Prevision of Phosphorus Adsorption in Extremadura (Spain) Vertisols and there’s relation with some Soil Edaphic Properties

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Abstract - In the region of Extremadura, located in southwestern Spain, Vertisols represent an important resource for rain-fed agriculture. Phosphorus (P) is the major limiting plant nutrient, and, its availability is a critical factor in the agricultural use of these soils. The sorption and their prediction by soil properties is important 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. Phosphate sorption was investigated in surface-samples of nineteen Vertisols in Extremadura (Spain) by uniform-surface and two-surface Langmuir equations. The 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: Fe₃⁺, ACCE, clay, and total surface area in a multiple-regression analysis. The equations obtained could offer a rapid estimation of P-sorption in Vertisols.

Key-Words: Extremadura, Phosphorus Adsorption, Vertisols, Soil Edaphic Properties

1 Introduction

Vertisols are traditionally seen as one of the most fertile soils of Extremadura in Spain and an important feature of rainfed agriculture. Phosphorus is the main limiting factor of crop nutrition, and its availability is a critical issue in the agricultural use of these soils [1]. 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 [2, 3]. 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 [4].

Previous studies [5, 6] 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 [4, 7].

In this paper we intent 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.

2 Materials and Methods

For this study 19 topsoil samples (0-30 cm) were collected, in the province of Badajoz (Extremadura, Spain). These soils were classified as Vertisol by FAO (Cromoxerent Entice, y Pelloxerent Cromoxerent Typical). Table 1 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 [8].

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 [9].

Total surface area, was determined using ethylene glycol monoethyl ether following the recommendations of [10].

\[ \text{K.MAP.C} = \frac{\text{Pa}}{(1 + \text{K.C})} \]

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 [4, 15, 16] like the equation presented here:

\[ \text{Pa} = \left[ \text{K’. MAP’.C} / (1 + \text{K’. C}) \right] + \left[ \text{K’’.MAP”.C} / (1 + \text{K”. C}) \right] \]

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 [17].

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**Table 1: Statistic summary for the analysis perform during the study**

<table>
<thead>
<tr>
<th>Clay</th>
<th>O. C.</th>
<th>pH</th>
<th>CEC.</th>
<th>C.C.A.</th>
<th>Fe-CDB</th>
<th>FeO</th>
<th>Al-CDB</th>
<th>AIO</th>
<th>AST</th>
</tr>
</thead>
<tbody>
<tr>
<td>g kg(^{-1})</td>
<td>g kg(^{-1})</td>
<td></td>
<td>Cmol kg(^{-1})</td>
<td>g kg(^{-1})</td>
<td>g kg(^{-1})</td>
<td>g kg(^{-1})</td>
<td>g kg(^{-1})</td>
<td>m(^2) g(^{-1})</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>429</td>
<td>9.88</td>
<td>7.68</td>
<td>46.89</td>
<td>13.05</td>
<td>5.95</td>
<td>1.17</td>
<td>0.73</td>
<td>0.11</td>
</tr>
<tr>
<td>STD. Desv</td>
<td>83.6</td>
<td>3.29</td>
<td>0.42</td>
<td>10.75</td>
<td>13.41</td>
<td>5.56</td>
<td>0.49</td>
<td>0.28</td>
<td>0.04</td>
</tr>
<tr>
<td>Variance</td>
<td>6995</td>
<td>10.84</td>
<td>0.18</td>
<td>115.76</td>
<td>179.94</td>
<td>30.96</td>
<td>0.24</td>
<td>0.08</td>
<td>0.00</td>
</tr>
<tr>
<td>Minimum</td>
<td>305</td>
<td>5.60</td>
<td>6.60</td>
<td>27.00</td>
<td>2.00</td>
<td>1.42</td>
<td>0.56</td>
<td>0.29</td>
<td>0.01</td>
</tr>
<tr>
<td>Maximum</td>
<td>610</td>
<td>17.80</td>
<td>8.20</td>
<td>68.00</td>
<td>52.00</td>
<td>22.42</td>
<td>2.20</td>
<td>1.30</td>
<td>0.19</td>
</tr>
</tbody>
</table>

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

Figure 1 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).

As shown in Table 2 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 [5] regarding vertisols. However, the results obtained in this study are similar to those obtained by [4] 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.

