

Competitive Interaction between Phosphate and Citrate on Goethite

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Interaction between various species in natural systems may affect the adsorption of these species and thereby their mobility and bioavailability. Recently an ion adsorption model has been developed, based on the surface structure of metal (hydr)oxides and the structure of surface complexes identified by spectroscopy. This model has been applied to the adsorption of phosphate and weak organic acids on goethite in single anion systems. We studied the interaction between phosphate and citrate on goethite, which is important for a better understanding of the competitive binding of phosphate and organic matter in natural systems. Citrate adsorption in the presence of phosphate decreased strongly over a wide pH range, whereas phosphate adsorption was only affected at pH values below 7, with the largest interaction around pH 5. Competition for binding sites appeared to be an important factor in determining the competitive adsorption of phosphate and citrate when taking into account that a larger number of surface groups is involved in the complexation of citrate compared with phosphate. Competitive adsorption was predicted satisfactorily by applying model parameters from the single anion experiments, using surface complexes coordinated to three or four surface groups for citrate and to one or two surface groups for phosphate.

Introduction

The sorption of phosphate on metal (hydr)oxides in soils and sediments influences the mobility and bioavailability of phosphate in terrestrial and aquatic systems. Organic matter present in these systems may interact with metal (hydr)oxides, thereby changing the sorption characteristics of metal (hydr)oxide surfaces. Natural organic matter and humics isolated from aquatic systems were shown to compete with phosphate for sorption on iron (hydr)oxides (1–3).

Sorption of natural organic matter on iron oxides is dominated by ligand exchange between carboxyl/hydroxyl groups and oxygen/water groups at the surface (3), a binding mechanism that has also been demonstrated for small organic acids (4, 5). Therefore, studying the influence of small organic acids on phosphate adsorption might provide a better understanding of the interaction of organic matter and phosphate on metal (hydr)oxides.

In soils, such small organic acids may be present because they may be released by roots and microorganisms and by the decomposition of organic matter (6–8). In the presence

of small organic acids, an increase in the mobilization of phosphate was observed for soils with a high content of iron and aluminum (hydr)oxides on which phosphate was sorbed (8–13). The effectiveness by which phosphate is desorbed from soils and metal (hydr)oxides depends on the number of carboxyl groups of the acid (12, 14, 15). On the pH-dependent competitive interaction between phosphate and organic acids/anions on metal (hydr)oxides, only few data are available (14–16). In this study, we examine the competitive adsorption of phosphate and citrate on goethite and the influence of pH and the anion concentrations on the competition.

Infrared spectroscopy studies of the binding of citrate on goethite showed that the three carboxyl groups of citrate are all involved in the coordination to the surface (4). In a study in which the adsorption behavior of different small organic acids on goethite was compared, citrate was assumed to be bound as a bidentate complex and, in addition, by hydrogen bonds between surface groups and the remaining carboxyl groups. This results in the complexation of citrate with three or four surface groups of goethite (17).

The simultaneous adsorption of citrate and phosphate on goethite can be predicted with the CD-MUSIC surface complexation model (18). The model uses surface complexes proposed from spectroscopy studies and is based on a reasonable approximation of the surface structure of goethite. In this study, the surface complexes and model parameter values that were successfully used to describe the adsorption of citrate and phosphate on goethite in single anion systems (17, 19) are used as a starting point.

Materials and Methods

The goethite used had a BET specific surface area of 96.4 m² g⁻¹ and a pristine point of zero charge (PPZC) of 9.2 (goethite I; 19). All solutions were prepared with distilled demineralized water and stored in polyethylene plastic to avoid contamination with silica. The pH-dependent adsorption of citrate and phosphate on goethite was determined in batch adsorption experiments in 0.01 M KNO₃. In blank treatments with citrate, no evidence for microbial degradation was found. In most experiments, following the addition of phosphate and/or citrate, the suspensions were equilibrated for 20 h in an end-over-end shaker. In one set of experiments, the influence of the order of addition of phosphate and citrate was studied by adding phosphate 24 h after citrate, or vice versa, and equilibrating the suspensions for another 20 h. The adsorption of phosphate and citrate was calculated from the difference in the initial total concentration of the anion in the system and the final concentration in solution. The concentrations mentioned below are initial total concentrations in the system.

