RESEARCH ARTICLE

SABRAO Journal of Breeding and Genetics
57 (2) 729-739, 2025
http://doi.org/10.54910/sabrao2025.57.2.29
http://sabraojournal.org/
pISSN 1029-7073; eISSN 2224-8978

STANDARDIZATION OF PHOSPHORUS ISOTHERMS THROUGH LANGMUIR AND MODIFIED FREUNDLICH EQUATION TO COMPUTE P-DOSES FOR DIFFERENT TEXTURED SOILS

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SUMMARY

Phosphorus plays a crucial role in promoting plant growth and development. However, Pakistani soils face phosphorus deficiency due to their mineralogical characteristics and high pH levels, resulting in instant adsorption of applied phosphorus. Key factors affecting phosphorus accessibility in these soils include clay mineral composition, sesquioxide levels, pH, and free $CaCO_3$ presence. The current study aimed to develop phosphorus adsorption isotherms using Langmuir and Modified Freundlich equations and determine phosphorus application rates for maximum yield. The experiment comprised 11 treatments, i.e., T_1 (Control), with the 10 doses consisting of increasing levels of phosphorus concentration in $CaCl_2$ solution: T_2 (10 ppm), T_3 (20 ppm), T_4 (30 ppm), T_5 (40 ppm), T_6 (50 ppm), T_7 (60 ppm), T_8 (70 ppm), T_9 (80 ppm), T_{10} (90 ppm), and T_{11} (100 ppm). An analysis of collected samples for texture determination used the hydrometer method. After determining the soil textural class of both soils, phosphorus adsorptions evaluation for both textures utilized P concentration in calcium chloride. Phosphorus adsorption curves exposed a higher P fixation happening at less phosphorus contents, whereas high phosphorus quantities resulted in less fixation for clay loam and sandy loam soils.

Keywords: Phosphorus, isotherm, soil texture, adsorption, and Freundlich model

Communicating Editor: Prof. Naqib Ullah Khan

Manuscript received: September 29, 2024; Accepted: November 27, 2024.

Citation: Zafar A, Sarwar G, Sarfraz M, Manzoor MZ, Gul S, Luqman M (2025). Standardization of phosphorus isotherms through Langmuir and modified Freundlich equation to compute p-doses for different textured soils. *SABRAO J. Breed. Genet.* 57(2): 729-739. http://doi.org/10.54910/sabrao2025.57.2.29.

Key findings: The study concluded the Langmuir model performed efficiently even at lower P concentrations, while the modified Freundlich model was most suitable at medium to high P concentrations. Hence, the modified Freundlich model is the best option for calculating theoretical P doses for field applications.

INTRODUCTION

Phosphorus is the second most important macro nutrient essential for plant growth. It is a vital component of biomolecules, such as, DNA and RNA, and plays a key role in processes like photosynthesis and energy transfer (Marschner, 2023). Phosphorus is crucial for maintaining soil fertility and regulating metabolic pathways in plants. Its availability directly affects crop production and yield. A shortage of phosphorus in soil can lead to reduced crop production and metabolic reactions, stunted plant growth, and decreased leaf area index and leaf number (Abell *et al*., 2020). Applying organic phosphorus in the fields is irrelevant when launching inorganic phosphorus in the market due to its excessive availability (Haygarth *et al*., 2016).

The soils of Pakistan are mostly calcareous and alkaline, with factors, such as, calcium carbonate content, sesquioxide levels, pH, clay mineral composition, and soil reactions, significantly influencing phosphorus availability. These factors can impact the solubility, fixation, and overall availability of phosphorus for plant uptake, making it essential to consider them when managing phosphorus fertilization in Pakistani soils. The nature of alkalinity in Pakistani soils is mostly due to an abundant use of brackish and deteriorated class of water for irrigation (Shafqat *et al*., 2016). Globally and in Pakistan, approximately 80%–90% of soils in arid and semi-arid regions are phosphorus deficient. Alarmingly, over 90% of Pakistan's soils suffer from P deficiency. With the world's rock phosphate reserves projected to be depleted within the next 50–80 years, the situation is critical. In the years 2007–2008, the cost of phosphatic fertilizers rose steeply by seven times worldwide due to the decreasing rock phosphate supply (Cordell *et al*., 2009b). Neutral pH (6.0–7.0) is most suitable for phosphorus availability. Below and above this pH, the applied phosphorus becomes fixed with acidic and basic cations, making it unavailable to plants. These soils' saturation with Ca results from the applied P forming insoluble complexes and converting into non-labile fraction (Veneklaas *et al*., 2012).

