorption pattern of P at different treatments of P alone, P + HA, and P+FYM.

4. CONCLUSIONS

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