

Phosphate Sorption by Almería Soils

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Because phosphate (P) deficiency is a serious problem in soils from warm arid and semiarid regions, adsorption-desorption of P on Almería (southeastern Spain) soils from aqueous solution at 303 K was studied. Effect of ionic strength was examined by using 0.01 or 0.1 M KCl as a suspending medium. Adsorption data for P and the soils studied were compared using the Langmuir adsorption equation. Adsorption capacity values (X_m) ranged from 51.4 (volcanic soil) to 409.7 mg of P kg⁻¹ (brown lime soil) for adsorption of P in a 0.01 M KCl supporting medium and from 109.2 (alluvial soil) to 424.1 mg of P kg⁻¹ (brown lime soil) in a 0.1 M KCl supporting medium. Values of X_m are always greater in the 0.1 M KCl supporting medium than in the 0.01 M KCl one. The adsorption of phosphate was correlated with soil organic matter content. Of P initially adsorbed, 31.3-74.8% could be desorbed in four equilibrations. Phosphate desorption was inversely related to the product of the b and X_m Langmuir equation parameters.

INTRODUCTION

The reaction between phosphate (P) and soil is one of the most frequently studied subjects in soil science. One reason for this is the widespread occurrence of phosphate deficiency. Another reason is the complex nature of the problem. Adsorption and desorption reactions are affected by experimental variables such as concentration of P, pH, concentration of electrolyte, period of reaction, and temperature (Barrow, 1974, 1979, 1984; Berkheiser et al., 1980).

One of the main variables which affect P sorption is the ionic composition, both species and concentration, of the suspending solution (Ryden and Syers, 1975; Bolan et al., 1986).

The P sorption process is controlled by other factors. In tropical acid soils, the amounts of oxides and hydroxides of aluminum and iron, which form the major components of the soil surface, play important roles in determining P sorption characteristics (Bigham et al., 1978; Juo and Fox, 1977; Le Mare, 1981). Other soil properties such as clay content and organic matter content may also play a part in the retention of added P (Hall and Barker, 1971; Saunders, 1965; Owen, 1953; Ahenkorah, 1968).

We investigated the adsorption-desorption process of P on soil using adsorption isotherms obtained for eight Mediterranean soils typical of Almería (East-Andalucía, Spain). We analyzed the effect of ionic strength by using 0.01 or 0.1 M KCl as suspending medium.

In addition, correlations between the characteristic adsorption parameters and soil properties such as clay and organic matter content, soil mineralogy, specific surface area, cation-exchange capacity, calcium carbonate, exchangeable calcium, assimilable phosphorus, and free (i.e., amorphous and crystalline) iron oxides were studied.

MATERIALS AND METHODS

The soil samples represent major soil types of Almería Province listed by the Environmental Agency of Andalucía (Junta de Andalucía, 1984). They are listed in Table I. Air-dried samples of less than 2 mm were analyzed by standard methods described in Jackson (1982) and Black (1965). Soil pH was determined in a 1:2.5 soil/water suspension using a glass electrode, organic matter content by the Walkley-Black method, and clay content by the hydrometer method. Cation-exchange capacity and exchangeable calcium were determined by the barium acetate method, and

assimilable phosphorus was determined by the Watanabe and Olsen method using a 0.5 M NaHCO₃ extracting solution.

Calcium carbonate was determined according to the Galet method (López and López, 1978). Free iron oxides were extracted with citrate-bicarbonate-dithionite (Mehra and Jackson, 1960) and determined by atomic absorption. Specific surface area was determined from N₂ adsorption isotherms at 77.4 K, using the BET equation (Adamson, 1982). Properties of the soil and taxonomic classification are given in Table I. A complete discussion about the characteristics of these soils is given in previous papers (Valverde et al., 1987; Socías, 1990). Soil mineralogy was analyzed using a semiquantitative X-ray method (Table II).

