Study of Arsenate Adsorption on Iron Oxide by in situ ATR-FTIR Spectroscopy

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Abstract

Stabilization of arsenic contaminated soils by iron oxides has been proposed as a remediation technique to prevent leaching of arsenate into the environment. However, fundamental studies are needed to establish under which conditions the complexes formed are stable.

A new method based on ATR-FTIR spectroscopy was adapted to study the adsorption of arsenate species on iron oxides. The measurements required the use of D$_2$O as solvent.

The amount of arsenate complexes adsorbed on the iron oxide increased with decreasing pH in the range studied, viz. pH 4-12. Arsenate complexes adsorbed at pH 4 desorbed from the film to some extent as the pH was increased to 8.5 or 12. The stability of arsenate complexes adsorbed on the iron oxide evidently changed with the change in pH, most likely due to the electrostatic repulsion between the negatively charged oxoanion and the more negatively charged iron oxide as the pH increased.

From competitive adsorption experiments it was found that arsenate species were more strongly bonded to the iron oxide than phosphate species. Furthermore, it was found that two different phosphate complexes formed on the iron surface at pH 4, one deuterated and the other one de-deuterated. The complexes showed very different stability. The deuterated phosphate complex was desorbed easily from the iron oxide film as arsenate was added to the system whereas the de-deuterated phosphate complex only desorbed slightly from the film upon adding arsenate.

This work has increased the fundamental knowledge of the iron oxide/arsenate/phosphate system, which will be of importance for the development of more effective soil remediation techniques.
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List of papers

The thesis is based on the following papers.


**Paper II: Adsorption of As(V) on iron oxide nanoparticle films studied by in situ ATR-FTIR spectroscopy.** I. Carabante, J. Kumpiene, M. Grahn, A. Holmgren, J. Hedlund. Colloids and Surfaces A. Physicochemical and Engineering Aspects, Volume 345, Nr 1-3, 2009, 106-113

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Introduction

Arsenic in the environment

Arsenic is the 20th most abundant element in natural systems, the 14th element in seawater and the 12th in the human body. However, arsenic is also very toxic. Long term exposure to low levels of arsenic may lead to cancer or skin diseases such as blackfoot disease, whilst exposure to a high amount of arsenic is lethal.

Inorganic arsenic in water can be found in two different oxidation states: As (III), the main species of which are arsenic trioxide, sodium arsenite and arsenic trichloride; and As (V), the main species of which are arsenic pentoxide, arsenic acid and arsenates. In comparison, As (III) shows higher mobility in soils and higher toxicity for human beings than As (V), however As (V) is the predominant specie in oxidizing conditions.

From 2001 the maximum arsenic concentration recommended in drinking water was changed from 50 µg/l to 10 µg/l by the World Health Organization (WHO). However, no toxicity for arsenic concentrations in water below 50 µg/L has been reported. Most countries changed their legislation to follow the WHO recommendation. As a result, areas considered to be arsenic contaminated increased significantly. Countries such as Argentina, Bangladesh, China, Chile, Mexico and Nepal have retained their limit at 50 µg/l due to the high arsenic content in natural water and also due to the technical and economical limitations with regard to reducing arsenic levels in drinking water. Even though countries such as China, Mexico, Argentina, Nepal, Chile, USA or Vietnam all have areas with high arsenic concentrations, West Bengal in India and Bangladesh are the areas in which the greatest population is exposed to high arsenic concentrations in ground water. The origin of arsenic contamination is often natural abundance in the environment. However, contamination can also be due to human activities, such as a result of carbon combustion in China, mining activities in Mexico or from arsenic based pesticides used in many countries.
CCA (copper, chromate, arsenate) is a wood preservative based on a copper, chromium and arsenic mixture that was introduced in the 1930s. As a consequence of inappropriate industrial methods of CCA wood preservative impregnation, many of the impregnation sites are now contaminated with high concentrations of arsenic in the soil. Remediation of arsenic contaminated soils is typically done by excavating the soil followed by controlled land filling. However, this method disrupts the environment and is expensive. Chemical amendment is an alternative to this method. Arsenic mobility and bioavailability is reduced in the soil by the addition of an appropriate chemical to avoid leaching of the contaminant to the environment. The addition of iron compounds, aluminium oxides and to a lesser extent manganese oxides to the soil has been reported as possible amendments to reduce leaching of arsenate to the environment. The high affinity of iron oxides for arsenic in combination with its low cost and abundance have made it an interesting adsorbent material for arsenic contaminated soil remediation but also for arsenic removal from water. Amorphous aluminium oxides showed a higher arsenic adsorption capacity than did iron oxides. However, iron compounds are preferred due to their high abundance and as they may be produced from cheap industrial by-products or wastes. Although good initial results have been obtained in the different tests regarding the use of iron compounds as soil amendments to arsenic contaminated soils, this method is still at a development stage and more data is needed to establish both the preferred conditions as well as the conditions to be avoided. The effect of parameters such as pH, redox potential and the presence of other organic and inorganic species are examples of important issues to be understood, as is the long-term stability of arsenic in the soil. Good understanding of the influence of these parameters needs to be established before chemical amendment can be accepted as a commercial remediation method. In the present work, the stability of arsenate adsorbed on iron oxides was studied as a function of the pH value of the solution and the presence of phosphate species in solution. These two parameters are very important. The stability of adsorbed arsenate on iron oxide may be influenced by the pH, as well as pH, of the water, since the speciation of arsenic oxoanion and the charge of the iron oxide surface are controlled
by this parameter. On the other hand, the presence of phosphate in the soil water, due to natural abundance or external addition such as fertilizers, compete with arsenate species for the adsorption sites of the iron oxide and affects therefore the stability of arsenate complexes adsorbed on the metal oxide. 12-18

