



## Phosphorus Adsorption and Phosphorus Use Efficiency in Calcareous Alkaline Soils Influenced by Humic Acid

Muhammad Numan Khan<sup>1</sup>, Dost Muhammad<sup>2</sup>, Sajjad Raza<sup>1\*</sup>, Abdul Haseeb<sup>3</sup>,  
Mubasher Nasir<sup>1</sup>, Asad Shah<sup>4</sup>, Farmanullah Khan<sup>2,5</sup> and Tanveer Ali<sup>1</sup>

<sup>1</sup>College of Natural Resources and Environment, Northwest Agriculture & Forestry University, Yangling, Shaanxi-712100, China.

<sup>2</sup>Department of Soil and Environmental Sciences, The University of Agriculture, Peshawar, Pakistan.

<sup>3</sup>Department of Horticulture, The University of Agriculture, Peshawar, Pakistan.

<sup>4</sup>College of Resources and Environment, Huazhong Agricultural University, Wuhan, China.

<sup>5</sup>Directorate of Soil and Water Conservation, Khyber Pakhtunkhwa, Peshawar, Pakistan.

### Authors' contributions

*This work was carried out in collaboration between all authors. Authors MNK and DM designed the study, wrote the protocol and wrote the first draft of the manuscript. Authors AH and MN managed the literature searches. Authors AS, FK and TA did majority of the analyses work of the study. Author SR supervised and managed the experimental and publication process. All authors read and approved the final manuscript.*

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### ABSTRACT

The effect of lignitic coal derived humic acid (HA) was evaluated on phosphorus adsorption and desorption capacity in calcareous alkaline soils collected from Research Farm of the University of Agriculture, Peshawar, Pakistan. The P adsorption capacity was determined by adding 0, 10, 20, 40, 60, 120, 240 and 360 mg P L<sup>-1</sup> (initially P applied, IPA) to 5 g soil with absence (alone P) or presences of 0.15% HA (P+HA) solution in duplicate. The mixture was shaken on horizontal shaker

\*Corresponding author: E-mail: [sajjad.raza@nwsuaf.edu.cn](mailto:sajjad.raza@nwsuaf.edu.cn); [sjad.rza@gmail.com](mailto:sjad.rza@gmail.com)

for 30 h continuously followed by 5 min centrifugation at 2500 rpm to collect the aliquot/supernatant. The soils were then added 45 mL distilled water followed by same shaking and centrifugation for desorption studies. The P+HA treatments yielded significantly higher EPC (equilibrium phosphorus concentration) and lower P adsorption ( $x/m$ ) at each level of IPA than alone P rendering that HA reduced the P adsorption. The P adsorbed ( $x/m$ ) expressed in percent of alone P ( $X_{ad}$ ) and the ratio of  $x/m$  to ECP ( $K_d$ ) simply decreased with each increments of IPA in case of alone P but first increased and then decreased in case of P+HA indicating different behavior of P in presences of HA solution. The higher  $X_{ad}$  and  $K_d$  in case of alone P revealed its comparatively higher affinity and more adsorption of P at any levels of IPA than the soil which received HA treatments. Similarly, the P+HA treated soils produced comparatively higher desorption of P at any IPA than the alone P treated soils suggesting that HA not only reduces the adsorption but can also increase their release from the soil surfaces into solution. The alone P was best fit to Langmuir modified two surface model whereas the P+HA was best fit to Freundlich isotherm models. These results indicated that humic acid application can improve the P use efficiency in field condition through changings in dynamics of P sorption and hence should be applied for better crop nutrient management.

*Keywords: Humic acid; phosphorous adsorption; desorption; calcareous soil.*

## 1. INTRODUCTION

Phosphorus is an important element for all living organisms. Its concentration in plants range from 0.2–0.8% of plant dry matter [1,2]. It plays vital role in several physiological processes like photosynthesis, respiration, energy storage and transfer, and cell enlargement [3]. If the soil is deficient in P, the plants cannot grow well or can't give an economical production.

Pakistani soils are deficient (80-90%) in P [4] and needs supplemental P application to support optimum crop production. Most of the soils in Pakistan are calcareous, alkaline in reaction and contain less than 1% organic matter [5]. Application of phosphorus in Pakistan is also highly unbalanced, the ratio of N:P application in Pakistan is around 3:1 which is way less than the required ratio of 1:1 or 2:1 for most crops.