Phosphorus in Pakistani soils is largely in adsorbed form, making it insufficient for optimal plant reproductive growth. Addressing this deficiency requires farmers to rely on phosphatic fertilizers, with approximately 85% of the world's rock phosphate being used annually for fertilizer production (Cordell *et al*., 2009a). However, the direct application of rock phosphate can be functional to soils, reducing production costs. This can proceed by either directly applying finely ground rock phosphate or converting it into various fertilizer forms. Rock phosphate's low solubility (10%) makes it a more effective phosphorus source in acidic soils. However, in alkaline soils common in Pakistan, conventional phosphorus fertilizers are more suitable (Sabah *et al*., 2016). For enhance solubility, organic sources like press mud, farmyard manure, and poultry manure have been useful. Integrating rock phosphate with compost also increases solubility, as microbial decomposition produces organic and inorganic acids solubilizing rock phosphate, releasing phosphorus for plant uptake (Weil and Brady, 2022). The use of crop residue sources for the fodder and fuel purpose reduced the dependence of crop production on this material, which resulted in enhanced use of chemical fertilizers. But, these organic sources gained the superlative importance in agriculture due to its beneficial effect on soil fertility and nutrient supply to plants. The use of organic sources, along with inorganic nutrient sources, improved plant growth and enriched the soil fertility status. This strategy also improved the physical and chemical conditions of the soil. It enhanced the nutrient use efficiency of the plants (Gutser *et al*., 2005).

Many organic sources of phosphorus prevail, which can serve judiciously to enhance P availability (Nobile *et al*., 2018). The rising rates of phosphorus fertilizers heightened the attention of scientists to seek alternative sources of P. Continuous use of chemical fertilizers and growth of exhaustive crops made the soil's phosphorus and organic matter deficient and damaged the soil chemistry. The need to resolve this problem requires emphasizing the deficiency of organic matter. Both these serious issues limiting the production can ease out by the integrated use of organic and inorganic sources of phosphorus (Arcand *et al*., 2010). Integrated use of inorganic fertilizer with organic source increased yield of crops like rice and wheat (Sarwar *et al*., 2020). Phosphorus extraction from organic sources occurs by microorganisms' decomposing organic manures. Other soil fauna, i.e., symbiotic free-living bacteria and soil flora, viz., fungi, were also participants in enhancing P availability in plants through various mechanisms (Richardson and Simpson, 2011). The Langmuir adsorption equation explains adsorption by assuming an adsorbate behaves as an ideal gas at isothermal conditions. According to the model, adsorption, and desorption are reversible processes. On the other hand, the Freundlich Adsorption isotherms depict curves showing the variations in gas adsorbed by the solid at a constant temperature and pressure. Hence, the latest study sought to construct P adsorption isotherms and fit data on the Langmuir and Modified Freundlich equations to compute P doses for rising soil solution of P to gain maximum yield.

MATERIALS AND METHODS

The collected soil samples underwent analysis for texture determination. After determining the appropriate texture, checking phosphorus adsorption continued on both textures—clay loam with sand = 32%, silt = 34%, and clay = 34%, and sandy loam with sand = 55%, silt = 30%, and clay = 15%—by making the P concentration in calcium chloride. The experiment has 11 treatments (Table 1).