Iron oxides

Two oxidation states of iron, Fe (II) and Fe (III), can be found in the different structures of iron oxides, hydroxides and oxide-hydroxides. Hereafter, the term iron oxide will for simplicity be used for referring to iron oxides hydroxides and oxide-hydroxides. Iron oxides are relatively abundant in natural systems, such as soils, rocks and ground water.19 There are 16 iron oxides, the most relevant of which are presented in Table 1.

<table>
<thead>
<tr>
<th>Oxide-hydroxides and hydroxides</th>
<th>Oxides</th>
</tr>
</thead>
<tbody>
<tr>
<td>Goethite α-FeOOH</td>
<td>Hematite α-Fe₂O₃</td>
</tr>
<tr>
<td>Akaganéite β-FeOOH</td>
<td>Maghemite β-Fe₂O₃</td>
</tr>
<tr>
<td>Lepidocrocite γ-FeOOH</td>
<td>Magnetite Fe₃O₄</td>
</tr>
<tr>
<td>Feroxyhyte δ-FeOOH</td>
<td></td>
</tr>
<tr>
<td>Ferricydrate Fe₅O₄H·4H₂O</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Most relevant iron oxides.19

Goethite (α-FeOOH) is an iron oxide hydroxide representing one of the highest thermodynamic stabilities within the iron oxides. As a result, it is by far the most common iron oxide in soils and rocks. It has a hexagonal close packing (hcp) of anions (O²⁻ and OH⁻). Hematite (Fe₂O₃) presents a very similar structure to goethite based on a hexagonal close packing of the anion (O²⁻). This iron oxide is also very stable thermodynamically and is thus also very abundant in natural systems. Magnetite (Fe₃O₄) is one of the three iron oxides containing iron in the divalent state as it, in addition to
Fe(II), also contains Fe (III) in its structure. It is well known for its magnetic properties and is an important iron ore. Magnetite has a face-centered cubic crystal structure. Ferricydrite (Fe₃O₄H·4H₂O) is sometimes denoted amorphous iron oxide, even though it represents a hcp anion crystalline structure. It is only present as nano-particles and is poorly XRD crystalline and crystal growth lead to further crystallization of a more stable iron oxide phase. It is widely abundant in surface environments. Three polymorphs of goethite (FeOOH) are found in nature: lepidocrocite (γ-FeOOH), which has a cubic close packing (ccp) of the anions, akaganéite (β-FeOOH), which has a body centered cubic packing (bcc) of anions and ferrihydrite (δ-FeOOH), which has a poorly crystalline structure. Lepidocrocite occurs in soil, rocks and biota, usually as a product of Fe²⁺ oxidation whereas akaganéite occurs rarely in nature and usually in Cl-rich media such as marine environments. Maghemite (α-Fe₂O₃) is isostructural with magnetite, however, only iron in the trivalent state is present in its structure. It occurs in soils as an oxidation product from magnetite.

The iron oxides have shown good performance as adsorbents, for instance, they have relatively high affinity for several inorganic oxoanions such as sulphate, phosphate or arsenate. They have also shown ability to adsorb gold particles on synthetic hematite. Goethite, in combination with activated carbon fiber, has been used for NO, SO₂ and NH₃ adsorption. The cosmetics industry has been taking advantage of the adsorption capacity of hematite to remove any arsenic trace elements and thus to reduce the toxicity of the products. Hematite has also been used for sensor studies due to its adsorption capacity, such as with fluor and water (humidity) in gases. Moreover, both natural and synthetic iron oxides are widely used as pigments since they show a high tinting strength, i.e. capacity to impart colour to other substances. Hematite as a pigment shows a red colour and it is used in e.g. paints and varnishes due to its high resistance to acids and bases. The paints containing hematite can be normally used for interior, exterior, and metallic pieces since the paints are resistant to heat and ultraviolet radiation because of the high thermal stability of the iron oxide. Magnetite has a black colour and is used as a pigment mainly for paints but also in the textile industries. It is also used in glass production, giving a green, blue or black colour to the glass. At the same time it also increases the water resistance of the glass, since the Fe-Si-
O formed in the superficial layers of the glass protect this layers from water penetration.\textsuperscript{20}

Iron oxides are also used as catalysts. Hematite, for instance, catalyzes the dehydrogenation of ethyl benzene to styrene.\textsuperscript{19}

**Adsorption Theory**

In the adsorption process, molecules from a gas or a liquid bind to the surface of a solid or a liquid. The molecules which are extracted from a phase and concentrate at the surface of a solid or liquid are called adsorbate whereas the material where the adsorbate is adsorbed is called adsorbent. The reverse process, in which the molecules migrate from the surface of a solid or liquid to a gas or a liquid is called desorption.\textsuperscript{21}