Table 2 - Parameters of sorption derived from Langmuir's equation for uniform surfaces and two surfaces

<table>
<thead>
<tr>
<th>Sample n°</th>
<th>Uniform surface</th>
<th>Heterogeneous surfaces</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MAP  mg kg(^{-1})</td>
<td>K 103  L kg(^{-1})</td>
</tr>
<tr>
<td>1</td>
<td>721</td>
<td>12.1</td>
</tr>
<tr>
<td>2</td>
<td>450</td>
<td>16.7</td>
</tr>
<tr>
<td>3</td>
<td>260</td>
<td>14.6</td>
</tr>
<tr>
<td>4</td>
<td>1504</td>
<td>10.6</td>
</tr>
<tr>
<td>5</td>
<td>1456</td>
<td>5.0</td>
</tr>
<tr>
<td>6</td>
<td>1585</td>
<td>5.2</td>
</tr>
<tr>
<td>7</td>
<td>2566</td>
<td>3.8</td>
</tr>
<tr>
<td>8</td>
<td>1010</td>
<td>7.8</td>
</tr>
<tr>
<td>9</td>
<td>860</td>
<td>11.8</td>
</tr>
<tr>
<td>10</td>
<td>658</td>
<td>8.9</td>
</tr>
<tr>
<td>11</td>
<td>1749</td>
<td>8.1</td>
</tr>
<tr>
<td>12</td>
<td>885</td>
<td>9.3</td>
</tr>
<tr>
<td>13</td>
<td>1854</td>
<td>5.1</td>
</tr>
<tr>
<td>14</td>
<td>810</td>
<td>10.9</td>
</tr>
<tr>
<td>15</td>
<td>298</td>
<td>23.6</td>
</tr>
<tr>
<td>16</td>
<td>150</td>
<td>13.9</td>
</tr>
<tr>
<td>17</td>
<td>1455</td>
<td>6.9</td>
</tr>
<tr>
<td>18</td>
<td>1394</td>
<td>6.0</td>
</tr>
<tr>
<td>19</td>
<td>1511</td>
<td>5.2</td>
</tr>
</tbody>
</table>

The graphic representation of C/Pa over C (figure 1) shows that the relationship is curvilinear. This fact is in line with the results found by other researchers [4, 18, 19, 20].

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
inclusion, 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 2) and a better regression coefficient.

These results also prove that in all the analysed 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 3. 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 [5, 21, 22] 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 favour the formation of iron crystalline oxide, closely related with the iron extracted with the citrate-dithionite-bicarbonate [23, 24, 25].

Table 3 - Simple linear correlation coefficients between P sorption parameters and relevant soil properties.

<table>
<thead>
<tr>
<th>pH</th>
<th>Clay</th>
<th>C.O.</th>
<th>CCA</th>
<th>Fe,CD</th>
<th>Al,CD</th>
<th>Fe₀</th>
<th>Al₀</th>
<th>AST</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAP</td>
<td>0.502</td>
<td>0.508</td>
<td>0.240</td>
<td>0.417</td>
<td>0.628</td>
<td>0.617</td>
<td>0.217</td>
<td>0.048</td>
</tr>
<tr>
<td>MAP'</td>
<td>0.351</td>
<td>0.433</td>
<td>0.163</td>
<td>0.592</td>
<td>0.295</td>
<td>0.352</td>
<td>0.421</td>
<td>0.199</td>
</tr>
<tr>
<td>MAP''</td>
<td>0.406</td>
<td>0.207</td>
<td>0.165</td>
<td>-0.040</td>
<td>0.900</td>
<td>0.629</td>
<td>0.065</td>
<td>-0.124</td>
</tr>
<tr>
<td>MAPT</td>
<td>0.415</td>
<td>0.221</td>
<td>0.170</td>
<td>-0.026</td>
<td>0.897</td>
<td>0.633</td>
<td>0.082</td>
<td>-0.111</td>
</tr>
</tbody>
</table>

*Organic carbon; ** Active CaCO₃ equivalent; 'P maximum sorption; "P maximum sorption in high energy places; '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.

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 [26]. 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 [27, 28] among other investigators. On the other hand [22], working in organic soils and [3] working in different kind of soils from eastern India found that the organic carbon and MAP are significantly and negatively correlated.

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 places was the Fe-CBD.

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:

\[
\text{MAP} = -509 + 72.25 \times 21.60 + X_1 \times X_2 \times X_3 + 20.20, \quad R^2 = 0.850
\]

Where \(X_1\) is Fe-CBD, clay content is \(X_2\) and \(X_3\) 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 (\(X_1\)) and Fe-CBD (\(X_2\)), being as follows:

\[
\text{MAPT} = -3809 + 25.40 = X_1 + X_2 - 386, \quad R = 0.954
\]

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.

4 Conclusions

The results puts in evidence that for the Vertisols studied in this work, the Langmuir equation for two surfaces better describes the adsorption of P than the Langmuir equation for uniform surfaces. 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. 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 explain 90% of the P maximum adsorption variation (MAPT).

References:


