Assessing Soil Edaphic Properties' influence in Phosphorus Adsorption in Vertisols - Extremadura (Spain)

L. Loures, J. Nunes, A. López-Piñeiro, A. Loures and A. Navarro

Abstract*—** Vertisols are soils rich in clay that are traditionally seen as one of the most fertile soils of Extremadura in Spain and as an important feature of rainfed agriculture, in which Phosphorus (P) constitutes the main limiting factor of crop nutrition, and its availability is a critical issue in the agricultural use of these soils. In this regard sorption prediction throughout soil properties constitutes an important factor for understanding fertilizer-P behavior in soils over time, and it serves as a guide for determining the amount of P available to plants and the effectiveness of P fertilizers. In tis regard the adsorption exerted by different components of the soil in the edaphic P is of vital importance, since it can serve as a guide for determining the amount of available P in the short and long term for plants and can even lead to more effective fertilization with this element. The present research investigates Phosphate sorption in surface-samples of nineteen Vertisols in Extremadura (Spain) using uniform-surface and two-surface Langmuir equations, which constitute important tools for estimating the availability of phosphorus and to adjust the concentration of phosphorus in the soil solution, determining the amount of phosphorus adsorbed per mass unit, as well as the constant related to the adsorption energy. The present research enabled us to conclude that phosphate sorption maxima (PAM) deduced from the uniform-surface Langmuir equation ranged from 150 to 2566 mg P kg-1, with a mean value of 1115 mg P kg-1. The calculated sorption maxima (TPAM) for the two-surface Langmuir model ranged from 410 to 15406 mg P kg-1 and the mean value (3845 mg P kg-1) increased about 3 times compared to the basic Langmuir equation. The two surface Langmuir model fit the sorption data better than the uniform layer model. Therefore, an underestimation of the P-sorption was observed when the traditional Langmuir equation was used. Total surface area was highly correlated with sorption maxima: r= 0.700 for PAM and 0.900*** for TPAM. The prediction of the PAM and TPAM was improved by combining all or several of following soil properties: Fed, ACCE, clay, and total surface area in a multiple-regression analysis. The equations obtained could offer a rapid estimation of P-sorption in Vertisols.

***Keywords*—** Adsorption Capability, Extremadura, Phosphorus, Soil Properties, Vertisols

I. INTRODUCTION

AGRICULTURAL landscapes are continuously changing as a result of complex and interacting natural processes coupled with planned and unplanned actions by man [1, 2, 3, 4 and 5]. However, this on-going transformation has raised global concerns as is the need to rethink rain-fed agricultural practices in order to protect the environment, and the Extremadura region (fig 1), located in southwestern Spain, in which Vertisols represent an important resource for rain-fed agriculture, is no exception.

Fig 1 – Geographic location of the Spanish Extremadura – adapted from Google images

Vertisols are traditionally seen as one of the most fertile soils of Extremadura in Spain and an important feature of rain-fed agriculture. Vertisols are soils rich in clay, generally found in Spain, in the provinces of Andalusia and Extremadura. In the first region there are typically darker Vertisols (Chroma <2) and in the second one they have a more brown color (Chroma> 2) (fig. 2 and 3). The color contrast is due to the organic matter content, which is always very low. The reasons for this darker tone are the complexation of colloids and

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organic smectites and the presence of finely divided oxide of manganese. The brown color is due to the low levels of montemorionite, the high content of well-drained iron oxyhydroxides or to a combination of all these characteristics. Vertisols are difficult soils to manage due to its high clay content, but have high natural fertility and appear especially in regions of smooth topography. They are therefore able to withstand the changes in a culture system based on the requirements of the market [6].