Two kinds of adsorption reactions are well-known: chemical adsorption and physical adsorption. Chemical adsorption implies a (covalent) chemical bond between a specific adsorption site of the adsorbent and the adsorbate. On the other hand, in physical adsorption, weak chemical interactions, such as van der Waals- and hydrogen bonding occur between adsorbent and adsorbate and, therefore, the chemical structure of adsorbate and adsorbent do not undergo major chemical changes as a result of the adsorption. Chemical adsorption is normally associated with a higher enthalpy of adsorption and slower kinetics of adsorption than physical adsorption. Since chemical adsorption implies that the adsorbent reacts with a specific adsorption site of the adsorbent, there is an upper limit to how much that may adsorb on the surface i.e. when the adsorbate has covered all the sites available resulting in a monolayer covering the surface. On the other hand, in physical adsorption, multilayers are frequently formed. This is because the adsorbate molecules can adsorb on each other via van der Waals- or hydrogen bonding forces.

The amount of adsorbate that adsorbs on a particular adsorbent depends basically on the chemical activity of the adsorbate and adsorbent, the concentration of the adsorbate, and the temperature at which the adsorption takes place, apart from the presence of other molecules that could simultaneously adsorb.\textsuperscript{21} To measure or study the adsorption process, adsorption isotherms are typically recorded. Adsorption isotherms show the
amount adsorbed at equilibrium as a function of the concentration of the adsorbate in the fluid.

The type I adsorption isotherm shown in Figure 1 is a typical adsorption isotherm for a chemical adsorption process. However, certain physical adsorption processes may also present this type of isotherm. At low concentrations, the amount adsorbed increases as the concentration of the adsorbate is increased in the fluid. At a certain point, the adsorbate covers the whole surface of the adsorbent and any increase in the concentration does not lead to an increase in the amount adsorbed. The other type of curves shown in Figure 1 illustrates different isotherms encountered where multilayer adsorption occurs. A type II isotherm corresponds to formation of a monolayer on the adsorbent surface, related to chemical or physical adsorption, followed by the adsorption in a multilayer adsorption fashion, as a consequence of a physical adsorption, as the concentration of the adsorbate is increased in the fluid. A type III isotherm represent a process in which the monolayer formation is a slow process (weaker adsorbent-adsorbate interaction) followed by a faster multilayer adsorption (higher adsorbent-adsorbent interaction). Type IV and V adsorption isotherms usually occur due to multilayer adsorption onto the surfaces of pores in the adsorbent.21

Figure 1. The five adsorption isotherm curves as classified by Brunauer.21

To describe the different isotherms observed experimentally, several different models have been devised. One of the most popular models is the Langmuir adsorption model, which is a mathematical model mainly describing type I isotherms, see equation 1. It was derived based on three assumptions: only monolayer adsorption is possible, the adsorption takes place at specific sites, and the heat of adsorption is independent of surface coverage.
The fractional loading, \( \theta \), is defined as the relation between loading \((q)\) or surface concentration at a particular concentration in the fluid bulk divided by the saturation loading \((q_s)\) i.e. the surface concentration at monolayer coverage, \( K \) is the adsorption constant and \( a \) is the concentration of the adsorbate in the fluid bulk.

Another adsorption model frequently encountered is the Freundlich adsorption model. Even though this model was based on the empirical application of equation 2 to experimental data, this model can also be derived for a model in which the heat of adsorption varies exponentially with surface coverage.22 However, the experimentally calculated parameters for this equation (2) normally only fits the adsorption data taken in a small concentration, or pressure, range.21

\[
q = k \cdot a^n
\]  

(2)

The parameters \( k \) and \( n \) in the equation are fitted constants and \( q \) is the loading.

**Adsorption of arsenate on iron oxides**

The adsorption of ions on iron oxides involves interactions between the adsorbate and the hydroxyl group of the iron oxide.19 This phenomenon was clearly demonstrated when the adsorption of arsenate on goethite was studied using IR spectroscopy.23 The surface chemistry of the iron oxides varies with pH. At low pH, the hydroxyl groups at the surface of the iron oxide are doubly protonated \((\equiv \text{Fe-OH}_2^+)\) and the surface charge of the iron oxide is thus positive. At a certain pH, the hydroxyl group is protonated with only one proton \((\equiv \text{Fe-OH})\) and thus the surface charge of the iron oxide is neutral. This pH is called the point of zero charge and typical pH values for the point of zero charge ranges between 5.5 and 9 for different iron oxides.19 A maximum adsorption of arsenate has been observed at acidic pH values around 3-4.24 25 At these
pH values, the electrostatic attraction between the negative oxoanion and the positive charge of the iron oxide surface favours adsorption. At pH lower than 3, fully protonated arsenate (H₃AsO₄) species are present in solution and electrostatic attraction is no longer possible resulting in a lower adsorption. At pH values above the point of zero charge, the iron oxide is negatively charged, and repels the negatively charged arsenate oxoanion. As the arsenate oxoanion and the iron oxide surface can not come close enough due to their repulsion, adsorption is not occurring at these pH values.

