Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

Phosphate desorption kinetics from goethite as induced by arsenate

Virginia Puccia [a,*], Carina Luengo [a], Marcelo Avena [a,b]

[a] INQUISUR, Departamento de Química, Universidad Nacional del Sur, Bahía Blanca, Argentina
[b] Consejo de Investigaciones Científicas y Técnicas de Argentina (CONICET), Argentina

ABSTRACT

The kinetics of the arsenate-induced desorption of phosphate from goethite has been studied with a batch reactor system and ATR-FTIR spectroscopy. The effects of arsenate concentration, adsorbed phosphate, pH and temperature between 10 and 45 °C were investigated. Arsenate is able to promote phosphate desorption because both oxoanions compete for the same surface sites of goethite. The desorption occurs in two steps: a fast step that takes place in less than 5 min and a slow step that lasts several hours. In the slow step, arsenate ions exchange adsorbed phosphate ions in a 1:1 stoichiometry. The reaction is first order with respect to arsenate concentration and is independent of adsorbed phosphate under the experimental conditions of this work. The rate law is then $r = k_r[As]$, where r is the desorption rate, k_r is the rate constant and $[As]$ is the arsenate concentration in solution. The values of k_r at pH 7 are 1.87×10^{-5} L m^{-2} min^{-1} at 25 °C and 7.95×10^{-5} L m^{-2} min^{-1} at 45 °C. The apparent activation energy of the desorption process is 51 kJ mol^{-1}. Data suggest that the rate-controlling process is intraparticle diffusion of As species, probably As diffusion in pores. ATR-FTIR spectroscopy suggests that adsorbed phosphate species at pH 7 are mainly bidentate inner-sphere surface complexes. The identity of these complexes does not change during desorption, and there is no evidence for the formation of intermediate species during the reaction.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Phosphate and arsenate are of major concern in environmental chemistry. Phosphate is not toxic, but is one of the main species responsible for eutrophication of fresh water bodies [1,2]. It is often added to soil as a plant nutrient. Arsenate is toxic and carcinogenic. Health problems related to its high concentration in groundwaters have been worldwide recognized [3,4]. It can be present as a natural contaminant or it may be added to soils as a pesticide.

The mobilization of phosphate and arsenate in the environment is significantly influenced by adsorption–desorption processes on mineral surfaces. Many studies have been performed regarding adsorption–desorption of these anions and their protonated species on different solid phases [5–8]. In particular, ferric oxides and hydrous ferric oxides have been widely studied due to their abundance in soils and sediments [9–13]. Understanding the reactions between these solids and phosphate and arsenate is a key factor for understanding and modelling their environmental behaviour.

Phosphorus and arsenic are both Group 15 (5A) elements of the periodic table, and thus phosphate and arsenate are species that have very similar structure [14] and chemical reactivity. They have very similar adsorption behaviour on solid surfaces [15,16]. On goethite, for example, they both adsorb with high affinity in an ample interval of pH [17–19], and the adsorption decreases by increasing the pH. Gao and Mucci [17] showed that under the same experimental conditions the adsorbed amount of phosphate and arsenate under equilibrium or near equilibrium situations only differs by around 10 or 20%. Adsorption constants of arsenate and phosphate on goethite are rather similar [18], indicating that they have the similar reactivity and react with the same surface sites. In addition, Luengo et al. [19] have also shown that the adsorption kinetics on a goethite sample is very similar in an ample range of pH, temperature and initial anion concentration. Such as these, there are several other articles showing the similarities in the adsorption of phosphate and arsenate on goethite [20–22].

The similarities in the adsorption of phosphate and arsenate are not only apparent from macroscopic adsorption data. There is also spectroscopic evidence indicating that both anions form the same kind of surface complexes with goethite. Tejedor-Tejedor and Anderson [23], for example, suggested by using CIR-FTIR spectroscopy that phosphate adsorbs at neutral pH values mainly through the formation of bidentate surface complexes. The same conclusions were obtained by Luengo et al. [24], who monitored the adsorption kinetics of phosphate on goethite by ATR-FTIR, and suggested that the mentioned bidentate complexes are the main surface species during adsorption at pH 7.5. On the other hand,

* Corresponding author at: Departamento de Química, Universidad Nacional del Sur, Av. Alem 1253, 8000 Bahía Blanca, Argentina. Tel.: +54 291 4595101x3593; fax: +54 291 4595160.
E-mail address: vpuccia@uns.edu.ar (V. Puccia).

O'Reilly et al. [25] found with EXAFS the same kind of inner-sphere surface complexes formed by arsenate at the goethite surface at pH 6. Although it is sometimes difficult to prove with FTIR, EXAFS or other spectroscopies the exact nature of the adsorbed species, data suggests that both phosphate and arsenate form inner-sphere complexes with the same kind of surface groups in goethite.

In view of the similarities in their structure, reactivity and type of surfaces complexes formed at the goethite surface, phosphate and arsenate must compete for adsorption sites on this solid. Indeed, phosphate has been reported to suppress the adsorption of arsenate (and *vice versa*) on goethite and many other oxides, clay minerals and soils [16]. Similar competing behaviour was shown by Manning and Goldberg [15] on goethite and gibbsite, although they propose in addition that some surface sites were uniquely available for either phosphate or arsenate. Hongshao and Stanforth [21] also reported competing behaviour on goethite when both anions were added simultaneously to a goethite suspension.

The competition can be also studied by desorption experiments. Hongshao and Stanforth [21], for example, induced phosphate desorption from goethite by adding arsenate, and *vice versa*. By quantifying simultaneously the concentration in solution of both anions, they could monitor the displacement of the adsorbed anion by the competing one at different times. Frau et al. [26] studied the effects of phosphate and other ions on the desorption kinetics of arsenate from ferrihydrite-bearing natural samples. They showed that phosphate is a strong competitor of arsenate. Such as these, there are many other articles reporting desorption of phosphate by arsenate or *vice versa* [15,16,22,25,27,28].

