Adsorption of a soil humic acid at the surface of goethite and its competitive interaction with phosphate

J. Antelo [a,*], F. Arce [a], M. Avena [c], S. Fiol [a], R. López [a], F. Macías [b]

[a] *Dep. de Química Física, Facultad de Química, Universidad de Santiago de Compostela. Avenida de las Ciencias s/n, Santiago de Compostela, 15782, Spain*
[b] *Dep. de Edafología y Química Agrícola, Facultad de Biología, Universidad de Santiago de Compostela, Spain*
[c] *Dep. de Química, Universidad Nacional del Sur, Bahía Blanca, Argentina*

Abstract

In order to be able to make predictions about the bioavailability and transport of contaminants and nutrients in soils, detailed knowledge is required about the adsorption of natural organic matter on the surface of oxides, as well as the processes of competition with the different ions present in the soil. With this aim, experiments investigating the adsorption of a soil humic acid (SHA) on goethite were carried out at pH 4.5, 7.0 and 10.0 and ionic strengths of 0.1 and 0.01 M, and the competition between SHA and phosphate was analysed by performing adsorption isotherms and electrophoresis experiments. Adsorption of SHA was clearly dependent on pH and ionic strength, decreasing with increasing pH or decreasing ionic strength. The results show that SHA and phosphate compete for the goethite surface, since the presence of phosphate decreases the adsorption of SHA and the presence of SHA decreases the adsorption of phosphate. Under certain conditions of pH, a decrease in phosphate adsorption of up to 45% and a decrease of SHA adsorption between 20 and 35% is produced. Furthermore, experiments performed by varying the order of addition of adsorbates to the goethite dispersion suggest that equilibration is attained more quickly when the adsorbates are added simultaneously than when one of the adsorbates is added before the other.
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1. Introduction

Both natural organic matter (NOM) and mineral oxides exert important effects on chemical speciation and the transport of nutrients and contaminants in soils and sediments. In natural systems, both types of substances are present at the same time and may interact with each other, forming surfaces that are relatively resistant to biodegradation. This mutual interaction may affect the role of mineral surfaces as reactive surfaces in natural environments, because their chemical properties – such as surface charge, colloidal stability and the adsorption capacity relative to other species present in solution – may be significantly altered (Tipping and Higgins, 1982; Murphy et al., 1990; Ali and Dzombak, 1996).

Natural organic matter consists of a mixture of well-defined weak organic acids and organic compounds that do not have a defined chemical structure. The latter predominate in the natural organic matter of soils and water, and are mainly composed of humic substances (Schnitzer and Khan, 1972). Humic substances (humic acids and fulvic acids) may constitute more than 80% of the organic matter of a soil and represent approximately 60% of the dissolved organic C in aquatic systems (Stevenson, 1994), and are therefore involved in the geochemical processes that occur in natural environments.

Many of the studies investigating the role of organic matter in adsorption processes on mineral surfaces (Du et al., 1999; Lenhart and Honeyman, 1999; Masset et al., 2000) have focused on metal cations, particularly those that occur as contaminants in natural environments. These types of systems are complex, because as well as the interactions of the cations and organic matter with the surface, there also exist interactions between the cations and either the dissolved organic matter or the organic matter that is adsorbed

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on the mineral surface. Although the competition between the organic matter and anions is not such a complex process, this type of system has not been well studied and existing studies have involved simple organic acids (Geelhoed et al., 1998; He et al., 1999; Grafe et al., 2001).

On the other hand, phosphorous is an element of major concern in environmental chemistry, as it is essential for plant growth in soils and is the nutrient that usually limits algal growth and eutrophication in surface waters (Klapper, 1991). It is well known that phosphate shows a relatively strong affinity for metal (hydr)oxides, especially iron and aluminum (hydr) oxides (Hiemstra and van Riemsdijk, 1996; Manning and Goldberg, 1996). The affinity of phosphate for the mineral surface depends not only on the anion binding capacity, but also on attractive or repulsive electrostatic interactions with the charged mineral surface. Many researchers have investigated phosphate adsorption reactions on oxide minerals using macroscopic and spectroscopic techniques. Phosphate is strongly adsorbed at low pH values and shows pH dependence, with adsorption decreasing as pH increases (Antelo et al., 2005). Moreover, phosphate adsorption is also dependent on ionic strength, increasing as ionic strength increases (Barrow et al., 1980; Antelo et al., 2005).

Most studies on the effect of organic matter on the adsorption of phosphate (Hingston et al., 1971; Sibanda and Young, 1986; Violante et al., 1991; Violante and Gianfreda, 1993) have been carried out using iron and aluminum oxides, as these are mainly responsible for the fixation of phosphate in soils. From the results obtained in such studies it has been concluded that di- and tricarboxylic organic acids reduce the adsorption of phosphate, whereas monocarboxylic acids have an insignificant effect on the adsorption of this anion. Noteworthy amongst these studies is that of Sibanda and Young (1986), who investigated the competitive adsorption of phosphate and humic substances on goethite and gibbsite, and reached the conclusion that humic substances block some surface sites, thereby reducing the adsorption of phosphate.