The chemical structure of the arsenate complexes formed on the iron oxide has been extensively studied using Extended X-ray Absorption Fine Structure (EXAFS) and FTIR. Bidentate binuclear complexes have traditionally been reported as the most thermodynamically stable complex formed and thus the most probable. The literature is, however, contradictory regarding the formation of monodentate complexes. In a recent publication, it was, based on EXAFS and FTIR measurements, concluded that the only complex formed on the goethite surface was the monodentate species. On the other hand, it has also been concluded that monodentate species only occurred at low surface coverage, whereas bidentate binuclear complexes formed at higher surface coverage. Nevertheless, another study concluded that the peak assigned to monodentate complex was instead due to a bidentate mononuclear complex. In another publication, the conclusion was that the formation of monodentate and bidentate mononuclear complexes were not very likely since they are thermodynamically unstable. Furthermore, in the latter study, the peak previously assigned to a bidentate mononuclear complex was assigned to the As-O-O-As structure. As illustrated above, many studies aiming at elucidating the structure of arsenate complexes adsorbed on iron oxides have been carried out, however the results are contradictory and the system is thus yet not fully understood.

The kinetics of adsorption of arsenate on iron oxides has been studied previously, and two distinct adsorption regimes were observed. In the first step, a fast adsorption was observed followed by a second step with significantly slower adsorption kinetics. It was proposed that arsenate was adsorbing as monodentate complex in the first relatively fast step, whereas in the second slower step, the monodentate complex reacted forming
a bidentate complex. On the other hand, it was reported the presence of two different adsorption sites in the other study. The fast adsorption corresponded to arsenate adsorption on more accessible adsorption sites whereas the subsequent slow adsorption process was due to arsenate adsorption on less accessible sites.

Moreover, the influence of carbonate on the adsorption of arsenate on iron oxide has been studied. In general, it was found that the final amount of arsenate adsorbed on iron oxide was not dependent on the presence of carbonate species in the system whereas the kinetics of adsorption was slightly influenced by the presence of carbonate. At pH 8 the arsenate adsorption rate was reduced by the presence of carbonates whereas it was enhanced at pH 4 and pH 6.

Phosphate and arsenate adsorption on iron oxides are very similar, with regard to pH dependence, higher adsorption capacity at low pH, and that only a small amount is adsorbed. When arsenate was pre-adsorbed on iron oxides, the adsorption of phosphate was drastically reduced, but the reduction of arsenate adsorption was not so high for the experiment carried out at opposite conditions. Arsenate thus seemed to be more strongly adsorbed on iron oxides than was phosphate.

The adsorption of phosphate on iron oxide has been studied using ATR-FTIR spectroscopy. Protonated binuclear bidentate complexes were predominantly adsorbed at pH values between 3 and 6. At pH>7.5, however, non-protonated binuclear bidentate complexes were predominantly adsorbed.
In situ ATR-FTIR spectroscopy

ATR-FTIR spectroscopy has proven to be a powerful tool for adsorption studies on synthetic and natural mineral surfaces.37-41

In the ATR technique, the incident IR beam is totally reflected inside an ATR crystal, see Figure 2. At each reflection, the electric field of the IR radiation probes the vicinity of the crystal surface where the sample is placed. The intensity of the electric field probing the sample decreases exponentially with the distance from the surface of the ATR crystal according to equation 3

\[ E = E_0 \exp \left( -\frac{2 \pi}{\lambda_i} \left( \sin^2 \theta - n_{21}^2 \right)^{1/2} Z \right) \]  \hspace{1cm} (3)

where \( E_0 \) is the intensity of the electric field at the surface of the ATR crystal (at \( Z = 0 \)), \( \lambda_i \) is the wavelength of the infrared radiation in vacuum (\( \lambda \)) divided by the refractive index of the ATR crystal (\( n_1 \)), \( n_{21} \) is the ratio of the refractive index of the sample medium (\( n_s \)) divided by the refractive index of the ATR crystal (\( n_1 \)), \( \theta \) is the angle of incidence, and \( Z \) is the distance perpendicular from the surface of the ATR crystal.

Total reflection of the IR beam in the ATR crystal occurs when the refractive index of the sample (\( n_s \)) is significantly lower than the refractive index of the ATR crystal (\( n_1 \)) and when equation 4 is fulfilled.42

\[ \sin^2 \theta - n_{21}^2 \geq 0 \]  \hspace{1cm} (4)

The depth of penetration, \( d_p \), is defined as the distance from the ATR crystal at which the intensity of the electric field has decreased to a value of \( e^{-1} \) (37%) of the intensity at the surface of the ATR crystal, and accordingly, it is a rough measure of the distance sampled. For a two-layer system (ATR crystal and sample) the penetration depth is given by equation 5
As shown by equation 5, the depth of penetration depends on the refractive indices of both the ATR crystal and the sample as well as of the wavelength of the incident beam. Thus, the depth of penetration increases with decreasing wavenumber. In the present work, the depth of penetration in the frequency range 1000-800 cm⁻¹ is ~1µm. Since the technique only probes the vicinity of the crystal, it is a powerful tool for studying the properties of thin films and their surface chemistry.

\[ d_p = \frac{\lambda}{2\pi n_i \left( \sin^2 \theta - n_3^2 \right)^{1/2}} \]  (5)

**Figure 2.** Schematic representation of the IR beam propagating in the ATR element.
Scope

The first objective of this study was to develop a new method based on ATR-FTIR spectroscopy to facilitate in-situ studies of the adsorption of arsenate on iron oxides.

