

Kinetics of phosphate adsorption on goethite: Comparing batch adsorption and ATR-IR measurements

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Abstract

The adsorption kinetics of phosphate on goethite has been studied by batch adsorption experiments and by in situ ATR-IR spectroscopy at different pH, initial phosphate concentrations and stirring rates. Batch adsorption results are very similar to those reported by several authors, and show a rather fast initial adsorption taking place in a few minutes followed by a slower process taking place in days or weeks. The adsorption kinetics could be also monitored by integrating the phosphate signals obtained in ATR-IR experiments, and a very good agreement between both techniques was found. At pH 4.5 two surface complexes, the bidentate nonprotonated $(\text{FeO})_2\text{PO}_2$ and the bidentate protonated $(\text{FeO})_2(\text{OH})\text{PO}$ complexes, are formed at the surface. There are small changes in the relative concentrations of these species as the reaction proceeds, and they seem to evolve in time rather independently. At pH 7.5 and 9 the dominating surface species is $(\text{FeO})_2\text{PO}_2$, which is accompanied by an extra unidentified species at low concentration. They also seem to evolve independently as the reaction proceeds. The results are consistent with a mechanism that involve a fast adsorption followed by a slow diffusion into pores, and are not consistent with surface precipitation of iron phosphate.

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1. Introduction

Phosphate is of major concern in environmental chemistry. It is essential for plant growth in soils and has been recognized as one of the main nutrients that controls eutrophication in surface water bodies [1,2]. Its transport and fate in soils and aquifers must be well understood to better evaluate its environmental impact.

It is well known that the mobilization of phosphate in the environment is markedly influenced by mineral surfaces. Adsorption at mineral surfaces determines the quantity of phosphate that is retained in the solid phase of soils, groundwaters and surface waters and therefore is one of the primary processes that affect and control the transport and bioavailability of this anion [3].

Many articles have been published so far on the adsorption of phosphate on minerals in equilibrium or near equilibrium conditions. Most of them deal with the adsorption on goethite ($\alpha\text{-FeOOH}$), which is one of the most common and stable crystalline iron (hydr)oxides in natural systems. There is abundant information on the effects of pH on phosphate adsorption on goethite. The adsorption occurs in an ample range of pH, increasing by decreasing pH. The interaction is so strong that phosphate adsorbs even under conditions where the solid surface is negatively charged [4,5]. There is also considerable information on the effects of ionic strength on the adsorption. The experiments show that ionic strength has a relatively small influence on the adsorption behavior [6], suggesting small competition with supporting electrolyte ions. Other articles also investigate the effects of goethite crystal morphology on phosphate adsorption–desorption [5], and competition between phosphate and other anions for the goethite surface [7–9]. Spectroscopic studies are less abundant but they provide very useful infor-

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mation on the identity of the surface species that phosphate forms when adsorbed at the iron (hydr)oxide–water interface. Tejedor-Tejedor and Anderson [10], for example, used CIR-FTIR spectroscopy to study phosphate adsorption on goethite and concluded that phosphate adsorbs at the surface through the formation of three different inner-sphere surface complexes: a monodentate nonprotonated complex, and two bidentate complexes, one protonated and one nonprotonated.

Although much less studied than adsorption under equilibrium or near equilibrium conditions, phosphate adsorption kinetics at the goethite–water interface is also documented in the literature [5,11]. The interest in studying phosphate adsorption kinetics is not only theoretical but also practical. It gives fundamental information on the adsorption mechanism, and valuable practical information that makes it possible to evaluate and predict the rate at which phosphate is sorbed by the solid phase in soils and sediments of surface waters. Strauss et al. [5] investigated the effects of pH, phosphate concentration and crystallinity of goethite on the adsorption kinetics of phosphate between 30 min and 6 weeks. The data reveals that in most goethites there is a fast initial adsorption process that takes place in a few minutes, followed by a slower process that may last for several days or even weeks. This two-step adsorption seems to be normal for phosphate adsorption on goethite [11], and on many other mineral and soil surfaces [12–15]. Several mechanisms have been proposed to explain the two-step adsorption, although there are still some controversies about the mechanism involved in the slow process, and more research is still needed.

All kinetic studies regarding phosphate adsorption on goethite rely on macroscopic adsorption data. No spectroscopic study has been published so far, and thus there is a lack of information about the type of phosphate species that become adsorbed as a function of time. This information could be very important to elucidate the adsorption mechanism.

This article presents a study of the phosphate adsorption kinetics at the goethite water interface. The effects of varying pH, initial phosphate concentration and stirring rate are investigated. In some selected cases, batch adsorption experiments were combined with *in situ* ATR-IR spectroscopy in order to monitor the evolution of the adsorbed phosphate species as a function of the reaction time. This gives new insights into the adsorption mechanism.

