PHOSPHORUS SORPTION ISOTHERMS IN SOILS OF THE SEMIARID REGION OF BRAZIL

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ABSTRACT - The soils of the Semiarid region of Brazil lack studies regarding sorption processes and availability of phosphorus (P). Therefore, the objective of this work was to quantify the sorption of P in ten soils representative of the Semiarid region of Brazil and correlate them with the soil phosphorus storage capacity. The P concentrations in the equilibrium solutions used to model the sorption isotherms were: 0, 5, 10, 15, 20, 30, 40, 55, 70, and 80 mg L\(^{-1}\) for the soils Typic Quartzipsamment (Neossolo Quartzarenico), Typic Hapludox (Latossolo Vermelho Amarelo), Typic Hapludult (Argissolo Vermelho Amarelo), Typic Quartzipsamment (Neossolo Flúvico), and Typic Dystrudept (Cambissolo Haplico); and 0, 10, 15, 25, 40, 55, 80, 100, 130, and 150 mg L\(^{-1}\) for the soils Typic Calciudolls (Chernossolo Rendzico), Typic Dystrudept (Cambissolo Haplico), Typic Dystrudept (Cambissolo Haplico), Typic Hapludult (Argissolo Vermelho Amarelo), and Typic Hapludult (Vertissolo Haplico). The Langmuir and Freundlich sorption isotherms were fitted to non-linear regression models and the values of the model parameters were estimated. The sorption isotherms were adequate to quantify the sorption of P in the soils of the Semiarid region of Brazil, with maximum P sorption capacity varying from 50.4 mg kg\(^{-1}\) to 883.5 mg kg\(^{-1}\). The sorption of P was higher in soils with more clayey textures, alkaline, and rich in iron and calcium, denoting the importance of evaluating the effect of these characteristics on the sorption of P in these soils.

Keywords: Precipitation. Adsorption. Soil phosphorus storage capacity.

ISOTERMAS DE SORÇÃO DE FÓSFORO EM SOLOS DO SEMIÁRIDO

RESUMO - Os solos do semiárido brasileiro ainda não foram suficientemente estudados quanto aos processos de sorção e de disponibilidade de fósforo (P). Nesse sentido objetivou-se com este trabalho quantificar a sorção de P em dez solos representativos da região semiárida e correlacioná-las com o Fator Capacidade de Fósforo do Solo (FCP). As concentrações de P das soluções de equilíbrio utilizadas para o ajuste dessas isoteremas corresponderam a 0; 5; 10; 15; 20; 30; 40; 55; 70 e 80 mg L\(^{-1}\) de P para os solos Neossolo Quartzarenico (Entisol), Latossolo Vermelho Amarelo (Oxisol), Argissolo Vermelho Amarelo (Ultisol), Neossolo Flúvico (Entisol) e Cambissolo Háplico (Inceptisol); e a 0; 10; 15; 25; 40; 55; 80; 100; 130 e 150 mg L\(^{-1}\) de P para os solos Chernossolo Rêndzico (Mollisol), Cambissolo Háplico (Inceptisol), Cambissolo Háplico (Inceptisol), Argissolo Vermelho Amarelo (Ultisol) e Vertissolo Háplico (Vertisol). As isoteremas de Langmuir e de Freundlich foram ajustadas por meio da técnica de regressão não-linear e estimados os valores dos parâmetros desses modelos. As isoteremas mostraram-se adequadas para quantificar a sorção de P nos solos do semiárido, com valores de capacidade máxima de sorção de P (CMSP) variando de 50,4 mg kg\(^{-1}\) a 883,5 mg kg\(^{-1}\). O P foi servido em maior quantidade nos solos mais argilosos, alcalinos e ricos em ferro e cálcio, evidenciando a importância da avaliação dessas características na sorção de P nesses solos.

Palavras-chave: Precipitação. Adsorção. Fator capacidade de P.
INTRODUCTION

The sorption of phosphorus (P) in soils is the main cause of low efficiency of applications of P fertilizers, since most P fertilizers applied are usually sorbed to the soil and a small part are available to plants (NOVAIS; SMITH, 1999).