The second objective was to study the stability of arsenate complexes on iron oxide. A good understanding of the stability of the arsenic complexes adsorbed on iron oxides is very important to develop depuration methods for arsenic contaminated systems using the adsorption ability of iron oxides, since these methods have been proposed for soil remediation or water depuration. The stability of arsenate adsorbed on iron oxide was evaluated when two parameters were changed. These parameters were pD, which is a parameter comparable to pH, but which refers to the deuteron (D+) concentration, and the phosphate concentration.
Experimental

Synthesis and film preparation

The iron oxide 6-line ferrihydrite, was synthesized by adding 1 ml of a 0.7 M solution of iron (III) chloride (FeCl$_3$·6H$_2$O; Riedel-de Haën, p.a. 99%) drop wise to 50 ml of boiling distilled water. The resulting solution was kept boiling under vigorous agitation for 5 minutes. During this time, the colour of the solution altered from yellowish to brown-red. The brown-red solution was allowed to cool down and was subsequently dialyzed against distilled water in a dialysis membrane (MWCO 12-14000; Spectra/Por Dialysis membrane; Spectrum laboratories) for approximately 24 hours. The distilled water was changed several times during the dialysis. The separation of ferric and chloride ions from the synthesis solution by the dialysis resulted in a pH change from 1.5 before the dialysis to approximately 5 by the end of the purification stage.

The purified iron oxide suspension was thereafter diluted by the addition of equal amounts (by mass) of methanol (CH$_3$OH; Kebo lab, >99.8%) to obtain better wetting properties of the iron oxide suspension. The ATR crystals (ZnSe; Crystan; trapezoidal 52 mm x 20 mm x 2 mm, 45° edge cut) were coated with a particle film by applying a small amount of the suspension on the ATR crystal. The suspension on the crystal was allowed to dry in air, which resulted in iron oxide films.

Iron oxide characterisation

The film morphology was investigated using scanning electron microscopy (SEM). A Phillips XL 30 microscope was used in the first work (paper II) to investigate gold coated samples. A FEI Magellan 400 microscope was used in the last work (paper III) to investigate samples without gold coating.
Electrophoresis (ZetaCompact) was used in order to determine the zeta potential of dilute iron oxide suspensions in 0.01M KNO₃ at pH values from 4 to 11.5. The data was evaluated applying the Smoluchowski equation.

A part of the dialyzed synthesis solution was freeze dried to obtain an iron oxide reference powder.

X-Ray Diffraction (XRD) measurements were performed on freeze dried powder of the iron oxide using a Siemens D5000 diffractometer running in Bragg-Brentano geometry.

Nitrogen adsorption at liquid nitrogen temperature was measured using a Micrometrics ASAP 2010 instrument. The powder sample was degassed at a temperature of 140°C for about 24h prior to the measurements. The sample was degassed at this temperature in order to avoid phase transformation of the ferrihydrite to hematite at higher temperatures.

**ATR-FTIR measurements**

A Bruker IFS 66v/s FTIR-spectrometer equipped with a DTGS (Deuterated TriGlycine Sulphate) detector was used for recording the infrared spectra. All spectra were recorded at a resolution of 4 cm⁻¹ and as a result of co-adding 200 scans.

Figure 3 shows a schematic figure of the experimental set-up. All experiments were carried out using deuterium oxide (D₂O, Aldrich, 99 atom % D) as solvent, since water is interfering with the absorption bands from arsenic species. The pD values of the solutions were controlled with a pH-stat (Metler Toledo, T70) which added either deuterium chloride (DCI; Aldrich; 99 atom % D) or sodium deuteroxide (NaOD; Aldrich; 99+ atom % D) solutions. The liquid solution was pumped by a peristaltic pump from the solution vessel into the stainless steel flow cell mounted in the spectrometer. The flow cell comprised two liquid compartments of about 2.5 cm³ each.
connected in series. After being in contact with both sides of the ATR crystals, the solution was recirculated back to the vessel. In order to minimize absorption of CO₂ from the air the solutions were continuously bubbled with argon gas (AGA, 99%).

**Figure 3.** Schematic figure of the experimental set-up used to perform the in situ ATR-FTIR measurements. The ATR crystal, which is represented in the drawing by the yellow prism, was mounted in the flow cell (coloured in grey) and the iron oxide film on the ATR crystal is shown in brown.