2. Materials and methods

2.1. Goethite synthesis and general characterization

Goethite was prepared using a procedure similar to that described by Atkinson et al. [16]. Briefly, a 5 M NaOH solution was added dropwise (10 mL min^{-1}) to a 0.1 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution until the pH was 12. The resulting ferrihydrite dispersion was aged at 60°C during 3 days and then it was dialysed at room temperature against doubly-distilled water until the conductivity was lower than $10 \mu\text{S cm}^{-1}$. After that, the dispersion was freeze-dried in order to obtain a dry powder.

Powder X-ray diffraction was measured with a Phillips PW1710 diffractometer between 10° and 70° 2θ using $\text{CuK}\alpha$ radiation. Transmission electron microscopy was performed using a Phillips CM-12 microscope. Transmission FTIR spectra were obtained with a Nexus 470 spectrophotometer, and the BET surface area was measured by N_2 adsorption with a Micromeritics ASAP 2000 V3.03 instrument.

2.2. Batch adsorption kinetics

Phosphate adsorption kinetic experiments were carried out in a cylindrical, water-jacketed reaction vessel covered with a glass cap. Mixing was done by a magnetic stirrer, and carbon dioxide contamination was avoided by bubbling water-saturated N_2 . The reaction temperature was maintained at $25 \pm 0.2^\circ\text{C}$ by circulating water through the jacket with a FAC (Argentina) water bath/circulator.

Before starting a kinetic experiment, a stock goethite dispersion (12.5 g L^{-1}) was prepared by adding solid goethite to a 0.1 M KNO_3 solution. The pH of the resulting dispersion was then adjusted to the desired value by adding HNO_3 or KOH solutions. Paralelly, 100 mL of a 0.1 M KNO_3 solution containing a known concentration of phosphate were placed in the reaction vessel, and the stirring (450 rpm, except for the cases where effects of stirring rate were investigated), N_2 bubbling and water circulation were switched on. Once the temperature reached $25 \pm 0.2^\circ\text{C}$, the pH of the KNO_3 /phosphate solution was adjusted to the same pH value of the stock goethite dispersion. The kinetic experiment was started by adding 2.4 mL of the stock dispersion to the KNO_3 /phosphate solution in the reaction vessel. This time was set as the initial time of the adsorption reaction. At different reaction times, a 5 mL aliquot was withdrawn, centrifuged at 5000 rpm during 5 min and the supernatant extracted for phosphate analysis. The reaction was followed for 360 min and the pH was continuously checked and kept constant by adding minute volumes of concentrated KOH or HNO_3 solutions.

Phosphate concentration was measured by the method proposed by Murphy and Riley [17], using an Agilent 8453 UV–vis diode array spectrophotometer equipped with a 1-cm quartz cell. The detection limit was around $1 \mu\text{M}$. Adsorbed phosphate was calculated from the difference between the initial phosphate concentration and the concentration of phosphate that remained in the supernatant solution.

In all experiments, the pH was measured with a Crison GLP 22 pH meter and a Radiometer GH2401 combined pH electrode. The stirring was controlled with an IKA RH KT/C magnetic stirrer.

2.3. ATR-FTIR adsorption kinetics

Adsorption kinetics was also followed by ATR-FTIR spectroscopy using a ZnSe crystal. A stock goethite dispersion (10 g L^{-1}) was prepared by dispersing solid goethite in a 0.1 M KNO_3 solution. The resulting dispersion was shaken during one hour and its pH was adjusted to the desired value (either 4.5, 7.5 or 9.0). Several drops of this dispersion were placed on top of

the ZnSe crystal and let dry under vacuum overnight in order to form a dry goethite film. The film was then rinsed with water to eliminate the excess of goethite particles that did not adhere well to the crystal. Then, the film was covered with a 0.1 M KNO_3 solution having the desired pH and a blank spectrum was recorded in the 800–4000 cm^{-1} wavenumber range. After this, the electrolyte solution was withdrawn and a new 0.1 M KNO_3 solution having the same pH and containing 6×10^{-5} M phosphate was added. This time was set as the initial time of the adsorption reaction. Spectra were then recorded as a function of time. Experiments were performed with a Nicolet Magna 560 FTIR equipped with either a MCT-A or a DTGS detector. The only important difference between these two detectors is that MCT-A is more sensitive than DTGS, giving less scattering of data. Additional experiments were performed in absence of the goethite film in order to record the spectra of dissolved phosphate species in the KNO_3 solution.

Each spectrum is the result of 256 co-added interferograms. The spectral resolution was 2 cm^{-1} in all cases. The working temperature in these experiments was $25 \pm 2^\circ\text{C}$.

3. Results and discussion

3.1. General characteristics of the synthesized goethite

X-ray diffraction indicated that the synthesized sample was a well-crystallized goethite, and no evidences for other iron oxides phases were detected. Goethite particles had their typical acicular shape [18] with a length of around 600 nm and a width of around 40 nm. The specific surface area was $57 \text{ m}^2 \text{ g}^{-1}$. Transmission FTIR spectra were also typical of goethite, showing characteristic absorption bands at around 3155, 893, 796 and 640 cm^{-1} . Very weak and not well defined vibrations also appeared at around 1260 and 1400 cm^{-1} , which seem to indicate some surface contamination with carbonate. Elemental analysis and model calculations revealed that this carbonate contamination may affect around 7% of the goethite surface sites [19].

