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Phosphorus adsorption and its relationship to the physical and chemical characteristics with different soil classes

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In order to determine the characteristics of phosphorus adsorption using the Langmuir and Freundlich isotherms and its relationship with some of the chemical and physical properties of soils, a study was developed at the Embrapa Soil Laboratory with soil samples (0 - 30 cm) from four classes of topsoil: Orthic Chromic Luvisols, Eutrophic Cambisols, Fluvic Neossol and Eutrophic Cambisols Typical. The hyperbolic model of the Langmuir isotherm was fitted by the non-linear regression technique. We performed a correlation analysis between the isotherm parameter values and soil characteristics that reflected the Phosphate Maximum Capacity. The values of remaining phosphorus ranged from 16.28 to 43.73 mg L^{-1} for the soils. For the Langmuir isotherm, the maximum phosphorus adsorption capacity (MPAC) values ranged from 0.2793 to 0.3954 mg g^{-1} of soil. The RY soil had the largest amount of adsorbed phosphorus (0.3954 mg g^{-1}), giving this soil a high MPAC.

Key words: Tropical soils, phosphorus, buffering capacity.

INTRODUCTION

In Brazil, most soil has a high degree of weathering, with large amounts of iron and aluminum oxides and clays of the kaolinite group of minerals that have surface charges that vary according to the reaction of the soil solution (Schaefer et al., 2008). Thus, the soil can behave as either a source or a drain of P, acquiring most of the P added to the soil by linkage to colloids and making it unavailable to plants. As the degree of weathering of these soils is increased, they become more electropositive, adsorbing anions such as phosphates (Novais and Smyth, 1999; Carvalho Filho et al., 2015).

Many of these weathered soils, and even some less weathered, despite having levels of P that are not significant, only have a small amount of P available due

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Table 1. Physical and chemical characteristics of the soils in accordance with the methodology of Embrapa (1997).

Characteristics	Sois			
	TCo	CXbe	RY	CXve
pH H_2O (1:2,5)	6.8	6.6	6.8	6.5
Ca^{+2} ($mmol_c$ dm^{-3})	76.9	182.1	145.3	31.0
Mg^{+2} ($mmol_c$ dm^{-3})	29.5	39.3	63.5	20.5
Na^{+} ($mmol_c$ dm^{-3})	1.1	0.7	1.1	0.5
K^{+} ($mmol_c$ dm^{-3})	5.1	13.5	4.8	6.2
SB ($mmol_c$ dm^{-3})	112.6	235.6	214.7	58.2
H+Al ($mmol_c$ dm^{-3})	12.4	38.0	28.1	12.4
T ($mmol_c$ dm^{-3})	125.0	273.6	242.8	70.6
V (%)	90	86	88	82
Al^{+3} $mmol_c$ dm^{-3})	0.5	0.5	0.5	0.5
P mg dm^{-3} ($Melich^{-1}$)	296.2	286.8	8.90	22.5
P mg dm^{-3} (RTA)	75.0	130.5	10.5	18.0
M.O (g kg^{-1})	11.2	28.8	20.9	10.2
Prem (mg L^{-1})	43.73	16.28	27.34	41.34
MPAC (mg g^{-1})	0.279	0.297	0.395	0.293
Sand (g kg^{-1})	726.4	716.8	450.1	726.6
Silt (g kg^{-1})	138.0	28.3	234.8	148.0
Clay (g kg^{-1})	135.6	254.9	330.0	125.4

TCo: Chromic Orthic Luvisol; CXbe: Eutrophic Haplic Cambisol; RY: Fluvic; CXve: Typical Eutrophic Cambisol.

to the low solubility of their forms of P and, by the strong interaction of phosphate with the soil, forming compounds of low solubility in soils linked to different combinations of iron, aluminum, calcium and organic matter (Rolim Neto et al., 2004; Bortoluzzi et al., 2015; Fink et al., 2016; Brito Neto et al., 2017). Despite its importance for the growth and development of plants, P is a macronutrient that is required in only small quantities, yet it is one of the elements that limit productivity in most cultures (Gatiboni et al., 2007) due to the adsorption phenomenon that is common to all soils. In northeastern Brazil, different classes of soil occur, from the least to the most weathered, with different energies of adsorption of P.

The reactions of adsorption and the precipitation of P in the soil begin as soon as P is added, so that in acidic and highly weathered soils, a portion of the P is adsorbed on the surface of clay minerals, such as iron and aluminum oxides, and another part precipitates with Fe and Al present in soil solution. However, in a few weathered soils with pH ranging from neutral to alkaline, part of the P added is adsorbed onto the surface of clay minerals and another portion precipitates with Ca in the soil solution. According to Gérard (2016), the P adsorption capacity of clay minerals may be similar to or higher than that of iron and aluminium oxides depending on the specific surface area of the particular soil components.