These characteristics correspond to the main edaphic ones, one can find in the Vertisols in the region of Spanish Extremadura, as reported by several authors [7, 8, 9, 10, 11, 12 and 13]. Vertisols are soils which after the 18 cm surface had been mixed, have 30% or more clay in all horizons to a depth of at least 50 cm, that in some periods, of most years (except when watered, open slits, from the surface, at least 1 cm wide, to a depth of 50 cm. These soils are very rich in terms of nutrients, in neutral to slightly alkaline pH and possess a high water retention capacity. They present generally high chemical fertility, but are very heavy and have poor aeration.

Fig 2 – Example of the appearance of a dark Vertisol. Source: Vertisol atlas nacional de espanha.

Fig 3 – Example of the appearance of a red Vertisol. Source: Vertisol atlas nacional de espanha.

These soils are characterized by having a high plasticity, being hard and very difficult to work when dry (fig 4). Despite their high water retention capacity, they present a water loss greater than would be predictable on the basis of the potential evaporation zone where they are implanted. This is due to the formation of cracks which increase greatly the surface through which water may be lost.

Among the most common in the Spanish Extremadura Vertisols, we have the following: Luvic Vertisol - it is said that a soil possesses luvic characteristics when B has a horizon with a cation exchange capacity greater than 24 cmol (+) 1 kg of clay in its entire thickness and degree of saturation with bases (method of ammonium acetate) of 50% or more on the whole horizon, to a depth of 100 cm from the ground surface. Calcic Vertisol - These are Vertisols with calcic horizon or concentrations of white limestone powder depth less than 125 cm.

Fig 4 – Appearance of a dryed Vertisols (Chroma >2) Source: Vertisol atlas nacional de espanha.

In this type of soil, phosphorus is the main limiting factor of crop nutrition, and its availability is a critical issue in the agricultural use of these soils [14]. The adsorption exerted by different components of the soil in the edaphic P is of vital importance, since it can serve as a guide for determining the amount of available P in the short and long term for plants and can even lead to more effective fertilization with this element [15, 16].

In this sense, the Langmuir adsorption isotherms are converted into important tools for estimating the availability of phosphorus and to adjust the concentration of phosphorus in the soil solution, to determine the amount of phosphorus adsorbed per unit mass, as well as the constant related to the adsorption energy [17].

Previous studies [18, 19] have revealed that both Fe and Al extracted by dithionite-citrate-bicarbonate (Fe-Al-CBD) are the parameters that best predict the maximum sorption in soils of Mediterranean climate. By contrast, other researchers conclude that the Fe and Al extracted with oxalate correlated, and therefore better predict, the maximum adsorption of phosphorus that the Fe-Al-CBD and CBD [17, 20].

This paper intents to examine phosphorus adsorption in surface samples from Extremadura Vertisols, comparing the results obtained by applying the Langmuir equation for uniform surfaces and uneven surfaces and to characterize the soil properties that best correlate with the adsorption of phosphorus, establishing the regression equations that allow an accurate prediction of the same.

1.1 General characteristics from typical Vertisols

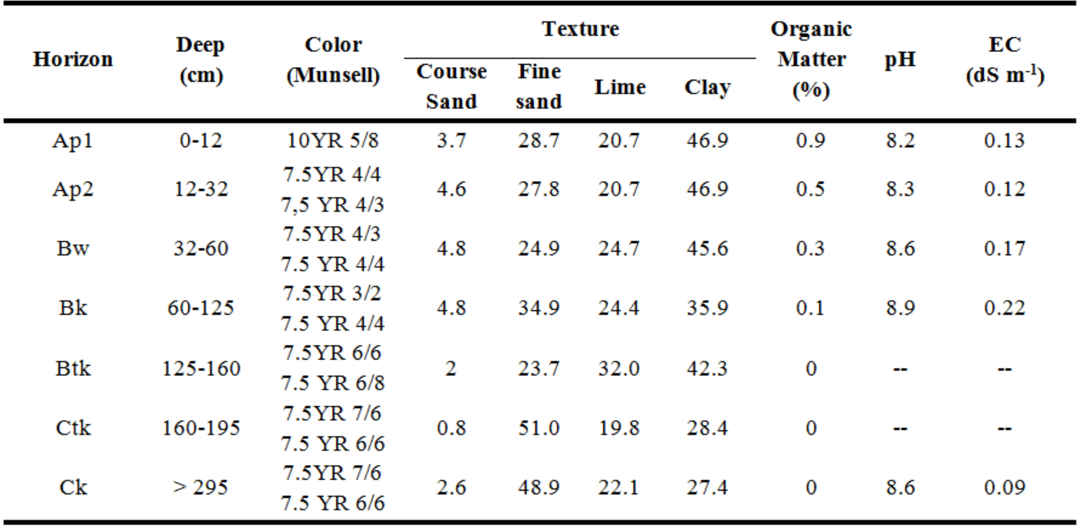
As one can see on table 1 and table 2, typical Vertisols presents some distinctive characteristics from other soil typologies which go beyond the ones mentioned before.