Several regression models for description and quantifying of P sorption in soils have been used in studies about P sorption processes, and the Langmuir and Freundlich sorption isotherms stand out among these models (COSTA et al., 2014; HADGU et al., 2014; TAMUNGANG et al., 2016; BRITO NETO et al., 2018).

The use of Langmuir and Freundlich sorption isotherms enables the evaluation of effects of several soil characteristics on the sorption of P in soils (SIMS; PIERZYNSKI, 2005). These effects have been found mainly for maximum P sorption capacity (MPSC), clay contents, remaining P (P-rem), iron and aluminum oxide contents, pH, organic matter contents, and exchangeable aluminum contents (HADGU et al., 2014; ALBUQUERQUE et al., 2016; SANTOS et al., 2016; TAMUNGANG et al., 2016; ARRUDA et al., 2017; BRITO NETO et al., 2018; SANTOS et al., 2018; TEIXEIRA; SOUSA; VALE, 2018). The Soil Phosphorus Storage Capacity (SPSC) denotes the soil capacity to retain P in the solution; P-rem and MPSC are the most determinant characteristics of the SPSC (BROGGI et al., 2011).

Despite the importance of studies about sorption of P, most studies in Brazil have not considered soils of the Semiarid region. Moreover, little information is found about this process in these soils, such as the studies of Godinho et al. (1997), Moreira et al. (2006), and Bezerra et al. (2013), who evaluated soils in the sates of Rio Grande do Norte and two soils were from sediments of the Barreiras Group: one Typic Hapludult (Argissolo Vermelho Amarelo) in Mossoró, RN (AVM; 05° 25’26.4°S; 037°11’19.9°W); and one Typic Hapludult (Argissolo Vermelho Amarelo) in Mossoró, RN (VHM; 05° 25’26.4°S; 037°12’26°W); one soil was from alluvial sediments: Typic Quartzipsamment (Neossolo Flávio) in Carnaubais, RN (NFC; 05°22’33.2°S; 036°50’42.2°W); one soil was from arenite: Typic Quartzipsamment (Neossolo Quartzarênico) in Russas, CE (NQR; 05°01’58.3°S; 038°07’12.7°W); and two soils were from sediments of the Barreiras Group: one Typic Hapludult (Argissolo Vermelho Amarelo) in Mossoró, RN (AVM; 05°09’58.5°S; 037°11’57.6°W); and one Typic Hapludox (Latossolo Vermelho Amarelo) in Mossoró, RN (LVM; 04° 56’13.8°S; 037°27’30.0°W) (BRASIL, 1971).

The soil samples were air dried, crushed, sieved to obtain the bulk soil, and characterized for chemical and physical attributes, according to Teixeira et al. (2017) (Table 1). The remaining P (P-rem) was analyzed according to Alvarez V. et al. (2000), by shaking the soil samples with a CaCl₂ 0.01 mol L⁻¹ solution and 60 mg L⁻¹ of P for five minutes, and leaving it to rest for decantation for 16 hours. The P contents in the extract was then quantified by molecular absorption spectrophotometry (BRAGA; DEFEILPO, 1974).

The Langmuir and Freundlich sorption isotherms were modeled according to Farias et al. (2009) and Alvarez V. et al. (2000). The P concentrations in the equilibrium solutions used to model the sorption isotherms were: 0, 5, 10, 15, 20, 30, 40, 55, 70, and 80 mg L⁻¹ for the soils Typic Quartzipsamment (Neossolo Quartzarenico), Typic Hapludox (Latossolo Vermelho Amarelo), Typic Hapludult (Argissolo Vermelho Amarelo), Typic Quartzipsamment (Neossolo Flávio), and Typic Dystrudept (Cambissolo Haplico); and 0, 10, 15, 25, 40, 55, 80, 100, 130, and 150 mg L⁻¹ for the soils Typic Calciudolls (Chernossolo Rendzico), Typic Dystrudept (Cambissolo Haplico), Typic Dystrudept (Cambissolo Haplico), Typic Hapludult (Argissolo Vermelho Amarelo), and Typic Hapludult (Vertissolo Haplico).