Soil texture

Soil texture is the relative proportion of sand, silt, and clay. Soil sample of 50 g, placed in a 500-ml beaker, received a 50 ml of 1% sodium hexametaphosphate solution and 250 ml of distilled water. The mixture was left to stand overnight. Afterward, stirring the soil for 10 min used a mechanical stirrer. The volume adjustment of the suspension ensued to obtain the desired level before putting into a 1000-mL graduated cylinder. Readings from a Bouyoucos hydrometer incurred recordings both in four seconds and two hours after mixing the suspensions. The International Textural Triangle, which offers a categorization

Table 1. Description of experimental treatments.

Treatments	Description
T_1	Control
T_2	10 ppm P concentration in $CaCl_2$ solution
T_3	20 ppm P concentration in $CaCl_2$ solution
T_4	30 ppm P concentration in $CaCl_2$ solution
T_5	40 ppm P concentration in $CaCl_2$ solution
T_6	50 ppm P concentration in $CaCl_2$ solution
T_7	60 ppm P concentration in $CaCl_2$ solution
T_8	70 ppm P concentration in $CaCl_2$ solution
T_9	80 ppm P concentration in $CaCl_2$ solution
T_{10}	90 ppm P concentration in $CaCl_2$ solution
T_{11}	100 ppm P concentration in $CaCl_2$ solution

system based on the proportions of sand, silt, and clay in the soil, helped identify the soil textural class (Moreno-Maroto and Alonso-Azcarate, 2022).

Construction of phosphorus adsorption isotherm and model application

The use of adsorption isotherms measured the residual effect of phosphatic fertilizer and adsorption capacities of the soil and evaluated the P requirement of soils and crops. The main objectives of phosphatic fertilizers were to assess the phosphate adsorption abilities of soils, developing P adsorption isotherms and evaluating sorption records on Langmuir and Modified Freundlich models. These will determine P quantities to get the solution of P quantity essential for higher yields of plants.

Methodology

Dissolving the salt of $CaCl_2$ in distilled water prepared the solution of desired concentrations. Taking a 2.5 g of soil sample bore mixing with 25 ml of 10 mM $CaCl_2.2H_2O$ solution containing varying P concentrations, ranging from 0 to 100 µg P/ml (0, 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100). The mixture sustained shaking on an end-over-end shaker for 24 hours to reach equilibrium. Determining the phosphate concentration in the final solution used the Olsen method (Olsen *et al.,* 1977), employing the Langmuir and Freundlich equations for calculations. The difference between the initial and final P concentrations in the solution became the amount of P adsorbed by the soil.

The Langmuir Model

In 1916, Langmuir anticipated a model based on the relation between adsorbed and free gaseous molecules. On the bases of this, he derived the Langmuir Equation, which represent an association b/w as the amount of exchange sites used for adsorption and pressure. The Langmuir model helps to compute the required energy for P sorption and P adsorption extreme of soil. All the adsorption isotherm models (Langmuir, Freundlich, and Redlich-Peterson isotherm models) fitted well and perfectly described the phosphorus adsorption (Sarkar *et al.,* 2022). The Langmuir model functioned fine on lesser P amounts. It does not provide a straightforward route when c/x is designed against c for a widespread choice of P absorption.

The common form of the Langmuir model is

$$X = \frac{kbC}{(1+C)} \dots\dots\dots\dots\dots (1)$$

Where

X = P adsorbed (µg g^{-1} soil P)
C = solution P concentration (mg L^{-1} P)
K = coefficient
b = maximum P adsorbed (mg L^{-1} P)

The linear form of the Langmuir model is

$$\frac{C}{X} = \frac{1}{kb} + \frac{C}{b} \dots\dots\dots\dots\dots (2)$$

1/k and b are calculated by fitting the linear form to the original data
1/k = constant
b = inverse of slope
1/b = slope
1/kb = intercept
Plot b/w C/X against C to give a straight line, provided the data fits into the Langmuir model.

