

## Research Article

# Optimizing Available Phosphorus in Calcareous Soils Fertilized with Diammonium Phosphate and Phosphoric Acid Using Freundlich Adsorption Isotherm

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In calcareous soils, phosphorus (P) retention and immobilization take place due to precipitation and adsorption. Since soil pH is considered a major soil variable affecting the P sorption, an acidic P fertilizer could result in low P adsorption compared to alkaline one. Therefore, P adsorption from DAP and phosphoric acid (PA) required to produce desired soil solution P concentration was estimated using Freundlich sorption isotherms. Two soils from Faisalabad and T. T. Singh districts were spiked with 0, 10, and 20 % CaCO<sub>3</sub> for 15 days. Freundlich adsorption isotherms ( $P = aC^{b/a}$ ) were constructed, and theoretical doses of PA and DAP to develop a desired soil solution P level (i.e., 0.20 mg L<sup>-1</sup>) were calculated. It was observed that P adsorption in soil increased with CaCO<sub>3</sub>. Moreover, at all the levels of CaCO<sub>3</sub>, P adsorption from PA was lower compared to that from DAP in both the soils. Consequently, lesser quantity of PA was required to produce desired solution P, 0.2 mg L<sup>-1</sup>, compared to DAP. However, extrapolating the developed relationship between soil CaCO<sub>3</sub> contents and quantity of fertilizer to other similar textured soils needs confirmation.

## 1. Introduction

In calcareous soils, phosphorus (P) retention and mobilization take place due to precipitation and adsorption; however, it is not always easy to distinguish between the two mechanisms. Water soluble P fertilizers applied to soil react with the soil constituents to form less soluble phosphates. When added to soil containing large amounts of calcium, soluble P is usually precipitated as dicalcium phosphate or octacalcium phosphate [1]. At low P concentration up to 0.4 mg L<sup>-1</sup>, active CaCO<sub>3</sub> and/or Fe dithionite could result in P adsorption whereas, at high concentration, precipitation could be predominant over the adsorption process [2]. The reactivity of CaCO<sub>3</sub> in soils depends upon the specific surface area of the carbonate and on its total surface area [3]. It has been demonstrated [4] that Ca<sup>2+</sup> is dominant ion in soil solution of calcareous soils and it is possible that formation of less soluble complexes with weak acid anions

like orthophosphate is due to unavoidable dominance of this ion. The dynamics of P is managed by calcite, which strongly holds P and consequently maintains low P concentration in soil solution. It was noted [2] that low CaCO<sub>3</sub> showed an upper limit of P adsorption varying from 1.4 to 3.5 mg P kg<sup>-1</sup> that was not modified by further increment of P in solution. Conversely, in soil with high CaCO<sub>3</sub> content, P adsorption increased up to the maximum experimental concentration of P in solution (2 g L<sup>-1</sup>).

As the soil pH is considered a major soil variable affecting the P sorption, thus an acidic P fertilizer could result in low P adsorption compared to basic one resulting in less amount of fertilizer required to produce P concentration in soil solution optimum for plant growth. Amount of P required to bring its desired concentration in soil solution could be better determined by P sorption isotherms [5, 6] instead of conventional soil P test; those do not take into consideration the physicochemical properties of soil. Although both

the Freundlich and Langmuir isotherms describe the adsorption phenomena satisfactorily [7], the former is preferred because it is capable of rigorous derivation and correlates well with soil properties [8]. Moreover, it is based on assumptions more realistic than some other cases; that is, an adsorption maximum is not obtainable from the isotherm that seems compatible with most of the observed P sorption by soils, at least, under normal laboratory conditions. Keeping in view the above facts, a laboratory study was conducted using Freundlich adsorption isotherm to assess the P adsorption capacity of two soils when treated with PA and DAP at varying levels of  $\text{CaCO}_3$ .

## 2. Materials and Methods

**2.1. Soil Preparation and Analyses.** Surface soil samples were collected from Faisalabad and T. T. Singh districts (hereafter referred to as S-I and S-II, resp.), air-dried, passed through a 2 mm sieve, mixed thoroughly, and stored in labeled plastic bottles. Samples were analyzed for various physiochemical properties like texture [9], pH of saturated paste ( $\text{pH}_s$ ), electrical conductivity of saturation extract ( $\text{EC}_e$ ) [10], available K [11], Olsen P [12], organic matter [13], and calcium carbonate [14].