From a practical standpoint, it is not easy to separate the reactions of adsorption or precipitation of P in soil; to do this, isotherms of Langmuir and Freundlich adsorption are used to describe the P (Novais and Smyth, 1999). In this regard, our aim with this work is to determine the adsorption capacity of P in four soil samples from Brazil's Northeastern region.

MATERIALS AND METHODS

The experiment was conducted at the Laboratory of Soils and Plant Nutrition at the National Center Cotton of Embrapa Algodão. Four soil samples with different chemical, physical and mineralogical characteristics, collected at a depth of 0 - 30 cm corresponding to the topsoil, were used. The soils were classified according to the Brazilian System of Soil Classification (Embrapa, 2006) as Orthic Chromic Luvisols (TCO), Eutrophic Cambisols (CXbe) Fluvic Neossol (RY) and Eutrophic Cambisols Typical (CXve). Soil samples were loosened, air dried and passed through 2 mm mesh sieves for chemical and physical characterization (Table 1) according to Embrapa (1997).

Subsoil samples were taken to determine the Prem, being determined in the equilibrium solution obtained after shaking a soil sample with 5 cm^{-3} of 50 mL of $CaCl_2$ 10 mmol L^{-1} containing 60 mg L^{-1} P for five minutes, and allowing it to settle for decantation for 16 h (Alvarez et al., 2000). The P equilibrium concentration solutions used for adjusting the Langmuir and Freundlich isotherms were based on the values of P-rem in the soil (Alvarez et al., 2000) and corresponded to 0.0, 10, 20, 40 and 80 mg L^{-1} P for soils with P-rem between 30 and 44 mg L^{-1}, 0.0, 18.75, 37.50, 75.0 and 150 mg L^{-1} P for soils with P-rem between 10 and 19 mg L^{-1} and 0.0, 13.75, 27.5, 55.0 and 110 mg L^{-1} P for soils with P-rem between 19 and 30 mg L^{-1}.