The Modified Freundlich Model

The Freundlich equation aligns with the adsorption model, where affinity decreases as adsorption increases. Similarly, Gregory *et al*. (2005) highlighted the advantages of the Freundlich model, noting its ability to accommodate and evaluate diversity, making it suitable for measuring heterogeneity on a large scale. The Freundlich equation has been successful to explain phosphate adsorption in soil (Zhou and Li, 2001; Hussain *et al*., 2003; Thakur *et al*., 2004). Compared with the Langmuir model, the Freundlich model has emerged to better describe phosphorus adsorption (Sidhu *et al*., 2004). While the modified Freundlich model is most suitable for medium to high P concentrations over a limited range, the original Freundlich model often provides a good description of adsorption. The proposed common form of the Freundlich model came from Le-Mare (1982).

$$P = aC^{b} \ldots\ldots\ldots\ldots\ldots..(1)$$

The modified form of the Freundlich model is a proposed formula for the soil by Freundlich and workers, as follows:

$$P = aC^{b/a} \ldots\ldots\ldots\ldots\ldots(2)$$

Where

a = amount of P adsorbed (mg g^{-1}),
C = solution P concentration (mg L^{-1} P)
b = maximum P adsorbed (mg L^{-1} P)
P = P adsorbed (mg g^{-1} soil P)

Olsen on available phosphorus

Weigh 5 g of air-dried soil into a 250 ml Erlenmeyer flask. Add 100 ml of 0.5 M $NaHCO_3$ solution (pH adjusted to 8.5). Shake the flask for 30 min on a mechanical shaker at 180 rpm. Run a blank sample in parallel, containing all reagents without soil. Filter the solutions using Whatman No. 42 filter paper. Take 5 ml of the filtrate and transfer it to a 50 ml volumetric flask. Add 5 ml of color developing reagent and fill up to the mark. Allow the samples to stand for 15 min. Record the absorbance on an Apel PD-303 S spectrophotometer at 880 nm wavelength (Watanabe and Olsen, 1965; Olsen *et al*., 1977).

RESULTS AND DISCUSSION

Construction of Langmuir and Freundlich model isotherms

Phosphorus adsorption curves (Figure 1) revealed the maximum phosphorus fixation occurred at low phosphorus concentrations, whereas high phosphorus concentrations resulted in reduced fixation for both soils. No P precipitation with soil constituents was evident at 100 µg ml^{-1}. As shown in Table 2, the percentage of phosphorus adsorbed in clay loam soils ranged from 96.4% to 48.2%, and in sandy loam soils, it ranged from 93.7% to 18.4%. This indicates the clay loam soil exhibited a higher phosphorus adsorption than the sandy loam soil. The curvilinear relationship observed in both soils suggests their adsorption energy was not constant. Generally, phosphorus adsorption increased with increasing phosphorus concentration for both soils.

Langmuir model for sorption data

The adsorption parameters for both soils differed significantly (Figure 2). The clay loam soil exhibited the highest values for bk, b, and k. The high r values (r > 0.95) indicated a strong correlation and excellent fitness of the data for both soils. The mean values for b, k, and the buffering capacity (bk) were 539.77 µg g^{-1}, 0.1538 mg g^{-1}, and 84.40 µg g^{-1}, respectively (Table 3), highlighting distinct differences in adsorption properties between the two soils.

Freundlich model for sorption data

In the Freundlich plots, it displayed the values of a, b, and r^2 were different for both soils. The b and a in clay loam soils appeared greater than in the sandy loam soils, with values of 33.24 µg g^{-1} and 24.15 ml g^{-1}, respectively, and a 0.52 mean r^2 value (Table 4). For Table 5, values of b for clay loam and sandy loam soils were comparable in both models, whereas in Table 6, the comparison of Langmuir and Modified Freundlich models for clay loam and sandy loam soils occurred and found quite successful.