The main aims of the present study were to investigate the adsorption of a soil humic acid (SHA) on goethite, as well as some factors that may affect this process, i.e. pH and ionic strength, and also to analyze the competition between phosphate and SHA for goethite. Goethite (α-FeOOH) was used as the mineral surface as it is one of the most abundant mineral (hydr) oxides in soils and has been used as a model system in numerous studies of the interaction of cations, anions or organic substances with mineral surfaces. For the competition study, a series of experiments were carried out to investigate the effect that the humic substance concentration and the order of addition of the species had on the adsorption of phosphate and SHA on goethite at different values of pH and ionic strength. The analysis of the adsorption results was made from a qualitative point of view. A full quantitative description is unavoidable at the moment, since the modelling of the interactions between the humic acids and mineral surfaces has not been solved in the way that is needed for the description of the results. Recent developments in the modelling of the binding of humic substances and metal (hydr)oxide (Weng et al., 2005; Weng et al., 2006a), hopefully will lead to the possibility to model this kind of data in the near future.

In addition, an electrophoretic study of the goethite-SHA-phosphate system was carried out to analyze the effect that the simultaneous adsorption of the two substances had on the surface charge, and to compare this effect with that observed when SHA or phosphate are adsorbed separately.

2. Materials and methods

2.1. Synthesis and characterization of goethite

Powdered goethite was prepared following a similar method to that proposed by Atkinson et al. (1967), and as previously described in greater detail (Antelo et al., 2005). The goethite sample was characterized using powder X-ray diffraction, transmission electron microscopy (TEM) and FTIR spectroscopy. The specific surface area was measured by the N_2 adsorption method and was found to be 70.8 m^2 g^{-1}. The point of zero charge (PZC) of the goethite sample was also determined with potentiometric titrations (Antelo et al., 2005). The PZC value, defined as the common intersection point of the different acid-base titration curves, was found to be 9.3 ± 0.1, which is similar to the PZC values of other goethite samples (Hiemstra and van Riemsdijk, 1996; Villalobos and Leckie, 2000).

2.2. Extraction and structural characterization of the soil humic acid sample

The SHA sample was extracted from the A horizon of a Humic Cambisol developed from granite and under eucalyptus (Monte Pedroso, Santiago de Compostela, NW Spain) by the method recommended by the International Humic Substances Society (Swift, 1996). The SHA sample was characterized by elemental analysis, UV spectroscopy, CPMAS ^{13}C NMR and acid-base potentiometric titrations. The main characteristics of the SHA are shown in Table 1.

2.3. Soil humic acid adsorption isotherms

To obtain the adsorption isotherms of SHA on goethite, additions of different volumes of a SHA solution to suspensions of iron hydroxide were carried out, so that the initial concentration

Table 1
Analytical characteristics of SHA

Elemental analysis (%)				E_4/E_6
C	H	N	Ash	4
50.81	3.72	4.40	<1	

Relative ^{13}C intensity of each chemical shift region (%)					
$C_{aliphatic}$	$C-O_{aliphatic}$	$C_{aromatic}$	$C_{phenolic}$	$C_{carboxylic}$	$C_{carbonylic}$
32.0	31.1	19.7	3.5	10.5	5.3

Acid groups content — NICA-Donnan, mol Kg^{-1}	
Carboxylic	2.23
Phenolic	1.35

of SHA varied between 10 and 200 mg L^{-1} and that of goethite was 0.6 g L^{-1}. Ionic strengths of 0.1 and 0.01 M were used in the study and the pH was adjusted by adding small volumes of 0.05 M HCl or OH, to achieve pH 4.5, 7.0 and 10.0. The suspensions were maintained, with shaking, in a water bath at 25.0±0.1 °C for 18–24 hours, which is longer than the time required to ensure that humic substances adsorption equilibrium on goethite is reached. Special care was taken to avoid the presence of CO_2, keeping the goethite suspensions in a N_2 atmosphere.

The suspensions were then centrifuged for 30 min at 6000 rpm and the SHA concentration in the solution was determined by UV spectroscopy (Vermeer et al., 1998; Du et al., 1999), measuring the absorbance at 360 and 400 nm (UV–vis Spectrophotometer JASCO V-530). Prior to each measurement the pH was adjusted (pH ≈ 8.7) with a NaHCO$_3$ buffer solution, to achieve the conditions under which the calibration was carried out. The amount of SHA adsorbed was calculated by subtracting the measured free concentration from the initial amount of SHA in solution.

2.4. Competitive adsorption experiments

The competition experiments were carried out at pH 4.5 and 7.0. Four different concentrations of SHA were used at each pH (pH=4.5–40, 100, 130, 160 mg L^{-1}; pH 7.0–40, 60, 80 and 115 mg L^{-1}) and different volumes of phosphate solution were added so that the initial concentration of anion was between 0.01 and 0.2 mM. The concentration of goethite in the suspension was 0.6 g L^{-1} and the ionic strength was 0.1 M. Competition experiments were also carried out at 0.01 M ionic strength, pH 4.5 and with two concentrations of SHA (40 and 130 mg L^{-1}).

In the study of the competitive adsorption, three types of experiments were carried out:

Simultaneous addition of SHA and phosphate: Once the simultaneous addition of the two species was carried out, the pH of the suspensions was adjusted as indicated above and the samples were then shaken for 24–36 hours. According to He et al. (1999) and Grafe et al. (2001), this is the time necessary for the samples to reach equilibrium.

Prior adsorption of SHA: In this experiment the SHA was added first, the pH was adjusted and then the suspensions shaken for 18–24 hours. Once the SHA was adsorbed on the goethite, the phosphate was added, the pH was readjusted to the required value and the suspensions were shaken for 24–36 hours, thus ensuring the equilibrium of adsorption of phosphate on goethite covered with SHA.

Prior adsorption of phosphate: Some additional experiments were carried out to examine the effect of prior addition of phosphate. This experiment was carried out in the same way as the previous experiment, but reversing the order of addition of phosphate and SHA.

At the end of the reaction period in all the experiments the suspensions were centrifuged for 30 min at 6000 rpm. The SHA concentration in solution was measured as described before and

the phosphate concentration was measured using the method proposed by Murphy and Riley (1962). The amounts of SHA and phosphate adsorbed were calculated from the difference between the initial and final concentrations of the species in solution.

All three types of experiments were carried out in a constant temperature water bath at 25.0±0.1 °C and in N_2 atmosphere.

2.5. Electrophoresis experiments

For the experiments investigating electrophoretic mobility, suspensions of 0.015 g L^{-1} of goethite in 0.01 M KNO$_3$ were prepared. Phosphate was added to obtain two concentrations of the anion (10^{-4} and 10^{-5} M) and the SHA to obtain a concentration of 0.2 mg L^{-1}. Aliquots of these suspensions were then removed and small amounts of 0.05 M HCl or KOH were added to achieve a range of values between pH 3 and 11. The suspensions were shaken for 24 hours in a constant temperature water bath at 25.0±0.1 °C, and the electrophoretic mobility was then measured. Additional experiments were also carried out to study the electrophoretic mobility of goethite alone and in the presence of phosphate or SHA, in a similar way to that described above. The electrophoretic mobilities were measured with a Malvern Zetamaster 5002 instrument. The average of three different measurements was calculated. Zeta potential values were calculated from electrophoretic mobilities using the Smoluchowsky equation.

3. Results and discussion

3.1. Soil humic acid adsorption experiments

The adsorption isotherms of SHA at an electrolyte concentration of 0.1 M and at different pH values are shown in Fig. 1. All of these isotherms can be defined as type L isotherms, which can be described by the Langmuir equation and reflect the great affinity of the mineral surface for these types of substances. A decrease in the adsorption of SHA was observed with increasing pH, a pattern that is usually found in studies of adsorption of natural organic matter on mineral oxides (Du et al., 1999; Tombacz et al., 2000). There are no models in the literature that can explain completely the
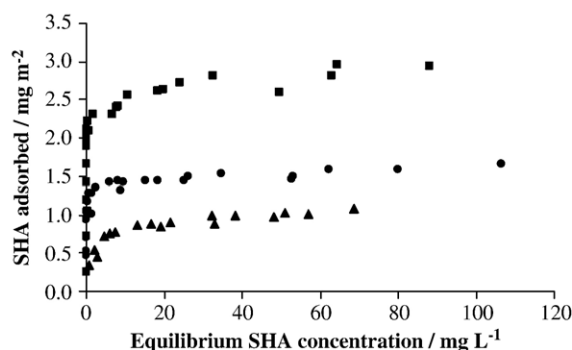

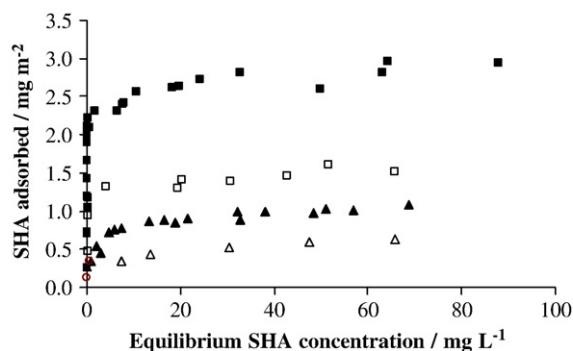Fig. 1. SHA adsorption on goethite in 0.1 M KNO$_3$. (■) pH 4.5; (●) pH 7.0; (▲) pH 10.0.

Fig. 2. Effect of ionic strength on SHA adsorption. Solid symbols, 0.1 M KNO₃; empty symbols, 0.01 M KNO₃. (■) pH 4.5; (▲) pH 10.0.

adsorption of humic acids on mineral surfaces. However, taking into account the latest insights that can be derived from the work by Weng et al. (2006b) on fulvic acid adsorption on goethite, the effect of pH on the adsorption seems to be a combined result of electrostatics, specific binding of SHA functional groups (mainly carboxylic) to goethite surface groups, and co-adsorption or co-desorption of protons at the SHA and goethite groups upon the humic adsorption. SHA is negatively charged at all pH values, whereas the goethite surface decreases its positive charge going from low pH to high pH, becoming negatively charged above its PZC (9.3). This indicates that the electrostatic attraction among the SHA and the goethite surface increases as the pH is decreased, resulting in a more favourable interaction and in a change in the degree of protonation of the SHA, facts that lead to higher adsorption (Weng et al., 2006b). As stated above, the interactions involved in the adsorption process are not only electrostatic, but there also exist specific non electrostatic interactions (Schlautman and Morgan, 1994; Vermeer et al., 1998). These types of interactions explain the adsorption of humic substances at pH values higher than the PZC, as under these conditions the electrostatic repulsions should lead to negligible adsorption.

The effect of ionic strength on SHA adsorption is shown in Fig. 2, in which, for reasons of clarity, only the results obtained for two pH values are included. It can be observed that an increase in adsorption is produced as the ionic strength of the medium increases. This pattern was also found in previous studies on the adsorption of humic substances on mineral oxides

(Kretzschmar et al., 1997; Tombacz et al., 2000). According to Jones and O'Melia (2000) this effect of the ionic strength is mainly given by changes in lateral electrostatic repulsion among adsorbed humic acid molecules. A decrease in the ionic strength results in increased lateral repulsions between adsorbed molecules, which lead to a reduced adsorption. According to the recent results of Weng et al. (2006a), the effect of changing the ionic strength is more complicated and involves not only electrostatics but also changes in the degree of protonation of the humic acid upon adsorption, mainly due to changes in the decay of the electric potential across the interface. In addition to the previous explanations, the variation in the ionic strength could induce conformational changes in humic acid molecules that may affect the adsorption process (Kretzschmar et al., 1997; Tombacz et al., 2000). Ions of the inert electrolyte exert a screening effect on the repulsion between the negative charges of the ionized groups of SHA, which at high ionic strength facilitates coiling or shrinking of the molecules, whereas at low ionic strength produces a more expanded structure (Ghosh and Schnitzer, 1980). In the latter conformation the molecules of SHA may occupy a larger area of the oxide surface, so that there will be a decrease in the adsorption.

3.2. The effect of SHA on phosphate adsorption

The adsorption isotherms of phosphate in the presence of SHA, corresponding to the simultaneous addition experiments at an ionic strength of 0.1 M, are shown in Fig. 3. They are compared to the phosphate adsorption isotherms in the absence of SHA obtained in a previous study (Antelo et al., 2005). The adsorption of phosphate decreases as the concentration of SHA increases. The results suggest that a competitive adsorption process between phosphate and SHA takes place. Phosphate ions are known to specifically bind goethite surface sites (Antelo et al., 2005), and thus functional groups of the SHA compete with phosphate for these adsorption sites. Electrostatic may also play an important role in the behaviour of the system. Since the adsorption of negatively charged SHA molecules should increase the negative electric potential near the goethite surface (or decrease the positive potential), the overall affinity of phosphate anions for the goethite surface should decrease in the presence of adsorbed SHA, resulting in a decreased phosphate adsorption. In addition to competition for surface sites and
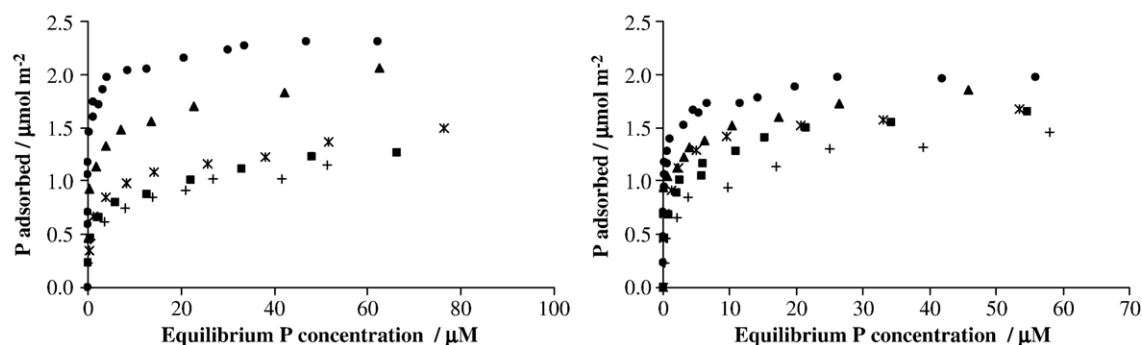

Fig. 3. Phosphate adsorption on goethite in the presence of SHA. Ionic strength 0.1 M KNO₃. Left, pH 4.5, (●) 0; (▲) 40; (∗) 100; (■) 130; (+) 160 mg L⁻¹ of SHA. Right, pH 7.0, (●) 0; (▲) 40; (∗) 60; (■) 80; (+) 115 mg L⁻¹ of SHA.
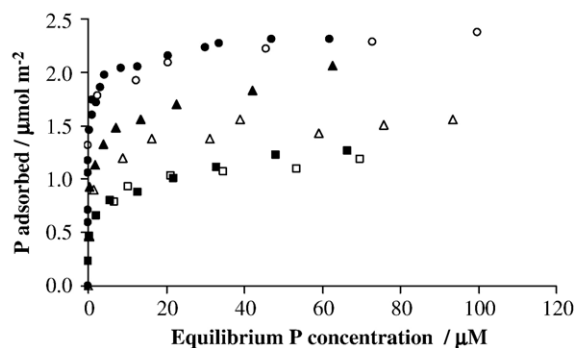
Fig. 4. Effect of ionic strength on phosphate adsorption in the presence of SHA at pH 4.5. Solid symbols, 0.1 M KNO_3; empty symbols, 0.01 M KNO_3. (●) 0; (▲) 40; (■) 130 mg L^{-1} of SHA.

electrostatics, some steric effects could also affect the adsorption of phosphate in the presence of SHA. Due to the relatively large size of the humic acid molecules, it is possible that adsorbed SHA molecules block part of the surface and decrease the availability of surface sites for phosphate adsorption (Simeoni et al., 2003).

Fig. 3 also shows that the effect of the presence of SHA on phosphate adsorption is stronger at low pH than at high pH. In fact, SHA reduces phosphate adsorption by 45% at pH=4.5 and by 25% at pH=7.0 (in both cases at the highest SHA concentration). This is in line with the explanations presented above, because a larger amount of SHA is adsorbed at low pH.

The effect of ionic strength on the phosphate adsorption isotherms in the presence of SHA is shown in Fig. 4. In the absence of SHA, there is no important effect of ionic strength, fact that has been observed and modelled in a previous publication (Antelo et al., 2005). Since phosphate specifically adsorbs at the goethite surface, changes in the ionic strength produce a very small and sometimes undetectable effect on the adsorption. The ionic strength has different effects on phosphate adsorption in the presence of SHA, depending on the concentration of the humic acid. At the lowest concentration of SHA a decrease in phosphate adsorption is observed with decreasing ionic strength, while at the highest SHA concentration, ionic strength is not observed to have any effect. The combination of two facts should be invoked to explain the results. On one hand,

the changes in SHA adsorption that take place by changing ionic strength. On the other hand, the conformational changes that adsorbed SHA may undergo upon changing ionic strength. The experiments showed that at low SHA concentrations the ionic strength had almost no effect on the adsorption of SHA. Therefore, it seems that the more expanded structure of SHA molecules is causing the decrease in phosphate adsorption at low ionic strength. On the contrary, at high SHA concentrations there was a marked decrease in the adsorption of SHA when the ionic strength was decreased, and thus an increase in phosphate adsorption should be expected. However, this increase in the adsorption appears to be compensated by the expansion of SHA under these conditions.

The effect of the order of addition of both species to the goethite suspensions is shown in Fig. 5. Each graph in the figure represents phosphate adsorption isotherms at a given SHA concentration, and compares the data with the phosphate adsorption isotherm in absence of SHA. Although the results obtained when SHA and phosphate were added simultaneously are nearly coincident to those obtained with previous adsorption of SHA, they do not coincide with the results obtained with previous adsorption of phosphate. In a study of the competition between arsenate and humic substances, Grafe et al. (2001) did not observe any differences on varying the order of addition of the species. In contrast, Violante et al. (1991) and He et al. (1999) observed differences in the adsorption of phosphate on carrying out the adsorption prior to, or simultaneously with simple organic acids with a shaking time up to 4 days. The observed differences clearly indicate that equilibrium has not been reached in some of the experiments, and that a slow kinetic is involved in some of them.

Depending on the order of adsorbates addition, phosphate adsorption has to approach equilibrium in different directions. For example, when only phosphate is added at the beginning of the experiment, there will be an important phosphate adsorption that should coincide with the phosphate adsorption isotherm in absence of SHA. Afterwards, once SHA is added, the competition among SHA and phosphate should induce a decrease in phosphate adsorption, and equilibrium has to be reached moving from high amounts of adsorbed phosphate to lower amounts of adsorbed phosphate. This decrease in phosphate adsorption is not observed for low SHA concentration (40 mg L^{-1}, graph in the left side), indicating that SHA
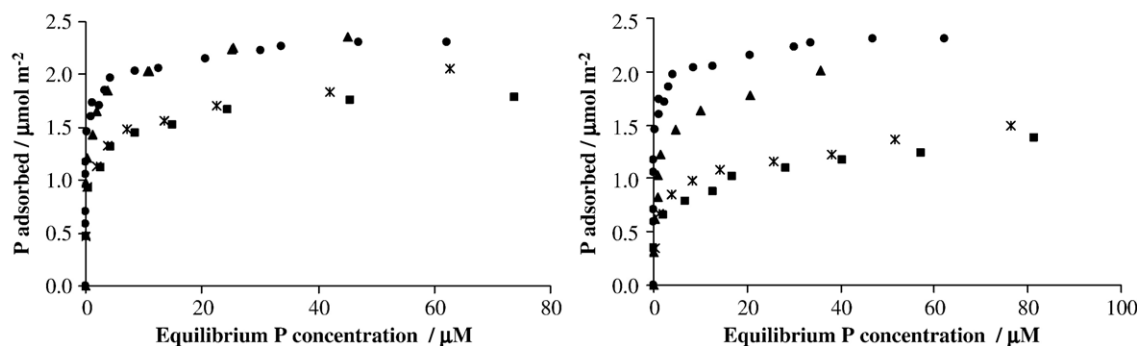

Fig. 5. Effect of the order of addition in the adsorption of phosphate on goethite at pH 4.5 and ionic strength 0.1 M KNO_3. Left, 40 mg L^{-1} of SHA. Right, 100 mg L^{-1} of SHA (●) in absence of SHA; (▲) previous addition of phosphate; (✳) simultaneous addition; (■) previous addition of SHA.
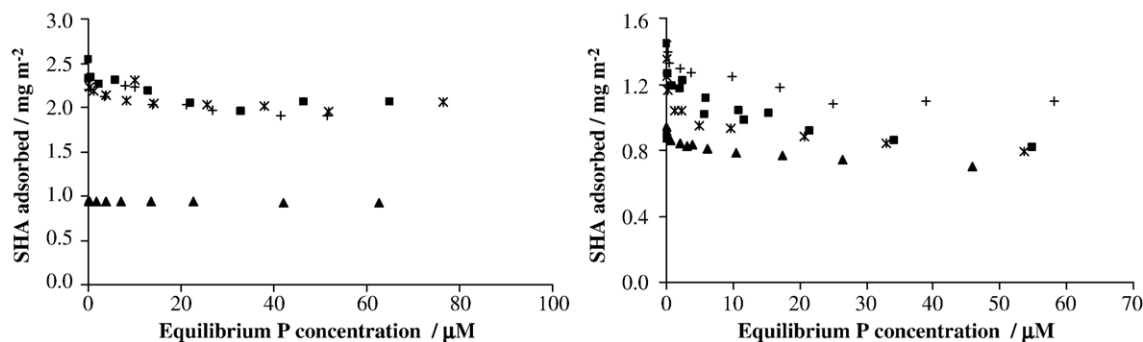
Fig. 6. Influence of phosphate on SHA adsorption on goethite in 0.1 M KNO$_3$. Left, pH 4.5, (▲) 40; (✳) 100; (■) 130; (+) 160 mg L^{-1} of SHA. Right, pH 7.0, (▲) 40; (✳) 60; (■) 80; (+) 115 mg L^{-1} of SHA.

does not displace adsorbed phosphate quickly. For high SHA concentration (100 mg L^{-1}, graph in the right side) some phosphate is desorbed by the presence of SHA. On the contrary, when only SHA is added at the beginning of the experiment, the subsequent addition of phosphate should induce a phosphate adsorption. Thus, phosphate has to be adsorbed by displacing some of the previously adsorbed SHA molecules, and equilibrium has to be reached moving from zero adsorbed phosphate to higher amounts of adsorbed phosphate. This phosphate adsorption seems to take place rather quickly since in both cases (with 40 and 100 mg L^{-1} SHA) an important adsorption is detected. In the third case, simultaneous addition of both adsorbates, phosphate and SHA should adsorb simultaneously at the goethite surface and compete for common sites. These two last types of experiments, previous addition of SHA and simultaneous addition of the adsorbates, lead to nearly coincident phosphate adsorption isotherms even though they approach equilibrium in different ways. Then, it is possible to speculate that the results obtained with these two experiments represent equilibrium or near equilibrium situations. Perhaps the experiments with previous addition of SHA still need an extra short time to reach complete equilibrium because phosphate adsorption isotherms under this condition are not exactly coincident with those obtained with simultaneous addition of adsorbates. Conversely, data obtained with previous addition of phosphate are far from those obtained with the other two types of experiments, indicating that they do not represent equilibrium situations.

3.3. Influence of phosphate on SHA adsorption

The effect of the presence of phosphate on SHA adsorption at 0.1 M ionic strength is shown in Fig. 6. In these experiments, phosphate and SHA were added simultaneously. For all concentrations of the humic acid there was a decrease in the adsorption of SHA on increasing the concentration of phosphate in solution. At pH=7.0 the adsorption of SHA was reduced up to 35% by the presence of phosphate, whereas at pH=4.5 the decrease was less, up to 20%. For both pH values, at the lowest concentration of SHA there was a lower reduction in adsorption, apparently because at this concentration there are enough surface sites for both adsorbates, and thus competition is not very important. Grafe et al. (2001) found a similar behaviour for the adsorption of humic acid in the presence of arsenate ion, which is consistent with the similar adsorption behaviour of phosphate and arsenate on goethite at 0.1 M ionic strength (Antelo et al., 2005). A similar behaviour to that shown in Fig. 6 was found at 0.01 M ionic strength, although the adsorption of SHA was much lower than at 0.1 M ionic strength.

As with the investigation of the adsorption of phosphate, the effect of the order of addition of species on the SHA adsorption was analysed, and the data are shown in Fig. 7. In this case, only the data obtained on carrying out simultaneous adsorption and prior adsorption of SHA are shown. Furthermore, only two of the SHA concentrations are shown for each of the pH values and at 0.1 M ionic strength.

For the lowest concentration of SHA, no difference between the two types of experiments was observed and the reduction in
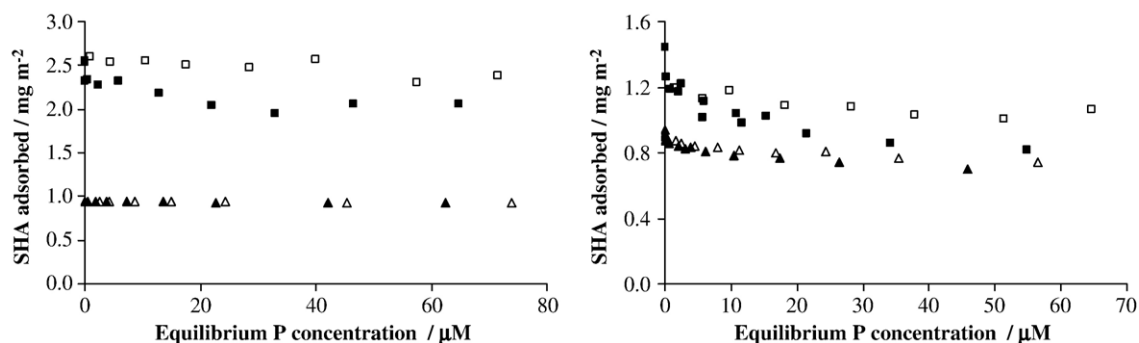

Fig. 7. Effect of the order of addition in the adsorption of SHA. Solid symbols, simultaneous addition; empty symbols, previous addition of SHA. Left, pH 4.5, (▲) 40; (■) 130 mg L^{-1} of SHA. Right, pH 7.0, (▲) 40; (■) 80 mg L^{-1} of SHA.

the adsorption was minimal, for reasons already explained above. For the highest concentration of SHA, although the results for both types of experiments are rather similar, adsorbed SHA is somewhat lower in the experiments involving simultaneous addition, especially at pH=4.5 and at high phosphate concentrations at pH=7.0. The results are in line with those obtained for phosphate adsorption in the presence of SHA, which show that in the experiments with previous addition of SHA the system may still need an extra short time for equilibration.

3.4. Electrophoresis

The electrophoretic mobility measures the movement of particles in suspension by the effect of an applied electric potential, and is directly related to the zeta potential, which usually reflects the net effective charge of the moving entity (Hunter, 1981). Thus, although it is difficult to measure the surface charge of a mineral oxide in the presence of several adsorbates such as phosphate and SHA, the electrophoretic mobility or zeta potential provides an estimate of the net charge of the moving particle. Furthermore, electrophoresis experiments allow determination of the isoelectric point, IEP, of variable charge particles. The IEP is defined as the pH at which the electrophoretic mobility, the zeta potential or the net charge of the moving particle is zero. Due to protonation–deprotonation reactions at the mineral surface and at adsorbed molecules, the net charge of the particle is usually positive at pH<IEP and negative at pH>IEP.