The adsorption of citrate was determined at 1 × 10⁻³ M with a goethite suspension density of 4 g L⁻¹ and at 1 × 10⁻⁴ M citrate with 0.5 g of goethite L⁻¹. For the latter citrate: goethite ratio, citrate adsorption was also determined in the presence of 1 × 10⁻⁴ and 6.5 × 10⁻⁵ M phosphate. The citrate concentration in solution was calculated from the measured dissolved organic carbon concentration (Skalar SK 12). Phosphate adsorption was determined in the presence of 1 × 10⁻⁴ M citrate at phosphate concentrations of 1 × 10⁻⁴, 8 × 10⁻⁵, and 6.5 × 10⁻⁵ M with 0.5 g of goethite L⁻¹. The phosphate concentration in solution was determined using the malachite green method (20) or the molybdenum blue method. Phase separation was performed by centrifuging the suspensions at 22000g for 25 min.

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TABLE 1. Surface Complexes of Phosphate and Citrate on Goethite and the Distribution of the Charge (z) of the Surface Complex over the Surface, the 1-Plane, and the d-Plane at the Head End of the Diffuse Double Layer (DDL)^a

surface complex	log K^b	FeOH ^{1/2-}	H ⁺	PO ₄ ³⁻	Cit ³⁻	z_{surface}^c	$z_{1\text{-plane}}$	$z_{d\text{-plane}}$	
Fe ₂ O ₂ PO ₂ ⁽²⁻⁾	30.0	2	2	1	0	-0.25	-1.75	0	
Fe ₂ O ₂ POOH ⁽⁻⁾	35.4	2	3	1	0	0	-1.0	0	
FeOPO ₃ ^(2 1/2-)	20.5	2	1	1	0	-0.3	-2.2	0	
Fe ₄ Cit ⁽⁻⁾	39.6	4	4	0	1	0.4	-0.4	-1.0	(Figure 1A)
Fe ₃ Cit ^(1 1/2-)	29.65	3	3	0	1	0.2	-0.7	-1.0	(Figure 1B)
Fe ₃ CitH ^(1/2-)	34.3	3	4	0	1	0.2	-0.2	-0.5	(Figure 1C)

^a Model parameter values are adapted from Geelhoed et al. (19) for phosphate and from Filius et al. (17) for citrate. The basic charging behavior of goethite is modeled with the parameter values of Geelhoed et al. (19). ^b Adjustments of log K : protonated bidentate phosphate, -0.1; citrate surface species with four surface groups, -0.2; citrate surface species with three surface groups, -0.1 because of altered charge distribution. ^c Adjusted charge distribution: more negative charge of citrate is attributed to the surface, resulting in less positive charge at the surface (0.2 instead of 0.3 for three surface groups and 0.4 instead of 0.6 for four surface groups) and less negative charge in the 1-plane. Note that the charge per surface oxygen is small.