**2.2. Development of  $\text{CaCO}_3$  Levels in Soils.** One kg of each soil was taken in plastic buckets, and three levels of  $\text{CaCO}_3$  (native, 10%, and 20%) were developed by mixing reagent grade salts with soils. The soils were wetted with distilled water to attain field capacity and equilibrated for 15 days at room temperature. At the termination of incubation, soils were mixed, dried, and passed through a 2 mm sieve and stored in plastic bottles for use in adsorption studies.

**2.3. Adsorption Isotherms.** Adsorption isotherms were constructed using a series of solutions with P concentrations (2.5, 5, 7.5, 10, 20, 40, and 80 ppm) prepared from each of DAP and PA in 0.01 M  $\text{CaCl}_2$ . To 2.5 g samples of the soils, 25 mL of the above-said P solutions was added and shaken for 24 h on a mechanical shaker. After equilibration, the samples were centrifuged for 15 min. at 4000 rpm and filtered through Whatman number 42 filter paper. Phosphorus concentration in the final solutions was determined following the method of Murphy and Riley [15]. The difference in P concentration of solutions before and after equilibrium was taken as the amount of P adsorbed. The sorption isotherms were examined by modified Freundlich equation proposed by Le Mare [16] as follows:

$$P = aC^{b/a}, \quad (1)$$

where  $P$  is amount of P adsorbed per unit of soil ( $\mu\text{g g}^{-1}$ ),  $C$  is equilibrium P concentration in soil solution ( $\mu\text{g mL}^{-1}$ ), and  $a$  and  $b$  are the amount of P adsorbed and the buffer capacities, respectively. The parameters  $a$  and  $b$  were estimated by regression of the logarithmic form of the data obtained from adsorption isotherms. Theoretical doses of PA and DAP fertilizers to develop a desired soil solution P level, that is,  $0.20 \text{ mg L}^{-1}$ , were calculated. A regression between

TABLE 1: Physiochemical properties of the soils used in adsorption studies.

Properties	Unit	Value	
		S-I	S-II
$\text{pH}_s$	—	7.20	7.30
$\text{EC}_e$	$\text{dS m}^{-1}$	1.40	3.86
$\text{CaCO}_3$	%	6.58	14.06
Organic matter	%	1.18	1.13
Olsen P	$\text{mg kg}^{-1}$ soil	15.56	9.35
Sand	%	15.53	20.12
Silt	%	47.45	47.54
Clay	%	37.53	32.52
Textural class	—	Silty clay loam	Silty clay loam

calculated quantities of P fertilizer and  $\text{CaCO}_3$  levels was developed to estimate requirement of P fertilizer for any level of soil  $\text{CaCO}_3$ .

## 3. Results and Discussion

**3.1. Freundlich Adsorption Isotherms for  $\text{CaCO}_3$  Amended Soils.** The physical and chemical properties of the soils are presented in Table 1. Both the soils were nonsaline, silty clay loam in texture, and slightly alkaline in reaction. After constructing the P adsorption isotherms, the data were subjected to examine the fitness of modified Freundlich equation. Linear plot of the modified Freundlich equation presented in Figure 1 and parameters of the equation (amount adsorbed ( $a$ ), buffer capacity ( $b$ )  $\text{mL g}^{-1}$ , and correlation coefficient ( $r^2$ )) are presented in Table 2. The goodness of the fit of the model was ascertained from  $r^2$  values ( $\geq 0.84$ ) which indicated high conformity of the adsorption data with the Freundlich model. These findings are in agreement with those of Chaudhry et al. [17] and Sarfraz et al. [18] who also reported dependence of the exponent of Freundlich equation on solution P concentration instead of time and temperature. A good fit of the P adsorption data to the Freundlich adsorption model over the Langmuir and Tempkin was also reported by Khan et al. [19].