The zeta potential curves corresponding to goethite and to goethite in the presence of phosphate, of SHA and of both substances are shown in Fig. 8. In the absence of phosphate and SHA, goethite shows an IEP value of 9.1, with zeta potential values that are positive at pH values lower than the IEP, and negative at higher pH values. Therefore at pH<IEP, goethite particles have a net positive charge and at pH>IEP they have a net negative charge. The presence of either phosphate or SHA in the goethite suspension leads to a substantial decrease in the zeta potential and the IEP, so that the particles have a negative charge within a wider range of pH values. The decrease in the IEP indicates that anionic species of phosphate and SHA are adsorbed on goethite under the investigated conditions (Hunter, 1981). Moreover, the fact that the lowest values of the IEP are found for the system containing phosphate and SHA indicates

that both substances are present together at the surface, contributing to further decrease the IEP.

The analysis of the magnitude of electrophoretic mobility or zeta potentials is sometimes not as straightforward as the analysis of IEP values. Even though the sign of the zeta potential reflects the sign of the net charge of the moving particle, its magnitude is not directly related to the magnitude of this charge in many cases, especially when large molecules such as polyelectrolytes or humic acids are adsorbed at the particle surface. The plane of shear may shift towards the solution side of the interface upon adsorption of this kind of molecules and thus the net charge of the moving particles becomes determined not only by the surface charge and the adsorbate charge but also by the presence of diffusely bound ions (co- and counterions). If no shift in the plane of shear occurs upon adsorption, an increase in the zeta potential will normally indicate an increase in the net charge of the particle and *vice versa*. Under this assumption, the magnitudes of the zeta potentials also indicate that both adsorbates decrease the net charge of the moving goethite particles, and that both adsorbates can reside together at the surface particles, which contributes to a further decrease in the charge.

4. Conclusions

The adsorption of SHA on goethite depends on the pH and ionic strength. The decrease in adsorption with increasing pH and with decreasing ionic strength seems to be mainly produced by electrostatic effects, although a complete quantitative description of the results should also take into account specific binding between SHA functional groups and goethite surface groups, co-adsorption or co-desorption of protons at the SHA and goethite groups upon the humic adsorption, and perhaps some changes in the humic acid structure.

Data for phosphate and SHA adsorption on goethite reveal that both adsorbates compete for the surface. Indeed, the addition of SHA decreases phosphate adsorption, and the addition of phosphate decreases SHA adsorption. The magnitude of the competition depends on the pH, with the greater decrease in the adsorption of phosphate at pH 4.5, and the greater decrease in the adsorption of SHA at pH 7.0. The results indicate that both adsorbates may compete for common surface sites, and that also electrostatics may play a role in the competition since both phosphate and SHA induce the development of negative charges at the particles surface.
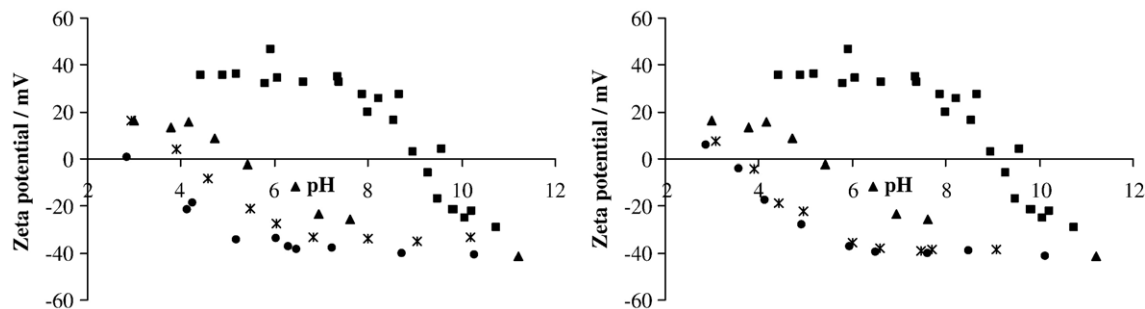

Fig. 8. Zeta potential of goethite in 0.01 M KNO$_3$ in the presence of 0.2 mg L^{-1} of SHA at two PO$_4$ concentrations. Left, 10^{-4} M of PO$_4$. Right, 10^{-5} M of PO$_4$. (■) goethite; (▲) goethite+SHA; (∗) goethite+PO$_4$; (●) goethite+SHA+PO$_4$.

The differences in adsorption of both phosphate and SHA on varying their order of addition show that equilibrium is not always attained under the studied conditions. Equilibrium seems to be reached when phosphate and SHA are added simultaneously, and near equilibrium situations are reached in the experiments with previous addition of SHA. On the contrary, experiments with previous addition of phosphate do not give indications of equilibration. The results indicate that in the experiments where one of the component is added first, the desorption of this component is rather slow (specially for phosphate) and thus equilibrium is attained more slowly that in the case of simultaneous addition.

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