Research Article

Phosphate sorption potential of some acid soils of Bangladesh as tested by Freundlich and Temkin equation

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Abstract

To investigate the phosphate sorption potential of soils, an incubation experiment was performed with five representative soil series of Bangladesh namely the Borkal (Typic Dystrudepts), the Pahartali (Aeric Endoaquepts), the Raojan (Aeric Endoaquepts), the Noapara (Typic Endoaquepts) and the Manu (Aeric Dystrudepts). Calcium chloride solution of 0.01 M containing 0, 1, 10, 25, 50 and 100 mg phosphorus dm^{-3} was used to equilibrate the soils and then the sorbed phosphate was measured. The phosphate sorption curves showed almost similar magnitude of changes. Phosphate sorption by the soils was observed in the order of Borkal>Noapara>Manu>Raojan>Pahartali soil series and reflected with the organic matter content of soils. Between Freundlich and Temkin equation, Freundlich model showed better fit to sorption data at higher P concentrations. The co-efficient of determination (R^2) values were used to compare the suitability and applicability of Freundlich and Temkin equation. Equilibrium P concentration (EPC_0) value (P concentration at zero fixation) was estimated by using Temkin adsorption equation and the values were between 0.05 mg dm^{-3} and 0.45 mg dm^{-3}. The highest EPC_0 was obtained for Pahartali and the lowest for Noapara soil series. Therefore, Freundlich equation may be more suitable for evaluating phosphate sorption capacities of agricultural soils.

Keywords: Phosphate, sorption, soil, Freundlich coefficient, Equilibrium phosphate concentration

Introduction

Phosphorus (P) is one of the most abundant and essential elements for crop development (1 and 2). Application of P fertilizers in soils either solid or liquid forms gradually leads to reaction between various soil components and orthophosphate ions ($H_2PO_4^-$, HPO_4^{2-}) transforming P from solution phase to less soluble phase. This type of transformation of P fertilizer from readily soluble to less soluble is relevant to as P retention/P fixation and has been reported by several authors (3-7).

Better management of P fertilizer can be achieved by studying the P sorption-desorption capacity of the soil that reflects the partitioning of P between soil solid phase and soil solution. Sorption is defined as the net accumulation of a sorbate at an interface between a sorbent and the solution phase. The sorption isotherms can be used to approximate the quantity of P that must

be added in soil to raise the P concentration in soil solution at equilibrium to a target, or maximum value (8). The relationship between labile P sorbed to the soil particle (clay) surface and solution P can be described by a quantity-intensity relationship or Q/I plot, which shows P sorption or desorption as a function of P in the equilibrium solution (9). The shape of the curve reflects P sorption capacity and the slope of the curve reflects the buffering capacity for freshly added P (10).

Adsorption isotherm is a common non-mechanistic technique that is used to assess substance adsorption. An adsorption isotherm is a graph of the equilibrium surface excess or amount of a compound adsorbed (e.g., in units of mmol kg^{-1} or mg kg^{-1}) plotted against the equilibrium solution concentration of the compound (e.g., in units of mmol L^{-1} or mg dm^{-3}) at

fixed temperature (thus the term isotherm), pressure, and solution chemistry (e.g., pH and ionic strength) (11). Various modeling approaches like Freundlich and Temkin equations have been used widely to describe P sorption reactions in soils. Gregory et al. (12) stated that advantage of Freundlich isotherm as unlimited sorption sites, which correlated better with a heterogeneous soil medium having different chemical/physical properties. The fitted Temkin equation is used to determine the equilibrium P concentration (EPC_0) of soils. The value of EPC_0 is defined as the P in solution at zero sorption, and is useful value for identification of source or sink for P exposed to surface runoff (13). Though several experiments have been conducted on phosphate sorption in soil but very few research have been conducted with soils of Bangladesh. Therefore, the present research work is conducted with a view to find out the effects of some soil properties on phosphate sorption of some acid soils of Bangladesh, to investigate the phosphate sorption potential of these soils and to evaluate the relationships among phosphate sorption parameters and selected soil properties**.**

