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Comparison of different models for phosphate adsorption in salt inherent soil series of Dera Ismail Khan

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Abstract

Soil samples from three different soil series of Dera Ismail Khan namely Zindani, Tikken and Gishkori were collected and used for sorption study. The physico-chemical properties of these soil series were found to be alkaline and calcareous in nature, with low organic matter and high ECe and sodium adsorption ratio (SAR). Three adsorption equations viz. Langmuir, Freundlich and Tempkin were used to describe P adsorption processes. The results of the study showed that maximum adsorbed P of Gishkori, Tikken and Zindani series was 235.49, 152.78 and 128.45 mg kg^{-1}, respectively. By applying various models, P adsorption data revealed that Freundlich equation (R^2 = 0.99) showed a better fit over the Langmuir equation (R^2 =0. 97) in all the three series. The Tempkin equation did not show a good fit to the data (R^2 = 0.89).

Key Words: Phosphorous, adsorption isotherm, langmuir, freundlich, tempkin models

Introduction

Phosphate adsorption is the process in which the ions are held on the active sites of the soil particle surfaces. The amount of phosphate adsorbed by soil increases as the amount of phosphate in solution increases and vice versa. Adsorption affects fate of P-source and the availability of phosphate to plants. The phosphate in fertilizers and manure is initially quite soluble and available. Adsorbed or precipitated inorganic phosphate undergoes desorption or dissolution reactions when moving from the solid to the solution phase. Adsorption isotherm can conveniently be described as the equilibrium relationship between the amount of adsorbed and dissolved species of phosphate at constant temperature in quantitative terms. Phosphate adsorption isotherm is an important criterion to study the interaction of the ions with the oxides and soil, and has been used to measure the adsorption capacity of the soil (Olsen and Watanabe, 1957). Adsorption is usually characterized by fitting of adsorption isotherm and their mathematical description using one or more adsorption equations. In general the two terms Langmuir isotherm and Freundlich isotherm models give the best fit to measured data (Bache and Williams, 1971; Holford *et al.*, 1974). The third common Tempkin equation was also used to describe the adsorption isotherm (Tempkin and Pyzhev, 1940).

Phosphate adsorption in alkaline calcareous soils is a most common phenomenon, due to the presence of different cations. Most of the soils in Pakistan are alkaline calcareous in nature, therefore P availability to plant is restricted. Rehman *et al.* (1991) reported that P was deficient in 68, medium in 29 and adequate in 3 percent of Dera Ismail Khan soils. Keeping in view the diversified behavior of phosphorus in alkaline calcareous soil and to understand the adsorption capacity of the soil, a study was carried out using three salt inherent soil series of Dera Ismail Khan (North West Frontier Province) with the objective to study the P adsorption isotherms of these salt inherent soil series and for further elaboration, the P adsorbed data were subjected to three important equations which best fit the P adsorption isotherm.

Materials and Methods

Soil samples and basic analytical methods

Three soil series namely Zindani, Tikken and Gishkori salt inherent series of Dera Ismail Khan (Soil Survey Staff, 1969) were selected to study the mechanism of P adsorption. The soil samples of surface soil were collected and analyzed for various physico-chemical analysis prior to adsorption studies.

Phosphorus sorption curves

The Phosphate adsorption studies were carried out by following the procedure given by Rao (1993). One gram of air dried soil was accurately weighed and 50 mL of solution (K_2HPO_4) containing 0.5, 1, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 µg P mL^{-1} were added and shaken for 24 hours at 25^{o}C. After equilibration, the soil suspensions were filtered through Whattman filter 42. Ten milliliter of extract of each of the sample and blank was taken in 50 mL volumetric flask with the help of pipette, 2 ml of 2.5 N H_2SO_4 was added and mixed thoroughly. Five milliliter of ascorbic acid was added, as the blue colour developed the P

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concentration was determined colorimetrically at wavelength of 882 nm.

The P adsorption data for the soils used in this study were fitted into the different adsorption equations. The data fitted in to the equations proposed by Holford *et al*. (1974), Le Mare (1982) and Dubus and Becquer (2001).

The Langmuir equation described in its linear form is as

$C/X = 1/ K_L b_L + C/b$ (Langmuir, 1918)

$X = K_f C^{1/n}$ (Freundlich, 1926)

$X = a + b \ln C$ (Tempkin and Pyzhev (1940)

Where

C = Equilibrium concentration of phosphorus in solution (mg P L^{-1})

X = mg of P adsorbed (mg P kg^{-1})

b_L = Adsorption maximum for Langmuir model (mg P kg^{-1})

K_L = Bonding energy constant of Langmuir model (L mg^{-1} P)

n = Empirical constant related to bonding energy of soil for phosphate

K_f = Proportionality constant for Freundlich model (mg kg^{-1})

a = Amount of P adsorbed of Tempkin model (mg P kg^{-1})

b = Buffer capacity of Tempkin model (mL g^{-1})