Agriculture plays a vital role in Pakistan's economy, but the country's calcareous and alkaline soils pose significant challenges. Several factors affect the availability of phosphorus in these soils, such as, calcium carbonate content, sesquioxides, pH, clay mineral composition, and soil reactions. Alarmingly, approximately 80%–90% of soils in Pakistan's arid and semi-arid regions, and over 90% of soils nationwide, are phosphorus-deficient. Phosphorus increases the reproductive growth of plants, as well as,

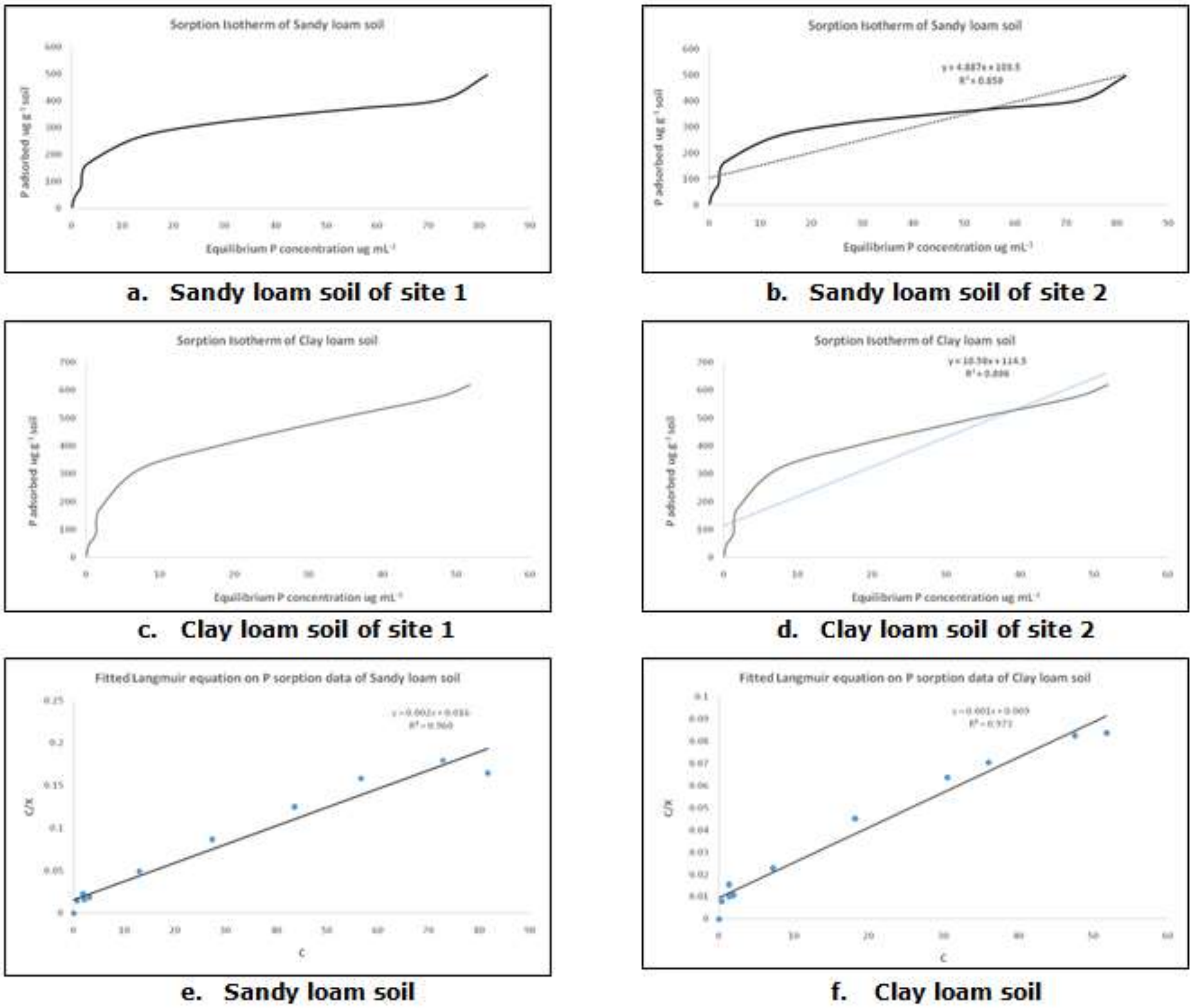
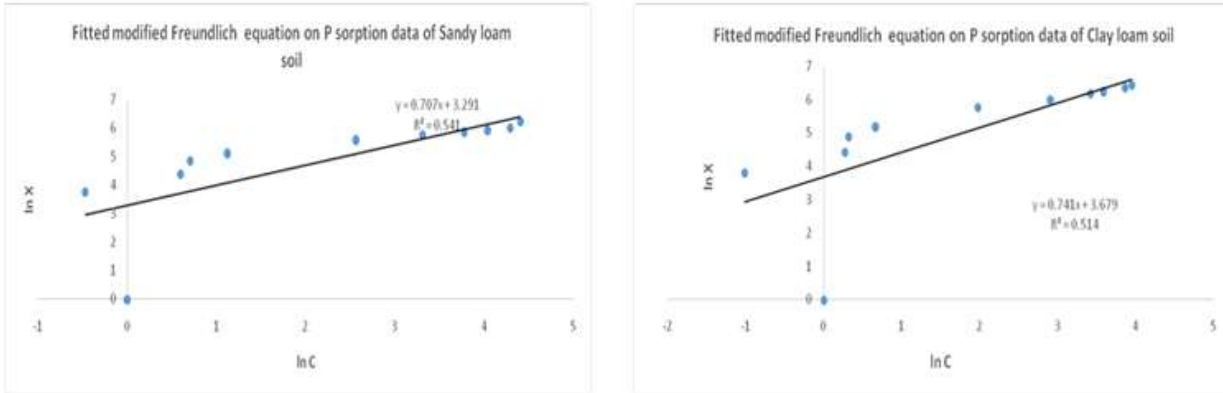