3.2. Phosphate adsorption kinetics

Fig. 1 shows the phosphate adsorption kinetics at pH 4.5 as measured by batch experiments. The different curves (adsorbed phosphate, P_{ads} , vs time, t) with solid symbols represent different initial phosphate concentrations. All curves have similar characteristics, showing an important and fast adsorption between $t = 0$ and 5 min, and a slower adsorption at longer times. Although adsorption seems to reach completion at around 300 min, some long-term kinetic experiments showed that adsorption continues after several days, but very slowly. For example, for an initial phosphate concentration of 5.47×10^{-5} M, P_{ads} increased by around 8% between 360 min and three days of reaction. Data in Fig. 1 are very similar to those reported in several other articles and, as it has been proposed by several authors, they suggest that adsorption takes place in at least two interconnected processes: a very fast initial process, which seems to take place in 5 min or less, followed

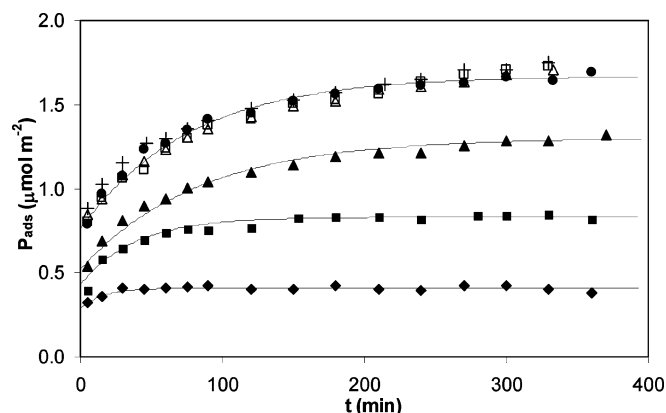


Fig. 1. Adsorption kinetics of phosphate on goethite. Solid symbols show experiments performed at constant stirring rate (450 rpm) and different initial phosphate concentrations: (●) 5.47×10^{-5} M, (▲) 2.73×10^{-5} M, (■) 1.37×10^{-5} M, (◆) 6.83×10^{-6} M. Other symbols show experiments performed at a constant initial phosphate concentration (5.47×10^{-5} M) and different stirring rates: (Δ) 600 rpm, (+) 400 rpm, (□) 200 rpm.

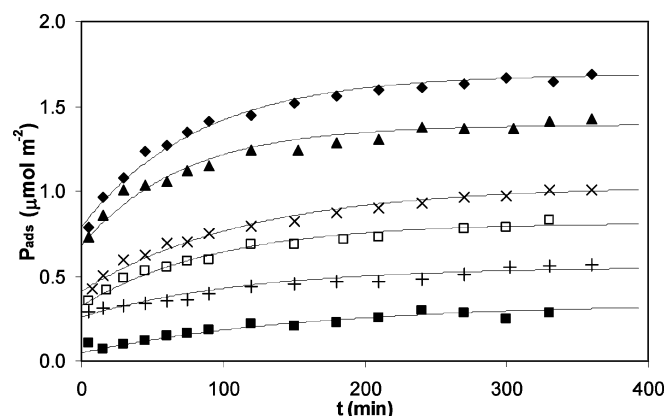


Fig. 2. Adsorption kinetics of phosphate on goethite at different pH: (◆) 4.5; (▲) 5.5; (×) 7.5; (□) 8.5; (+) 9.5; (■) 10.5. Initial phosphate concentration: 5.47×10^{-5} M.

by a slower process that takes place in hours or even days [5]. Fig. 1 also shows that phosphate adsorption does not depend on the stirring rate. This indicates that adsorption after 5 min of reaction is not controlled by a diffusion process in the aqueous side of the interface [20].

Fig. 2 shows the effects of pH on the adsorption of phosphate at a constant initial phosphate concentration (5.47×10^{-5} M). The behavior is similar to the reported by Strauss et al. [5]. At a given reaction time, P_{ads} decreases by increasing pH. The behavior at long times agrees with that reported by other authors who measured phosphate adsorption on goethite under equilibrium or near equilibrium conditions, showing that the affinity of phosphate for the goethite surface decreases by increasing pH [4,6,7]. The general trend of long-time data is also in agreement with model predictions [4,6], which indicate that under equilibrium conditions the decreased affinity of phosphate for the goethite surface is the result of a combined effect of the formation of different inner-sphere surface complexes between phosphate species and surface groups and electrostatic inter-