Results and Discussion

Physico – chemical properties of three soil series

Selected physico-chemical properties of the soil samples are presented in Table 1. Soil samples were collected from surface. All of the soils series are alkaline with the pH above 8. The texture of the Tikken and Gishkori are Clay loam, while Zindani soil has silt loam texture. All the three soils contain excessive amount of soluble salts with range of electrical conductivity around 4 dS m^{-1}. Also, the sodium adsorption ratio was found to be above 13 in Tikken and Gishkori. The organic matter content of the three soils was less than 1 percent in all the three soils. Calcium is the dominant cation present in the soil, with high amount of $CaCO_3$ value. The extractable P in soil was found deficient in three soil series, but Zindani soil contained more than Tikken and Gishkori. It may be due to the different factors as silty loam soil texture, low ECe, SAR and $CaCO_3$ (Hussain *et al*., 2006).

Phosphate adsorption Isotherms

The Phosphate adsorption isotherms of the three soil series used in the study were determined by plotting the equilibrium concentration of phosphate (C) against the amount of phosphate adsorbed (X). The adsorption isotherm of the three soil series shows that all the soil series have exhibited different curves. Comparing the highest amount of P adsorbed in the three soil series it is evident that each series has different capacities to adsorb P (Table 2). The result of the study showed that Gishkori soil had the highest value of maximum adsorption 235.49 mg kg^{-1}, followed by Tikken and Zindani series with maximum P adsorbed 152.78 and 128.45 mg kg^{-1} respectively. The highest value of adsorption in the Gishkori soil series may be due to more organic matter content and clay lattice. Similar adsorption isotherms have been reported in Rasulpur soil series by Sarfaraz *et al*. (2009).

The graphic representation of the adsorption isotherms of the three soils series had different curves (Figure1). The curves followed a smooth plateau pattern. It is evident from the curves that the rate of P adsorption increased with the increase in the concentration of P, but at certain point of higher concentration the level of P becomes almost constant with no more capacity to adsorb P.

Fitting the adsorption data to different equations

The sorption isotherms were examined according to the linear form of the two equations. When the sorption data was plotted in the Langmuir adsorption isotherm by taking C/X against C (Figure 2), showed a good fit. The slope of the plot was found less than 0.01. While the R^2 value was the highest observed (0.980) in Tikken series followed by Gishkori with value of 0.978 and the lowest was observed in Zindani series with value of 0.961 (Table 3). It was observed from the study that the Langmuir equation well fitted to the data on higher concentration of P. The comparison of the Langmuir adsorption maximum (b) for the three soil series showed that values of adsorption maximum, was 270.27, 217.39 and 121.95 mg kg^{-1} for Gishkori, Tikken and Zindani soils, respectively, (Table 4). It was observed that the Langmuir equation gave higher value of maximum adsorbed than the actual calculated values (Table 2). The binding energy was the highest for

Table 1. Physico-chemical properties of the three soil series

Soil Series	Soil Texture	pH	ECe (dSm^{-1})	SAR $(mmol\ L^{-1})^{1/2}$	$CaCO_3$ (%)	O.M. (%)	Olsen P (mg Kg^{-1})
Zindani	Silty loam	8.51	3.46	10.25	12.58	0.85	7.01
Tikken	Clay loam	8.46	4.35	14.36	13.01	0.93	5.32
Gishkori	Clay loam	8.33	5.59	13.22	15.67	0.99	5.01

Gishkori 0.063 L (mg P)$^{-1}$, followed by Zindani 0.061 and 0.027 L (mg P)$^{-1}$ for Tikken soil series. The lowest value of the binding energy constant was due to the alkaline nature of soil. Olsen and Watanabe (1957) reported 0.92 and 4.39 ml µg^{-1} in alkaline and acidic soil, respectively. Similar results of binding energy constant were reported by Hussain, *et al*. (2006) for the sodic soil.

Table 2. The Maximum adsorbed P by three soil series

Name of Soil Series	Maximum P adsorbed (mg Kg^{-1})
Zindani Series	105.45
Tikken Series	152.78
Gishkori Series	235.49

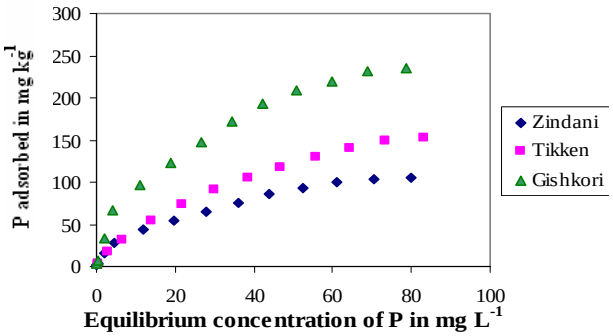

Figure 1. Phosphate adsorption isotherm of three soil series

The adsorption isotherm examined by the linear form of the Freundlich equation by plotting log C against log X (Figure 3) showed that a good linear fit to the data of the three series was observed. The exponent (b) found in the equation was greater that 0.5, with the maximum value of 0.758 observed in the Tikken series and the lowest was observed in the zindani series which yielded 0.608. Also the values observed were greater as compared to the Langmuir equation, with the highest R^2 value of 0.99 observed in Tikken soil series (Table 3).