Calcareous nature and high soil pH are the main factors responsible for reduced P availability in Pakistan. Majority of the phosphorus applied under above conditions becomes fixed through reaction with calcium by making insoluble di-calcium and octa-calcium phosphate compounds [6], which plants can't uptake. Adsorption and sorption including chemi-sorption and physio-sorption are the possible ways by which applied phosphorus gets fixed within the soil.

Many of the researchers have successfully confirmed the use of different adsorption equations in relation to phosphate adsorption [7,8]. The equation of Langmuir and Freundlich described the phenomena of adsorption in a

much better way [9]. The Langmuir and Freundlich isotherms were best fitted for P adsorption data for calcareous soils [10] 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  $\text{CaCO}_3$ . The phosphorus adsorption relationships were satisfactorily explained by the equations for soils which showed different slope of line except for Kari soil, which was not statistically significant and fit for Langmuir equation [7]. 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 [11]. The estimation of maize P requirement through adsorption isotherm model by fitting the data in Langmuir and modified Freundlich equations and concluded that P in the level of 22-67  $\text{mg kg}^{-1}$  is required to keep the level of soil solution in different soil series up to 0.2  $\text{mg P L}^{-1}$  [12]. According to the scale of P sorption [13] Pakistani soils requires 50-100  $\text{kg P}_2\text{O}_5 \text{ ha}^{-1}$  to keep a desired level of soil solution P for optimum growth production.

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 when added to saline-sodic silty clay soil, improvements were observed in the activities of alkaline phosphatase, urease, microbial activities, cation exchange capacity and moisture retention of soil [14]. It was concluded from field experiments that humic acid (HA) can supplement the chemical fertilizers to reduce the input cost of agricultural production [15]. It is believed that the application of HA can reduce the bonding energy thereby decreasing the adsorption capacity of P. With the above in mind, this study is therefore, conducted to evaluate the effect of humic acid on P adsorption and desorption capacity of calcareous soil.

## 2. MATERIALS AND METHODS

The effect of lignitic coal derived humic acid (HA) on phosphorus adsorption and desorption potential of strongly calcareous alkaline soils of Peshawar series was evaluated in a pot experiment conducted in the wire house of department of Soil and Environmental Sciences, The University of Agriculture, Peshawar during 2013. Soil samples were collected from Research Farm of the university and were air dried and sieved through 2 mm sieve. The treatments include addition of alone P (No HA) or P dissolved in 0.15% solution of HA (HA+P) during preparation of 1000 mg P solution (stock solution) from  $\text{KH}_2\text{PO}_4$  for the adsorption study. From the stock solution working solutions of 0, 10, 20, 40, 60, 120, 240 and 360 mg P  $\text{L}^{-1}$  were prepared by addition of distilled water.

### 2.1 Phosphorus Adsorption

The phosphorus adsorption isotherms were determined following the procedure [16] used by several researchers [17,18]. In this study, 50 ml solution containing 0, 10, 20, 40, 60, 120, 240 and 360 mg p  $\text{L}^{-1}$  (initially applied P, IPA) of both alone P and P+HA were applied to 5 gm soil in 250 mL open mouthed conical flasks. The soil plus respective P solution taken in duplicate were

shaken on horizontal shaker for 30 h continuously. The suspension were then transferred into the vial and centrifuged for 10 minutes to obtain the supernatant followed by filtration through Whatman No. 42. The P in the supernatants were determined through  $\text{NH}_4$ -molybdate method [19]. After diluting the sample by 21 fold, 1 mL of the diluted extract was taken into 25 mL flask and was added with 5 mL ascorbic acid mixed reagent (containing potassium tartarate, ammonium molybdate, and  $\text{H}_2\text{SO}_4$ ) and volume was adjusted to 25 mL. After making the volume the flasks were kept in dark for 15 minutes and then analyzed the P on spectrophotometer (Shimadzu, UV-1700). This concentration was represented as equilibrium P concentration (EPC). The difference between the IPA and EPC was assumed to be the adsorbed P  $\text{mg kg}^{-1}$  denoted by  $x/m$ .