Figure 1. Sorption isotherms for both soils.

Table 2. Amount of P adsorbed (mg kg^{-1}) in sandy loam and clay loam soils equilibrated with different phosphorus levels.

P added (mg L^{-1})	Amount of P adsorbed in sandy loam soil (mg kg^{-1})	Amount of P adsorbed in clay loam soil (mg kg^{-1})
0	0.0 (0)	0.0 (0)
10	9.4 (93.7%)	9.6 (96.4%)
20	18.2 (90.9%)	18.7 (93.5%)
30	28 (93.2%)	28.6 (95.4%)
40	36.9 (92.3%)	38.1 (95.2%)
50	37.1 (74.1%)	42.8 (85.6%)
60	32.7 (54.5%)	41.8 (69.7%)
70	26.5 (37.8%)	39.5 (56.4%)
80	23.4 (29.3%)	44 (54.9%)
90	17.2 (19.1%)	42.4 (47.1%)
100	18.4 (18.4%)	48.2 (48.2%)



a. Sandy loam soil **b. Clay loam soil**

Figure 2. Fitted Langmuir equation on phosphorus sorption data of both soils.

Table 3. Parameters of Langmuir model explaining sorption of P in both soils.

Soil textures	Maximum adsorption - b (µg g^{-1})	Affinity coefficient - k (mL g^{-1})	Maximum buffering capacity - bk (µg g^{-1})	Correlation coefficient (r^2)
Sandy loam	454.54	0.1375	62.49	0.9604
Clay loam	675.0	0.1701	106.31	0.9730
Mean	539.77	0.1538	84.40	0.9665

Table 4. Parameters of Freundlich model explaining sorption of P in both soils.

Soil textures	Maximum adsorbed - a (µg g^{-1})	Maximum buffering capacity - bk (µg g^{-1})	Correlation coefficient (r^2)	No. of values (n)
Sandy loam	26.87	18.96	0.54	11
Clay loam	39.61	29.35	0.51	11
Mean	33.24	24.15	0.52	11

Table 5. Comparison of b values of both models.