An aliquot of 2.5 cm³ of each soil sample was weighed and added to 125-mL Erlenmeyer flasks; 25 mL of a CaCl₂ 0.01 mol L⁻¹ solution containing P, according to each concentration, was then added. The flasks were horizontally shaken for 24 hours and the suspensions were filtered in qualitative filter paper. The P contents in the equilibrium solution (supernatant) was quantified by colorimetry.

MATERIAL AND METHODS

The sorption of phosphorus (P) was evaluated in samples of the 0-0.30 m layer of ten non-cultivated soils representative of the Semiarid region of Brazil at the Piranhas-Âçu (RN) and Jaguariibe (CE) River Valleys and correlate them with the SPSC.

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The Langmuir sorption isotherm of each soil was fitted to non-linear regression models (single region), which showed to be the best linearization technique (FARIAS et al., 2009), according to Equation 1:

\[ Q = \frac{(abC)}{(1 + aC)} \]  

where:
- \( Q \) = quantity of P sorbed in the soil,
- \( C \) = concentration of P in the equilibrium solution,
- \( a \) = constant of the model that estimates the binding energy of P to the soil, and
- \( b \) = constant of the model, whose estimate is the soil maximum P sorption capacity (MPSC).

This technique was also used for the model of the Freundlich sorption isotherm, using Equation 2:

\[ Q = kC^n \]  

where:
- \( Q \) = quantity of P sorbed in the soil,
- \( C \) = concentration of P in the equilibrium solution,
- \( k \) and \( n \) = constants of the model related to soil capacity to sorb P from the equilibrium solution.

The parameters of the models fitting the two P sorption isotherms were estimated and correlation analyses were carried out for the values of these parameters and for clay contents, MPSC, and P-rem.

### RESULTS AND DISCUSSION

The high coefficients of correlation between the data estimated by hyperbolical model of Langmuir and the observed data varied from 0.9634 to 0.9867 (Figures 1 and 2). This result indicates that this model adequately describes the sorption of phosphorus (P) in the soils studied, as found by CHAVES et al. (2009), FARIAS et al. (2009), CORRÊA, NASCIMENTO and ROCHA (2011), and HADGU et al. (2014).
Figure 1. Langmuir sorption isotherm for data of quantity of P sorbed in different soils.

NQR = Typic Quartzipsamment (Neossolo Quartzarênico); LVM = Typic Hapludox (Latossolo Vermelho Amarelo); AVM = Typic Hapludult (Argissolo Vermelho Amarelo); NFC = Typic Quartzipsamment (Neossolo Flúvico); CHA = Typic Dystrudept (Cambissolo Haplico); CHB = Typic Dystrudept (Cambissolo Haplico)
The sorption of P increased as the concentration of P in the equilibrium solution was increased in all soils studied. However, after reach the equilibrium of chemical reactions, this increase stopped, enabling the estimation of the maximum P sorption capacity (MPSC) by fitting the data to the Langmuir sorption isotherm (Figures 1 and 2, and Table 2).

This dynamic was also found by Godinho et al. (1997), Chaves et al. (2009), Pinto et al. (2013), and Rossi, Rollán and Bachmeier (2016), since the sorption of P decreases as the P adsorption sites in the soil colloids are saturated and the Al\(^{3+}\), Fe\(^{3+}\), and Ca\(^{2+}\) activities in the soil solution decrease due to the precipitation of these cations combined with P. Therefore, the P sorption stops because of increases in P concentration in the equilibrium solution (HADGU et al., 2014).

The MPSC varied from 50.40 mg kg\(^{-1}\) in the NQR to 883.45 mg kg\(^{-1}\) in the CHQ, which enables the distinguishing of three group of soils: NQR, LVM, AVM, and NFC, with low MPSC (mean of 78.9 mg kg\(^{-1}\)); CHA, CHB, and AVA, with intermediate MPSC (mean of 424.5 mg kg\(^{-1}\)); and CRM, CHQ, and VHM, with high MPSC (mean of 845.5 mg kg\(^{-1}\)).
The MPSC results found (Table 2) were similar to those found by Corrêa, Nascimento and Rocha (2011) for ten soils of the state of Pernambuco, Brazil (37.04 to 904.13 mg kg\(^{-1}\)), but they were higher than those found by Farias et al. (2009) for twelve soils of the state of Paraíba, Brazil (36.0 mg kg\(^{-1}\) to 435.3 mg kg\(^{-1}\)).