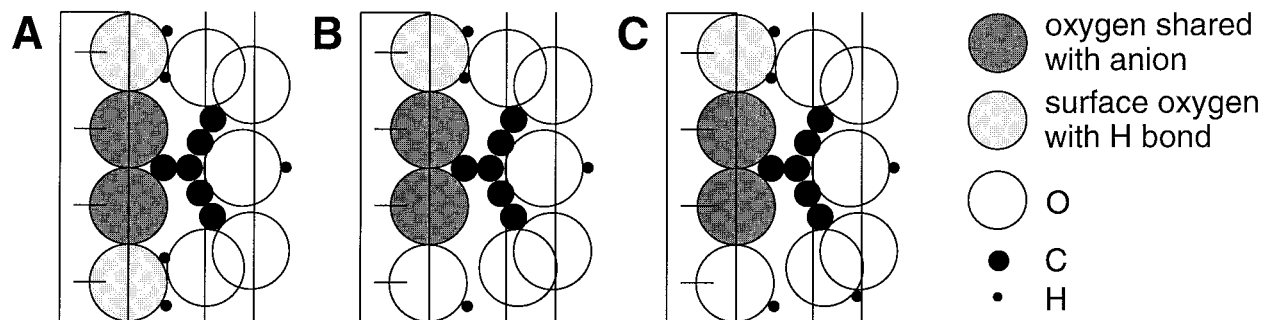


FIGURE 1. Schematic drawing of citrate surface complexes: (A) bidentate complex with two H-bonds between the surface and carboxylate groups, (B) bidentate complex with one H-bond, and (C) bidentate complex with one H-bond and one protonated carboxylate group.

In another set of experiments with relatively low phosphate loading of goethite, ³²P was added to determine phosphate in solution. Phosphate adsorption was determined at 2.1 × 10⁻³ M with 0.2 g of goethite L⁻¹ in the presence of 1 × 10⁻⁵, 1 × 10⁻⁴, and 1 × 10⁻³ M citrate. Per 20 mL of suspension, 0.3–5.8 kBq of carrier free ³²P was added. The influence of the order of addition was studied for 2.1 × 10⁻⁵ M phosphate and 1 × 10⁻⁴ M citrate. After equilibration, the suspensions were centrifuged at 15000g for 10 min after which the supernatant was centrifuged for another 10 min. The ³²P concentration in solution was determined using Cerenkov counting, and the ³¹P concentration in solution was calculated from the ³¹P:³²P ratio corrected for disintegration.

Dissolution of goethite by citrate during the experiments was not checked. The dissolution of goethite by citrate is larger at large citrate:goethite ratio and low pH. Model calculations using the solubility product of goethite (21) show that, for the system with 1 × 10⁻³ M citrate and 0.2 g of goethite L⁻¹ at pH 2.5–4; 5% of the goethite is dissolved at equilibrium. This corresponds to a decrease in the goethite surface area of about 2.5%. As a result, the surface coverage of citrate and phosphate, and their solution concentrations will slightly increase. For competitive systems with phosphate, the increase in the phosphate concentration in solution will be less than 1%.

Modeling Anion Adsorption

The adsorption of phosphate and citrate was modeled using a multi-site complexation (MUSIC) approach (18). The density of the various surface groups can be derived from the crystal structure of goethite. The surface groups differ in the coordination with underlying Fe atoms (n), leading to singly ($n = 1$), doubly ($n = 2$), or triply ($n = 3$) coordinated surface groups. Singly coordinated surface groups are considered to be reactive for protonation and anion adsorption. Doubly coordinated surface groups are uncharged over a wide pH range and, therefore, are regarded as not reactive. One-third of the triply coordinated surface groups can be

considered to be reactive for protonation (22). The charge of the surface groups is determined by the number of bonds with the Fe atoms (0.5 unit per bond) and the charge of the surface ligand (-2 for O, -1 for OH, 0 for OH₂). The model parameters, a.o. site density, capacitance, and affinity constants needed to describe the basic charging behavior of goethite are taken from Geelhoed et al. (19).

Phosphate and citrate exchange ligands with the surface, forming inner-sphere complexes (4, 23). The charge of these inner-sphere complexes is regarded as a spatial charge distributed over the surface, the d-plane at the head end of the diffuse double layer (DDL), and the intermediate 1-plane. Phosphate modeling is based on the formation of bidentate complexes, protonated bidentate complexes, and monodentate complexes, surface species that have been identified with in situ CIR-FTIR spectroscopy (23). The constants used (19) are given in Table 1. The adsorption of citrate at $I = 0.01$ M can be described with the complexes depicted in Figure 1. These complexes and their model constants (Table 1) are taken from Filius et al. (17). The charge of the citrate complexes attributed to the surface results from the protonation of surface groups, the oxygens shared between the surface and citrate, and the oxygens bound with H-bonds. Because of the large size of citrate, the remaining charge of the surface complex is distributed over the 1-plane and d-plane (Table 1) (17).