### 2.2 Phosphorus Desorption

The centrifuged soil samples, left over in the bottom of centrifuge bottles after collection of supernatants for P adsorption analysis, were added with 45 ml of distilled water followed by gentle shaking on reciprocating horizontal shaker for shaking. The suspension was then centrifuged on 25000 rpm for 10 minutes and the supernatant was analyzed for P through the already discussed  $\text{NH}_4$ -molybdate method. The equilibrium concentration of P at this time was assumed to be the desorbed P from the solid particles into solution.

### 2.3 Adsorption Isotherm Models

The adsorption isotherm models of Langmuir and Freundlich were applied to investigate P adsorption in the soil by comparing 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.

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

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

Whereas in the formula,  $x/m$  is the amount of P adsorbed ( $\text{mg P kg}^{-1}$ ), ' $K_L$ ' is bonding energy constant, ' $b$ ' is Langmuir adsorption maximum ( $\text{mg P kg}^{-1}$ ), EPC is the concentration of P in soil solution at equilibrium ( $\text{mg L}^{-1}$ ) ' $K_L b$ ' is also known as maximum buffering capacity of the soil system. The EPC/( $x/m$ ) was plotted against EPC which produced linear form where the  $1/K_L b$  represented the intercept and  $1/b$  as slope of the linear scatter graph. Such linear plots were developed for the soil which showed curvilinear shape rather than the straight line, and as such the multisite and multilayer adsorption isotherm model which is also known as the Modified Langmuir Adsorption Isotherm Model [20] was used as per the following formula:

$$\frac{x}{m} = b_1 - \frac{x/m_1}{k_1 \text{EPC}} + b_2 - \frac{x/m_2}{K_2 \text{EPC}}$$

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

The region I representing the first straight portion that may be associated to P adsorption while at high EPC precipitation may be responsible for the second straight line in region II [21]. Other scientist also reported that the P is mainly adsorbed on lime surface in calcareous soil when EPC is low while precipitation of P takes place as a Ca-P compound when EPC is higher [22].

Phosphorus buffering capacity is the potential of soil to resist changes in P soil solution concentration, when P added or removed from the soil [23,24]. The soil with high buffering capacity can release P to the soil solution slowly and reversible retention of P by collides of soil during that soil reaction [25]. An ideal model is comprehensive, when it can apply to a large range of condition without modification; it is practical when it confirm to the accepted theories of behavior; and it is analytical, when it can be applied to the most different condition [26].

The Freundlich equation implies that the energy of the adsorption on a uniform surface is independent of surface coverage [20] and that it decreases logarithmically as the fraction of the covered surface increases. The decrease in

energy of adsorption with increase in surface coverage is due to surface heterogeneity. It is usually used in a condition where the Langmuir equation fails [20].

The equation is expressed by the following formula was also used to check its fitness in the given conditions.

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

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

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

### 3. RESULTS AND DISCUSSION

The phosphorus adsorption and desorption capacity as influenced by P concentrations alone and in combination with humic acid (HA) was evaluated in calcareous alkaline soils. The results of the experiment are stated below.

#### 3.1 Phosphorus Adsorption as Influenced by HA Application

The P adsorption ( $x/m$ ) and equilibrium P (EPC) increased with increase in applied P levels (IPA) under soils treated with P alone and in combination with HA but showed different pattern. The P adsorption of soils treated with HA ranged between 14 to 925  $\text{mg kg}^{-1}$  at IPA levels from 0 to 360  $\text{mg L}^{-1}$  which was significantly lower than the P adsorption values of soils where the only P was applied (47 to 1072  $\text{mg kg}^{-1}$ ) (Table 1 and Table 2). This lower adsorption of P in HA treated soils resulted in significantly higher EPC ( $\text{mg L}^{-1}$ ) at each IPA level than soil which received P alone. P adsorption at any IPA or EPC levels was lower for P+HA treated soils than alone P (Fig. 1 and Fig. 2). The lower adsorption and higher EPC revealed that HA reduced the P adsorption over alone P application.