Most articles regarding adsorption, desorption and competition between phosphate and arsenate on solid surfaces are focussed on experimental data obtained under equilibrium or near equilibrium conditions. There is less information on the kinetics of these processes. This kind of information is valuable for a better understanding of the mechanisms of the adsorption–desorption processes of these oxoanions. Thus, the aim of this article is to study the desorption kinetics of phosphate from goethite as induced by the presence of arsenate. Phosphate is adsorbed first and then arsenate is added to promote phosphate desorption. The decrease in adsorbed phosphate is monitored as a function of time, and the effects of arsenate concentration, initial adsorbed phosphate, pH and temperature on the desorption rates are evaluated.

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. [29]. Briefly, a 5 M NaOH solution was added dropwise (10 mL min^{-1}) to a 0.1 M Fe(NO$_3$)$_3$·9H$_2$O solution until the pH was 12. The resulting ferrihydrite suspension was aged at 60 °C for 3 days and then it was washed with doubly distilled water until the conductivity was lower than 10 μS cm^{-1}. After that, the suspension was freeze-dried in order to obtain a dry powder. Teflon containers were used for the synthesis because pH 12, high temperature and long ageing times could lead to silicate contamination. All solutions were prepared with purified water, boiled and purged with N$_2$ to avoid carbonate contamination. Purging with N$_2$ was also performed during the mixing of the NaOH and the Fe(NO$_3$)$_3$·9H$_2$O solutions. Powder X-ray diffraction (measured with a Rigaku Geigerflex diffractometer between 2° and 40° 2θ using CuK$_\alpha$ radiation) showed that the synthesized sample was a well-crystallized goethite. Transmission FTIR spectrum (obtained with a Nexus 470 spectrophotometer) was also typical of goethite, showing its characteristic absorption bands at around 3155, 893, 796 and 640 cm^{-1} [18,23,28]. No signs of carbonate bands at around 1335 and 1490 cm^{-1} were found [30]. The N$_2$-BET surface area was

77.8 m^2 g^{-1} as measured with a Quantachrome Nova 1200e instrument. Scanning electron microscopy (performed with a Leo EVO-40 XVP instrument) showed that goethite is present as large particles having up to around 40 μm size. These particles, however, are aggregates of much smaller acicular particles of around 0.3 μm length (see supplementary material).

2.2. Batch experiments

Adsorption–desorption 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 N$_2$. The reaction temperature was maintained at 25 ± 0.2 °C (except for the cases where effects of temperature were investigated) by circulating water through the jacket with a FAC (Argentina) water bath/circulator.

Before starting an adsorption–desorption experiment, a stock goethite suspension (15.5 g L^{-1}) was prepared by adding solid goethite to a 0.1 M KNO$_3$ solution. The pH of the resulting suspension was then adjusted to 7.0 (or other desired value) by adding HNO$_3$ or KOH solutions. 100 mL of a 0.1 M KNO$_3$ solution containing a known concentration of phosphate (5.48 × 10^{-5} M) were placed in the reaction vessel, and the stirring (450 rpm), N$_2$ bubbling and water circulation were switched on. This initial phosphate concentration was the same in all batch experiments (except when the effects of initial adsorbed phosphate were investigated, where 3.55 × 10^{-5} and 2.03 × 10^{-5} M phosphate concentrations were also used) and was chosen to obtain high surface coverages, as deduced from adsorption isotherms (see below). Once the temperature reached the desired value, the pH of the KNO$_3$/phosphate solution was adjusted to 7.0 (or the other desired value) by adding HNO$_3$ or KOH. The experiment was started by adding 2.0 mL of the stock suspension to the KNO$_3$/phosphate solution in the reaction vessel to produce phosphate adsorption. At different adsorption times, a 4.0 mL aliquot of the well-mixed suspension was withdrawn, centrifuged at 1050 × g during 5 min and the supernatant extracted for phosphate analysis. The phosphate adsorption reaction was followed for 90 min.

The desorption kinetics experiment was started by adding a known volume of a 1.61 × 10^{-3} M arsenate solution, whose pH was previously adjusted to the working pH. This volume was chosen so that the ratio between total phosphate and total arsenate (P$_T$/As$_T$) in the vessel was either 1:3, 1:1 or 3:1 in molar/molar units in most cases. After the addition of arsenate, 5.0 mL aliquots of the suspension were withdrawn at different times, centrifuged and the supernatant separated for phosphate analysis. The desorption reaction was followed for 390 min in experiments performed at 25 ± 0.2 and 10 ± 0.2 °C. This time was shortened to 210 min for experiments performed at 45 ± 0.2 °C since at longer times some evaporation that significantly affected the results was detected.

Phosphate concentration in the supernatants was measured by the malachite green spectrophotometric method proposed by Linge and Oldham [31], after arsenate reduction with acidified sodium sulphite. In addition, in order to investigate if there was simultaneous adsorption of arsenate, the total anions concentration (phosphate + arsenate) was measured by the molybdenum blue method proposed by Tsang et al. [32], reading the absorbance at a wavelength of 880 nm, where both anions have the same molar extinction coefficient. UV–Vis spectra were recorded with an Agilent 8453 UV–Vis diode array spectrophotometer equipped with a 1-cm quartz cell.

In all experiments the pH was continuously checked and kept constant by adding minute volumes of concentrated KOH or HNO$_3$ solutions if necessary. 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.

Besides these kinetic experiments, a phosphate adsorption isotherm was performed by adding appropriate volumes of 1.61×10^{-3} M KH_2PO_4 to 0.2 mL of goethite suspensions (15.5 g L^{-1}) in 0.1 M KNO_3, at pH 7.0 and 25 °C. The suspensions were shaken for 90 min, followed by centrifugation and supernatant analysis. The same procedure was used to measure an adsorption isotherm for arsenate, using in this case appropriate volumes of 1.61×10^{-3} M KH_2AsO_4. Phosphate or arsenate concentrations were measured by the mentioned malachite green spectrophotometric method [31].