Soil textures	Freundlich model	Langmuir model
Sandy loam	18.96	454.54
Clay loam	29.35	625.0

Table 6. Comparison of Langmuir and Modified Freundlich models for two different textured soils.

Soil textures	Langmuir equation		Modified Freundlich equation	
	Model form	Linear form	Model form	Linear form
	X=(bkC)/1+(k)(C)		$P=aC^{b/a}$	
Sandy loam	X=(454)(0.137)C/1+(0.137)C	Y=0.0022x+0.016	$P= 26.8777C^{0.7070}$	Y=0.7071x+3.2913
Clay loam	X=(625)(0.170)C/1+(0.170)C	Y=0.0016x+0.0094	$P= 39.6107C^{0.7410}$	Y=0.7411x+3.6791
Mean	X=(539)(0.153)C/1+(0.153)C		$P=33.2442C^{0.7240}$	

enhancing the root stability by applying adequate quantity of phosphorus (Zhang *et al*., 2019). With global rock phosphate reserves expected to deplete within 50–80 years, the increasing prices of phosphoric fertilizers derived from rock phosphate are becoming a pressing concern. This situation highlights the need for sustainable soil management and fertilizer use practices to ensure long-term agricultural productivity.

Slight acidic to neutral pH (6.0–7.0) is most suitable for P availability. The quantity of phosphorus in the soil depends on the soil's properties and pH (Messiga *et al*., 2015). In acidic soils, the pH has primary control from hydrogen (H), iron (Fe), and aluminum (Al) ions. These ions are typically present in higher concentrations in acidic soils and contribute to their low pH. In contrast, alkaline soils have a higher pH due to the presence of calcium (Ca) and magnesium (Mg) ions. These ions are often more prevalent in alkaline soils and help maintain their higher pH. Additionally, in sodic soils (soils with high sodium content), sodium (Na) ions are crucial in controlling the pH. Sodic soils typically have a high pH due to the presence of sodium carbonate and other sodium-bearing compounds (Weil and Brady, 2022).

Soil pH is a vital characteristic providing complete understanding of the soil environment for plant growth, encompassing factors, such as, nutrient supply trend, fate of added nutrients, salinity/sodicity status, soil aeration, soil mineralogy, and regional weather conditions. In Pakistan, particularly in arid and semi-arid zones, the soil pH is usually alkaline, with values exceeding 8.00 in normal soils and up to 10.00 in sodic soils. A decrease in soil pH, achieved through effective land management strategies, is highly desirable. Therefore, efforts to reduce soil pH in alkaline and sodic soils can have a significant impact on agricultural productivity and soil health in Pakistan (Sarwar, 2005).

Pakistan soils are Ca saturated causing the applied P to form insoluble complexes and convert into non-labile fraction. The application of phosphorus fertilizers, along with nitrogen, is essential for optimal crop production. As rock phosphate is a primary source of phosphorus, not all forms can be favorable to produce phosphatic fertilizers. However, its application can be direct to soils through various methods, reducing the costs associated with chemical processing. Two approaches include direct application of finely ground rock phosphate to the soil and converting rock phosphate into other forms of fertilizers through various treatments. The efficiency of direct rock phosphate application is higher in acidic soils than in alkaline soils. Although it is a cost-effective source of phosphorus, its low solubility (10%) limits its use in Pakistan's predominantly alkaline soils (Sabah *et al.*, 2018).

Current laboratory research results signified the Freundlich model is best fit at medium to high P concentrations and is beneficial in our field experiments for the calculation of various P rates. The Freundlich equation matches with the adsorption model, wherein the affinity decreases with the increase in adsorption isotherms. It was evident that the Freundlich equation was optimal to explain the adsorption of phosphate in the soil (Thakur *et al*., 2004). The experiment revealed the Langmuir equation provided the best fit for phosphorus adsorption data across the soils, compared with the Freundlich and Temkin models. The good fit of the Langmuir model suggests that the phosphorus sorption affinity of the soils remained constant as surface saturation increased (Sarker *et al.,* 2024). Adsorption of P is finely vivid with the Freundlich model as compared with the Langmuir model (Sidhu *et al*., 2004).