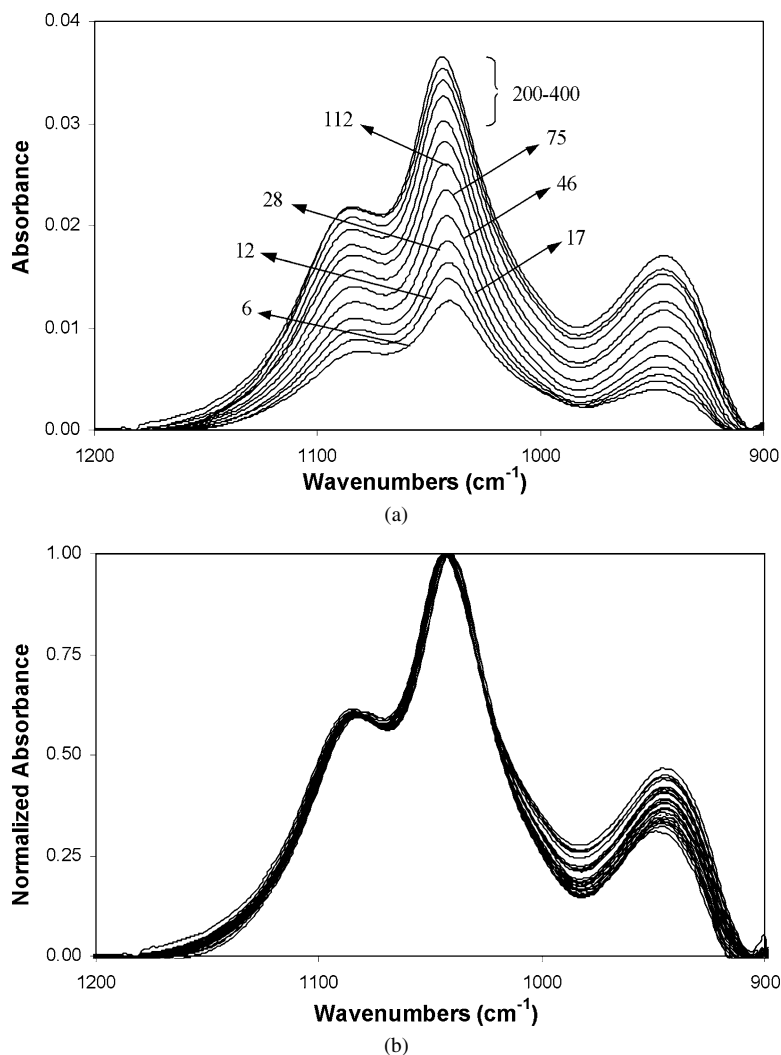


Fig. 3. (a) ATR-FTIR spectra of phosphate adsorbed on goethite at pH 9.0 at different times. (b) Normalized spectra. Times in minutes are indicated in the figure.

actions between phosphate species and the charged goethite surface.

Fig. 3 shows ATR-IR spectra of adsorbed phosphate at pH 9. Whereas Fig. 3a shows the effect of time on the spectra, Fig. 3b shows all the spectra after normalization with respect to the highest absorbance. Data analysis is focused in the 900–1200 cm^{-1} region, where bands associated with various phosphate vibrations are found [21]. The assignment of bands to different surfaces complexes is based mainly on the work by Tejedor-Tejedor and Anderson [10], who studied phosphate adsorption on goethite, and on the work by Arai and Sparks [22], who studied phosphate adsorption on ferrihydrite. There are still some controversies about phosphate peak assignments on goethite, especially after the thorough study by Persson et al. [23]. However, these authors performed IR spectra to dried goethite samples, and as the same authors indicate, significant shifts in bands positions can be produced by differences in water contents. Therefore, we keep to the assignments by Tejedor-Tejedor and Anderson [10] and by Arai and Sparks [22] whose experimental setups were very similar to ours. Three main bands are observed in the spectra at pH 9 (Fig. 3): one with a maximum at $945 \pm 4 \text{ cm}^{-1}$, a second and more intense one

at $1044 \pm 3 \text{ cm}^{-1}$, and a third one at $1089 \pm 3 \text{ cm}^{-1}$. The band at 945 cm^{-1} may be somewhat affected by baseline correction because of the strong adsorption of lattice goethite groups that starts at around 950 cm^{-1} and has a maximum at 893 cm^{-1} . The three observed bands correspond undoubtedly to inner-sphere surface complexes since their positions are different to those of phosphate ions in solution [10]. The intensity of the three IR bands increases with time, indicating an increased phosphate adsorption by increasing the reaction time. On the other hand, Fig. 3b shows that the shape of all spectra is very similar. There is no change in the bands position and only the relative intensity of the band at 945 cm^{-1} changes with time. We believe that this change is not an indication of a structural change of the adsorbed phosphate species but instead an effect of the important baseline correction that needs to be done at these wavenumbers.