In general this soil has a clay content of approximately 45%, normal values for the region of Extremadura [6 and 21]. The higher clay content appears in upper horizons, where the relationship between Limo and clay is also the lowest. The pH is alkaline and increases with depth, reaching its maximum in the Btk horizon, coinciding with the maximum concentration in carbonates. The cation exchange capacity decreases with depth and the exchangeable cations shows an uneven distribution over the profile. The Mg and Na are mainly in the middle of the soil section, reaching a peak on the horizon Ctk. The Ca / Mg ratio is around 3.5 in the top soil and progressively lowered until it reaches the horizon C about 0.2. The Na percentage in the soil exchange complex is between 8 and 10% in the Ctk and Cc horizons, however, the electrical conductivity indicates that there is no problem of soil salinity [6].

II. MATERIALS AND METHODS

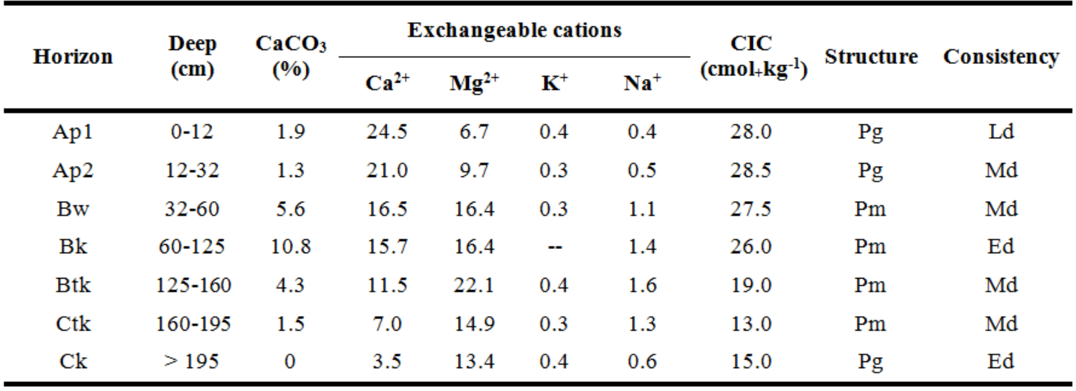
For this study 19 topsoil samples (0-30 cm) were collected, in the province of Badajoz (Extremadura, Spain). These soils

Table 1 - General characteristics from typical Vertisols



Horizon	Deep (cm)	Color (Munsell)	Texture				Organic Matter (%)	pH	EC ($dS\ m^{-1}$)
			Course Sand	Fine sand	Lime	Clay			
Ap1	0-12	10YR 5/8	3.7	28.7	20.7	46.9	0.9	8.2	0.13
Ap2	12-32	7.5YR 4/4 7,5 YR 4/3	4.6	27.8	20.7	46.9	0.5	8.3	0.12
Bw	32-60	7.5YR 4/3 7.5 YR 4/4	4.8	24.9	24.7	45.6	0.3	8.6	0.17
Bk	60-125	7.5YR 3/2 7.5 YR 4/4	4.8	34.9	24.4	35.9	0.1	8.9	0.22
Btk	125-160	7.5YR 6/6 7.5 YR 6/8	2	23.7	32.0	42.3	0	--	--
Ctk	160-195	7.5YR 7/6 7.5 YR 6/6	0.8	51.0	19.8	28.4	0	--	--
Ck	> 295	7.5YR 7/6 7.5 YR 6/6	2.6	48.9	22.1	27.4	0	8.6	0.09