Results and Discussion

Adsorption in Single Anion Systems. The adsorption of citrate on goethite decreased with increasing pH (Figure 2). At pH values above the PPZC almost no citrate was adsorbed. Below the PPZC, where goethite becomes positively charged, a strong increase in citrate adsorption was observed with decreasing pH. At low pH, the adsorption of citrate levels off because of increasing protonation of citrate in solution. Model calculations show that the electrostatic contribution to the total affinity of citrate for the goethite surface is relatively large (17, 24).

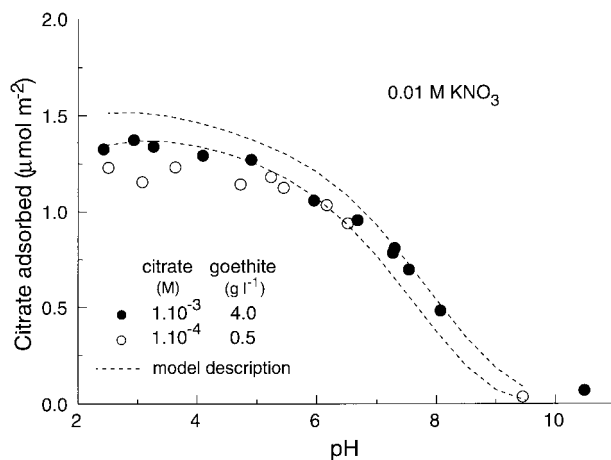


FIGURE 2. Citrate adsorption on goethite at two citrate:goethite ratios. Citrate adsorption was modeled using the model parameter values of Filius et al. (17).

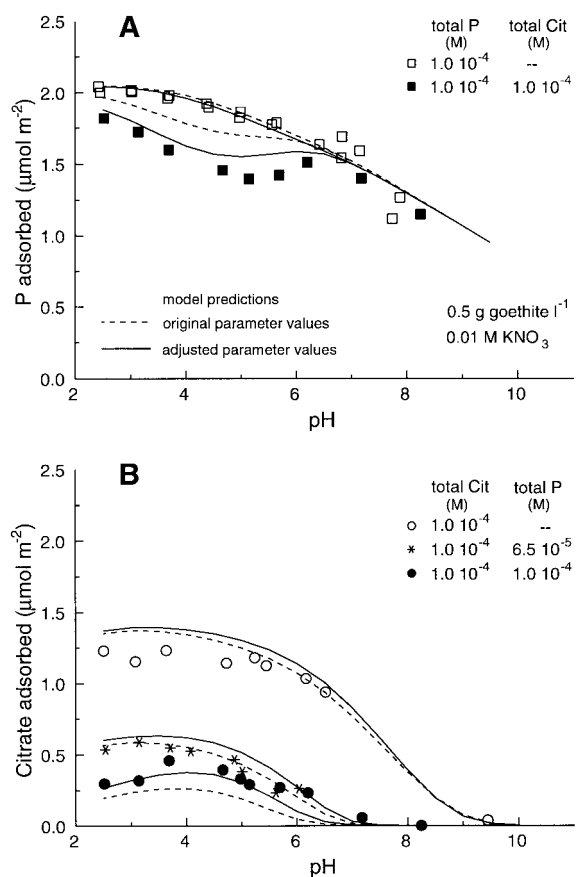


FIGURE 3. Single anion and competitive adsorption of (A) phosphate and (B) citrate at equal total concentrations of 1×10^{-4} M at 0.5 g of goethite L^{-1} . Data of phosphate adsorption without citrate are taken from Geelhoed et al. (19). Citrate adsorption was also determined at a lower total phosphate concentration of 6.5×10^{-5} M. Model calculations were performed with the original and adjusted model parameter values (Table 1).