The 1044 and 1089 cm^{-1} bands were already observed by Tejedor-Tejedor and Anderson [10] for phosphate adsorbed on goethite. With their experimental set up, they could not analyse the band at lower frequencies because of the strong absorption of lattice goethite groups. These authors have assigned these two bands to the nonprotonated bidentate complex $(\text{FeO})_2\text{PO}_2$, based on IR spectra of iron phosphate complexes

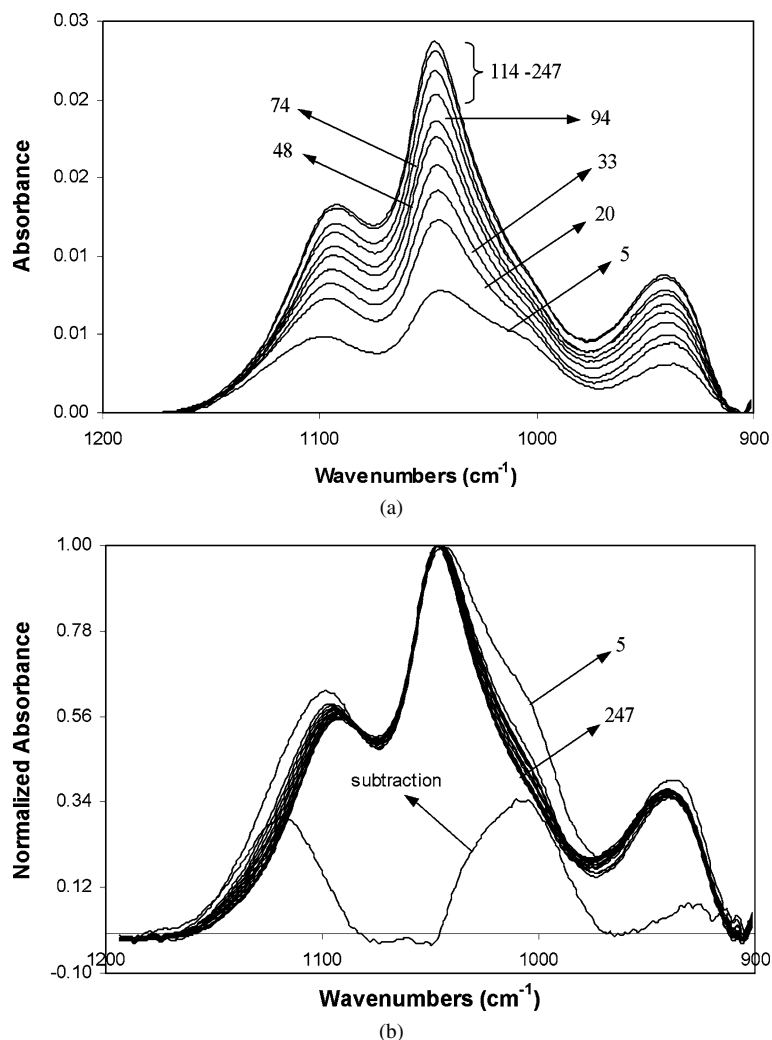


Fig. 4. (a) ATR-FTIR spectra of phosphate adsorbed on goethite at pH 4.5 at different times. (b) Normalized spectra. Times in minutes are indicated in the figure.

in solution. Arai and Sparks [22], on the other hand, found three IR bands for phosphate adsorbed on ferrihydrite: $\cong 952 \text{ cm}^{-1}$, $\cong 1021 \text{ cm}^{-1}$ (the most intense one) and $\cong 1088 \text{ cm}^{-1}$, which were assigned to the mentioned $(\text{FeO})_2\text{PO}_2$ complex on the basis of symmetry considerations and comparisons with IR spectra in D_2O . Considering that some variation in the bands positions may occur for phosphate complexes on goethite or ferrihydrite, this set of band resembles that of Fig. 3. Thus, ATR-IR data at pH 9 gives good evidence for the formation of the nonprotonated bidentate complex $(\text{FeO})_2\text{PO}_2$, whose surface concentration increases as the reaction proceeds. Although this is the most important surface complex at pH 9, other complexes may be also present at relatively low concentrations. According to Tejedor-Tejedor and Anderson [10], the nonprotonated monodentate complex $(\text{FeO})\text{PO}_3$ shows IR bands at 1001 and 1025 cm^{-1} , and the protonated bidentate complex $(\text{FeO})_2(\text{OH})\text{PO}$ shows its more intense bands at 1006 and 1123 cm^{-1} . Low concentrations of these complexes could be the responsible for the small changes in the shape of the spectra at around 1000 and 1130 cm^{-1} (Fig. 3b).

Experiments performed at pH 7.5 resulted in a spectral behavior that was very similar to that observed at pH 9 and thus

they are not shown here. Three bands at 942 ± 3 , 1042 ± 2 , and $1085 \pm 2 \text{ cm}^{-1}$ were observed, whose intensities increased as the reaction time increased. No change in the shape of the spectra was observed after normalization. Thus, at pH 7.5 the nonprotonated bidentate complex $(\text{FeO})_2\text{PO}_2$ is also the main species that populates the goethite surface.