Table 2 - General characteristics from typical Vertisols (cont.)



Horizon	Deep (cm)	$CaCO_3$ (%)	Exchangeable cations				CIC ($cmol_+ kg^{-1}$)	Structure	Consistency
			Ca^{2+}	Mg^{2+}	K^+	Na^+			
Ap1	0-12	1.9	24.5	6.7	0.4	0.4	28.0	Pg	Ld
Ap2	12-32	1.3	21.0	9.7	0.3	0.5	28.5	Pg	Md
Bw	32-60	5.6	16.5	16.4	0.3	1.1	27.5	Pm	Md
Bk	60-125	10.8	15.7	16.4	--	1.4	26.0	Pm	Ed
Btk	125-160	4.3	11.5	22.1	0.4	1.6	19.0	Pm	Md
Ctk	160-195	1.5	7.0	14.9	0.3	1.3	13.0	Pm	Md
Ck	> 195	0	3.5	13.4	0.4	0.6	15.0	Pg	Ed

Pg – Course Prismatic; Pm – Medium Prismatic; Ld – Slightly hard; Md – Very hard; Ed – Extremely hard were classified as Vertisol by FAO (Cromoxeret Entice, y Pelloxeret Cromoxeret Typical). Table 3 is a statistical summary of the main parameters. None of the selected soils were subjected to fertilization during the year preceding the samples collection. The climate of the area is characterized by having an annual rainfall ranging from 487 to 512 mm and an annual medium temperature oscillating between 15.6 and 16.1°C.

2.1 Soil analysis

Particle size analysis: The particle size was determined using the Robinson pipette. Prior were eliminated the organic matter content and the free sesquioxides.

pH: It was determined in a mixture of soil-water with a 1:1 ratio using a combined electrode Organic carbon: It was determined by oxidation with dichromate according to Nelson, and Sommers [22].

Cation exchange capacity: was determined by saturating the soil with NH4OAC 1N at pH 7, then washed this soil with ethanol. The ammoniacal nitrogen was extracted by NaOAC and determined by the Kjeldahl method.

Active calcium carbonate (ACC) was determined by the method of Drouineau [23].Total surface area, was determined using ethylene glycol monoethyl ether following the recommendations of Carter, Heilman and Gonzalez [24].

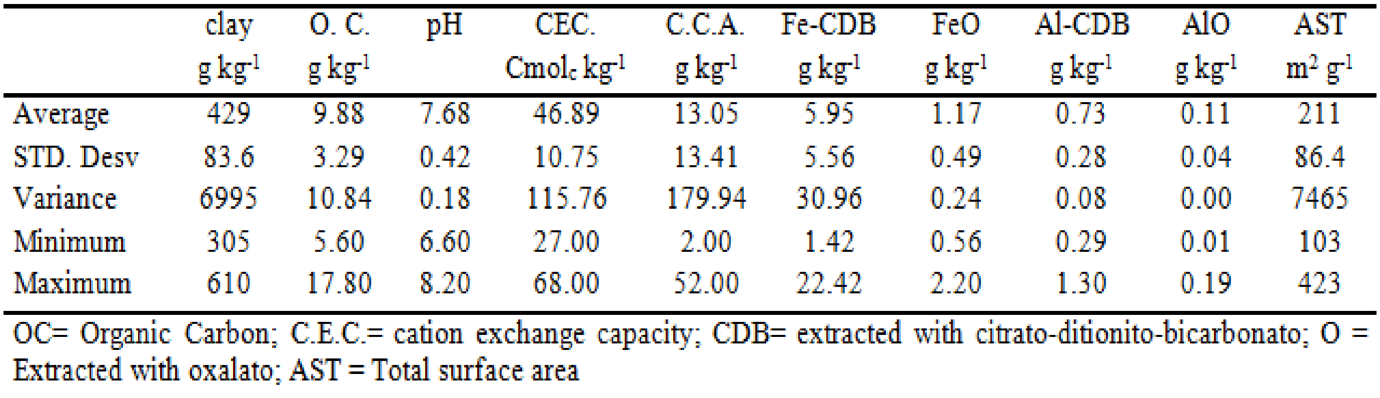
Fe and Al extractable with oxalate, were obtained by extraction with 0.2 M ammonium oxalate at pH 3 [25].