Materials and Methods

Soil sampling

With a view to study the phosphate sorption characteristics of soils, an experiment was conducted in the laboratory of the Department of Soil Science, University of Chittagong, Bangladesh. Five different soil series namely the Borkal (Typic Dystrudepts), the Pahartali (Aeric Endoaquepts), the Raojan (Aeric Endoaquepts), the Noapara (Typic Endoaquepts) and the Manu (Aeric Dystrudepts) were used in the study. Among them, Borkal and Manu are high hill soils and other three soils are alluvial soils. For each soil series, soil samples were collected randomly from the field at a depth of 0- 15 cm and homogenously mixed before taking a composite sample (2-3 kg). The soils were then air dried at room temperature ($298\pm2^{\circ}K$), grounded and passed through a 2 mm sieve.

Chemical analysis

The soil samples were analyzed for particle size, pH, organic matter and total and available P contents determinations. Bouyoucos hydrometer method was used to determine particle size analysis (14). The pH

of the soil was determined by using a soil to water ratio of 1:2.5. Soil organic carbon was determined by wet oxidation method. Chromic acid was used as oxidizing agent and the excess chromic acid left after the oxidation of organic carbon was determined volumetrically with standard ferrous sulphate solution, and the quantity of substance oxidized was calculated from the amount of chromic acid reduced (15). Total soil P was determined colorimetrically by ascorbic acid blue color method (16) after digestion with H_2O_2-H_2SO_4 (17) and the absorbance was measured by spectrophotometer at wave length of 882 nm. The available P of the soils was determined by the same procedure as mentioned above after extraction with 0.2 N CH_3COOH + 0.013 N HNO_3 + 0.015 N NH_4F + 0.25 N NH_4NO_3 + 0.001 M EDTA (Mehlich 3) (18).
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Phosphate Sorption Procedures

For phosphate sorption study, soil samples of 1 g were equilibrated into a 50 cm^3 centrifuge tube with 25 cm^3 of 0.01 mol dm^{-3} $CaCl_2$ solution containing 0, 1, 10, 25, 50 and 100 mg (equivalent to 0, 25, 250, 625, 1250 and 2500 mg P kg^{-1} soil) as KH_2PO_4. The soil samples containing phosphate as KH_2PO_4 in the $CaCl_2$ media were then incubated at room temperature ($298\pm1^{\circ}K$) for 24 h. This incubation time (24 h) was chosen according to the experiment conducted by Sharpley et al., (19). The incubation experiment was arranged in the laboratory according to completely randomized design. The mixtures were centrifuged and the supernatants were analyzed for P following the ascorbic acid blue color method (16). Phosphorus content was measured by a UV-Vis spectrophotometer (Optima SP-3000 nano, Tokyo, Japan) at 882 nm wavelength. Sorbed P was inferred from the difference between the concentration of soluble P added in the initial solution and the concentration of P in the solution at equilibrium. Each treatment was replicated three times.

The Freundlich equation:

$$S = K_f C^{1/n} \quad \text{-------------------------(i)}$$

The Freundlich equation is often used in its logarithmic form:

$$\log S = \log K_f + \ n \log C \ \text{----------------------(ii)}$$

Where, S denotes total sorbed P ($\mu g\ g^{-1}$), C denotes the amount of P in the solution after equilibration ($\mu g\ mL^{-1}$), K_f and n are empirical constants. The constant K_f represents the amount of P sorbed ($mmol\ kg^{-1}$) when C is 1 $mmol\ L^{-1}$.

The Temkin isotherm equation is:

$$S = a \log C + b \text{ -----------------------(iii)}$$

Where, S = sorbed P ($mg\ kg^{-1}$), C = equilibrium P concentration in solution ($mg\ dm^{-3}$), a and b are constants. The Temkin isotherm is valid only for an intermediate range of ion concentrations. The fitted Temkin equation is used to determine the equilibrium P concentration (EPC_0) for each of the soils, by determining the value of C when S equals zero.

Statistical analysis

Regression curve fitting equations were drawn by the Microsoft Office Excel program and Minitab (20).