2.3. ATR-FTIR experiment

The desorption of phosphate by addition of arsenate was also followed by ATR-FTIR spectroscopy as a complementary technique. A stock goethite suspension (5 g L^{-1}) in 0.1 M KNO_3 solution was shaken during one hour and its pH was adjusted to 7.0. Several drops of this suspension were placed on top of the ZnSe crystal of the ATR accessory 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 of pH 7 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 1×10^{-4} M phosphate was added. Spectra were then recorded as a function of time during 120 min to follow phosphate adsorption as previously described [24]. After this, the solution was withdrawn and a new 0.1 M KNO_3 solution now containing 1×10^{-4} M arsenate at pH 7 was added. This was set as the initial time for the desorption experiment. The spectra were recorded as a function of time during 92 min to follow phosphate desorption. Experiments were performed with a Nicolet Magna 560 FTIR equipped with a DTGS detector. 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 ± 2 °C.

3. Results and discussion

Fig. 1 shows the adsorption isotherms of phosphate and arsenate at pH 7. Both anions show very similar isotherms. This similarity, which has been reported in many other articles, reflects the similarity in the affinity of both anions for the goethite surface. Adsorption increases up to concentrations of around 2×10^{-5} M and then becomes almost independent on the concentration of oxoanions, nearly reaching a plateau value. The coincidence in the plateau values is consistent with ATR-FTIR [23,24] and EXAFS
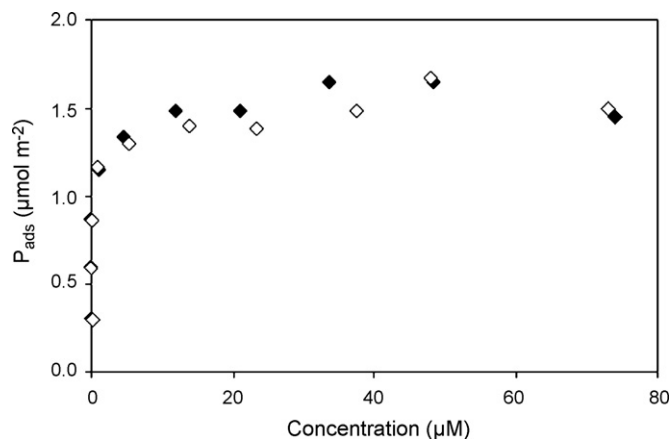
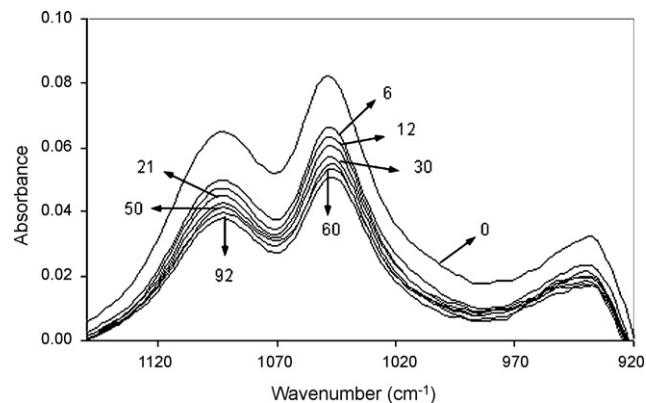**Fig. 2.** ATR-FTIR spectra of surface phosphate species during desorption after addition of arsenate at pH 7.0. Values of t_{des} in minutes are indicated in the figure.

[25] data, which show that both anions form very similar surface complexes on goethite, mainly bidentate complexes, occupying the same amount of sites at the surface per adsorbed oxoanion. These plateau values are also within the values normally found for goethites [18,24,33].

Fig. 2 shows the evolution in time of ATR-FTIR spectra of a goethite that has been first subject to phosphate adsorption, followed by an introduction of arsenate to induce phosphate desorption. The spectrum at the desorption time, t_{des}, zero is the spectrum registered immediately before the introduction of arsenate. The bands shown by the spectra are the typical ATR-FTIR absorption bands of adsorbed phosphate at pH around 7 [23,24], and they correspond to the mentioned bidentate surface complexes. Data shows that there is an important decrease in the intensity of the spectrum after 6 min of reaction and that this decrease is less marked at longer desorption times. The decrease in the signal indicates that phosphate desorbs after arsenate addition. Thus, desorption is relatively fast between 0 and 6 min and then becomes slower. Complete desorption is not expected in this kind of experiments since both phosphate and arsenate are present in the system at significant concentrations.

Fig. 2 also shows that the shape of all spectra is very similar. There is no change in the bands position and only their intensity is decreasing upon desorption. Thus, the presence of arsenate does not change the binding mode of phosphate, and phosphate remains adsorbed as a bidentate complex during desorption. There is no evidence for the formation of intermediate species during desorption. The data is analogous to the findings by O'Reilly et al. [25] for the reverse process. For the phosphate-induced desorption of arsenate from goethite, these authors found that arsenate remained always as a bidentate complex during desorption, since no changes in its binding mode were detected by EXAFS. Unfortunately, although Fig. 2 clearly indicates that arsenate is inducing phosphate desorption, the simultaneous adsorption of arsenate could not be monitored by ATR-FTIR. According to Parikh et al. [34] arsenate bands appear at 875 and 908 cm^{-1} on birnessite and hydrous manganese oxide. If this is the case for arsenate on goethite, this IR region is almost coincident with the strong absorption bands of goethite, impeding the analysis of arsenate bands by ATR-FTIR.

Fig. 3 shows the total anions (phosphate + arsenate) concentration in the supernatant as a function of time for several desorption experiments. Time zero in these experiments corresponds to the time of arsenate addition, and the first data point is obtained after 5 min of reaction. In all cases the sum of the concentrations of phosphate and arsenate in the supernatant remains constant in time. The invariability of total anions concentration as the reaction proceeds means that any amount of adsorbed arsenate is corresponded with the same amount of desorbed phosphate, i.e., arsenate ions

Fig. 1. Phosphate and arsenate adsorption isotherms on goethite in 0.1 M KNO_3 at pH 7 and 25 °C: (♦) phosphate; (◊) arsenate.
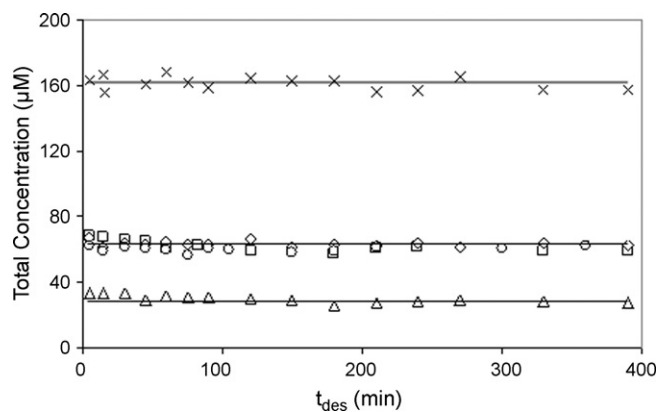
Fig. 3. Total (phosphate + arsenate) concentration in supernatant as a function of desorption time at pH 7 for the different experiments performed. ×, 25 °C and P_T/As_T 1:3; □, 10 °C and P_T/As_T 1:1; ○, 45 °C and P_T/As_T 1:1; ◇, 25 °C and P_T/As_T 1:1; △, 25 °C and P_T/As_T 3:1.

Fig. 4. Phosphate adsorption–desorption curves at pH 7 and 25 °C. The vertical dashed line indicates the time of arsenate addition. Phosphate concentration was 5.48×10^{-5} M in all experiments. P_T/As_T ratio: ◇, 3:1; ○, 1:1; □, 1:3. Lines in the desorption part of the figure show predictions with Eqs. (1) and (2) and parameters in Table 1.

exchange adsorbed phosphate ions in a 1:1 stoichiometry. A 1:1 exchange stoichiometry is expected at high surface coverages, close to surface saturation. Under this extreme condition, since there are no available sites at the goethite surface for arsenate adsorption, arsenate has to exchange with adsorbed phosphate and thus the total anions concentration in the supernatant remains unchanged. Similar exchange results were informed by Hongshao and Stanforth [21] mainly under conditions of high surface coverages. This behaviour is not so simple at low surface coverages, where arsenate has available surface sites for adsorption and it may simply adsorb without any exchange occurring [21].

The 1:1 stoichiometry deduced from Fig. 3 is true for times longer than 5 min, since the first data point was obtained at this desorption time. It is very difficult, however, to achieve the same conclusion for desorption times between 0 and 5 min. When the total anions concentration in the supernatant measured in the experiments is compared to a theoretical value calculated as the sum of phosphate remained in solution after phosphate adsorption plus added arsenate, the experimental values were around 10% (between 8% and 12%) lower than the calculated ones. An exact 1:1 stoichiometry between t_{des} 0 and 5 min requires a coincidence between these two values. The 10% difference may suggest that some arsenate is rapidly adsorbed first without any exchange occurring at the beginning of the reaction. However, since phosphate is near its adsorption maximum, the availability of adsorption sites for arsenate should be very low, and the 10% difference may be due to a systematic and unknown error, possibly related to some interference between phosphate and arsenate, which is rather common in this kind of spectrophotometric methods [32]. Fortunately, this possible error does not affect the quantification of phosphate, which is directly measured with the malachite green method [31]. It may affect, however, the quantification of arsenate, which has to be indirectly estimated from the difference between total anions concentration and phosphate concentration. Therefore, to avoid any error in the analysis of the results, reactions rates were quantified from the decrease in adsorbed phosphate (or from the increase in desorbed phosphate) as a function of time.

Fig. 4 shows the results of batch adsorption–desorption experiments at 25 °C at three different concentrations of added arsenate. The adsorbed amount of phosphate, P_{ads}, is plotted as a function of time. Time zero corresponds here to the beginning of the phosphate adsorption experiment, whereas the dashed line in the figure indicates the time of arsenate addition. Phosphate adsorption curves coincide because they were all done with the same initial phosphate concentration. The last adsorption points, in addition, coincide with the plateau values seen in the isotherms (Fig. 1). The kinetics of
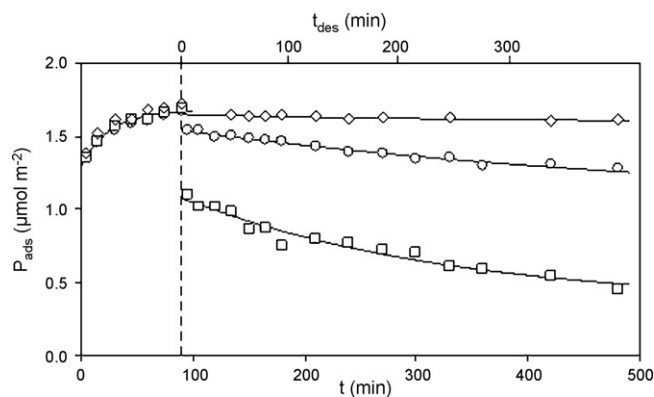
phosphate adsorption is in agreement with previously published data, showing a fast initial adsorption followed by a slower adsorption [10,19,21]. After arsenate addition, phosphate desorption takes place. As it occurs with adsorption, there are also two well distinguished steps in phosphate desorption (better seen for data obtained at high arsenate concentrations): a fast step that takes place between the time of arsenate addition and the first desorption point measured at 5 min of desorption, and a slower step taking place afterwards. The fast step is seen as an abrupt decrease in P_{ads} immediately after arsenate addition. All data points, therefore, belong to the slow step and thus all the measured rates correspond to this step [19]. The two-step process is in agreement with ATR-FTIR data (Fig. 2), that shows a relatively fast desorption up to 6 min of desorption, followed by a slower desorption at longer times.