Fe and Al extractable with citrate-bicarbonate-dithionite were determinate according to the methodology proposed by Mehra and Jackson [26].

2.2 Adsorption isotherms

The sorption isotherms were obtained by shaking the samples for 240 hours at a constant temperature of 25° C with a solution of 0.01 M CaCl2 containing different levels of KH2PO4, at a 1:10 ratio. The initial concentrations of P in the solutions were 25, 50, 100, 200, 300, 400 and 500 mgP L-1.

Table 3: Statistic summary for the analysis performed during the study



	clay g kg^{-1}	O. C. g kg^{-1}	pH	CEC. Cmol$_c$ kg^{-1}	C.C.A. g kg^{-1}	Fe-CDB g kg^{-1}	FeO g kg^{-1}	Al-CDB g kg^{-1}	AlO g kg^{-1}	AST m^2 g^{-1}
Average	429	9.88	7.68	46.89	13.05	5.95	1.17	0.73	0.11	211
STD. Desv	83.6	3.29	0.42	10.75	13.41	5.56	0.49	0.28	0.04	86.4
Variance	6995	10.84	0.18	115.76	179.94	30.96	0.24	0.08	0.00	7465
Minimum	305	5.60	6.60	27.00	2.00	1.42	0.56	0.29	0.01	103
Maximum	610	17.80	8.20	68.00	52.00	22.42	2.20	1.30	0.19	423

OC= Organic Carbon; C.E.C.= cation exchange capacity; CDB= extracted with citrato-ditionito-bicarbonato; O = Extracted with oxalato; AST = Total surface area

Three drops of toluene were added to inhibit microbial activity. After shaking the samples, they were centrifuged at 6500 g for 15 minutes and then the phosphorus was determined from the supernatant by the method of [27].

The amount of phosphorus adsorbed was calculated by the difference between initial and final amounts of P in solution. The Langmuir equation [28] was used to determine the adsorption parameters according to the following equation:

$$K.MAP.C = Pa / (1 + K.C)$$

Where Pa is the amount of P adsorbed (mg kg-1), K is a constant related to adsorption energy; MAP is the Langmuir maximum adsorption (mg kg-1) and C is the final concentration of P in balance solution (mg L-1), MAP and K were determined in the graphic representation of C/Pa over C, being the slope equal to 1/MAP and the point of intersection with the Y-axis equal to 1/(MAP.K).

The equation presented above assumes that P is adsorbed on a uniform surface. However and due to the heterogeneous nature of the P adsorption systems, it is expected that more than one parameter acts in the adsorption process. Thus if we assume that P is adsorbed on two different surfaces with different energies, the Langmuir equation that better describe this phenomenon is the equation for two surfaces [17, 29, 30] as the one presented here:

$$Pa = [K'. MAP'.C / (1 + K'. C)] + [K''.MAP''. C / (1 + K''. C)]$$

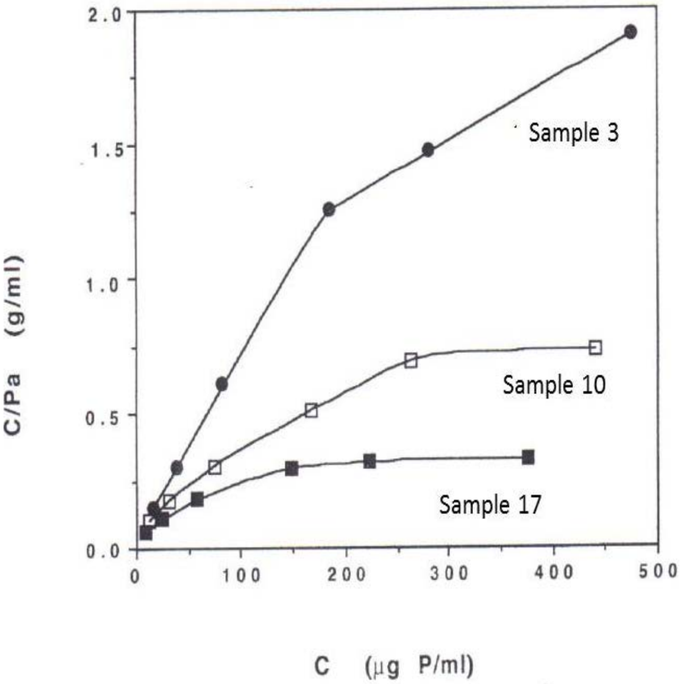
Where k' e K" are the energies for the adsorption sites of high and low energy, respectively. The maximum adsorption of P is represented by MAP' e MAP" for sites with high and low energy, respectively, and MAPT is the maximum adsorption of phosphorus (MAP '+ MAP").

The adsorption parameters derived from the Langmuir equation for heterogeneous surfaces were obtained in the graphic representation of Pa/Pa over C according to [31].

III. RESULTS AND DISCUSSION

Fig. 4 shows an example of the Langmuir isotherm for a selection of three soils, which have low, medium and high phosphorus adsorption (Pa is the amount of phosphorus adsorbed per weight unit and C is the concentration of P in the existing solution).

Fig 4 - Langmuir adsorption isotherms for three different



soils

As show in Table 3 MAP differ widely, presenting levels which vary between 150 and 2566 mg P kg-1, with an average value of 1115 mg P kg-1, indicating important differences in the behavior of soils with respect to P adsorption. Most of our soils have a high adsorption capacity of P in comparison with the results found by [18] regarding Vertisols.

However, the results obtained in this study are similar to those obtained by [17] in Alfisols and Vertisols. Observing Table 2 it's also possible to note that the adsorption energy (K) provides a wide range, although lower than that offered by the maximum adsorption capacity.

The graphic representation of C/Pa over C (figure 4) shows that the relationship is curvilinear. This fact is in line with the results found by other researchers [17, 32, 33, 34].

This result shows that in a heterogeneous system, as the soil, phosphate is adsorbed on two different surfaces and with different energies of adsorption and, in consequence, the Langmuir equation for two surfaces (heterogeneous surfaces), describe better the P adsorption than the Langmuir equation for uniform surfaces.

In figure 1, can be observed the existence of a first line segment with stronger inclination, for every presented sample this line portion correspond to a maximum adsorption capacity of P very small, but in which the retention is made with a very high energy, followed by another line segment, with a smoother slope, which would correspond to a large amount of P adsorbed, with a much smaller energy level much lower.

Because of this, when considering two simple linear regressions, one for each segment of the line, it's possible to obtain a best model for the adsorption of P (Table 4) and a better regression coefficient.

These results also prove that in all the analyzed samples, the estimated values of MAPT considering the Langmuir equation for distinct adsorption surfaces were higher than the values of MAP obtained from the Langmuir equation for uniform surfaces.