The adsorption experiments were carried out as follows: 0.01 and 0.1 M KCl aqueous solution containing initial KH₂PO₄ concentrations between 2 and 18 mg of P L⁻¹ were prepared. This concentration range is under the limit for which P precipitation might be initiated (Bolarin et al., 1980). Two grams of soil and 50 mL of a P solution were placed in a stoppered conical flask and shaken for 24 h (the time required for equilibrium to be reached between P adsorbed and P in solution) in a thermostated shaker bath at 303 ± 0.1 K. After shaking, the suspensions were centrifuged (10 000 rpm for 15 min), and the concentration of P in the supernatant liquid was determined by an ascorbic acid method (Murphy and Riley, 1962). The amount of P adsorbed was calculated by subtracting the final from the initial P concentration and adding the amount of P initially contained on potential adsorption sites in the soil.

Several drops of toluene were added to each suspension to control microbial activity. A KCl solution-soil containing no P was always included, and two replicates were analyzed at each P concentration for every soil type.

Desorption experiments were carried out as follows: 2 g of soil and 50 mL of 0.01 or 0.1 M KCl phase containing 10 mg of P L⁻¹ were placed in the corresponding adsorption stoppered conical flasks. After the initial adsorption equilibrium had been attained, suspensions were centrifuged and the supernatant solutions were poured off for analysis. Then 50 mL of 0.01 or 0.1 M KCl solution was added to the remaining soil, and this system was again shaken for 24 h to establish the new equilibrium. This treatment was also followed by centrifugation and determination of the new equilibrium concentration in the supernatant fluid. The amount of phosphate desorbed in this first rinse was calculated. This process was repeated four times. Blanks were included in each case, and all desorption experiments were carried out in duplicate.

RESULTS AND DISCUSSION

The adsorption isotherms were characterized in all cases by a sharp increase in the amount of P adsorbed, at low

Table I. Characteristics of the Soils

soil	taxonomic classification	pH	organic matter, g kg ⁻¹	clay, g kg ⁻¹	cation-exchange capacity, mmol kg ⁻¹	specific surface × 10 ⁻³ , m ² kg ⁻¹	calcium carbonate, g kg ⁻¹	exchangeable Ca ²⁺ , mmol kg ⁻¹	free oxides, g kg ⁻¹	assimilable P, mg of P ₂ O ₅ kg ⁻¹
AL-01	brown clay, Almanzora Alto	Xerorthents	8.5	20.2	131	16	294	4.9	18.9	18.1
AL-02	brown lime, Almanzora Bajo	Xerochrepts	8.9	25.5	143	14	704	9.0	9.1	52.9
AL-03	rendzine, Andarax Gádor	Rendolls	8.1	11.2	78	5	92	5.0	18.2	21.0
AL-04	saline, Campo de Dallas	Fluvaquents	8.2	28.4	41	13	453	7.7	12.8	50.2
AL-05	volcanic, Campo de Níjar	Haplargids	8.7	6.4	59	5	153	4.0	17.1	25.8
AL-06	desert, Campo de Tabernas	Camborthids	7.9	5.7	122	11	465	8.0	16.2	17.1
AL-07	brown lime, Los Vélez	Xerochrepts	8.1	35.5	141	43	569	11.8	19.0	45.0
AL-08	alluvial, Rio Nacimiento	Xerofluvents	8.0	15.7	117	8	92	5.4	22.1	23.9

Table II. More Important Minerals in Clay Fraction

soil	g kg ⁻¹ of soil			
	montmorillonite	illite	chlorite	kaolinite
AL-01	23.6	86.5	tr	21.0
AL-02	73.0	57.2	7.2	tr
AL-03	23.4	32.8	12.5	4.7
AL-04	3.7	32.8	3.3	
AL-05	1.8	48.4	3.5	3.5
AL-06	13.4	62.2	25.6	13.4
AL-07	35.3	79.0	26.8	
AL-08	26.9	53.8	7.0	29.3

equilibrium concentration, followed by a much more gradual increase at high equilibrium concentration of P (Figure 1).

Conformation of adsorption data to the Langmuir equation was tested by using a linear form

$$C/X = (1/bX_m) + C/X_m \quad (1)$$

where X is the amount of P sorbed per unit weight of soil, C is the concentration of P in the equilibrium solution, X_m is the maximum amount of P that can be sorbed in a monolayer, and b is an affinity constant.