**3.2. Calcium Carbonate and P Adsorption.** In adsorption equation,  $b$  represents the buffer power of the soil for P. The more the value of  $b$  is the more the P adsorption capacity of soil would be. The soils differed slightly in buffer capacities despite a large difference in native  $\text{CaCO}_3$  that might be due to similar proportion of active  $\text{CaCO}_3$  and its specific surface area in the soils which mainly govern P behavior. With the addition of  $\text{CaCO}_3$  in soils, the buffer capacity of the soils was increased (Table 3). Similarly, Samadi and Gilkes [20] and Samadi [21] reported that P adsorption in calcareous soil was related to  $\text{CaCO}_3$  contents. Castro and Torrent [22] found an increase in differences among P fertilizers for P adsorption with the increase in carbonate contents of the soil and attributed the fact to the precipitation of Ca-phosphate. However, Samadi [23] reported that both total and active  $\text{CaCO}_3$  were less important factors for P adsorption. This

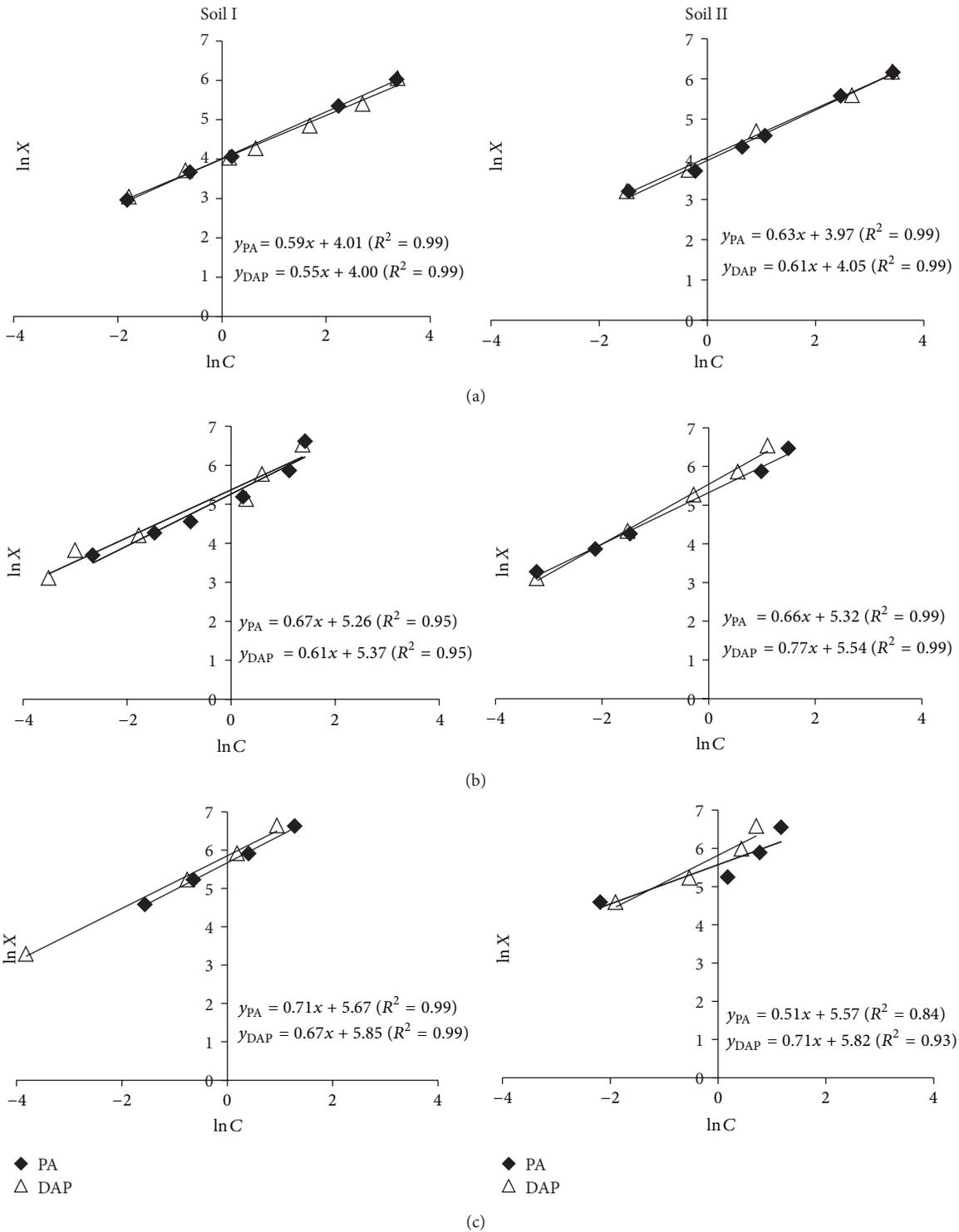


FIGURE 1: Freundlich isotherms for P adsorption: (a), (b), and (c) represent native, 10%, and 20% CaCO<sub>3</sub>, respectively.