The adsorption of phosphate and citrate in single anion systems at equal initial total concentrations is shown in Figure 3 (open symbols). Comparing the adsorption of phosphate and citrate at high pH ($pH \approx PPZC$) shows that phosphate is adsorbed in considerable amounts, whereas citrate is not adsorbed. This illustrates that phosphate has a much larger intrinsic affinity for the goethite surface than citrate. At low pH the adsorption of citrate is also smaller than the adsorption

of phosphate, but this can be explained from the larger number of surface groups involved in the adsorption of citrate as compared with phosphate. In situ spectroscopic studies of phosphate adsorbed on goethite have shown that phosphate is adsorbed as bidentate, protonated bidentate, and monodentate surface species (23). Using the CD-MUSIC model, an accurate quantitative description of the observed distribution of phosphate species on goethite related to phosphate loading and pH was obtained (18). At intermediate to low pH, the bidentate phosphate species are most abundant. Model calculations for citrate adsorption at low pH indicate that about 70% of the surface complexes is of type A (Figure 1), in which citrate is coordinated to four surface groups. The resulting predicted number of occupied surface groups at pH 3 in Figure 3 is $4.1 \mu\text{mol m}^{-2}$ for phosphate and $5.1 \mu\text{mol m}^{-2}$ for citrate. Compared with the total number of reactive surface groups of $5.7 \mu\text{mol m}^{-2}$, this shows that the surface coverage of goethite with citrate can become very high.

Adsorption in Competitive Systems. Anion adsorption in competitive systems is affected directly by competition for surface sites and indirectly by the change of the electrostatic charge in the plane of adsorption. The simultaneous addition of citrate and phosphate to goethite resulted in a decrease in the adsorption of both phosphate and citrate (Figure 3, filled symbols), indicating that phosphate and citrate compete for adsorption on the goethite surface. The adsorption of citrate was strongly decreased over the whole pH range, whereas phosphate adsorption was only affected below pH 7, an effect that is caused by the difference in the intrinsic affinities. Competition between organic and inorganic anions has also been observed for, for example, oxalate and phosphate, chromate or sulfate (16, 25, 26), and phthalic or chelademic acid and sulfate (27).

The surface coverage of goethite with phosphate or citrate in the single anion experiments was high, which implies that, when these anions are added together, direct competition for binding sites must take place. For the conditions in Figure 3, the decrease in the adsorption of citrate can largely be explained from nonelectrostatic site competition. At pH 4, phosphate adsorption amounts to $1.6 \mu\text{mol m}^{-2}$. Due to the difference in the number of surface groups involved in surface complexation, this would lead to a decrease in the adsorption of citrate of about $0.9 \mu\text{mol m}^{-2}$, which is close to what was observed experimentally. When a smaller amount of phosphate is present in the mixed system (Figure 3), the decrease in citrate adsorption caused by competition is less. The decrease in the adsorption of phosphate due to the presence of citrate was smaller than expected from direct site competition, indicating the influence of electrostatic interaction.

The influence of electrostatic interaction is also demonstrated by the results of the model calculations. Using the original model parameter values (17, 19), the influence of citrate on phosphate adsorption is underestimated, although the general trend in the pH dependence of competitive adsorption is predicted well (Figure 3). The competitive interaction between phosphate and citrate on goethite was enlarged by changing the distribution of charge of citrate. A small amount of negative charge, -0.1 valence unit, was shifted from the 1-plane to the surface, and the corresponding $\log K$ values were adjusted because of this (Table 1). Consequently, the contribution of the electrostatic energy to the total affinity of the $-$ citrate surface complexes changed, and this resulted in lower adsorption of protonated phosphate bidentate complexes. The adsorption of phosphate was further reduced by decreasing the intrinsic affinity constant of the protonated bidentate phosphate complex by $0.1 \log K$ unit. With the adjusted parameter values, the data of single anion adsorption (17–19) and adsorption interactions (19, 28) are still described well.