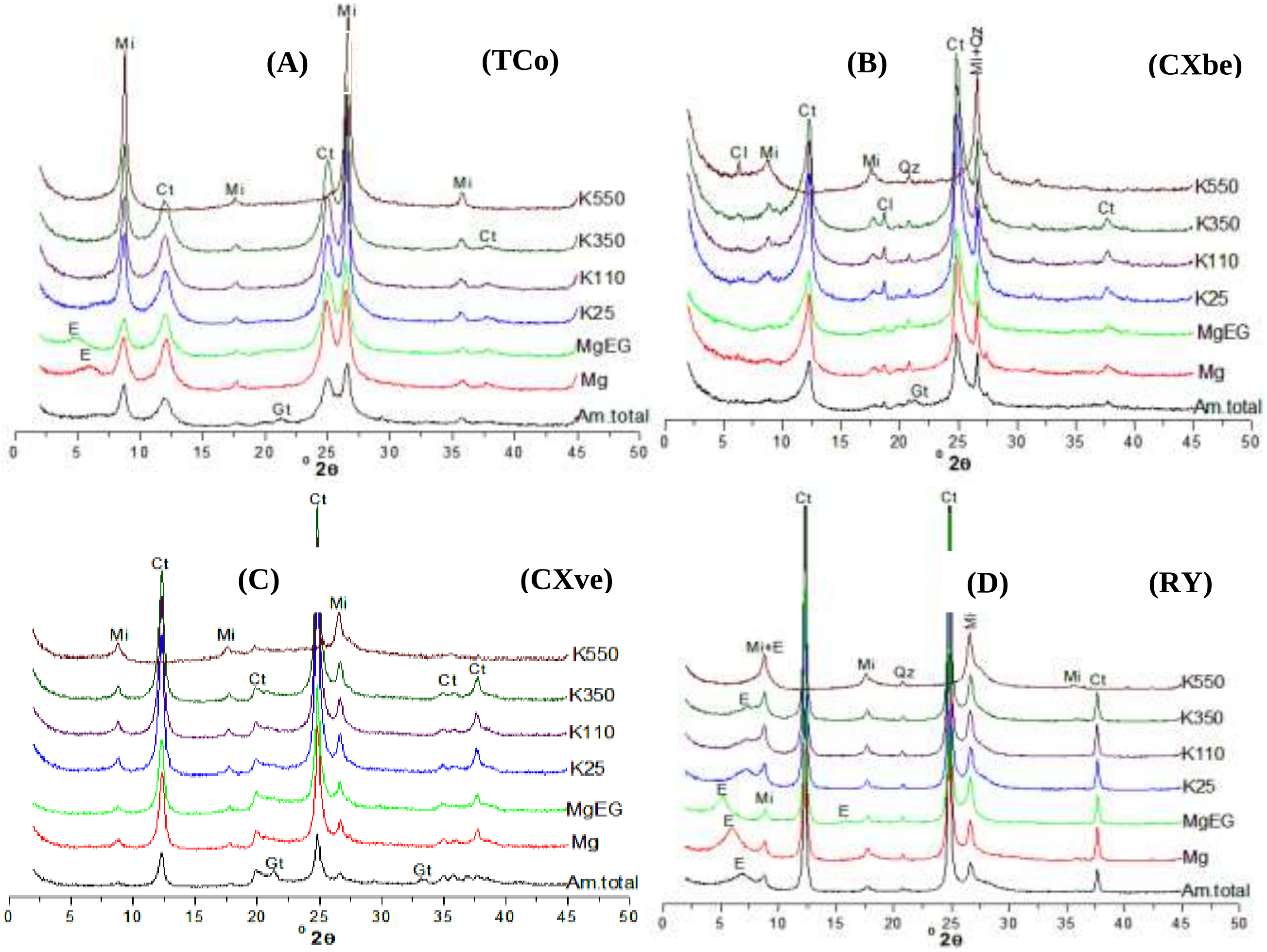

Figure 1. X-ray diffractogram of clay samples from (A) TCO, (B) CXbe, (C) CXve and (D) RY assembly-oriented CuKα radiation.

To determine the MPAC, 2.5 cm^{-3} of soil was used. Then, 25 mL of $CaCl_2$ 10 mmol L^{-1} was added to a 250-mL Erlenmeyer flask containing P according to the concentrations mentioned above. After horizontal shaking for 24 h, the suspensions were centrifuged at 3000 rpm for five minutes and then filtered. The content of P in the equilibrium solution was determined by colorimetry (Braga and Defelipo, 1974), which was performed in triplicate. From the data obtained in triplicate, Langmuir and Freundlich adsorption isotherms were constructed by plotting the amount of P adsorbed in the soil (Q) on the ordinate and the concentration of P in equilibrium solution (C) on the abscissa. The hyperbolic form of the Langmuir equation is given by the following expression:

$$X = \frac{(a+b+c)}{m\ (1+a.c)}$$

Where x/m is the amount of P adsorbed to the soil in mg P (x)/g soil (m), (b) is the MPAC (mg g^{-1}) of P in the soil, (c) is the concentration of P in the equilibrium solution (mg L^{-1}), and a is the constant related to the adsorption energy of the element in soil (mg L^{-1}) (Olsen and Watanabe, 1957). The constants and (b) were estimated by the linear Langmuir equation, obtained by transformation of the hyperbolic equation, which corresponds to: C/x/m= C+1/ab/b. The linear form of the Freundlich equation is given by the following expression: log (x/m)= log k+(1/n). log (c) Where: x/m is the mass of the solute associated with the solid phase (mg kg^{-1}), (c) is the solute concentration in equilibrium solution (mg L^{-1}), KF: is the coefficient of Freundlich adsorption (cm^3 kg^{-1}) and (n) is an estimate of the tuning parameter (dimensionless).

The clay fraction (Ø <0.002 mm) was separated in the Physics Laboratory of Embrapa Solos, according to Embrapa (1997). Simple linear regression equations were adjusted for the parameters of Langmuir and Freundlich isotherms, which were correlated with the soils' physical and chemical characteristics.

RESULTS AND DISCUSSION

X-ray diffraction indicated that the mineralogy of the clay fraction presented different characteristics among the soils analyzed. Minerals were identified from the following groups: kaolinite (Ka), Mica (Mi), smectite (E), chlorite (Cl), Goethite (Gt) and quartz (Qz). The TCO sample Figure 1A) revealed the presence of mica, kaolinite, smectite and goethite, where the order Mi>Ct>E>Gt

Table 2. Parameters of Langmuir and Freundlich isotherms estimated by linear regression fits to the soils.