**Adsorption experiments**

A background spectrum was recorded before each adsorption experiment. In paper II, a flow of D₂O was allowed to equilibrate with the iron oxide film for approx. 30 minutes before recording the background spectrum. In paper III, a 0.1M sodium chloride (NaCl, Merck; 99.5%) solution in D₂O was allowed to equilibrate with the iron oxide film for 5 hours before the background spectrum was recorded. The solutions were adjusted to the same pD as in the forthcoming experiment, i.e. pD 4 or 8.5. After recording the background spectrum, the appropriate amount of a stock solution of sodium hydrogen-arsenate hepta-hydrate (NaH₂AsO₄•7H₂O; Fluka; p.a. 98.5%) or sodium phosphate monobasic monohydrate (NaH₂PO₄•H₂O; Sigma-Aldrich; 98-102%) was added and the adsorption experiment started. During the different experiments, spectra were recorded continuously to observe the changes induced upon adsorption in situ. The concentration of the solutions after the experiments was analyzed using Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-
OES, Perkin Elmer optima 2000 DV) to confirm that the concentration of the oxoanion in solution remained constant during the experiment.
Results

Characterisation of the iron oxide particles and films

An X-ray diffractogram of the freeze dried iron oxide powder is shown in Figure 4. The peak positions were in good agreement with the reference pattern for 6-line-ferrihydrite peaks. The peaks were very broad, which showed that the crystal size of the iron oxide was very small as expected and reported previously for 6-line-ferrihydrite.

Figure 4. X-ray diffractogram of the freeze dried iron oxide powder. The vertical bars indicate the peak positions with their relative intensities and the Miller indices of the planes from the reference pattern of 6-line-ferrihydrite.

The surface area of the iron oxide freeze-dried powder was determined to 190 m²/g by applying the BET equation to N₂ adsorption data. The pore size distribution was also determined from N₂ adsorption data by the BJH method and most pores were found to be in the range from 2 to 10 nm. The pore size distribution corresponded to interparticle pores and it was assumed that the interparticle pores in the iron oxide film were the same as for the powder. A second XRD pattern recorded after the nitrogen adsorption experiment confirmed that no phase transformation had occurred during the adsorption measurements.
The Z-potential of the iron oxide surface in a 0.01M KNO₃ background electrolyte was determined as a function of pH, see Figure 5. The point of zero proton charge was estimated to be between 7.5 and 8, which is in good agreement with the values reported in the literature, viz. around 7.9. Even though all the adsorption experiments were performed in D₂O and not in H₂O, it was assumed that the iron oxide surface behaves in a similar way in both solvents, and thus the point of zero D⁺ charge was assumed to be in the same range as the point of zero proton charge.

![Figure 5](image)

**Figure 5.** Z-potential of the iron oxide as a function of pH in a 0.01M KNO₃ background electrolyte.

Figure 6a shows a top view SEM image of a gold coated iron oxide film. The film is composed of densely packed and very small, less than 20 nm, spherical particles. The gold coating may increase the observed particle size.

Figure 7 shows side view SEM images of two iron oxide films used in a) Paper II and b) Paper III. For each film, several images were recorded at different locations on the film and it was found that the film thickness was even. The film thickness for the film presented in Figure 7a was about 700-900 nm whereas the thickness of the film presented in Figure 7b was about 300-500 nm. The difference in thickness between the two films was mainly a result of that different amounts and concentration of iron oxide suspension was used. Both SEM images illustrates that the film was constituted of densely packed and very small spherical particles. The SEM image illustrated in Figure 7
b is more representative since it was recorded with a high resolution SEM and without any gold coating on the sample.

**Figure 6.** Top view SEM image of a gold coated iron oxide film (Paper II).

**Figure 7.** Side view SEM images of a) a gold coated iron oxide film (paper II) and b) an iron oxide film without gold coating (paper III). The thickness of the iron oxide film is indicated by an arrow.

**Spectroscopic differences between arsenate and phosphate species in solution and adsorbed on iron oxide.**

Figure 8 shows the spectra recorded from arsenate solutions (13 mM) at a) pD 4, b) pD 8.5 and c) pD 11.8. The signal in these spectra stems only from arsenate species in solution as discussed in Paper II. Three absorption bands at 908, 875 and 730 cm\(^{-1}\) appeared in the spectra recorded at pD 4 (Figure 8a) where D\(_2\)AsO\(_4^−\) is the predominant specie in solution (reaction 1).\(^1\) Only one absorption band at 856 cm\(^{-1}\) appeared in the
spectrum recorded at pD 8.5 (Figure 8b), at this pD the predominant arsenate species in solution is DAsO$_4^{2-}$. At pD 11.8, both DAsO$_4^{2-}$ and AsO$_4^{3-}$ species are present in solution (reaction 1). Hence the spectrum recorded at this pD (Figure 8c) shows an absorption band at 856 cm$^{-1}$ stemming from DAsO$_4^{2-}$ species in solution and another absorption band at 806 cm$^{-1}$ stemming from AsO$_4^{3-}$. It is thus possible to distinguish between the different arsenate species in solution using the ATR-FTIR technique. Figure 8d shows the spectra recorded after 5 hours of arsenate adsorption on an iron oxide film from a 0.03 mM solution at pD 4 (Paper II). The bands stemming from arsenate adsorbed on iron oxide were situated at 875 and 840 cm$^{-1}$, i.e. at different wavenumbers than the bands stemming from the dominating arsenate species in solution at this pD, viz. D$_2$AsO$_4^-$ which had absorption bands at 875 and 730 cm$^{-1}$. Therefore, Figure 8 illustrates the ability of the technique to distinguishing arsenate species adsorbed on an iron oxide film from arsenate species in solution. Moreover, the high adsorption capacity of the iron oxide film concentrated arsenate in the film. The signal thus stemming from arsenate species adsorbed on iron oxide from a 0.03 mM arsenate solution was more intense than the signal stemming from arsenate in solution even though the concentration of arsenate in solution was more than 400 times higher than in the adsorption experiment. This phenomenon suggests that iron oxide coated waveguides might be utilized as sensor probes for detecting arsenate in aqueous solutions.

$$H_3AsO_4 \rightarrow H_2AsO_4^- + H^+ \rightarrow HAsO_4^{2-} + H^++\rightarrow AsO_4^{3-} + 3H^+ \quad (1)$$
Figure 8. Spectra of a 13 mM arsenate solution recorded at a) pD 4, b) pD 8.5 and c) pD 11.8 using an uncoated ZnSe crystal. Spectrum d) was recorded from a 0.03 mM arsenate solution after 5 hours in contact with an iron oxide film.

Figure 9 shows spectra recorded using phosphate (60 mM) solutions at a) pD 4 and b) pD 8.5. The signal given in these two spectra originate from phosphate species in solution as discussed in Paper III. Three bands at 1180, 1084 and 940 cm\(^{-1}\) appeared in the spectrum recorded at pD 4. These bands were assigned to monoacid phosphate species, \(D_2PO_4^-\), since it is the predominant phosphate species in solution at this pD (reaction 2).\(^{34}\) At pD 8.5, two absorption bands were observed in the spectrum at 1084 cm\(^{-1}\) and 988 cm\(^{-1}\) and these were assigned to the predominant phosphate species at this pD, viz. \(DPO_4^{2-}\) (reaction 2). Figure 9 also shows the spectrum recorded of phosphate species adsorbed on an iron oxide film from a 0.03 mM phosphate solution at c) pD 4 and d) pD 8.5 after 5 hours of adsorption time. At pD 4, five absorption bands at 1124, 1084, 1035, 1014, 998 cm\(^{-1}\) assigned to adsorbed phosphate species were obtained, whereas at pD 8.5, bands assigned to adsorbed phosphate appeared at 1064 cm\(^{-1}\) and 1021 cm\(^{-1}\) (more detailed assignments are presented below). Figure 9 thus clearly
illustrates that phosphate species in solution and phosphate species adsorbed on the iron oxide film may unambiguously be distinguished from each other using ATR-FTIR spectroscopy. Again the iron oxide film exerts a concentrating effect such that the signal obtained from adsorbed phosphate species was higher than the signal obtained from species in solution although the concentration in the solution in the latter case was 2000 times higher.

$$H_3PO_4 \overset{pK_{a1}=2.16}{\rightarrow} H_2PO_4^- + H^+ \overset{pK_{a2}=7.21}{\rightarrow} HPO_4^{2-} + 2H^+ \overset{pK_{a3}=12.32}{\rightarrow} PO_4^{3-} + 3H^+ \quad (2)$$
Influence of pD on the adsorption/desorption of As(V) on iron oxide

Figure 10a shows spectra recorded at different adsorption times while a 0.03 mM arsenate solution at pD 4 was flowing over an iron oxide film. The intensity of the two bands at 875 cm\(^{-1}\) and 840 cm\(^{-1}\), assigned to arsenate species adsorbed on the iron oxide, increased with adsorption time. According to Beer’s law\(^{42}\), the increase in the intensity of these bands indicates an increase in the arsenate concentration on the iron oxide film and thus indicates that the adsorption continued throughout the whole experiment. Simultaneously, negative adsorption bands appeared in the 1700-1000 cm\(^{-1}\) region of the spectra, (see paper II). These bands were assigned to carbonate species adsorbed on the iron oxide film during film preparation. The decrease in intensity of the bands assigned to carbonate species occurred simultaneously as arsenate was adsorbing, which indicates that the arsenate replaced some of the carbonate species adsorbed on the surface. The intensity of the band at 840 cm\(^{-1}\), assigned to adsorbed arsenate, and the (negative) intensity of the band at 1409 cm\(^{-1}\), assigned to adsorbed carbonate, were plotted against time, see Figure 10b. The kinetic curves of arsenate adsorption and carbonate desorption shown in this Figure illustrate that none of the processes reached equilibrium after 5 hours reaction time. As stated in Paper II, desorption of carbonates from the film could be a limiting step for arsenate adsorption on the iron oxide. However, diffusion of arsenate species from the solution to less accessible adsorption sites on the iron oxide may also limit the rate of adsorption.