TABLE 2: Fitted Freundlich adsorption isotherms.

CaCO <sub>3</sub> level (%)	Phosphoric acid treated soils		DAP treated soils	
	S-I	S-II	S-I	S-II
Native	$P = 55.37C^{0.59}$	$P = 52.87C^{0.63}$	$P = 54.64C^{0.55}$	$P = 57.51C^{0.61}$
10%	$P = 192.87C^{0.64}$	$P = 216.15C^{0.68}$	$P = 215.29C^{0.61}$	$P = 242.52C^{0.77}$
20%	$P = 289.88C^{0.71}$	$P = 267.04C^{0.50}$	$P = 348.06C^{0.68}$	$P = 335.82C^{0.71}$

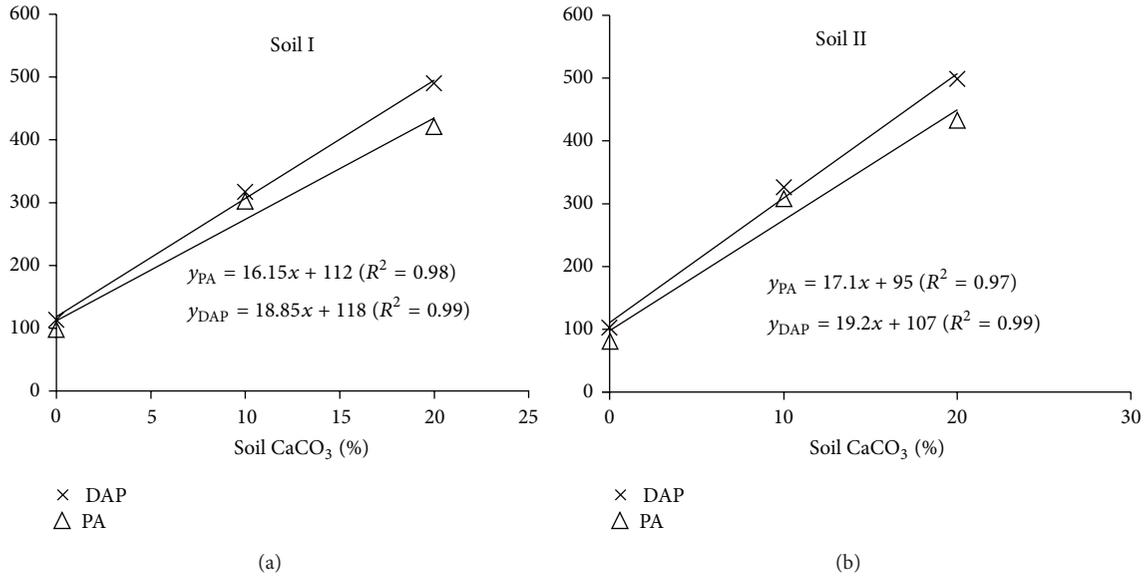


FIGURE 2: Relationship between soil CaCO<sub>3</sub> and P<sub>2</sub>O<sub>5</sub> requirement (kg ha<sup>-1</sup>) to achieve 0.2 mg L<sup>-1</sup> soil solution P.

TABLE 3: Buffer capacities of CaCO<sub>3</sub> enriched soils as determined from Freundlich adsorption isotherms.

CaCO <sub>3</sub> level (%)	PA		DAP	
	S-I	S-II	S-I	S-II
Native	33 ± 1.63*	33 ± 1.98	30 ± 1.72	35 ± 2.07
10%	128 ± 5.57	121 ± 3.40	145 ± 4.50	175 ± 8.89
20%	206 ± 11.95	211 ± 9.54	239 ± 9.01	248 ± 15.41

\* Means ± SE.