It may be concluded from the above results that the Freundlich model showed a better fit to the data particularly at lower concentration than the Langmuir and Tempkin models. Similar results have been observed for the Freundlich model over Langmuir and Tempkin by other workers including Dubus and Becquer (2001), Barrow (1978), Sanyal *et al.* (1993). The high conformity of the adsorption data with the modified Freundlich model (R^2 = 0.95) have been reported by Mehdi *et al.* (2008).

The Tempkin equation of the adsorption isotherm was obtained after plotting the X against ln C. It was observed

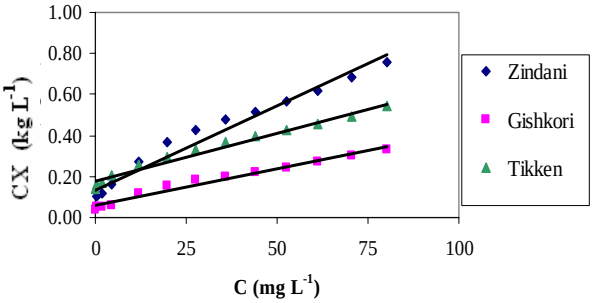

Figure 2. Langmuir isotherm for three soil series

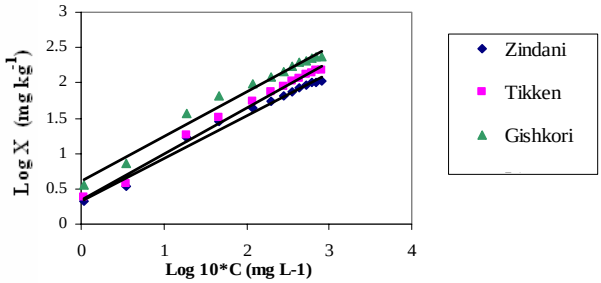

Figure 3. Freundlich equation for three soil series

that the Tempkin equation did not show a good fit to the data of the three soil series as compared with the Langmuir and Freundlich equations. The exponent (b) was found greater in all the three series, with maximum value of 38.35 mL g^{-1} found in the Gishkori series. The data well fitted the Gishkori soil with the value of 0.89, while the value for other two soil series was found inferior to Gishkori series (Table 3). In the simplified Tempkin equation, the adsorption energy decreases linearly with increasing surface coverage. The relationship between amounts of P adsorbed and the logarithm of concentrations of P should give a straight line if the model was suitable for describing adsorption isotherm. However, this was not found to be so in our study (Fig. 4). The Tempkin equation thus has limited value, despite its potential usefulness over large concentration ranges. These results agree with Sanyal *et al.* (1993) and Dubus and Becquer (2001).

Conclusion

The adsorption isotherm showed different curves for the three series. Comparing the three equations it may be concluded that the Langmuir and Freundlich equations provided a good fit to the data of the three soil series. Fitting sorption data to Freundlich and Langmuir equations gave R^2 values greater than 0.95. The Tempkin equation thus has limited value, despite its potential usefulness over large concentration ranges.

Table 3. Regression equations with R^2 value for three soil series

Soil Series	Model	Equation	R^2
Zindani	Langmuir	y = 0.008x + 0.134	0.962
	Freundlich	y = 0.608x + 0.324	0.987
	Tempkin	y = 16.747x - 19.968	0.884
Tikken	Langmuir	y = 0.005x + 0.170	0.980
	Freundlich	y = 0.759x + 0.050	0.991
	Tempkin	y = 28.402x - 59.111	0.876
Gishkori	Langmuir	y = 0.004x + 0.058	0.974
	Freundlich	y = 0.641x + 0.606	0.978
	Tempkin	y = 38.354x - 47.17	0.899

Table 4. Comparison of Langmuir Adsorption maximum and binding energy constant for three soils

Soil Series	Adsorption Maximum (b) (mg kg^{-1})	Bonding Energy Constant (K) (L mg^{-1} P)
Zindani	121.95	0.061
Tikken	217.39	0.027
Gishkori	270.27	0.063

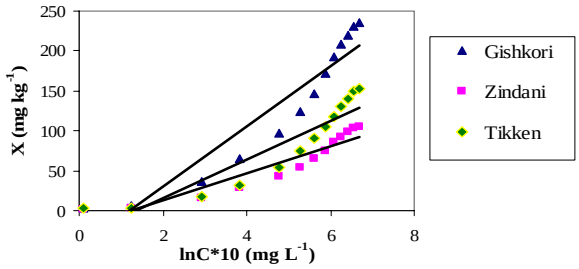

Figure 4. Tempkin Equation for three soil series

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