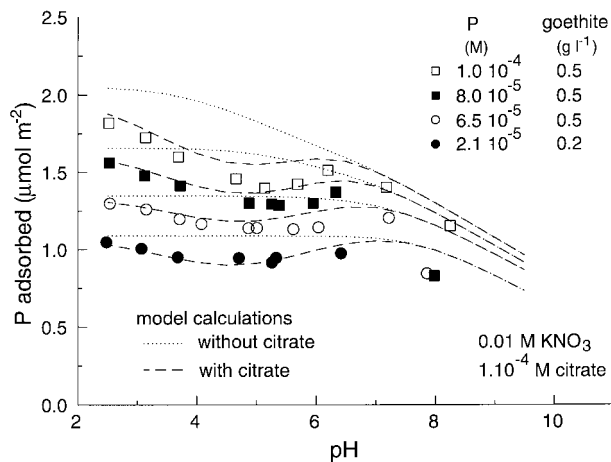


FIGURE 4. Phosphate adsorption on goethite at different phosphate loadings in the presence of an initial total concentration of 1×10^{-4} M citrate. Model calculations were performed with the adjusted parameter values for the presence (dashed lines) and absence of citrate (dotted lines).

The effect of citrate on phosphate adsorption at various phosphate loadings of goethite is shown in Figure 4. With decreasing phosphate loading of goethite, the effect of the presence of citrate on the amount of phosphate adsorbed becomes less. This may be attributable to a decreasing competition for binding sites, because a smaller part of the surface is covered with phosphate. Figure 5A shows that the presence of larger total concentrations of citrate increases the competitive interaction with phosphate. The increase in the phosphate concentration in solution caused by the competitive adsorption of citrate and phosphate is shown in Figure 5B. At the relatively low phosphate loading of goethite in this experiment, citrate had a very large effect on the phosphate concentration in solution. The phosphate concentration in solution increased 300–600-fold in the presence of a total concentration of 0.1–1 mM citrate. Even the presence of a low total concentration of citrate (1×10^{-5} M) resulted in an increase of the phosphate concentration in solution at low pH. The effect of the order of addition of phosphate and citrate on the phosphate concentration in solution, particularly when compared with the effect of competition, was relatively small (Figure 5B).

The competitive adsorption experiments carried out at relatively low phosphate loading (Figure 5) show that the presence of citrate had a much larger effect on the phosphate concentration in solution than on the amount of phosphate adsorbed. Adsorption isotherms of phosphate on goethite in the absence and presence of citrate (Figure 6) show that the relative increase in the phosphate concentration in solution caused by the presence of citrate increases with lower phosphate loading of goethite. Phosphate has a very high affinity for the goethite surface, which results in very small phosphate concentrations in solution when the surface coverage of goethite is low. As a result, a small decrease in phosphate adsorption caused by competition with citrate will lead to a very large relative increase in the phosphate concentration in solution. The competitive adsorption between phosphate and citrate decreases the affinity of phosphate for the goethite surface, which is illustrated by the larger slope of the phosphate adsorption isotherm in the presence of citrate (Figure 6).

Environmental Implications. In natural systems, the phosphate concentration in solution is generally low. Our experiments show that under these conditions competition between phosphate and organic compounds may result in a very large increase in the phosphate concentration in