Correlation coefficients were calculated between phosphate sorption and soil properties, phosphate sorption parameters and soil properties and among phosphate sorption parameters.

Results and Discussion

Physical and chemical properties of Soils

The physical and chemical properties of the studied soils are listed in Table 1. The pH of the soils ranged from 5.42 to 5.86. The highest and lowest clay content of the soil was obtained in Noapara (40%) and Pahartali (26%) soil series, respectively. The organic matter and total P contents of the soils were varied from 1.42 to 2.16% and 383 to 487 $mg\ kg^{-1}$, respectively. Total P concentration of the soils showed significant positive correlation (p= 0.05) with available (Mehlich 3 P) soil P. The Mehlich 3 extractable soil P was the highest of 18.6 $mg\ kg^{-1}$ in the Pahartali soil series and the lowest of 13.8 $mg\ kg^{-1}$ in the Borkal soil series.

Table 1. Physical and chemical properties of soils

Soil series	pH	Sand (%)	Silt (%)	Clay (%)	Textural class	Organic matter (%)	Total P ($mg\ kg^{-1}$)	Mehlich 3 P ($mg\ kg^{-1}$)
Borkal	5.42	30	32	38	Clay loam	2.09	383	13.8
Pahartali	5.86	44	30	26	Loam	1.42	487	18.6
Raojan	5.65	55	16	29	Silty clay loam	1.76	375	15.1
Noapara	5.45	31	29	40	Clay loam	2.16	392	14.8
Manu	5.74	17	50	33	Silty clay loam	1.85	456	15.7

**Phosphorus sorption behavior**

In all the soils, except for 0 $\mu g\ P\ mL^{-1}\ PO_4^{3-}$-P treatment, P-sorption occurred due to application of P at different rates. Some desorption was noticed at 0 $mg\ P\ dm^{-3}$ treatment (i.e., control). Desorption of P at control was also reported by several other scientists (21-22). In the present investigation, the amount of P sorption gradually increased with increasing P application in all the soil series. Naseri et al. (23) also reported an increase in P sorption with increasing P in equilibrium solution. The phosphate sorption isotherms of the studied soils have been constructed by plotting the equilibrium concentration of phosphate (P_{eq}) against the amount of phosphate sorbed (P_{sorb})

(Figure 1). From the sorption isotherms, it is obvious that the studied soil series showed different trends. Among the five studied soil series, Borkal and Noapara soil had the maximum and Pahartali had the minimum P adsorption capacity. On the other hand, P sorption capacity of Raojan and Manu soil series was intermediate between Borkal and Noapara, and between Pahartali soil series. Correlation studies showed that phosphate sorption was positively correlated with both organic matter (p< 0.05 to p< 0.001) and percent clay content (p< 0.05 to p< 0.001) of the experimental soils when phosphates were added at the rate from 1 to 100 $mg\ dm^{-3}$. Among the rates of phosphates applied, the best correlation was obtained

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at 100 mg dm^{-3}. The significant positive correlation between phosphate sorption parameters and clay contents of the soils might be due to the presence of higher number of positive charges of the surface of clay particles that can be reacted and bind the