It is generally recognized that the assumptions on which eq 1 is based do not strictly pertain to P sorption by soils. This is substantiated by the common failure of eq 1 to produce linear plots. This equation is based on the assumptions that the energy of adsorption is constant, which implies uniform sites and no interaction between P molecules, that the adsorption is on localized sites, which implies no translational motions of adsorbed molecules in the plane of the surface, and that maximum adsorption possible corresponds to a complete monomolecular layer (Adamson, 1982). However, the Langmuir model has been applied to up to 20 mg of P L⁻¹ of equilibrium concentration (Olsen and Watanabe, 1957; Weir and Soper, 1962). Thus, the model is useful over the specified equilibrium concentration since the X_m parameter may be used to compare the behavior of different soils in relation to the adsorption of phosphate. Several authors have concluded that the Langmuir equation should be regarded as strictly empirical and therefore should be essentially used as a curve-fitting procedure (Sibbesen, 1981; Goldberg and Sposito, 1984).

Because the equilibrium concentrations are, in all cases, less than 16 mg of P L⁻¹, we fitted the adsorption data to the Langmuir equation. Figure 2 shows the straight lines obtained for 0.01 and 0.1 M KCl media, the correlation coefficients being in all cases greater than 0.95 (all correlations were significant at the 0.001 probability level). For this reason and taking into account all of the above mentioned, the experimental adsorption data for P for the eight soils were compared using the Langmuir adsorption equation (Table III). By applying the analysis of variance technique, we conclude that, under the experimental conditions used, differences in P adsorption exist among the eight soils studied.

Table III. Langmuir Parameters and Correlation Coefficients

soil	0.01 M KCl			0.1 M KCl		
	X_m , mg of P kg ⁻¹	b , L (mg of P) ⁻¹	r	X_m , mg of P kg ⁻¹	b , L (mg of P) ⁻¹	r
AL-01	139.2	0.388	0.987	199.5	0.217	0.987
AL-02	104.3	0.383	0.990	212.4	0.232	0.989
AL-03	60.0	1.367	0.996	168.0	0.222	0.996
AL-04	355.0	0.766	0.984	405.3	0.585	0.996
AL-05	51.4	0.307	0.997	124.3	0.183	0.985
AL-06	87.4	1.133	0.985	146.5	0.730	0.993
AL-07	409.7	0.304	0.962	242.1	0.784	0.995
AL-08	93.7	0.406	0.993	109.2	0.458	0.999

The X_m values ranged between 51.4 (volcanic soil/AL-05) and 409.7 mg of P kg⁻¹ (brown lime soil/AL-07) for adsorption of P in a 0.01 M KCl supporting medium and between 108.9 (alluvial soil/AL-08) and 422.0 mg of P kg⁻¹ (brown lime soil/AL-07) for adsorption in a 0.1 M KCl supporting medium (Table III).

The X_m values are always greater in the 0.1 M KCl than in the 0.01 M KCl support medium. This fact might be explained by taking into account that an increase in ionic strength (from 0.01 up to 0.1 M KCl) decreases the thickness of the diffuse layer and thereby the volume of the linear solution (Ryden and Syers, 1975). Consequently, if the charge on the surface remains constant, the concentration of anions in the diffuse layer increases. For a given level of P addition, the proportion of chloride (Cl) relative to P in the outer solution increases with support medium concentration. The selectivity of the surface for P relative to Cl (Hingston et al., 1972) suggests that the proportion of Cl to P would not increase to the same extent in the inner solution. This assumption, in association with the effect of ionic strength on the concentration of anions in the inner solution, implies an increase in P concentration at the sorbing surface. In addition, a greater ionic strength solution will lead to some SiO₂ dissolution and removal of other species occupying potential adsorption sites, so the P adsorption will increase. The b values range between 0.30 (brown lime soil/AL-07) and 1.21 (rendzine soil/AL-03) for adsorption of P in a 0.01 M KCl supporting medium and between 0.16 (volcanic soil/AL-05) and 0.78 (brown lime soil/AL-07) in a 0.1 M KCl supporting medium (Table III).