Fig. 4 shows that an increase in arsenate concentration produces an increase in phosphate desorption. A similar behaviour is found for adsorption–desorption experiments at 45 °C and different concentrations of added arsenate (Fig. 5). In order to estimate the desorption rates, the amount of desorbed phosphate was calculated as:

$$P_{des} = P_1 + P_2(1 - e^{-kt_{des}}) \tag{1}$$

where P_{des} is the amount of desorbed phosphate during the desorption time t_{des}, and P_1, P_2 and k are constants. A similar equation was used successfully to fit the two-step adsorption of phosphate and arsenate on goethite [19] and can be equally used to fit here
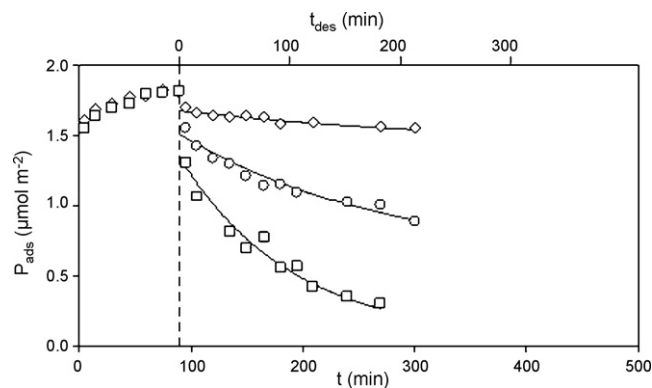
Fig. 5. Phosphate adsorption–desorption curves at pH 7 and 45 °C. The vertical dashed line indicates the time of arsenate addition. Phosphate concentration was 5.48×10^{-5} M in all experiments. P_T/As_T ratio: ◇, 3:1; ○, 1:1; □, 1:3. Lines in the desorption part of the figure show predictions with Eqs. (1) and (2) and parameters in Table 1.

Table 1
Best fitting parameters for experimental data.

P_T/As_T	P_T (mol L^{-1})	pH	T (°C)	P_1 (μmol m^{-2})	P_2 (μmol m^{-2})	k (min^{-1})	r_0 (μmol m^{-2} min^{-1})
3:1	5.48×10^{-5}	7.0	45	1.31×10^{-1}	2.46×10^{-1}	3.82×10^{-3}	9.39×10^{-4}
1:1	5.48×10^{-5}	7.0	45	3.00×10^{-1}	9.50×10^{-1}	5.00×10^{-3}	4.75×10^{-3}
1:3	5.48×10^{-5}	7.0	45	4.60×10^{-1}	1.30	1.00×10^{-2}	1.20×10^{-2}
3:1	5.48×10^{-5}	7.0	25	6.00×10^{-2}	9.00×10^{-2}	2.00×10^{-3}	1.8×10^{-4}
1:1	5.48×10^{-5}	7.0	25	1.01×10^{-1}	5.19×10^{-1}	2.00×10^{-3}	1.04×10^{-3}
1:3	5.48×10^{-5}	7.0	25	5.38×10^{-1}	7.31×10^{-1}	4.22×10^{-3}	3.08×10^{-3}
1:1	5.48×10^{-5}	7.0	10	0	3.54×10^{-1}	1.16×10^{-3}	4.11×10^{-4}
1:1	5.48×10^{-5}	4.5	25	3.03×10^{-1}	5.23×10^{-1}	9.00×10^{-3}	4.79×10^{-3}
1:1	5.48×10^{-5}	9.5	25	1.24×10^{-1}	$-$[a]	0	0
0.4:1	2.03×10^{-5}	7.0	25	7.40×10^{-2}	4.96×10^{-1}	2.00×10^{-3}	9.92×10^{-4}
0.7:1	3.55×10^{-5}	7.0	25	1.31×10^{-1}	3.83×10^{-1}	2.00×10^{-3}	7.66×10^{-4}

[a] Not estimated.

the two-step desorption process of phosphate. The value of P_1 represents the amount of phosphate that is desorbed during the fast process, which leads to the abrupt decrease in P_{ads} immediately after arsenate addition. The term $P_2(1 - e^{-kt_{des}})$ is the amount desorbed in the slower process. To fit data such as those plotted in Figs. 4 and 5, P_{ads} is calculated as

$$P_{ads} = P_{ads,0} - P_{des} \tag{2}$$

where $P_{ads,0}$ is the amount of adsorbed phosphate just before arsenate addition.

The phosphate desorption rate at any point of the slow process, r, can be known by differentiating Eq. (1) with respect to time

$$r = \frac{dP_{des}}{dt_{des}} = kP_2\,e^{-kt_{des}} \tag{3}$$

from which the initial desorption rate, r_0, can be estimated by evaluating Eq. (3) at $t_{des} = 0$,

$$r_0 = kP_2 \tag{4}$$

It must be noted that a good data fit with Eqs. (1) and (2) is not a prove for a certain adsorption mechanism. The data could be also well fitted with other kinetic equations such as the Elovich equation [35]. The equations are just used here to have a good estimation of r_0 from the use of all data points in the fitting. Table 1 lists the values of P_1, P_2, k and r_0 for all the conditions studied. It is clear that r_0 increases by increasing arsenate concentration at a given temperature. Moreover, r_0 vs. arsenate concentration plots (not shown here, see supplementary material) give straight lines for data at 25 °C (slope: 1.87×10^{-5} L m^{-2} min^{-1}, y-axis intercept:

0, $r^2 = 0.99$) and 45 °C (slope: 7.95×10^{-5} L m^{-2} min^{-1}, y-axis intercept: 0, $r^2 = 0.99$), showing a linear dependence between desorption rate and arsenate concentration.

Fig. 6 shows the effects of initial adsorbed phosphate (initial surface coverage with phosphate) on the desorption process. The shape of the desorption curves and the values of r_0 are very similar in all cases, indicating no effect of initial surface coverage on the desorption rate under the experimental conditions investigated.

Fig. 7 shows the effects of pH at constant phosphate and arsenate concentration. Although phosphate concentration was the same in all experiments, adsorbed phosphate (data before arsenate addition) varies with pH. The adsorption decreases slightly between pH 4.5 and 7.0, and strongly between 7.0 and 9.5. This is often found for phosphate adsorption on goethite, which shows a relatively small variation with pH in acidic media and a relatively strong pH dependency in alkaline conditions [15]. Desorption is strongly affected by pH. The higher desorption rate is found at pH 4.5, followed by a slower rate at pH 7.0. At pH 9.5 no desorption could be detected. Desorption seems to be so slow at this high pH, that most variations in P_{ads} and data scattering here are believed to reflect small pH changes during the experiment.