Soils	Langmuir equation	R^2	P-rem (mg L^{-1})	MPAC (mg g^{-1})	a (L mg^{-1})	FCPm (mL g^{-1})
TCo	C/q= 3.580C-12.59	0.98	43.73	0.2793	0.2843	0.0795
CXBe	C/q= 3.361C-13.32	0.99	16.28	0.2975	0.2523	0.0750
RY	C/q= 2.529C-12.17	0.98	27.34	0.3954	0.2078	0.0822
CXVe	C/q= 3.408C-10.18	0.98	41.34	0.2934	0.3348	0.0982

Soils	Freundlich equation	R^2	K	N
TCo	C/q= 0.866C-1.749	0.85	0.018	1.155
CXBe	C/q= 0.885C-1.731	0.85	0.014	1.064
RY	C/q= 0.880C-1.710	0.83	0.019	1.130
CXVe	C/q= 1.880C-0.940	0.92	0.020	1.137

Prem: Remaining Phosphorus; MPAC: Maximum capacity of adsorption of phosphorus; a: binding energy; FCPm: Factor maximum capacity of phosphorus; k and n: Freundlich isotherm parameters.

indicates an estimate of the relative prevalence of each mineral held based on the XRD patterns. A sample of CXbe (Figure 1B) revealed the existence of kaolinite, mica, chlorite, quartz and goethite, and the estimate of the prevalence of these minerals was in accordance with the order Ct>E>Cl>Qz>Gt according to the XRD patterns.

Analysis of a sample of CXve revealed the presence of minerals such as kaolinite, mica, and goethite in the order Ct>E>Gt, demonstrating the predominance of these minerals in this soil (Figure 1C). The x-ray diffractogram for RY demonstrated the presence of kaolinite, smectite, mica and quartz in this order: Ct>E>E>Qz, representing the predominance of these minerals in the soil (Figure 1D), since the absence of goethite demonstrates the preservation of soil minerals, which may contribute to P availability to plants.

The high coefficients of determination obtained from the linearized equations of the Langmuir and Freundlich isotherms (Table 2) indicate that the mathematical models were adequately effective in quantifying the adsorbed P in these soils. The values for P-rem varied from 16.28 to 43.73 mg L^{-1}; these may be considered soils with an intermediate capacity of adsorption, according to the criteria presented by Alvarez et al. (2000) and Saadi et al. (2000).

The determination of P-rem assists in the interpretation of P and its critical level in the soil, allowing inferences about the buffering capacity of the soil (Grilli et al., 2007). TCO had a higher Prem (43.73 mg L^{-1}), characterizing it as a soil that has low Phosphate Maximum Capacity (PMC). CXbe presented the lowest Prem value (16.28 mg L^{-1}), indicating that the different soils have different P adsorption capacities, these being directly related to the chemical, physical and mineralogical properties of the soils (Table 2). Godinho et al. (1997), working with soils of the Rio Grande do Norte semi-arid region, obtained values of P-rem that ranged from 32.11 to 44.63 mg L^{-1}, which had a lower amplitude than those observed in this study. Rogeri et al. (2016) working with soils from Rio Grande do Sul region, obtained values of P-rem from 17.6 to 47.5 mg L^{-1}.

The values for MPAC (Table 2) according to the Langmuir model ranged from 0.2793 to 0.3954 mg g^{-1} soil. For the RY soil, which adsorbed the greatest amount of P (0.3954 mg g^{-1} soil), giving it a greater degree of soil weathering, possibly due to the higher content of clay, Ca and MO, this adsorption can be classified as very high according to the criteria established by Alvarez et al. (2000). The clay fraction is the most active portion of this phenomenon due to its high specific surface area (Ranno et al., 2007). This occurs because of the greater density of Lewis acid sites (Novais and Smyth, 1999) in the colloids on the soil's surface.

Based on the determination coefficients, it was observed that the Langmuir model was more efficient than the Freundlich in determining the MPAC in the soils, although there was variation in the k values (0.014 to 0.020) and the n values were higher than one in all of the soils, characterized with large amounts of active sites (Sposito, 1989) (Table 2). This amount of adsorbed P is consistent with the value obtained for the P-rem in RY (27.34 mg L^{-1}), characterized as a soil with a great capacity to adsorb P. This result is largely due to the granulometric and mineralogical constituents of the soil, which had the highest clay content among the soils, although the main constituent mineral, kaolinite, was one of the main factors that contribute to the adsorption of P, due to the 1:1 mineralogical structure, compared with the oxidized components, so was the predominant clay content.