To determine the factors that affect adsorption of P by soil, the adsorption capacities of the eight soils, represented by X_m values, were correlated with soil properties (Table IV). The analysis shows that X_m values are not at all correlated with clay content, pH, calcium carbonate, percentage of montmorillonite and illite in the clay fraction and free iron oxides; correlation coefficients range from -0.02 (for percentage of clay, 0.01 M KCl medium) to 0.60 (for CaCO₃, 0.1 M KCl medium). The analysis shows that X_m values are correlated with organic matter content and, to a lesser extent, with cation-exchange capacity, specific surface area, assimilable phosphorus, and exchangeable calcium.

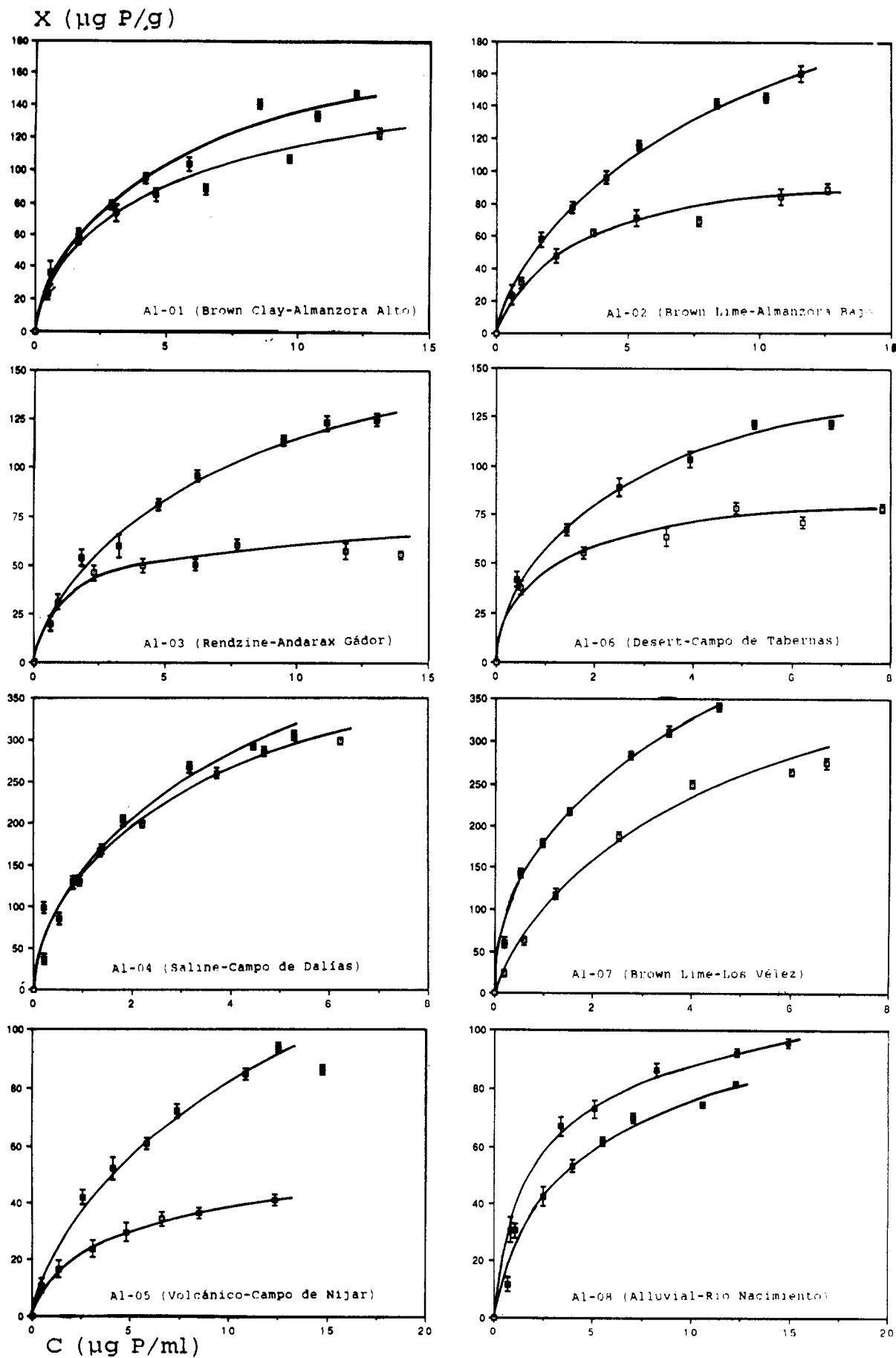


Figure 1. Adsorption isotherms of phosphate ions on the soils studied. (○) 0.01 M KCl as support medium; (●) 0.1 M KCl as support medium.