Since there is a 1:1 exchange stoichiometry, the overall desorption reaction can be written as a simple exchange process:

$$P_{ads} + As \rightarrow As_{ads} + P \tag{5}$$

where P_{ads} and As_{ads} denote adsorbed phosphate and arsenate species respectively, whereas P and As denote phosphate and arsenate species in solution respectively. The rate law for this process
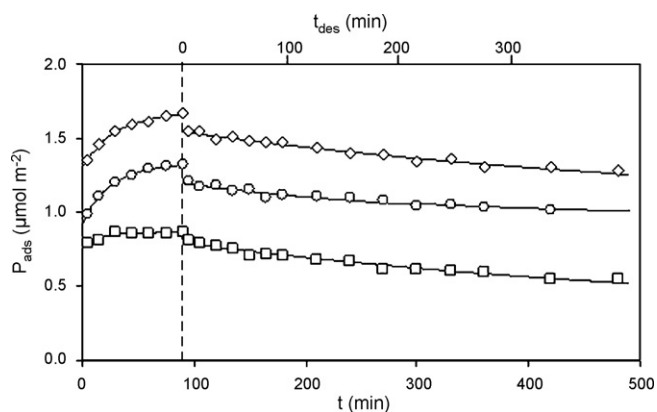
Fig. 6. Phosphate adsorption–desorption curves at different initial concentration of phosphate at pH 7 and 25 °C. The vertical dashed line indicates the time of arsenate addition. Arsenate concentration was 5.30×10^{-5} M in all experiments. Initial concentration of phosphate: ◊, 5.48×10^{-5} M; ○, 3.55×10^{-5} M; □, 2.03×10^{-5} M. Lines in the desorption part of the figure show predictions with Eqs. (1) and (2) and parameters in Table 1.
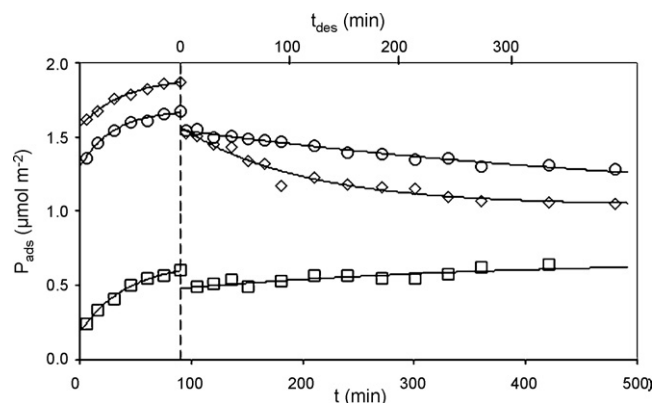
Fig. 7. Phosphate adsorption–desorption curves at different pH for a P_T/As_T ratio 1:1 at 25 °C. The vertical dashed line indicates the time of arsenate addition. Phosphate concentration was 5.48×10^{-5} M in all experiments. pH: ◊, 4.5; ○, 7.0; □, 9.5. Lines in the desorption part of the figure show predictions with Eqs. (1) and (2) and parameters in Table 1.

is defined as

$$r = k_r P_{ads}^n [As]^m \qquad (6)$$

where $[As]$ is the concentration of arsenate species in solution, k_r is the rate coefficient or rate constant, and n and m are the partial reaction orders. The linear dependency between rate and arsenate concentration indicates that $m = 1$, and the independence of the rate with initial adsorbed phosphate indicates that $n = 0$. Thus, the rate law can be written as a pseudo first order rate equation

$$r = k_r [As] \qquad (7)$$

and the value of k_r is directly the slope of the r_0 vs. arsenate concentration curve.

Actually, the overall reaction given by Eq. (5) surely occurs in several steps involving at least [36,37] i) transfer of As from the solution bulk to the goethite surface (this may include diffusion in bulk solution and intraparticle diffusion such as pore diffusion), ii) chemical reaction exchange of As for P (this could include chemical binding of As to the goethite surface followed by the chemical detachment of P), and iii) transfer of displaced P species from the goethite surface to the solution bulk. Any one or more of these steps can be the rate-controlling step, and some information about it can be obtained from the rate law. If either transfer of As to the surface or chemical binding of As to the goethite surface is rate-controlling, the rate should be dependent on arsenate concentration and independent of initial adsorbed phosphate, in agreement with the rate law shown by Eq. (7). If either chemical detachment of P or transfer of displaced P to the solution is rate-controlling, the rate should depend on both, arsenate concentration and initial adsorbed phosphate, which is not the case found here. Additional evidence for a mechanism involving As transport or As binding as rate-controlling steps can be obtained from pH effects on the desorption rate. A pH increase will increase the net negative charge (or reduce the net positive charge) of the surface, resulting in a slower attachment of anionic As species, and a slower reaction rate. The opposite pH effect is expected for a mechanism having P detachment or P transfer from the surface as the rate-controlling step.

The effects of temperature are better visualized in Fig. 8, which shows the adsorption–desorption curves at 10, 25 and 45 °C for a 1:1 P_T/As_T ratio. An increase in temperature increases the desorption rate of phosphate. The apparent activation energy, E_{app}, of the process can be estimated by applying the Arrhenius equation to the studied system:

$$k_r = A\, e^{-E_{app}/RT} \qquad (8)$$
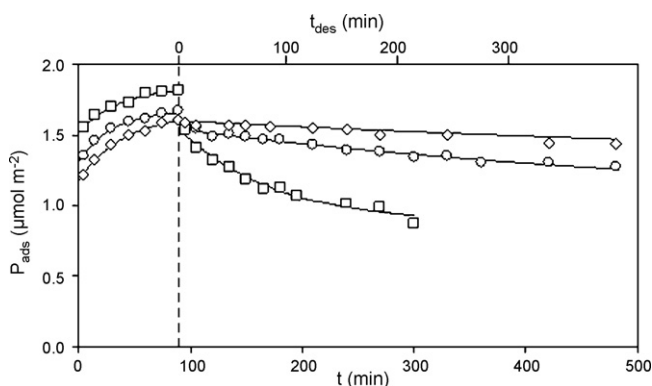
Fig. 8. Phosphate adsorption–desorption curves at different temperatures for a P_T/As_T ratio 1:1 at pH 7. The vertical dashed line indicates the time of arsenate addition. Phosphate concentration was 5.48×10^{-5} M in all experiments. Temperature: $\diamond$, 10 °C; $\bigcirc$, 25 °C; $\square$, 45 °C. Lines in the desorption part of the figure show predictions with Eqs. (1) and (2) and parameters in Table 1.