Some authors consider that the clay content is mainly responsible for variations in soil PMC (Moughli et al., 1993; Vilar et al., 2010; Oliveira, 2015) it is common to find a significant positive correlation between soil clay contents and MPAC in the literature. There was a wide variation in values for energy of adsorption (a) for the four soils. Although RY had a high adsorption of P, this soil had a lower binding energy (0.2078 mg L^{-1}) between phosphate ions and soil colloids; thus, it may be inferred that despite the high value of MPAC, P is adsorbed by a relatively low binding energy and may become available to plants more easily (Table 2). A similar behavior was observed for the value of the maximum adsorption capacity of phosphorus (FCPm) in this same soil, with the second highest value, which is characterized as a soil that is highly resistant factor in its intensity, since the greater the value of FCPm in the soil, the greater the resistance to change in factor intensity (I), either by the addition or removal of P.

For the two cambisoils (CXbe and CXve), the MPAC values were very close to one another, 0.2975 mg g^{-1} soil for CXbe and 0.2934 mg g^{-1} soil for CXve in the Langmuir model, despite having a wide divergence in Prem values. However, the Freundlich model was more efficient for quantifying the P adsorbed to CXve and CXbe, with k values of 0.020 and 0.014, respectively, and n values greater than one, showing a high number of active sites of adsorption. Although these soils present almost the same value for MPAC, they have significantly different levels of clay; CXbe presented the highest P content (254.9 g kg^{-1}), with CXve lagging behind with 125.4 g kg^{-1} (Table 2). According to Novais and Smyth (1999), the clay fraction is the most active contributor to this phenomenon because of its high specific surface area, due to the higher density of Lewis acid sites on the surfaces of colloids.

Different values were also observed for adsorption energies of P in the two FCPm cambisoils. The higher energy of adsorption was observed for CXve (0.3348 mg L^{-1}) and the lower in CXbe (0.2523 mg L^{-1}), demonstrating a behavior contrary to the values of MPAC for these soils. This behavior is directly related to the fact that the amount of goethite in CXve is greater than in CXbe, even with this greater amount of adsorbed P (Table 2). These results approach those found by Moreira et al. (2006) in four soils (Typic, Acrisol, and Regolíticos Typic Oxisol) from different regions of Ceará State in Brasil, with MPAC values ranging from 0.1099 to 0.3448 mg g^{-1} soil.

The value of MPAC has been used on the recommendation of P. However, according to Novais and Kamprath (1979), using just MPAC to predict the amount of soil P for plant growth is insufficient, since other factors, intensity and capacity, are required in the process of predicting the responses of plants to fertilization. According to Novais and Smyth (1999), the need for more extensive measurements (amount adsorbed) and other intensive factors (quality of adsorption), called FCPm (MPAC × adsorption energy), may become clearer, with MPAC tending to a constant and adsorption energy varying with the status of P in the soil.

Among the soils, TCO had the smallest amount of adsorbed P (0.2793 mg g^{-1} soil) by the Langmuir model; however, it had the second highest value for the binding energy of P (0.2843 L mg^{-1}) (Table 2). This smaller amount of adsorbed P can be directly related to the amount of clay present in the soil (135.6 g kg^{-1}) among the more sandy soils, and the low content of organic matter in the soil (Table 2). According to Fink et al. (2016), the role of organic matter is ambivalent, since it can adsorb P as well as block the adsorption sites that occur on the surfaces of clays and oxides of iron and aluminum. However, this high value for the binding energy can be related to the presence of goethite in the mineralogical composition of the soil, causing the phosphate ions to become more strongly adsorbed to soil colloids.

The Freundlich isotherm parameters were less efficient in quantifying P than the Langmuir, with 0.018 for the k value and 1.155 for the n value (Table 2). The Fe and Al oxides are taken as constituents of the clay fraction, and as more effective for P adsorption (Fink et al., 2016), with goethite being considered the main component of the clay fraction responsible for this phenomenon in the soils of Central Brazil (Fink et al., 2016). The higher P adsorption capacity of soils in relation to their hematite Goethite content was also found by Curi and Franzmeier (1984) and can be credited, according to Frossard et al. (1994), to the differences in accessibility of the surface phosphate OH^- groups. By affecting the extent of the mineral's reactive surface, the morphology of the iron oxide crystals also influences P adsorption (Camargo et al., 2015).

Conclusions

The values of maximum adsorption capacity for phosphorus (MPAC) in the soils ranged from 0.2793 to 0.3954 mg g^{-1}, with a positive correlation between MPAC and the clay content.

The Langmuir isotherm was more efficient in determining the MPAC of the soil compared to the Freundlich isotherm. Also, P adsorption parameters (MPAC, Prem, and the constant k of the Freundlich equation) are reliable variables to characterize phosphorus adsorption.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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