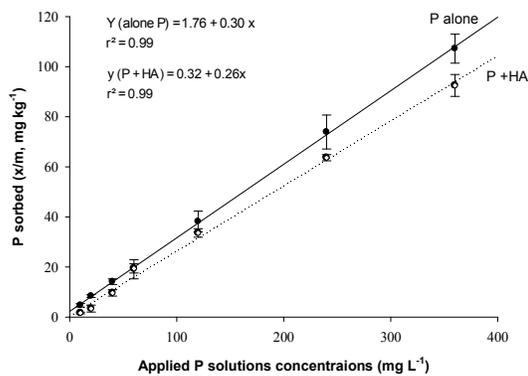
**Table 1. Physico-chemical properties of soil used for experiment**

EC ( $\mu\text{S/cm}$ )	pH	SOC ( $\text{mg/kg}$ )	Available P ( $\text{mg/kg}$ )	Available K ( $\text{mg/kg}$ )	Total N ( $\text{mg/kg}$ )	$\text{NO}_3^-$ -N ( $\text{mg/kg}$ )	$\text{NH}_4^+$ -N ( $\text{mg/kg}$ )
79.5	8.24	16770	41.9	91.75	990	4.56	2.12

**Table 2. Effect of HA application on P adsorption characteristics**

	Initial P applied (IPA)	Equilibrium P (EPC)	P adsorbed (X/m)		X <sub>ad</sub>	K <sub>d</sub>	(EPC)/(X/m)
	mg/L	mg/L	mg/L	mg/kg	%		
Phosphorous alone	0	2.83	-	-	-	-	-
	10	5.30	4.70	47	47.00	8.87	0.113
	20	11.60	8.40	84	42.00	7.24	0.138
	40	25.86	14.14	141	35.36	5.47	0.183
	60	40.90	19.10	191	31.83	4.67	0.214
	120	81.85	38.15	382	31.79	4.66	0.215
	240	166.10	73.90	739	30.79	4.45	0.225
	360	252.80	107.20	1072	29.78	4.24	0.236
Phosphorous + humic acid	0	4.10	-	-	-	-	-
	10	8.61	1.39	14	13.90	1.61	0.619
	20	15.16	4.85	48	24.23	3.20	0.313
	40	30.34	9.67	97	24.16	3.19	0.314
	60	40.56	19.44	194	32.39	4.79	0.209
	120	86.40	33.60	336	28.00	3.89	0.257
	240	170.70	69.30	693	28.88	4.06	0.246
	360	267.50	92.50	925	25.69	3.46	0.289

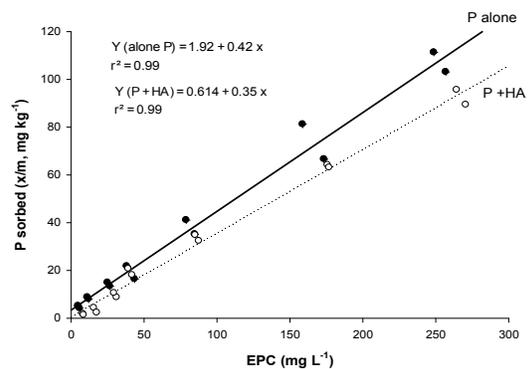
X<sub>ad</sub> = Ratio of adsorption (%) with applied P, K<sub>d</sub> = Ratio of adsorbed P with equilibrium [P]



**Fig. 1. Adsorption isotherms relationship of applied P solution concentrations (IPA) with incremental P adsorption influenced by HA application in calcareous soils**

The P adsorbed (x/m) expressed in percent of IPA (X<sub>ad</sub>) and the ratio of x/m to ECP denoted as distribution co-efficient (K<sub>d</sub>) simply decreased from 47.00 to 29.78 and from 8.87 to 4.24, respectively with increase in IPA from 10 to 360 mg P L<sup>-1</sup> in alone P treated soils. While in HA treated soil, X<sub>ad</sub> and K<sub>d</sub> first increased and then decreased to 25.65 and 3.46 respectively at IPA 360 mg P L<sup>-1</sup>, indicating different pattern and comparatively lower P adsorption in HA treated soils. It is an established criteria that high X<sub>ad</sub> and K<sub>d</sub> values indicate more efficient removal of P from the soil solutions by soils [18]. The higher X<sub>ad</sub> K<sub>d</sub> 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 treatments. It was reported Hussain et al. [27] that organic matter significantly decreased P adsorption. The lower X<sub>ad</sub> and K<sub>d</sub> in initial lower IPA levels further revealed that the role of HA in reducing the P adsorption could be more important at lower P concentration than higher IPA or EPC levels.