negatively charged phosphate ions in the solution. Similar results were also reported by other investigators (24-27) who stated that the adsorption of P in soils increases with the increasing of clay contents in soils.
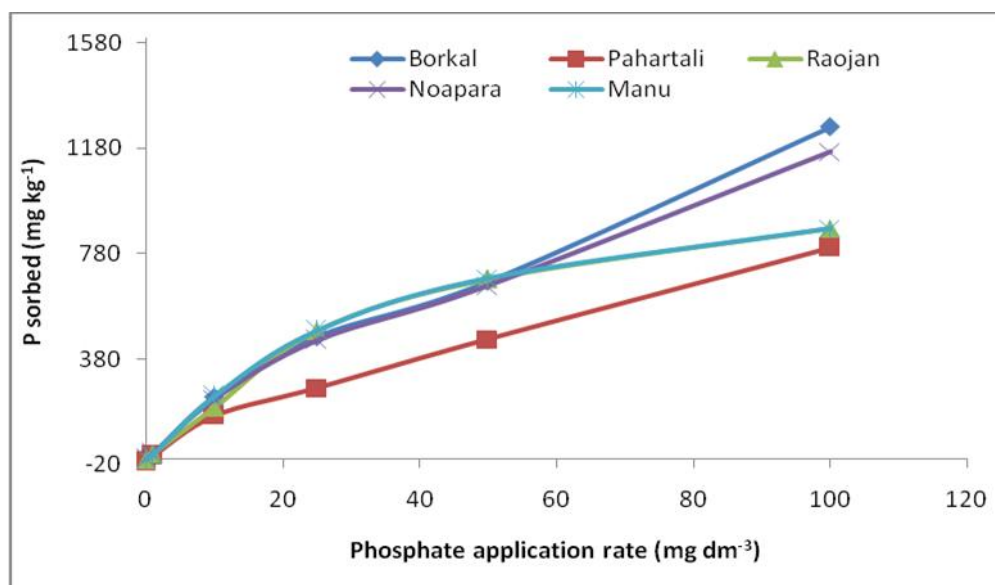
Figure 1. Trend of phosphate sorption in different soils with different rates of P application

Phosphate adsorption isotherms

The adsorption isotherms were examined by the linear form of the Freundlich adsorption equation by plotting logS against logC (Figure 2), and all the soils showed a good fit except Manu soil series. The R^2 value was highest in Noapara and Pahartali soils series (0.95), followed by Raojan (0.93), Barkal (0.80) and Manu (0.64) (Table 2). Sorption parameters were also calculated from Freundlich equation (Figure 3). The Freundlich exponent, n, represents the heterogeneity

of surface sites having different affinities for phosphate retention by soil. Fitting with Freundlich equation, the highest n was found in Pahartali soil series (0.74), followed by Borkal (0.61), Raojan(.61) Noapara (0.57) and Manu (0.51) soil series. Freundlich coefficient K$_f$, which is a measure of the amount of P sorption sites, ranged from 38 to 135 mg kg^{-1} in the studied soils. According to Freundlichparameter K$_f$, Noapara, soil has the highest sorption sites followed by Manu, Borkal, Raojan, and Pahartali.

Table 2. Phosphorus sorption parameters

Soil Series	K$_f$ (mg/kg)	n	EPCo (mg/dm^3)
Borkal	124	0.61	0.33
Pahartali	38	0.74	0.45
Raojan	101	0.61	0.11
Noapara	135	0.57	0.05
Manu	120	0.51	0.26

The sorption data were also fitted to the Temkin equation and the R^2 values were between 0.83 and 0.93 (Figure 3). Equilibrium P concentration (EPC$_0$) value, which is the solution P concentration at zero

fixation, was estimated by using Temkin adsorption equation and the values were between 0.05 to 0.45. The highest EPC$_0$ was obtained for Pahartali and the lowest for Noapara soil series.