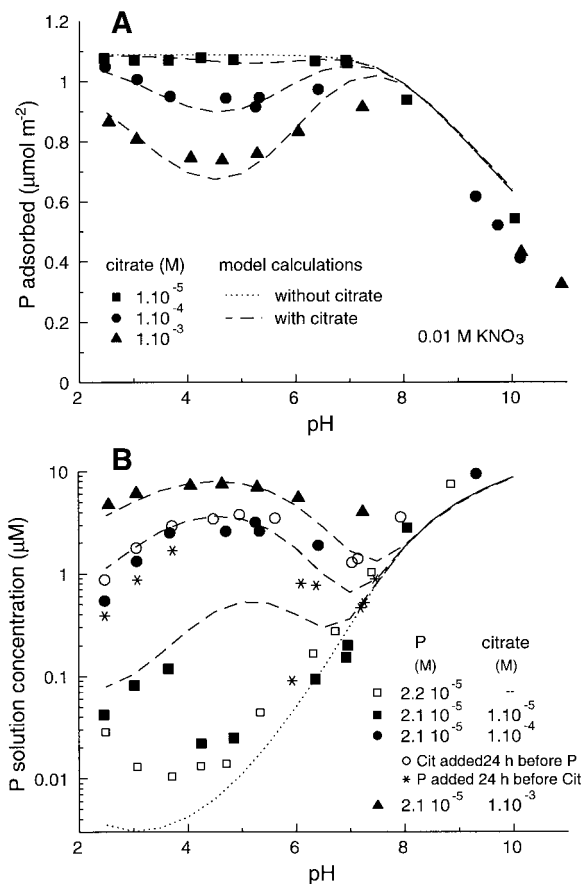


FIGURE 5. Influence of the initial total concentration of citrate on (A) the amount of phosphate adsorbed and (B) the phosphate concentration in solution for an initial total concentration of 2.1×10^{-5} M at $0.2 \text{ g of goethite L}^{-1}$. Also the measured phosphate concentration in solution in the absence of citrate is shown (data taken from ref 19). For 1×10^{-4} M citrate, the effect of different orders of addition on the phosphate concentration in solution is indicated. Model calculations were performed with the adjusted parameter values.

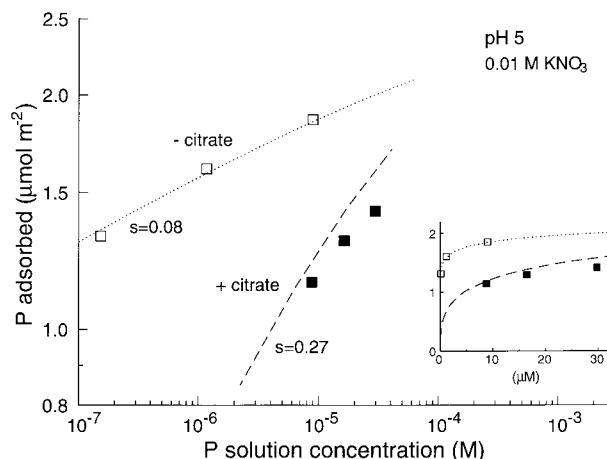


FIGURE 6. Phosphate adsorption isotherms at pH 5 in the absence of citrate and in the presence of an initial total concentration of 1×10^{-4} M citrate at $0.5 \text{ g of goethite L}^{-1}$. Data are interpolated from Figure 4 and from ref 19. Model calculations were performed with the adjusted parameter values. The slopes ($s = \Delta C_s / \Delta C$) of the isotherms are indicated for the concentration ranges at which they were calculated.

solution (Figure 6). The mobility and bioavailability of phosphate are directly related to the phosphate concentration

in solution (29) and will therefore increase strongly as a result of competitive adsorption.

The adsorption mechanisms of natural organic matter and small organic anions are similar (3), which implies that the mechanisms that determine competitive adsorption may be comparable as well. Competition for binding sites appeared to play an important role in the competitive interaction between phosphate and citrate. For organic compounds such as humic and fulvic acids, a large number of surface groups may be involved in the coordination to the surface, which suggests that these compounds can compete relatively strongly with anions such as phosphate.

The presence of natural organic matter is likely to decrease the affinity of phosphate for adsorption on metal (hydr)-oxides by competitive adsorption. Therefore, it is essential to take the competitive interaction of phosphate and organic matter into account in the modeling of the bioavailability and mobility of phosphate in natural systems.

Acknowledgments

We thank Dr. B. J. M. Verduin of the Department of Virology, Wageningen Agricultural University, for the use of the isotope laboratory; Mr. A. J. Korteweg, Department of Physical and Colloid Chemistry (WAU), for carrying out the BET surface area measurements; and Mr. R. P. J. J. Rietra for performing the potentiometric titrations of goethite.