The levels of MAPT vary between 410 and 15 406 mg P kg-1, with an average value of 4295 mg P kg-1, consequently, a significant underestimation (about 4 times less) of P adsorption was observed when the traditional Langmuir equation was used, since in this case the values of MAP vary between 150 and 2566 mg P kg-1, with an average value of 1115 mg P kg-1. In all soils analysed, the MAP" levels are higher than those corresponding to MAP' with mean values of 3674 mg P kg-1 and 495 mg P kg-1 respectively, indicating that most of P was adsorbed on sites of low energy and therefore can consider itself as easily available to plants.

The results obtained in the simple correlation analysis between the different edaphic properties and adsorption parameters are presented in Table 5.

It is possible to verify that the property that shows higher correlation with MAP is AST followed by Fe-CBD. The close relationship between MAP and Fe-CBD corroborate the results obtained by [18, 35, 36] among other authors, which conclude that Fe-CBD is a very important property in the characterization of P adsorption produced in Mediterranean region.

The edaphoclimatic conditions in Mediterranean soils favor the formation of iron crystalline oxide, closely related with the iron extracted with the citrate-dithionite-bicarbonate [37, 38, 39].

The correlation between the amount of clay (r = 0.508 **) and MAP is low, although statistically significant. Similar correlation coefficient (r = 0.502 **) is obtained by relating the pH with MAP, demonstrating that P adsorption tends to increase when increasing the pH value in soil where the Ca is the dominant cation in the exchange complex. Similar results were obtained by [40].

Also active calcium carbonate provides a positive and significant correlation (r = 0.471 *) with MAP, putting in evidence the importance of CaCO3 in the adsorption of P in Mediterranean soils. In contrast, the correlation between organic carbon and MAP (r = 0.240) was not statistically significant. Similar results were obtained by [41, 42] among other investigators. On the other hand [36], working in organic soils and [16] working in different kind of soils from eastern India found that the organic carbon and MAP are significantly and negatively correlated.

Table 4 - Parameters of sorption derived from Langmuir's equation for uniform surfaces and two surfaces

Sample n°	Uniform surface			Heterogeneous surfaces						
	MAP mg kg^{-1}	K103 L kg^{-1}	r	MAP' mg kg^{-1}	K103 L kg^{-1}	r	MAP'' mg kg^{-1}	K103 mg kg^{-1}	r	MAPT mg kg^{-1}
1	721	12.1	0.960	405	52.7	0.990	871	2.5	0.997	1276
2	450	16.7	0.980	291	76.5	0.901	467	2.8	1.000	757
3	260	14.6	0.965	152	116.0	0.960	299	2.6	0.999	451
4	1504	10.6	0.973	803	36.9	0.933	1268	4.3	0.983	2071
5	1456	5.0	0.882	384	51.7	0.941	4227	0.8	0.989	4612
6	1585	5.2	0.860	356	101.0	0.933	3268	1.2	0.971	3624
7	2566	3.8	0.818	571	43.1	0.832	12801	0.5	0.985	13372
8	1010	7.8	0.958	390	47.2	0.953	1301	2.4	0.954	1691
9	860	11.8	0.987	436	45.6	0.977	591	6.1	0.996	1026
10	658	8.9	0.935	395	30.4	0.938	4430	0.3	1.000	4825
11	1749	8.1	0.990	817	20.8	0.978	1074	5.6	0.976	1891
12	885	9.3	0.980	398	41.7	0.989	761	4.2	0.999	1158
13	1854	5.1	0.888	606	29.5	0.978	6850	0.6	0.961	7456
14	810	10.9	0.965	468	39.8	0.891	720	3.5	0.937	1188
15	298	23.6	0.982	194	266.0	0.969	216	5.1	0.996	410
16	150	13.9	0.958	264	82.9	0.955	504	2.4	0.990	806
17	1455	6.9	0.871	603	37.2	0.941	14803	0.2	0.995	15406
18	1394	6.0	0.917	641	22.6	0.971	3243	1.0	0.982	3884
19	1511	5.2	0.880	627	22.5	0.968	6258	0.5	0.917	7155