Fig. 4 is equivalent to Fig. 3, and shows data recorded at pH 4.5. The intensity of the IR bands increases as time increases, indicating an increased phosphate adsorption. The three bands assigned to the $(\text{FeO})_2\text{PO}_2$ complex can be also observed at pH 4.5. However, there is a change in the shape of the normalized curves as the reaction time increases, suggesting that at least one extra surface complex is present at significant and detectable concentrations. This change is mainly produced in the $970\text{--}1044 \text{ cm}^{-1}$ range, where a shoulder at around 1008 cm^{-1} can be observed, and in the $1080\text{--}1160 \text{ cm}^{-1}$ range. Tejedor-Tejedor and Anderson [10] showed that two bands, one with a maximum at 1006 cm^{-1} and other with a maximum at 1123 cm^{-1} , appeared at low pH in the spectra of phosphate on goethite. They assigned these bands to the monoprotonated bidentate complex $(\text{FeO})_2(\text{OH})\text{PO}$. Deconvolution of the spectra allowed them to identify a third band for this complex, at

982 cm^{-1} , which was around four times less intense than those at 1006 and 1123 cm^{-1} . The position of these bands coincides well with the spectral changes observed in Fig. 4b, and suggests that $(\text{FeO})_2(\text{OH})\text{PO}$ is the extra surface complex at pH 4.5. Similar results were found by Arai and Sparks [22] for phosphate adsorption on ferrihydrite. They proposed the formation of the $(\text{FeO})_2(\text{OH})\text{PO}$ complex at pH < 7.5, although they left open the possibility that other protonated complexes (protonated monodentate or monodentate with hydrogen bonding) instead of $(\text{FeO})_2(\text{OH})\text{PO}$ could be present.

In order to gain more insights into the characteristics of the spectrum of the extra complex formed at pH 4.5, a subtraction of the normalized spectrum at 247 min from the normalized spectrum at 5 min is shown in Fig. 4b. The so obtained difference spectrum shows a band at 1009 cm^{-1} , another band at 1121 cm^{-1} , and a weak band at around 930 cm^{-1} . This difference spectrum is very similar to the spectrum attributed to the $(\text{FeO})_2(\text{OH})\text{PO}$ complex by Tejedor-Tejedor and Anderson [10], except for the weak band at 930 cm^{-1} , which is outside the wavenumber range investigated by these authors. It is necessary to remark that the shape of the difference spectrum shown in Fig. 4b may not coincide exactly with the shape of the spectrum of the $(\text{FeO})_2(\text{OH})\text{PO}$ complex. They will coincide if no $(\text{FeO})_2(\text{OH})\text{PO}$ complex exists at the surface at 247 min or longer times, fact that is not completely true (see below). In spite of this, the spectral subtraction is very useful because it makes it possible to identify with good accuracy the position of the bands assigned to the protonated bidentate complex.

Although not shown here, we have also investigated the changes in absorbance in the 1200–1600 cm^{-1} range during the kinetic runs. This is a range where adsorbed carbonate shows important vibrations [21,24,25], and where variations in absorbance should have been detected if adsorbed phosphate displaced significant amounts of carbonate impurities. No changes were observed at any time indicating that possible carbonate impurities, if exist, are not participating at significant extent in the phosphate adsorption process.

An important conclusion of the work by Tejedor-Tejedor and Anderson [10] is that the integrated absorption coefficients for all phosphate surface complexes should be the same. This opens the possibility of quantifying the relative adsorption of phosphate as a function of time from ATR-IR data by integrating the IR absorption bands. This has been carried out by deconvolution of the spectra into several peaks in the 900–1200 cm^{-1} range. No constraints for amount of peaks or peak positions are actually needed in this deconvolution. The only important fact is to obtain a good fit of the spectra in order to accurately evaluate their areas, which should be proportional to the amount of adsorbed phosphate. However, spectral deconvolution under certain constraints may be helpful to identify and quantify the different surface complexes and to follow their evolution as the adsorption reaction proceeds. Three gaussians corresponding to the $(\text{FeO})_2\text{PO}_2$ complex and three gaussians corresponding to the $(\text{FeO})_2(\text{OH})\text{PO}$ complex were used in the deconvolution. The position of the bands of the nonprotonated complex was constrained to wavenumbers around 947, 1044 and 1089 cm^{-1} ; the positions of the bands of the protonated complex were con-

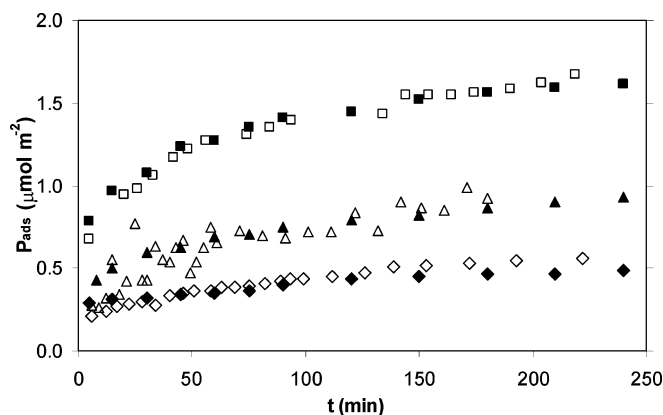


Fig. 5. Comparison of the adsorption kinetics of phosphate as measured by batch and ATR-IR experiments. Batch: (◆) pH = 9.0; (▲) pH = 7.5; (■) pH = 4.5; ATR-IR: (◇) pH = 9.0; (△) pH = 7.5; (□) pH = 4.5.