TABLE 4: Quantities of P<sub>2</sub>O<sub>5</sub> (kg ha<sup>-1</sup>) required to achieve 0.2 mg L<sup>-1</sup> soil solution P.

CaCO <sub>3</sub> level (%)	PA		DAP	
	S-I	S-II	S-I	S-II
Native	98 ± 6.29*	78 ± 5.69	113 ± 7.94	99 ± 5.89
10%	302 ± 8.67	298 ± 12.49	317 ± 14.42	316 ± 9.50
20%	421 ± 14.65	419 ± 8.60	490 ± 20.13	483 ± 12.98

\* Means ± SE.

discrepancy in results has been answered by Peña and Torrent [24] as the inability of the standard methods used for the determination of total and active CaCO<sub>3</sub>.

**3.3. Phosphorus Requirement as a Function P Source.** It was observed that, at all the levels of CaCO<sub>3</sub>, P adsorption from PA was lower compared to that from DAP in both the soils. Consequently, lesser quantity of PA was required to produce desired solution P, 0.2 mg L<sup>-1</sup>, compared to DAP (Table 4). Lower P adsorption and/or precipitation from PA compared to DAP might be due to higher acidity produced by PA in alkaline soil. Although there is limited information available comparing the effect of acidic and alkaline P source on its adsorption/precipitation in soil, our results are in line

with the information available so far. According to Lu et al. [25], SSP being an acidic P fertilizer performed better than DAP for P uptake and soil test levels on alkaline calcareous soil. Similarly, in a two-year field experiment Chaubey and Kaushik [26] reported higher grain yield of wheat with SSP compared to DAP and attributed the low yield with DAP to more P fixation as a result of alkaline soil pH around its granule. Wijewardena [27] observed that the highest available P content in soils after potato and vegetables harvest soils for consecutive four seasons with TSP compared to imported and local Siri Lankan rock phosphates was lesser in acidity.

**3.4. Phosphorus Requirement as a Function of CaCO<sub>3</sub>.** Regression between soil CaCO<sub>3</sub> and solution P is presented in Figure 2 for both soils and P sources. Using these equations, the amount of P fertilizer required for any level of CaCO<sub>3</sub> could be calculated. Use of Freundlich P sorption isotherm, which relates soil solution P concentration with quantity of P adsorbed in soil, to predict P fertilizer requirement of a specific soil is better approach rather than using soil test. It may be due to that soil test only provides information about the plant available P [28] and does not estimate the amount of fertilizer P needed unless calibrated for a particular test. But extrapolating the developed relationship between soil CaCO<sub>3</sub> contents and quantity of fertilizer to other similar textured soils needs confirmation. If it holds true, then it would be quite promising, time saving, and accurate approach for predicting P fertilizer requirement to achieve the desired level of soil solution P.

#### 4. Conclusion

In semiarid regions, CaCO<sub>3</sub> is the dominant soil constituent limiting P availability to plants by adsorption and precipitation reactions. Therefore, P addition to such soil could be

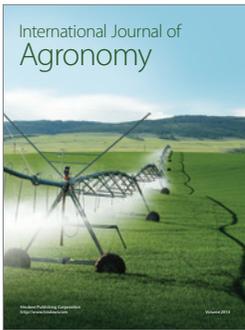
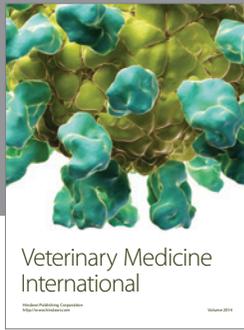
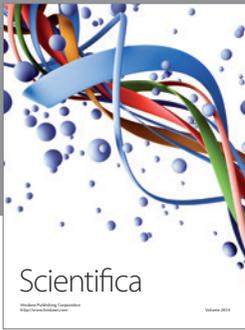
rationalized depending upon  $\text{CaCO}_3$  contents of soil. A good fit of the adsorption data to the modified Freundlich model in the present study suggests that external P requirement of plants could be better determined using this adsorption model rather than using soil test P values depicting available phosphorus. Moreover, using an acidic P source instead of alkaline one could result in lesser P adsorption and/or fixation in alkaline calcareous soils.

### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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