Table 2. Estimates of parameters of Langmuir and Freundlich sorption isotherms for ten soils of the Semiarid region of Brazil.

| Soil    | Langmuir sorption isotherm | Freundlich sorption isotherm |
|---------|---------------------------|-----------------------------|
|         | MPSCa \(k\) \(n\)        | \(a\) \(k\) \(n\)          |
| NQR     | 50.4016 \(1.6799\) \(32.2002\) \(8.0169\) |                     |
| LVM     | 87.2600 \(1.6620\) \(51.7796\) \(7.0150\) |                     |
| AVM     | 100.8756 \(1.1825\) \(61.3122\) \(6.2908\) |                     |
| NFC     | 77.4201 \(0.5662\) \(39.5007\) \(6.0314\) |                     |
| Mean    | 78.9893 \(1.2727\) \(46.1982\) \(6.8385\) |                     |
| CHA     | 383.3451 \(0.6750\) \(153.6844\) \(3.5894\) |                     |
| CHB     | 435.6351 \(0.2415\) \(144.1645\) \(3.8662\) |                     |
| AVA     | 454.3834 \(0.3286\) \(153.4291\) \(3.3355\) |                     |
| Mean    | 424.4545 \(0.4150\) \(150.4260\) \(3.5970\) |                     |
| CRM     | 879.4527 \(0.3277\) \(292.9840\) \(3.4277\) |                     |
| CHQ     | 883.4568 \(1.0791\) \(405.9710\) \(4.1263\) |                     |
| VHM     | 773.5344 \(0.2140\) \(225.9578\) \(3.3113\) |                     |
| Mean    | 845.4813 \(0.5403\) \(308.3043\) \(3.6218\) |                     |

NQR = Typic Quartzipsamment (Neosolo Quartzarênico) in Russas (CE); LVM = Typic Hapludox (Latozossolo Vermelho Amarelo) in Mossoró (RN); AVM = Typic Hapludult (Argissolo Vermelho Amarelo) in Mossoró (RN); NFC = Typic Quartzipsamment (Neosolo Flávico) in Carnaubais (RN); CHA = Typic Dystrudept (Cambissolo Haplico) in Afonso Bezerra (RN); CRM = Typic Calciudolls (Chernossolo Rendzico) in Mossoró (RN); CHB = Typic Dystrudept (Cambissolo Haplico) in Baraúna (RN); CHQ = Typic Dystrudept (Cambissolo Haplico) in Quixeré (CE); AVA = Typic Hapludult (Argissolo Vermelho Amarelo) in Apodi (RN); VHM = Typic Hapludert (Vertissolo Haplico) in Mossoró (RN); MPSC = maximum P sorption capacity; \(a\) = binding energy of P to the soil; \(k\) and \(n\) = constants of the model related to soil capacity to sorb the P from the equilibrium solution.

The variations found in the present work denote the large diversity of soil physical, chemical, and mineralogical characteristics of the Semiarid region of Brazil, mainly due to clay, Ca\(^{2+}\), Al\(^{3+}\), and Fe\(^{3+}\) contents in the soil solution, pH, and mineralogy of the clay fraction (contents of kaolinite and iron and aluminum oxides), which affect the P adsorption and precipitation in soils.

The high coefficients of correlation between the data estimated by the Freundlich model and the observed data varied from 0.8673 to 0.9899 (Figures 3 and 4), denoting that this model was also able to adequately describe P sorption in the soils studied. The values found for the constant \(k\) of the Freundlich model (Table 2) also enabled the formation of three groups of soils: NQR, LVM, AVM, and NFC, with low P sorption capacity; CHA, CHB, and AVA, with intermediate; and CRM, CHQ, and VHM, with high P sorption capacity.

The main soil characteristics related to soil phosphorus storage capacity (SPSC) estimated by the sorption isotherms (MPSC and \(k\)) presented high correlations to P-rem (\(r = -0.949**\) for MPSC; \(r = -0.902**\) for \(k\)) and clay (\(r = 0.915**\) for MPSC; \(r = 0.820**\) for \(k\)) (Table 3). In addition, the correlation between MPSC and \(k\) was also high (\(r = 0.954**\)). This indicates that the clay contents and P-rem are good estimators of SPSC, and both can be used for interpretation of P contents (Mehlich-1) and recommendation of soil P fertilizers for crops grown in these soils.