Phosphorus is a macro nutrient essential for optimum crop growth and animal health. The soil's ability to supply P in an available form gains influences from sorption capacity and P binding energies in soil. These properties usually come from sorption isotherms that are time-consuming and difficult for routine analysis (Dunne *et al.,* 2020). Phosphorus adsorption curves revealed both soils fixed maximum P at low concentrations, without any attachment of P by soil ingredients up to 80 µg/ml. A previous study showed sandy loam soil adsorbed 59% of P (ranging from 44% to 85%), while clay loam soil adsorbed 72% of P (ranging from 60% to 95%). This indicates clay loam soil fixed more P than sandy loam soil, likely due to its higher clay and $CaCO_3$ contents. Numerous studies have reported similar findings, highlighting the significant role of clay and $CaCO_3$ in P adsorption. For instance, Bertrand *et al*. (1999) claimed calcite powerfully holds P, preserving little P absorptions in soil solution. White (1980) also stated P adsorption happens on external of soil carbonates, with scums accumulative soil surface area beyond that of clean calcite.

Phosphorus obsession amounts were more for clay, clay loam, sandy loam, and loamy sand soils, correspondingly, through supplementary phosphorus. Subsequently, extra P is essential to increase the soil test rate in clay soils associated to loam and sandy soils (Chaudhry *et al*., 2003). Both soils displayed a rounded association between phosphorus adsorption and equilibrium P concentration. Normally, P adsorption augmenting results by increasing symmetry P content in clay loam and sandy loam soils. Sequence of rise in soil solution P through additional P amounts was sandy loam soil > clay loam soil. This suggests the rate of increase in soil solution P varies among soils, potentially due to differences in soil properties and P adsorption mechanisms (Sarfraz, 2014).

The Langmuir model adsorption parameters exhibited significant variations between soils, with clay loam soil showing higher values of bk, b, and k than with sandy loam soil. Various soil constituents, including clay content, clay type, $CaCO_3$ content, P concentration, Al and Fe oxides, and soil pH, impact P fixation in soils (Chaudhry *et al*., 2003). High r^2 rates (>0.95) showed a strong linear correlation between the variables, with average rates of 455.46 μg g^{-1}, 0.206 mL g^{-1}, and 95.43 μg g^{-1} for b, k, and maximum buffering capacity, respectively. The mean r2 value of 0.99 was important and optimistic, representing durable link among b and k. The Langmuir model accurately describes adsorption capacity for low equilibrium P ranges, with bk being a reliable indicator of soil adsorption capability (Holford, 1997). Research has consistently shown that clay content is a critical factor in P sorption, with increasing clay content leading to enhanced P sorption in both soils (Biswas and Tomer, 1997).

Langmuir and Freundlich models can be applicable to differentiate soils based on equilibrium P concentration within their valid ranges. However, their applicability varies depending on the P absorption. Freundlich formula is more appropriate for minute to average symmetry P concentrations. The "a" value of the Freundlich formula is valuable for soils crosswise on an extensive series of symmetry absorptions. Given the high phosphorus sorption in both soils, a modified Freundlich model was effective to calculate P doses (Sarfraz, 2014). This method allows for more accurate predictions of P requirements, considering the unique characteristics of each soil.

CONCLUSIONS

The Langmuir model effectively described phosphorus sorption at lower concentrations, whereas the modified Freundlich model excelled at medium to high concentrations. Subsequently, the modified Freundlich model was the selected method for calculating theoretical phosphorus doses in field applications. Based on these conclusions, the study recommended using P sorption approach, with the P requirement determined under clay loam and sandy loam soils. Phosphorus sorption technique is more useful than routine methods since it integrates P intensity, quantity, and buffering capacity aspects of the soil, which play an important role in controlling P flux.

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