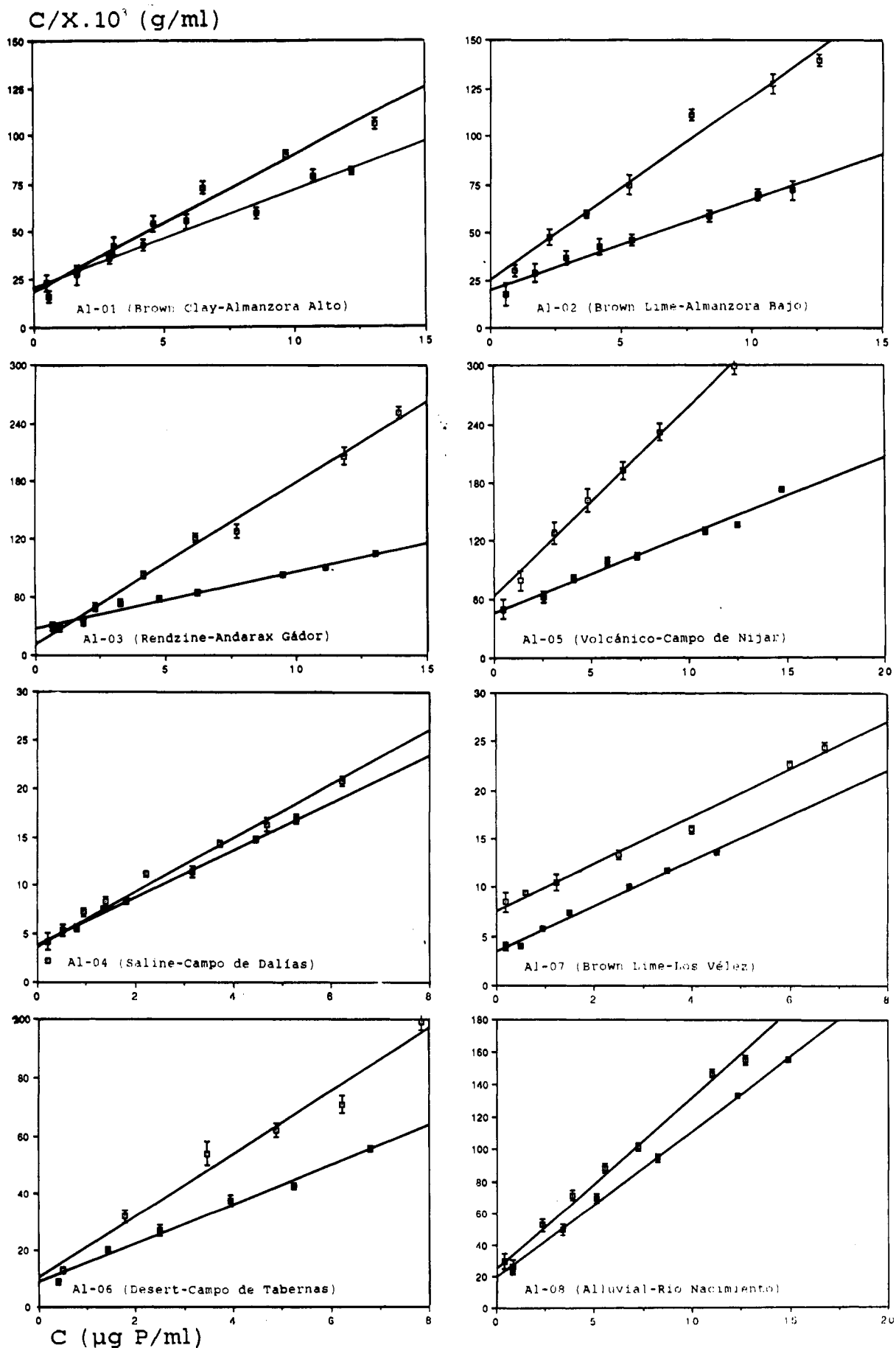


Figure 2. Application of the Langmuir equation to the experimental data points corresponding to adsorption of phosphate ions on the soils studied. (O) 0.01 M KCl as support medium; (●) 0.1 M KCl as support medium.