where A is the Arrhenius pre-exponential term, R the gas constant and T the absolute temperature. According to this equation, a $\ln(k_r)$ vs. T^{-1} plot should be a straight line with slope $E_{app} R^{-1}$. This plot for data between 10 and 45 °C (not shown here) did result to be linear (slope, -6094 K^{-1}, $r^2 = 0.99$) leading to a value of 51 kJ mol^{-1} for E_{app}. This value means that the rate decreases by a factor of around 10 by decreasing the temperature from 45 to 10 °C.

Besides providing the temperature dependence of the rate of reaction, the magnitude of the activation energy can be also helpful in the evaluation of the rate-controlling process. Sparks [36], for example, indicates that typical values of E_{app} are <21 kJ mol^{-1} for diffusion-controlled processes in water, and that particle-controlled processes have higher values: 20–40 kJ mol^{-1} for diffusion-controlled processes in pores within the particles, and 42–84 kJ mol^{-1} for processes controlled by chemical reactions at mineral surfaces. Lasaga [37], on the other hand, states that diffusion-controlled processes in solution have E_{app} values <21 kJ mol^{-1}, but that reactions where the breaking of bonds in crystals is rate-controlling should have relatively high E_{app} values, similar to those of diffusion in solids (83–336 kJ mol^{-1}). He also points out that most activation energies for a wide variety of mineral-solution processes lie within these two ranges (in the range 42–84 kJ mol^{-1}), and attributes these relatively low values to the catalytic effect of adsorption or to the presence of surface defects. Agbenin and van Raij [38], on the other hand, interpreted activation energy values between 42 and 49 kJ mol^{-1} for phosphate desorption from soils to intraparticle diffusion processes.

An E_{app} of 51 kJ mol^{-1} allows to rule out diffusion in solution, and indicates that the rate control is within the particle, either As diffusion in pores or As chemical binding to the surface. Diffusion in pores is in agreement with the interpretation given by Agbenin and van Raij [38], and chemical binding is in agreement with the E_{app} ranges provided by Sparks [36] and Lasaga [37]. Chemical binding, however, appears to be very rapid for As on goethite. Grossl et al. [39] have shown that this binding has time scales in the order of milliseconds, which is much faster that the times scales found in this work.

4. Conclusions

Phosphate desorption from goethite is induced by arsenate because both oxoanions have similar structure and reactivity, and thus they compete for the same surface sites of goethite. As it occurs with phosphate adsorption, the desorption occurs in two steps: a fast step that takes place between the time of arsenate addition and the first desorption point measured at 5 min of desorption, and a slower step that lasts several hours. This two-step desorption can be deduced from both, batch desorption experiments and ATR-FTIR measurements. Batch desorption data indicate that there is a 1:1 exchange between arsenate and phosphate during the slow step, and the process is first order with respect to arsenate concentration and independent of initial adsorbed phosphate. The rate law, together with pH effects and the apparent activation energy of the desorption process suggest that the rate-controlling process is intraparticle diffusion of As species, probably As diffusion in pores. ATR-FTIR indicates that at pH 7 the adsorbed phosphate species are mainly bidentate inner-sphere surface complexes. The identity of these complexes does not change during desorption, and there is no evidence for the formation of intermediate species during the reaction.

Acknowledgments

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.colsurfa.2009.07.026.

References

[1] H. Klapper, Control of Eutrophication in Inland Water, Ellis Horwood, Chichester, UK, 1991.

[2] B.M. Spears, L. Carvalho, R. Perkins, A. Kirika, D.M. Paterson, Spatial and historical variation in sediment phosphorus fractions and mobility in a large shallow lake, Water Res. 40 (2006) 383–391.

[3] P.L. Smedley, D.G. Kinniburgh, A review of the source, behavior and distribution of arsenic in natural waters, Appl. Geochem. 17 (2002) 517–568.

[4] J.D. Paoloni, M.E. Sequeira, C.E. Fiorentino, Mapping of arsenic content and distribution in groundwater in the southeast pampa, Argentina, J. Environ. Health 67 (2005) 50–53.

[5] N.S. Bolan, N.J. Barrow, A.M. Posner, Describing the effect of time on sorption of phosphate by iron and aluminium hydroxides, J. Soil Sci. 36 (1985) 187–197.

[6] B. Bar-Yosef, U. Kafkafi, R. Rosenberg, G. Sposito, Phosphorus adsorption by kaolinite and montmorillonite: I. Effect of time, ionic strength, and pH, Soil Sci. Soc. Am. J. 52 (1988) 1580–1585.

[7] R.L. Parfitt, Phosphate reactions with natural allophane, ferrihydrite and goethite, J. Soil Sci. 40 (1989) 359–369.

[8] T.H. Hsia, S.L. Lo, C.F. Lin, D.Y. Lee, Characterization of arsenate adsorption on hydrous iron oxide using chemical and physical methods, Colloids Surf. A 85 (1994) 1–7.

[9] C. Colombo, V. Barrón, J. Torrent, Phosphate adsorption and desorption in relation to morphology and crystal properties of synthetic hematites, Geochim. Cosmochim. Acta 58 (1994) 1261–1269.

[10] R. Strauss, G.W. Brümmer, N.J. Barrow, Effects of crystallinity of goethite: II. Rates of sorption and desorption of phosphate, Eur. J. Soil Sci. 48 (1997) 101–114.