Literature Cited

- (1) Tipping, E. *Geochim. Cosmochim. Acta* **1981**, *45*, 191–199.
- (2) Hawke, D.; Carpenter, P. D.; Hunter, K. A. *Environ. Sci. Technol.* **1989**, *23*, 187–191.
- (3) Gu, B.; Schmitt, J.; Chen, Z.; Liang, L.; McCarthy, J. F. *Environ. Sci. Technol.* **1994**, *28*, 38–46.
- (4) Cornell, R. M.; Schindler, P. W. *Colloid Polym. Sci.* **1980**, *258*, 1171–1175.
- (5) Tejedor-Tejedor, M. I.; Yost, E. C.; Anderson, M. A. *Langmuir* **1992**, *8*, 525–533.
- (6) Hoffland, E.; Findenegg, G. R.; Nelemans, J. A. *Plant Soil* **1989**, *113*, 161–165.
- (7) Leyval, C.; Berthelin, J. *Agric. Ecosyst. Environ.* **1989**, *28*, 313–319.

- (8) Afif, E.; Barrón, V.; Torrent, J. *Soil Sci.* **1995**, *159*, 207–211.
- (9) Earl, K. D.; Syers, J. K.; McLaughlin, J. R. *Soil Sci. Soc. Am. J.* **1979**, *43*, 674–678.
- (10) Lopez-Hernandez, D.; Flores, D.; Siegert, G.; Rodriguez, J. V. *Soil Sci.* **1979**, *128*, 321–326.
- (11) Lopez-Hernandez, D.; Siegert, G.; Rodriguez, J. V. *Soil Sci. Soc. Am. J.* **1986**, *50*, 1460–1462.
- (12) Hue, N. V. *Soil Sci.* **1991**, *152*, 463–471.
- (13) Gerke, J. Z. *Pflanzenernähr. Bodenkn.* **1992**, *155*, 339–343.
- (14) Nagarajah, S.; Posner, A. M.; Quirk, J. P. *Nature* **1970**, *228*, 83–85.
- (15) Parfitt, R. L. *Plant Soil* **1979**, *53*, 55–65.
- (16) Violante, A.; Colombo, C.; Buondonno, A. *Soil Sci. Soc. Am. J.* **1991**, *55*, 65–70.
- (17) Filius, J. D.; Hiemstra, T.; Van Riemsdijk, W. H. *J. Colloid Interface Sci.* **1997**, *195*, 368–380.
- (18) Hiemstra, T.; Van Riemsdijk, W. H. *J. Colloid Interface Sci.* **1996**, *179*, 488–508.
- (19) Geelhoed, J. S.; Hiemstra, T.; Van Riemsdijk, W. H. *Geochim. Cosmochim. Acta* **1997**, *61*, 2389–2396.
- (20) Novozamsky, I.; Van Dijk, D.; Van der Lee, J. J.; Houba, V. J. G. *Commun. Soil Sci. Plant Anal.* **1993**, *24*, 1065–1076.
- (21) Lindsay, W. L. *Chemical equilibria in soils*; John Wiley & Sons: New York, 1979.
- (22) Hiemstra, T.; Venema, P.; Van Riemsdijk, W. H. *J. Colloid Interface Sci.* **1996**, *184*, 680–692.
- (23) Tejedor-Tejedor, M. I.; Anderson, M. A. *Langmuir* **1990**, *6*, 602–611.
- (24) Hingston, F. J.; Atkinson, R. J.; Posner, A. M.; Quirk, J. P. *Nature* **1967**, *215*, 1459–1461.
- (25) Mesuere, K.; Fish, W. *Environ. Sci. Technol.* **1992**, *26*, 2365–2370.
- (26) Karlton, E. *Eur. J. Soil Sci.* **1998**, *49*, 113–120.
- (27) Ali, M. A.; Dzombak, D. A. *Environ. Sci. Technol.* **1996**, *30*, 1061–1071.
- (28) Venema, P.; Hiemstra, T.; Van Riemsdijk, W. H. *J. Colloid Interface Sci.* **1997**, *192*, 94–103.
- (29) Geelhoed, J. S.; Van Riemsdijk, W. H.; Findenegg, G. R. *Plant Soil* **1997**, *197*, 241–249.

Received for review October 17, 1997. Revised manuscript received April 17, 1998. Accepted April 24, 1998.

ES970908Y