**Fig. 2. Adsorption isotherms showing relationship of equilibrium phosphorus solution concentrations with incremental P adsorption as influenced by HA application in calcareous soils**

It was also reported that addition of humic acids to soil with P fertilizer significantly increased the amount of water soluble phosphate, strongly retarded the formation of occluded phosphate and increased P uptake and yield by 25% [28].

Similarly, while evaluating the role of organic residue, limestone and gypsum application on phosphorus adsorption by low land soils, observed reduced P adsorption with organic residue and limestone [29]. They concluded that the reduced P adsorption could be associated to increase in soil pH and reduction in exchangeable Al with these applications. The gypsum application did not affect the P adsorption in the given experiment. The application of organic matter may bind the solution P and thus prevent it from being adsorbed on soil surfaces. Dissolved organic carbon (DOC), dissolved organic P (DOP) are less adsorbed than solution inorganic PO<sub>4</sub> on young andesitic soils [30]. Yusran, [31] also concluded that application of organic residues reduced the P adsorption of soil. Sarir et al. [32] stated that HA is more effective in recovery of added P than FYM in an incubation experiment. Wandruszka, [33] reported that both surface reactions and precipitation of P take place in soil, especially in the presence of calcite and limestone but addition of HA material appear to increase recovery of Olsen P that could be associated to formation of complexes between inorganic P and humates that prevent them from being adsorbed.

### 3.2 Adsorption Isotherm Equation

By plotting the (EPC)/(X/m) against EPC gives the Langmuir Adsorption Model which produced curvilinear form in case of alone P but did not fit such form in case of P+HA treatments (Fig. 3, Fig. 4). Curvilinear Langmuir plots were also observed in other soils by various scientists [18,27,34]. Manzoor, [35] also reported the curvilinear Langmuir plot in the same soil. The curvilinear behavior suggested that originally the soil had varying bonding energy for P adsorption and the adsorption capacity of soil decreased with each additional increment of IPA. Gunary, [36] stated that the curvilinear relationship mean that the soil would adsorb a small amount of P less firmly and so on. However, Syers et al. [37] were of the opinion that two or more population of sites in soils having different affinity for P might be the reason for curvature.

The assumption of constant energy of adsorption, adsorption on specific sites and monolayer adsorption on which the simple Langmuir adsorption isotherm equation relies [20] were fully (100%) satisfied in case of alone P as obvious from the curvilinear shape of the relation. However, the regression in it was poor only 0.56.

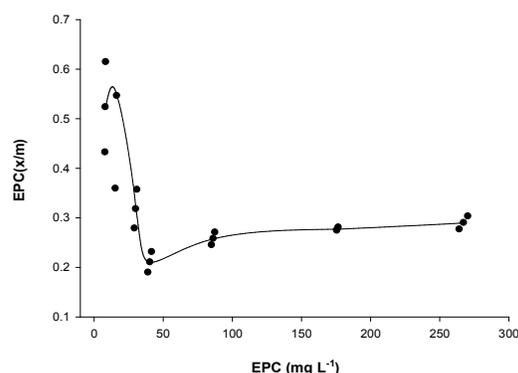


Fig. 3. Langmuir isotherm for calcareous soil applied with P alone

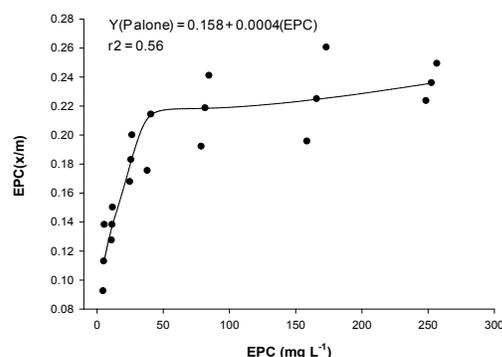


Fig. 4. Langmuir isotherm for calcareous soil P+ HA

Because of deviation from the simple Langmuir equation and curvilinearity in the soil of Peshawar soil form multisite and multilayer adsorption as expressed by the following modified Langmuir Model was applied as given by [20].

$$\frac{x}{m} = b_1 - \frac{x/m_1}{K_1 EPC} + b_2 - \frac{x/m_2}{k_2 EPC}$$

Where the subscripts 1 and 2 refer to the region (or mechanism) 1 and 2 respectively.