However, although the coefficient of correlation between clay and P-rem was good (\(r = -0.841**\) (Table 3), the comparison between some soils showed that P-rem is a better estimator of SPSC than clay contents. This was found for the comparison between the CHQ and AVA; although these soils had practically the same clay contents (Table 1), the MPSC of the CHQ (883.5 mg kg\(^{-1}\)) was practically 2-fold that of the AVA (455.5 mg kg\(^{-1}\)) (Table 2). The difference in MPSC between CHQ and AVA is not explained by the difference between clay contents, but is clearly shown by the P-rem and Fe\(_2\)O\(_3\) contents of these soils; the P-rem and Fe\(_2\)O\(_3\) contents were 11.6 mg L\(^{-1}\) and 121.39 g kg\(^{-1}\) for CHQ, and 25.9 mg L\(^{-1}\) and 44.12 g kg\(^{-1}\) for AVA, respectively (Table 1), denoting the importance of iron oxides for the P adsorption in these soils.
Figure 3. Freundlich sorption isotherm for data of quantity of P sorbed in different soils.

NQR = Typic Quartzipsamment (Neossolo Quartzarênico); LVM = Typic Hapludox (Latossolo Vermelho Amarelo); AVM = Typic Hapludult (Argissolo Vermelho Amarelo); NFC = Typic Quartzipsamment (Neossolo Flúvico); CHA = Typic Dystrudept (Cambissolo Haplico); CHB = Typic Dystrudept (Cambissolo Haplico)
CRM = Typic Calciudolls (Chernossolo Rendzico); CHQ = Typic Dystrudept (Cambissolo Haplico); AVA = Typic Hapludult (Argissolo Vermelho Amarelo); VHM = Typic Hapludert (Vertissolo Haplico)

**Figure 4.** Freundlich sorption isotherm for data of quantity of P sorbed in different soils.

**Table 3.** Coefficients of simple linear correlation between parameters of the Langmuir and Freundlich sorption isotherms and soil characteristics that denote the phosphorus storage capacity of ten soils in the Semiarid region of Brazil.

|            | MPSC (2) | a      | k      | n      | Clay |
|------------|----------|--------|--------|--------|------|
| P-rem      | -0.949** | 0.677  | -0.902** | 0.916** | -0.841** |
| Clay       | 0.915**  | -0.632** | 0.820*  | -0.765** | - |
| n          | -0.807** | -      | -      | -      | - |
| k          | 0.954*   | -      | -      | -      | - |
| a          | -0.563*  | -      | -      | -      | - |

* = significant at 5%; ** = significant at 1%; ns = not significant; constants of the Langmuir sorption isotherm: MPSC = maximum P sorption capacity, and a = binding energy of P to the soil; k and n = constants of the Freundlich model related to soil capacity to sorb the P from the equilibrium solution.
The P-rem (Table 1) and MPSC (Table 2) found denote that the SPSC of these soils has high variation. CHQ, for example, present a MPSC 17.5-fold that of NQR, which had the lowest SPSC. The highest MPSC values were found in CRM, CHQ, and VHM (Table 2), which presented high pH, and Fe$_2$O$_3$, Ca$^{2+}$, and clay contents (Table 1).

Mota, Assis Júnior and Amaro Filho (2004) evaluated the mineralogy of a Typic Dystrudept (Cambissolo Haplico) in Chapada of Apodi, RN, Brazil, and found higher iron and aluminum oxide contents than those found in a Typic Hapludox (Latossolo) and a Typic Hapludult (Argissolo) in this same region. Moreover, Moreira et al. (2006) evaluated the sorption of P in four soils of Ceará, Brazil, and found higher sorption of P in a Typic Dystrudept (Cambissolo Háplico); they attributed this result to the interaction between several factors, including the high total iron contents and free and amorphous iron oxides in this soil. These minerals are probably the main responsible for the high MPSC of soils (SANTOS et al., 2011).