When comparing the adsorption parameters derived from the application of the Langmuir equation for two surfaces, it is noted that AST is most strongly correlated with MAP" and MAPT then with MAP' and MAP. The active calcium carbonate gives the best correlation coefficient with MAP ', whereas the Fe-CBD do the same thing with MAP", indicating that ACC was the main adsorbent of P in high energy places while at low energy was the Fe-CBD.

Table 5 - Simple linear correlation coefficients between P sorption parameters and relevant soil properties.

	pH	Clay	C.O.^{a}	CCA^b	Fe-CDB	Al-CDB	Fe$_O$	Al$_O$	AST
MAP^c	0.502**	0.508**	0.240NS	0.417*	0.628**	0.617**	0.217NS	0.048NS	0.708***
MAP'^{d}	0.351NS	0.433*	0.163NS	0.592**	0.295NS	0.352*	0.421*	0.199NS	0.451**
MAP''^{e}	0.406**	0.207NS	0.165NS	-0.040NS	0.900***	0.629**	0.065NS	-0.124NS	0.897***
MAPT	0.415**	0.221NS	0.170NS	-0.026NS	0.897***	0.633**	0.082N	-0.111NS	0.900***

^{a}Organic carbon; ^{b} Active $CaCO_3$ equivalent; ^{c}P maximum sorption; ^{d}P maximum sorption in high energy places; ^{e}P maximum adsorption in low energy places; CDB= Extracted with citrate-bicarbonate dithionite; o= Extracted with com oxalate; *,**,*** significant at 0.05, 0.01 y 0.001 probability levels respectively; NS= not significant.

Considering the objective of finding equations that can predict more accurately the maximum adsorption of phosphorus from properties routinely analyzed in the laboratory, a series of multiple regression analyzes were carried out. From the different combinations tested, the equation that best predicts MAP is:

MAP = -509 + 72.25 21.60 + X1 X2 X3 + 20.20, R = 0.850

Where X1 is Fe-CBD, clay content is X2 and X3 is CCA. These three variables represent and predict more than 80% of P maximum adsorption.

The equation that best predicts MAPT were the one that included in the multiple regression analysis the variables AST (X1) and Fe-CBD (X2), being as follows:

MAPT -3809 + 25.40 = X1 + X2 386, R = 0.954

These variables explain more than 91% of the MAPT variation. The results suggest that for the soil considered in this study, the maximum adsorption of P can be quickly and accurately estimated by the inclusion of CBD and Fe-AST in a multiple regression analysis.

IV. CONCLUSIONS

The obtained results puts in evidence that for the studies Vertisols, the Langmuir equation for two surfaces better describes the adsorption of P than the Langmuir equation for uniform surfaces. Furthermore it’s possible to notice that the traditional Langmuir equation underestimates (4 times lower) the levels of P adsorption when compared with Langmuir adsorption equation applied to two distinct surfaces, values that are considered to be highly significant considering the main objectives of the present research.

Moreover, that present research highlighted the fact that the Langmuir adsorption theory is well suited for describing ion adsorption in complex systems like soils, which have multiple ions, highly heterogeneous surfaces, and a variety of adsorption sites on the particle surfaces, indication that corroborates with findings presented in previous studies [43, 44 and 45].

The inclusion of soil properties routinely analyzed in the laboratory, such as the content of clay, Fe-CBD and CCA explains 80% of maximum adsorption variation of P (MAP). Finally, the inclusion of Fe-CBD and AST in multiple regression analysis explains 90% of the P maximum adsorption variation (MAPT).

In sum it is possible to say that equations obtained throughout the present research offer a rapid and appropriate framework for estimating P-sorption in Vertisols.

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