The graph yielded two curve line for each the soil treated with alone P; one at low equilibrium [P] (EPC) and the other at higher EPC. The region I representing the first straight portion may be associated to P while at high EPC precipitation may be responsible for the second straight line in region II [21]. Barrow, [22] also reported that the P is mainly adsorbed on lime surface in calcareous soil when EPC is low and

precipitation of P takes place as a Ca-P compound when EPC is higher.

The data were plotted according to the above linear model in Fig. 5 and Fig. 6 which produced linear relationships with  $r^2$  values of 0.98 and 0.96 in case of alone P and P+HA respectively. It states that Freundlich adsorption isotherm model was fit under some conditions.

Values of K representing the adsorption coefficient of soil was 11.22 in case of alone P which sharply dropped to 1.53 when P+HA was added to soil (Table 2). Similarly the value of N representing inverse of the slope of graph was 1.237 for alone P which decreased to 0.847 in case of P+HA. Since the lower n or higher 1/n value indicates more heterogeneity [38] suggesting that application of HA increased the heterogeneity of soil. Javid, [39] reported that K is the adsorbed P that would sustain a unit P concentration in equilibrium solution. This employs that lower K in case of P+HA would have lower P adsorption capacity at low P concentration than in case of alone P. Cole et al. [40]; Holford and Mattingly, [41] suggested that at low [P], adsorption is expected while at higher P the dominant mechanism is precipitation. Kuo and Lotse, [19] suggested that P may replace an adsorbed water molecule, bicarbonates or hydroxyl ion when it is adsorbed by calcite.

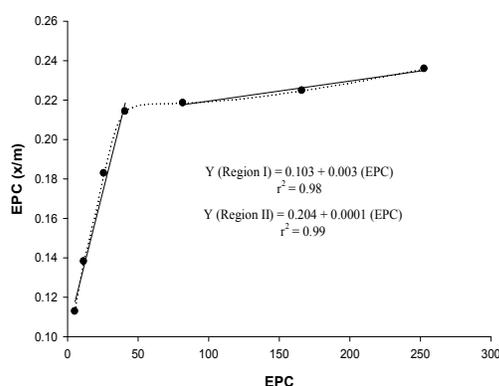
DOM obtained from humus soil (DOMH), rice straw (DOMR), and pig manure (DOMP) reduced maximum Hg (mercury) adsorption capacity up to 40% over control in order of DOM H (250.00 mg kg<sup>-1</sup>) < DOMR (303.03 mg kg<sup>-1</sup>) < DOMP (322.58 mg kg<sup>-1</sup>) < control (416.67 mg kg<sup>-1</sup>). They also reported that DOM of all types promoted the Hg desorption which corroborate our results where the P adsorption decreased and desorption increased with HA application [42]. It was reported that Andisols usually fix large amounts of phosphate 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 [43].

Zhiyou et al. [44] while studying the influence and mechanism of soil-derived humic acid (SHA) on adsorption of P onto particles in soils and by

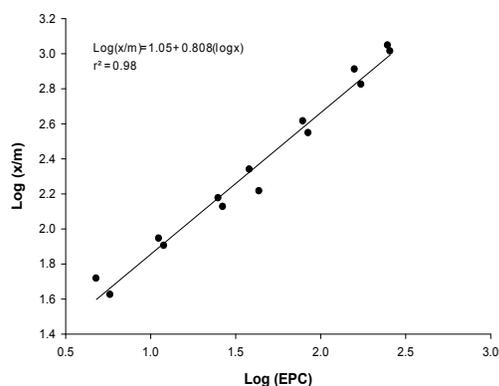
synthetic goethite (α-FeOOH) reported that addition of SHA can significantly reduce the amount of PO<sub>4</sub> adsorption as much as 27.8%. It was concluded that both generated electrostatic field and competition for adsorption sites were responsible for the mechanism by which SHA inhibited adsorption of PO<sub>4</sub> by goethite.