strained to wavenumbers around 930, 1009 and 1126 cm^{-1} . A very good spectral fit was found in all cases ($R^2 > 0.995$), and the areas of the spectra could be accurately evaluated making it possible to compare adsorption kinetics measured by ATR-IR and batch experiments. This comparison is shown in Fig. 5. A very good agreement can be observed at the three investigated pH, indicating that the kinetics of phosphate adsorption on goethite can be followed by integrating the ATR-IR signal. This agreement is also consistent with the fact that adsorption kinetics after 5 min of reaction does not depend on diffusional processes in the solution side of the interface. In fact, if these processes were the rate controlling ones, no coincidence would have been expected between both types of experiments, since batch adsorption was performed under stirring, whereas ATR-IR was performed in a relatively quiet system, with no external stirring.

The deconvolution of spectra was very consistent for data obtained at pH 4.5. The six mentioned gaussians were necessary to obtain a good spectral fit. The peak positions for the nonprotonated complex were 952 ± 2 , 1047 ± 1 and 1092 ± 3 cm^{-1} , and their relative areas were around 0.3/1/0.7 in all the cases. The peak positions for the protonated complex were 933 ± 1 , 1012 ± 3 and 1122 ± 4 cm^{-1} , and their relative areas were always around 0.25/1/0.3. This consistency suggests that a reliable evolution in time of the surface concentrations of the $(\text{FeO})_2\text{PO}_2$ and $(\text{FeO})_2(\text{OH})\text{PO}$ complexes can be obtained. In contrast, the deconvolution of spectra for data obtained at pH 7.5 and 9 was not so consistent. Although using six gaussians produced a very good spectral fit, the peak positions and their relative areas changed illogically, especially for the peaks assigned to the $(\text{FeO})_2(\text{OH})\text{PO}$ complex. Moreover, similar fit could also be achieved with four gaussians: the three gaussians corresponding to the $(\text{FeO})_2\text{PO}_2$ complex, which is surely present at this pH, plus an extra gaussian with maximum at 1012 ± 4 cm^{-1} . In spite of these problems in deconvolution, the results indicate that at pH 7.5 and 9 $(\text{FeO})_2\text{PO}_2$ is the dominant surface complex, and that at least other surface complex (either $(\text{FeO})_2(\text{OH})\text{PO}$, $(\text{FeO})\text{PO}_3$ or other) is also present. A rough estimation suggests that the concentration of $(\text{FeO})_2\text{PO}_2$ should represent around 80% of the total P_{ads} .

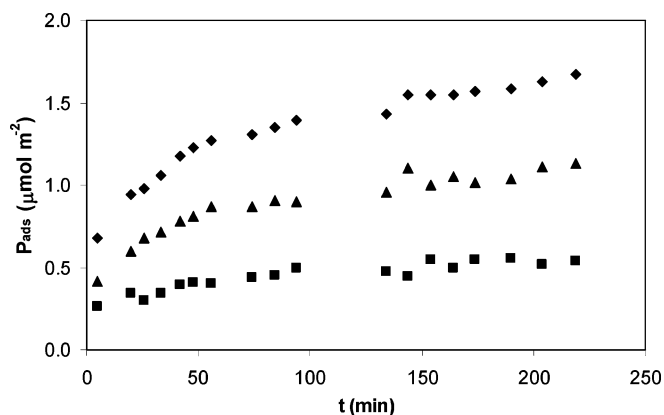


Fig. 6. Evolution in time of the concentration of surface complexes at pH 4.5: (◆) total; (▲) bidentate nonprotonated $(\text{FeO})_2\text{PO}_2$; (■) bidentate protonated $(\text{FeO})_2(\text{OH})\text{PO}$.

Fig. 6 shows the evolution in time of the surface concentration of $(\text{FeO})_2\text{PO}_2$ and $(\text{FeO})_2(\text{OH})\text{PO}$ complexes at pH 4.5. The concentration of both complexes increases as the reaction proceeds, and there are some changes in the relative concentration of both species between 5 and 220 min. In fact, whereas $(\text{FeO})_2\text{PO}_2$ represents 61% of P_{ads} at 5 min, it becomes 68% of P_{ads} at 220 min. These changes, although detectable, are relatively small and it seems that both complexes adsorb and evolve in time rather independently. No figures equivalent to Fig. 6 can be constructed for data obtained at pH 7.5 and 9, since the surface concentration of the species accompanying $(\text{FeO})_2\text{PO}_2$ is relatively low and could not be accurately quantified. However, what is clear from ATR-IR data obtained at pH 7.5 and 9, is that the predominant species, $(\text{FeO})_2\text{PO}_2$, and its accompanying species evolve equally in time since the shape of the spectra does not change as the reaction proceeds.