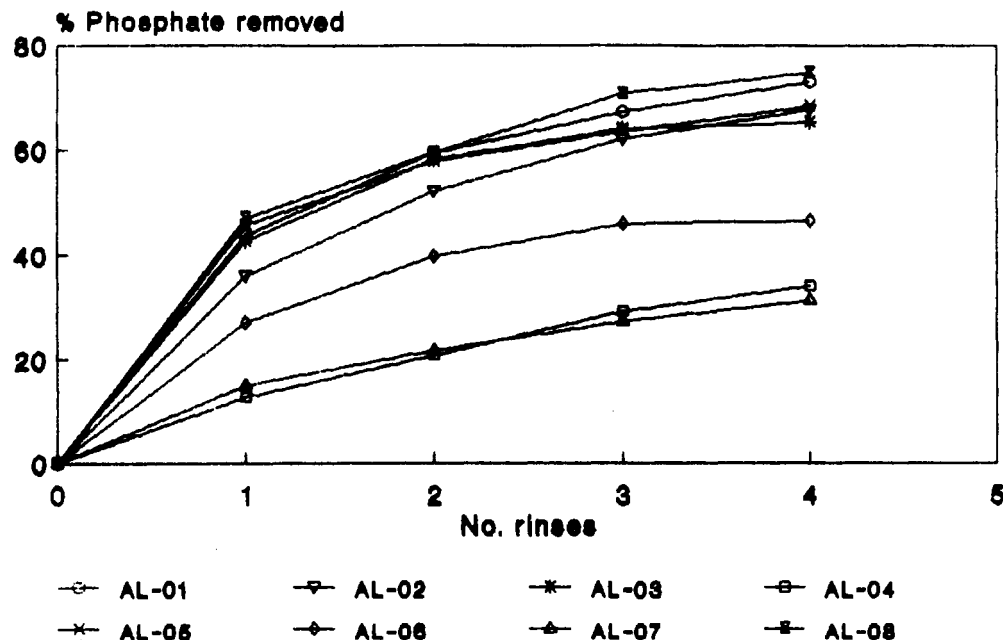


Figure 3. Phosphate ions removed from the soils after four consecutive rinses using 0.01 M KCl as support medium. (Standard deviations of the point replicates are less than 4.96.)