**Table 3. Comparative equilibrium parameters of the Freundlich adsorption isotherm equation for the given treatments of alone P and P+HA**

Parameters	P alone	P+HA
Intercept	1.05	0.185
Slope	0.808	1.18
Square r	0.98	0.96
Adsorption maximum (K)	11.22	1.53
N value	1.237	0.847



**Fig. 5. Two surface layer adsorption model of Langmuir adsorption isotherm for P adsorption in calcareous soil series**



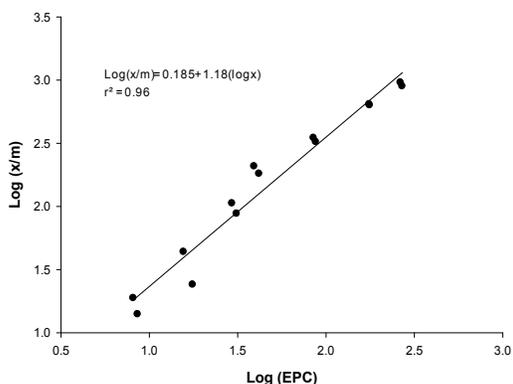
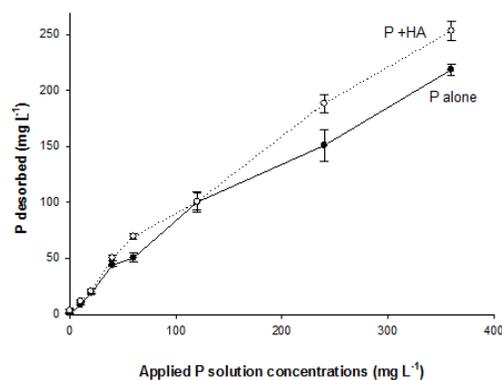
**Fig. 6. Freundlich Isotherm for P alone**

**Table 4. Effect of HA application on P desorption characteristics in the given alkaline calcareous soil of Peshawar series**

Applied P level IPA (mg L <sup>-1</sup> )	Solution P (mg L <sup>-1</sup> )		Desorbed P (mg L <sup>-1</sup> )	
	P alone	P+HA	P alone	P+HA
0	0.11	0.35	0.96	3.18
10	0.93	1.30	8.34	11.70
20	2.13	2.26	19.13	20.30
40	4.88	5.61	43.90	50.46
60	5.61	7.71	50.50	69.39
120	11.14	11.15	100.23	100.39
240	16.77	20.92	150.89	188.26
360	24.28	28.13	218.53	253.13

### 3.3 Desorption of Phosphorus

The P+HA treated soils produced comparatively higher desorption of P at any IPA than the alone P treated soils (Table 3, Fig. 8). The desorbed P ranged from 3.18 to 253 mg P L<sup>-1</sup> at 0 to 360 mg IPA L<sup>-1</sup> in P+HA treated soils that were higher than the desorbed P (0.96 to 218 mg P L<sup>-1</sup>) observed in P alone treated soils. This indicated that HA increased desorption of P from soil into the solution that could be associated to the chelating effect of HA. This could be one of the reasons that HA application increased the efficiency of phosphatic fertilizers. Khattak et al. [14] demonstrated that HA reduced the P fertilizer requirements of maize, wheat and sugar beet by 50%. However, it should be noted that the desorbed values of P at any level of IPA except 0 seem relatively higher. Since the soils were not rinsed before desorption so it seems likely that some residual P left over in the soils after carried over to the ECP. Nevertheless, the difference in desorbed P between the P+HA and alone P at any level IPA level demonstrated that application of HA increased desorption of P.

**Fig. 7. Freundlich Isotherm of P+HA****Fig. 8. Desorption of P as influenced by HA application in alkaline calcareous soil**

## 4. CONCLUSION AND RECOMMENDATIONS

The adsorption of P increased with increase in EPC and levels of IPA and was higher for alone P than P+HA suggesting that application of HA reduced the P adsorption. The adsorption isotherm was fit to Langmuir models in case of alone P only but the Freundlich model was fit to both alone P and P+HA. The lower K and N values in case of P+HA suggested reduction in P adsorption with addition of humic acid. The P+HA also produced comparatively higher desorption of P at any IPA than alone P treated soils. This indicated that HA increased desorption of P from soil into the solution that could be associated to the chelating effect of HA. The lower adsorption and higher desorption of P with application of humic acid could be one the mechanisms that explain associated improvement in P use efficiency with HA application in field conditions.

Conjunctive use of HA and phosphatic fertilizers is recommended to enhance the P use efficiency

and decrease the P adsorption on soil colloidal particles.

## COMPETING INTERESTS

Authors have declared that no competing interests exist.

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