3.3. The slow adsorption step

Although phosphate adsorption kinetics on goethite can be interpreted as the result of at least two interconnected adsorption steps, there is no much information regarding the mechanisms of these processes at the molecular level. Actually, it is physically unrealistic to make a clear separation between the two mentioned steps and to identify when the initial fast step finishes or when the slow step begins. However, there is a general agreement in that both steps take place at very different time scales. In fact, the initial fast adsorption process is interpreted as an adsorption reaction whereby dissolved phosphate species bind rapidly surface groups at the goethite surface. This kind of reactions usually takes place in milliseconds for the case of ion adsorption at oxide surfaces [26,27]. The second process is much slower and takes place in days or even weeks. Since ATR-IR and batch adsorption experiments are usually performed at times longer than a few minutes of reaction, these techniques can provide useful information about the slow process.

Martin et al. [28] suggested that the slow step is a slow precipitation of iron phosphate at the surface. Van Riemsdijk et al. [15], on the other hand, suggested that it represents a slow diffu-

sion of the anion through a growing coating of iron phosphate. Anderson et al. [11] proposed that the fast initial adsorption to a goethite particle was followed by a slow and progressive coagulation due to phosphate that bonded and bridged primary particles. Later, Torrent et al. [12] suggested that this step is a slow diffusion of phosphate to the surface of pores located between domains of contiguous crystals or between aggregated particles. Strauss et al. [5], provided further lines of evidences for this diffusion mechanism. They were able to successfully predict the effects of pH, temperature and initial phosphate concentration on the adsorption kinetics of phosphate on goethite samples of varying crystallinity and surface area with a model that assumed a fast initial adsorption reaction connected to a diffusive penetration towards the center of the particle. Their studies on phosphate release by concentrated HCl and NaOH solutions were also consistent with this mechanism.

Batch experiments do not allow to distinguish among iron phosphate precipitation at the surface of goethite, diffusion of phosphate through a coating of iron phosphate, phosphate bridging of goethite particles and diffusion into pores. However, ATR-IR provides useful information in this respect. ATR-IR results are not compatible with the first two mechanisms since they show no indication of the formation of iron phosphate during the sorption reaction. In fact, the IR absorption bands of several crystalline or amorphous iron phosphates are different to those observed in Figs. 3 and 4 [23,29] suggesting that iron phosphate is not formed within our experimental conditions. Moreover, a sorption process that combines a fast adsorption followed by a slow formation of iron phosphate would be reflected in changes in the spectra as the reaction time increases. These changes are certainly not observed at pH 7.5 and 9. Although some changes are observed at pH 4.5, the general trend observed in Fig. 6 is that both adsorbed complexes evolve rather independently giving no evidence for the formation of iron phosphates. ATR-IR results seem to be also incompatible with the bridging mechanism because it requires that phosphate changes its bonding arrangement as the second step progresses. Even though there are still some controversies about phosphate peak assignments on goethite, as it was indicated in Section 3.2, the invariability of the peaks positions as reaction proceeds indicate that ATR-IR results are more compatible with surface diffusion into pores, where surface complexes that are formed after the first minutes of reaction migrate rather slowly into the pores without changing appreciably their identity.

4. Conclusions

ATR-IR has shown to be a useful technique to follow phosphate adsorption kinetics on goethite. Under certain conditions, the technique is able to distinguish the formation of different surface complexes at the goethite–water interface during the adsorption reaction, and to monitor the evolution in time of these species. According to the peak assignments by Tejedor-Tejedor and Anderson [10] and by Arai and Sparks [22], at pH 4.5 the formation of both, $(\text{FeO})_2\text{PO}_2$ and $(\text{FeO})_2(\text{OH})\text{PO}$ species is detected from the beginning of the experiments. Although there are some changes in the relative concentrations of

these species as the reaction proceeds, the changes are relatively small and the species seem to evolve rather independently. At pH 7.5 and 9, on the other hand, the dominating surface species is $(\text{FeO})_2\text{PO}_2$, although one or more extra species may be accompanying it at low surface concentrations. Even though the net surface concentration of these species increases as the reaction proceeds, their relative concentration does not change. The results are consistent with a mechanism that involves a fast adsorption followed by a slow diffusion into pores.

Besides the usefulness of ATR-IR to study adsorption kinetics of systems where one type of adsorbing ion is present, the technique appears to be very promising for studying adsorption kinetics and competition among different ions. For example, the technique could be useful to study competition between carbonate and phosphate for goethite surface sites by investigating the ATR-IR signals in the 1200–1600 and the 900–1200 cm^{-1} ranges respectively. This kind of study could be very useful to gain information on the dynamics of processes that control the transport and fate of phosphate in soils and aquifers. In addition, ATR-IR also may become very helpful in the development of theoretical models that describe adsorption kinetics at the mineral–water interface. Among several models of adsorption kinetics, the one developed by Strauss et al. [5] seems to be the only model that takes into account both, phosphate adsorption on charged external surfaces and phosphate diffusion into pores. This model, however, needs to be improved and modified in order to consider the formation of the different inner-sphere surface complexes that were detected by ATR-IR, and much work is still needed in this respect.

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