The P-rem denotes not only the soil chemical and physical characteristics that affect the sorption of P, but also mineralogical characteristics; the minerals of the clay fraction of CHQ probably had higher P sorption capacity than those of AVA. Moreira et al. (2006) and Broggi et al. (2011) found no trend of higher sorption of P in soils with higher clay contents, denoting the greater importance of the mineralogy of the clay fraction for the MPSC, when compared to clay contents.

The four sandy soils (NQR, LVM, AVM, and NFC) presented the lowest MPSC (Table 2), which is probably related to the low clay contents and high P-rem of these soils (Table 1). The sorption of P in sandy soils is lower because of the low quantity of mineral colloids that can adsorb P (SIMS; PIERZYNSKI, 2005).

The results found are consistent with those obtained by Arruda et al. (2017), who evaluated six soils and found higher P-rem in the most clayey soils. Similarly, Chaves et al. (2009) found higher MPSC in more clayey soils; and Jalali and Jalali (2016) found that limestone soils in Iran presented differences in P contents (extracted by different methods) and indicated a strong effect of soil texture on the sorption of P, presenting a lower SPSC in more sandy soils and a higher SPSC in clayey soils.

A high clay content does not always mean high sorption of P; however, the positive correlation found for clay contents and MPSC ($r = 0.915**$) denotes the importance of this granulometric fraction for the explanation of P sorption processes in the soil. Moreover, the most clayey soils were, in general, those with higher sorption of P (Tables 1 and 2). This positive correlation between sorption of P and clay contents is related to the large surface area of clays when compared to sand and to a larger number of positive charges that react and strongly connect to negatively charged phosphate ions in the soil solution (HADGU et al., 2014).

Farias et al. (2009) evaluated two soils groups in the state of Paraíba, Brazil, and found significant high correlation between MPSC and clay for a group of six less weathered soils, but found no significant correlation between MPSC and clay for a group of six more weathered soils. They attributed this result to the effect of the mineralogy of the clay fraction on the sorption of P, mainly in more weathered soils.

Corrêa, Nascimento and Rocha (2011) evaluated soils in the state of Pernambuco, Brazil, and found positive and significant correlation between MPSC and clay contents; they reported that clay content and attributes can estimate the MPSC, and the clay type is important because of a large MPSC variation resulted from different clays in soils. The use of only one soil attribute, such as clay contents, as a criterion to recommend P fertilizers may result in errors, and the P-rem may be used, since it is a more reliable measure of SPSC (PINTO et al., 2013; ROGERI et al., 2016).

The correlations found between the constant $a$ related to the energy of sorption of P and P-rem ($r = 0.677*$) and clay contents ($r = -0.632**$) were statistically significant, but low ($r < 0.700$). Thus, the binding energy of P to these soils is not surely lower in more clayey soils or in those that have lower P-rem.

The sorption of P was higher in soils with more clayey textures, alkaline, and rich in Ca$^{2+}$ and Fe$_2$O$_3$, such as the soils CHQ, AVA, and VHM. In these soils, the adsorption of P to the mineral colloidal surfaces are probably as important as the precipitation of P bound to Ca$^{2+}$, which has not the same energy of the P bound to iron and aluminum oxides, and can be used by plants, as reported by Santos et al. (2011).

Chaves et al. (2009) evaluated two soils of the Semiariad region of Brazil and found that the energy of adsorption of P was higher in the soil with lower clay contents. In addition, Matos et al. (2017) evaluated the sorption of P in soils of the Brazilian Amazon region and found that the binding energy of P to active sites decreases by being repelled by negative charges of clays. According to Novais and Smith (1999), it is not clear whether the P binding energy estimated by the Langmuir sorption isotherm can be a measure of the energy of P retention in the soil. In this context, Farias et al. (2009) and Chaves et al. (2009) evaluated soils of the Semiariad region of Brazil and found no correlation between soil clay content and the binding energy estimated by the Langmuir sorption isotherm.
CONCLUSIONS

The sorption of phosphorus (P) was higher in soils with more clayey texture, alkaline, and rich in iron and calcium.

The clay contents and P-rem in the soils studied were correlated with the maximum P sorption capacity of soils, but P-rem was superior to clay contents regarding the estimation of maximum P sorption capacity of the soils.

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