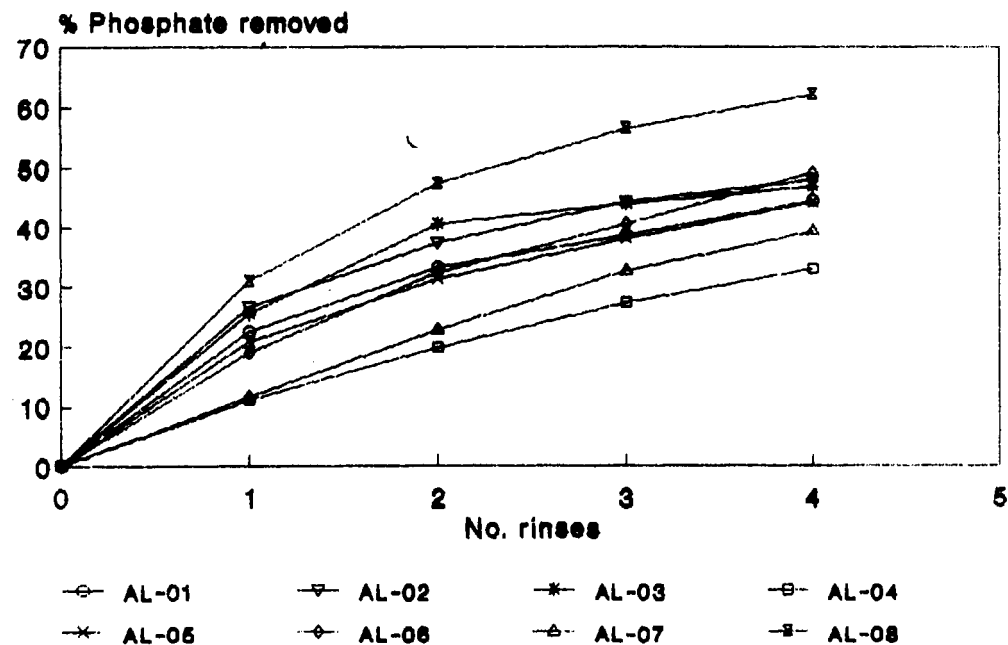


Figure 4. Phosphate ions removed from the soils after four consecutive rinses using 0.1 M KCl as support medium. (Standard deviations of the point replicates are less than 4.96.)

Percentages of P removed after four rinses (Figures 3 and 4) range between 31.3 for soil AL-07 and 74.8 for soil AL-08 in a 0.01 M KCl support medium and between 33.0 for soil AL-04 and 62.0 for soil AL-08 in a 0.1 M KCl support medium. This variation of the P removed was, in general, inversely related to that obtained for the X_m values. This fact appears to be natural since the soil with a major P adsorption capacity also presents a lesser P desorbed percentage and vice versa.

To verify the above, percentages of P desorbed were correlated with the inverse of the apparent equilibrium constant, K_a , corresponding to the adsorption process, which can be calculated as the product of the Langmuir equation parameters b and X_m (López González et al., 1978). Note that although b may be related to the adsorption energy, it is not an indicator of the surface available for phosphate ions. A relative indicator of the soil affinity for phosphate (when the experimental data

Table IV. Correlation Coefficients between Phosphate Adsorption and Soil Characteristic

soil characteristic	r	
	0.01 M KCl	0.1 M KCl
pH	-0.23	-0.11
organic matter	0.85 ^c	0.86 ^c
clay	-0.01	-0.12
cation-exchange capacity	0.77 ^b	0.73 ^b
specific surface area	0.80 ^b	0.75 ^b
calcium carbonate	0.52	0.58
exchangeable calcium	0.71 ^b	0.72 ^b
free iron oxides	-0.08	-0.26
assimilable phosphorus	0.64 ^a	0.72 ^b
montmorillonite	-0.04	0.04
illite	0.18	0.09

^{a-c} Significant at 0.05, 0.02, and 0.01 probability levels, respectively.

points agree with the Langmuir equation) is the apparent equilibrium constant (K_a). Correlations were performed

between K_a^{-1} and percentages desorbed after the first and fourth rinses; correlation coefficients obtained were, respectively, 0.90 and 0.81 for P adsorption on the soils in the 0.01 N KCl medium and 0.93 and 0.69 for P adsorption in the 0.1 N KCl medium.

CONCLUSIONS

The adsorption of phosphate on Almería soils in a 0.1 M KCl support medium is between 1 and 3 times greater than that corresponding to a 0.01 M KCl support medium. Soils AL-07 and AL-05 (0.01 M KCl medium) and AL-07 and AL-08 (0.1 M KCl medium) have, respectively, the greatest and least adsorption capacities. The adsorption of P seems dependent on the organic matter content of the soils.

Desorption percentages are inversely correlated with the product of the b and X_m Langmuir equation parameters, which represents the soil affinity for the phosphate ions.

All of the above-mentioned results are important for agriculture and for the environment since a reassessment of phosphorus application practices is needed to minimize phosphate eutrophication of lakes and ponds and conserve phosphate resources while maximizing crop yield.

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