Figure 2. Phosphate sorption equation for the soils fitted by the Freundlich equation, (a) Borkal, (b) Pahartali, (c) Raojan, (d) Noapara and (e) Manu soil series.
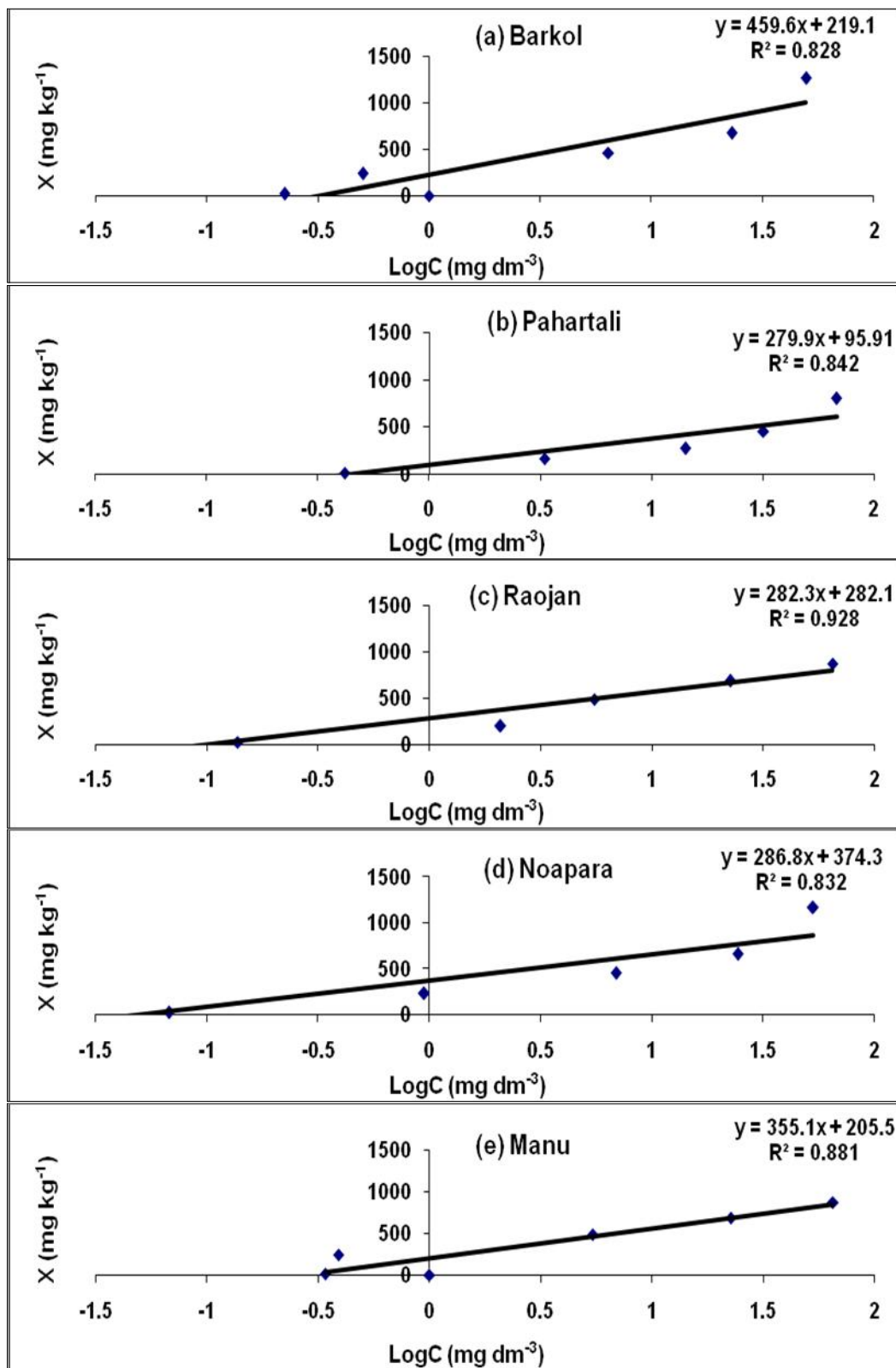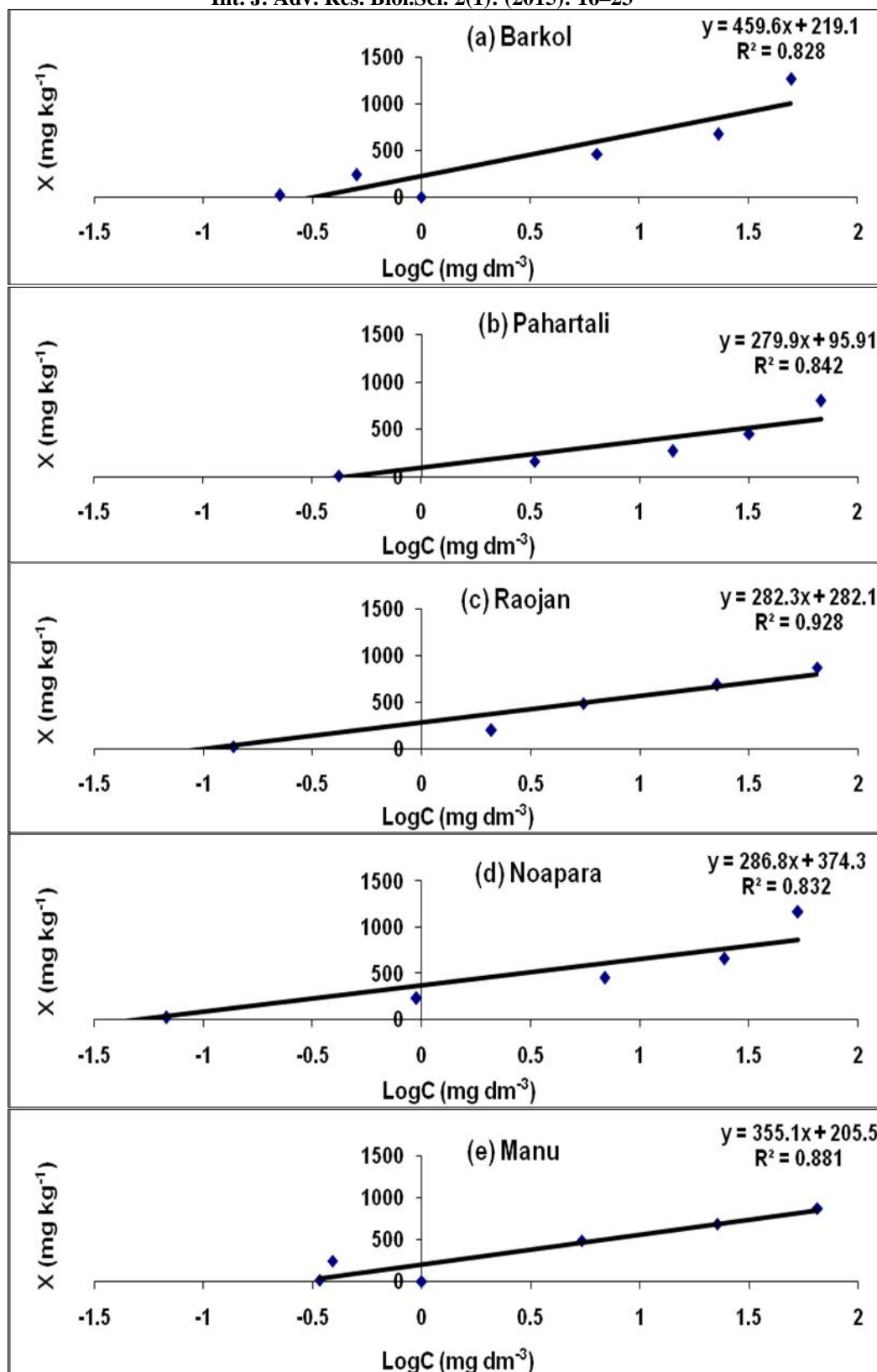
Figure 3. Phosphate sorption equation for the soils fitted by the Temkin equation, (a) Borkal, (b) Pahartali, (c) Raojan, (d) Noapara and (e) Manu soil series.

As EPC_0 value estimates P intensity in soil, higher EPC_0 value suggests greater P desorption from soil particles or sediments. It was observed that phosphate sorption parameters such as P-sorption capacities (k_f), Freundlich constant n, and EPC_0 were positively correlated with both soil contents of clay and organic matter. However, among phosphate sorption parameters, positive correlation was found between phosphate sorption capacities (k_f) and Freundlich constant n ($p<0.05$) but negative correlation was found between phosphate sorption capacities (k_f) and EPC_0 values ($p<0.05$) whereas Freundlich constant n was positively correlated with EPC_0 values ($p<0.05$).

Conclusion

The magnitude of phosphate sorption capacity of different soils varied considerably among the soils. Soil organic matter and clay content played vital role to enhance phosphate retention capacity and hence phosphate sorption parameters such as K_f, n and EPC_0 were positively correlated with both the soil parameters. Considering the coefficient of determination (R^2) values of Freundlich and Temkin equations, Freundlich equation may be more suitable for evaluating phosphate sorption capacities of agricultural soils.

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