[11] K.P. Raven, A. Jain, R.H. Loeppert, Arsenite and arsenate adsorption on ferrihydrite: kinetics, equilibrium, and adsorption envelopes, Environ. Sci. Technol. 32 (1998) 344–349.

[12] M. Grafe, M.J. Eick, P.R. Grossl, Adsorption of arsenate (V) and arsenite (III) on goethite in the presence and absence of dissolved organic carbon, Soil Sci. Soc. Am. J. 65 (2001) 1680–1687.

[13] P. Lakshmipathiraj, B.R.V. Narasimhan, S. Prabhakar, G. Bhaskar Raju, Adsorption of arsenate on synthetic goethite from aqueous solutions, J. Hazard. Mater. 136 (2006) 281–287.

[14] A.J. Bridgeman, G. Cavigliasso, Density-functional investigation of bonding in tetrahedral MO_4 anions, Polyhedron 20 (2001) 2269–2277.

[15] B.A. Manning, S. Goldberg, Modeling competitive adsorption of arsenate with phosphate and molybdate on oxide minerals, Soil Sci. Soc. Am. J. 60 (1996) 121–131.

[16] A. Violante, M. Pigna, Competitive sorption of arsenate and phosphate on different clay minerals and soils, Soil Sci. Soc. Am. J. 66 (2002) 1788–1796.

[17] Y. Gao, A. Mucci, Acid base reactions, phosphate and arsenate complexation, and their competitive adsorption at the surface of goethite in 0.7 M NaCl solution, Geochim. Cosmochim. Acta 65 (2001) 2361–2378.

[18] J. Antelo, M. Avena, S. Fiol, R. López, F. Arce, Effects of pH and ionic strength on the adsorption of phosphate and arsenate at the goethite-water interface, J. Colloid Interface Sci. 285 (2005) 476–486.

[19] C. Luengo, M. Brigante, M. Avena, Adsorption kinetics of phosphate and arsenate on goethite. A comparative study, J. Colloid Interface Sci. 311 (2007) 354–360.

[20] F.J. Hingston, A.M. Posner, J.P. Quirk, Competitive adsorption of negatively charged ligands on oxide surfaces, Discuss. Faraday Soc. 52 (1971) 334–342.

[21] Z. Hongshao, R. Stanforth, Competitive adsorption of phosphate and arsenate on goethite, Environ. Sci. Technol. 35 (2001) 4753–4757.

[22] F. Liu, A. De Cristofaro, A. Violante, Effect of pH, phosphate and oxalate on the adsorption/desorption of arsenate on/from goethite, Soil Sci. 166 (2001) 197–208.

[23] M.I. Tejedor-Tejedor, M.A. Anderson, Protonation of phosphate on the surface of goethite as studied by CIR-FTIR and electrophoretic mobility, Langmuir 6 (1990) 602–611.

[24] C. Luengo, M. Brigante, J. Antelo, M. Avena, Kinetics of phosphate adsorption on goethite: comparing batch adsorption and ATR-IR measurements, J. Colloid Interface Sci. 300 (2006) 511–518.

[25] S.E. O'Reilly, D.G. Strawn, D.L. Sparks, Residence time effects on arsenate adsorption/desorption mechanisms on goethite, Soil Sci. Soc. Am. J. 65 (2001) 67–77.

[26] F. Frau, R. Biddau, L. Fanfani, Effect of major anions on arsenate desorption from ferrihydrite-bearing natural samples, Appl. Geochem. 23 (2008) 1451–1466.

[27] B.A. Manning, S. Goldberg, Modeling arsenate competitive adsorption on kaolinite, montmorillonite and illite, Clay Clay Miner. 44 (1996) 609–623.

[28] M. Pigna, G.S.R. Krishnamurti, A. Violante, Kinetics of arsenate sorption-desorption from metal oxides: effect of residence time, Soil Sci. Soc. Am. J. 70 (2006) 2017–2027.

[29] R.J. Atkinson, A.M. Posner, J.P. Quirk, Adsorption of potential-determining ions a the ferric oxide-aqueous electrolyte interface, J. Phys. Chem. 71 (1967) 550–558.

[30] M. Villalobos, J.O. Leckie, Surface complexation modeling and FTIR study of carbonate adsorption to goethite, J. Colloid Interface Sci. 235 (2001) 15–32.

[31] K.L. Linge, C.E. Oldham, Interference from arsenate when determining phosphate by the malachite green spectrophotometric method, Anal. Chim. Acta 450 (2001) 247–252.

[32] S. Tsang, F. Phu, M.M. Baum, G.A. Poskrebyshev, Determination of phosphate/arsenate by a modified molybdenum blue method and reduction of arsenate by $S_2O_4^{2-}$, Talanta 71 (2007) 1560–1568.

[33] T. Hiemstra, W.H. Van Riemsdijk, A surface structural approach to ion adsorption: the charge distribution (CD) model, J. Colloid Interface Sci. 179 (1996) 488–508.

[34] S.J. Parikh, B.J. Lafferty, D.L. Sparks, An ATR-FTIR spectroscopic approach for measuring rapid kinetics at the mineral/water interface, J. Colloid Interface Sci. 320 (2008) 177–185.

[35] J. Zhang, R. Stanforth, Slow adsorption reaction between arsenic species and goethite (α-FeOOH): diffusion or heterogeneous surface reaction control, Langmuir 21 (2005) 2895–2901.

[36] D.L. Sparks, Enviromental Soil Chemistry, Academic Press, Amsterdam, 2003.

[37] A.C. Lasaga, Kinetic Theory in the Earth Sciences, Princeton University Press, Princeton, 1998.

[38] J.O. Agbenin, B. van Raij, Kinetics and energetics of phosphate release from tropical soils determined by mixed ion-exchange resins, Soil Sci. Soc. Am. J. 65 (2001) 1108–1114.

[39] P.R. Grossl, M. Eick, D.L. Sparks, S. Goldberg, C.C. Ainsworth, Arsenate and chromate retention mechanisms on goethite. 2. Kinetic evaluation using a pressure-jump relaxation technique, Environ. Sci. Technol. 31 (1997) 321–326.