Figure 10. a) Spectra of arsenate adsorbed on an iron oxide film at different times of adsorption from a 0.03 mM solution at pD 4. a) 1.5 min. b) 6.5 min. c) 11.5 min. d) 36.5 min. e) 66.5 min. f) 116.5 min. g) 191.5 min. h) 300 min. b) (□) Peak height of the band at 840 cm\(^{-1}\) assigned to arsenate species adsorbed on iron oxide and (○) peak height of the band at 1409 cm\(^{-1}\) assigned to carbonate species vs. time.
Figure 11 shows spectra of arsenate species adsorbed on the iron oxide film from a 0.03 mM arsenate solution at different pD values ranging from 4 to 12, and after 70 minutes of adsorption time (for details, see Paper II). Two bands assigned to arsenate adsorbed on iron oxide can be observed in spectra recorded at pD 4, 6 and 8. The bands appearing in the spectra recorded at pD 4 and 6 were situated at 875 and 840 cm\(^{-1}\) whereas they shifted to 855 and 830 cm\(^{-1}\) in the spectrum recorded at pD 8.5. The observed shifts are probable due to de-deuteration of the adsorbed arsenate species, as elaborated in Paper II. Further, the absorption bands were more intense at lower pD values, indicating that arsenate adsorbed to a larger extent at lower pD values. This conclusion was based on the assumption that the molar absorptivities of the arsenate species adsorbed were very similar and thus independent of the pD value. Spectra recorded at pD 10 only showed weak bands indicating very low adsorption of arsenate at this pD, and at pD 12, no bands from adsorbed arsenate could be observed in the spectrum. The observed adsorption behaviour, with less adsorption at higher pD values, may be expected since the iron oxide surface is more positively charged at lower pD values and the electrostatic attraction between the iron oxide surface and the negatively charged oxoanion would thus favour the adsorption. On the other hand, at pD 10 and 12, the surface of the iron oxide is negatively charged and thus the electrostatic repulsion between iron oxide surface and the negatively charged oxoanions would hamper the oxoanion adsorption.
Figure 11. Spectra of arsenate adsorbed on iron oxide at different pH values after 70 min of adsorption from a 0.03 mM arsenate solution.

Figure 12 shows the intensity of the band at ~840 cm\(^{-1}\) after 5 hours of adsorption on an iron oxide at different arsenate concentration in solution at pH 4 (○) and pH 8.5 (●), for further experimental details see Paper III. Since the molar absorptivity of the arsenate complexes adsorbed on the iron oxide at pH 4 and 8.5 was considered to be the same, it is thus possible to conclude about the adsorbed amounts. At each concentration in solution, the adsorbed amount was higher at pH 4 than at pH 8.5 as would be expected from the electrostatic interactions as discussed previously. Moreover, in the whole range studied, the adsorbed amount increased with increasing arsenate concentration in solution. Therefore, arsenate did not reach monolayer coverage in the concentration range studied. Even after 5 hours of adsorption, equilibrium was not reached, these curves are thus rather pseudo equilibrium adsorption isotherms than true adsorption isotherms, however the shape of the kinetic curves indicate that after 5 hours of adsorption the equilibrium is reasonably close.
Figure 12. Peak height of the ∼840 cm⁻¹ absorption band stemming from arsenate adsorbed on iron oxide at pseudo equilibrium (5 hours of adsorption) plotted versus arsenate concentration at (⊙) pD 4 and (■) pD 8.5.

Figure 13 shows plots of the absorbance from arsenate adsorbed on an iron oxide film from a 0.03 mM solution at pD 4 plotted versus adsorption time, thus indicating the kinetics of adsorption. After 300 minutes, the pD was changed to either 8.5 (△) or 12 (□) while keeping the arsenate concentration constant. As the pD was changed from 4 to 8.5, arsenate immediately desorbed from the iron oxide and after 5 hours approximately 20% of the arsenate originally adsorbed had desorbed from the surface. However, when the pD was changed from 4 to 12, about 65% of the arsenate had desorbed after the same time. At both pD’s, the desorption of arsenate was very fast within the first 40 minutes followed by a slower desorption process in the remaining part of the experiment.
As discussed in Paper II, two kinds of interactions may occur between the arsenate and the metal oxide: the formation of a D-bonded outer-sphere complex due to a physical adsorption; and also a hydroxyl group may be expelled from the iron oxide surface, leading to the formation of an inner-sphere complex, with the formation of a Fe-O-As chemical bond, as a consequence of chemical adsorption. Even though it is not straightforward to distinguish between these two kinds of interactions, rinsing experiments may possibly indicate which of the two complexes is the most probable. Since D-bonded outer-sphere complexes are associated to lower adsorption energy than the inner-sphere complexes, the latter is expected to desorb to a lesser extent in a rinsing experiment. Consequently, a rinsing experiment was devised. Figure 14 shows the spectra recorded at different times while pre-adsorbed arsenate was rinsed by pure D$_2$O adjusted at the same pD as in the pre-adsorption viz. pD 4 (a) and 8.5 (b), see Paper II for details. Figure 14a illustrates that arsenate barely desorbed from the iron oxide film at pD 4 during the 200 minutes of rinsing and about 90% of the arsenate pre-adsorbed was still adsorbed after the rinsing experiment. On the other hand, significant desorption of arsenate was observed in the rinsing experiment performed at pD 8.5 as shown in Figure 14b. These experiments thus indicate that the arsenate
complexes are more strongly bonded to the iron oxide surface at pD 4 than at pD 8.5. The weaker adsorption bond at the latter pD may be explained by the decrease in the electrostatic attraction between arsenate species and iron oxide surface at pD 8.5 combined with the hypothesis that a higher fraction of D-bonded complexes were formed.

Figure 14. Spectra recorded at different desorption times, from 1.5 to 300 minutes (the times at which spectra were recorded follows a<b<c<d<e for the two figures) at a) pD 4 and b) pD 8.5. Before desorption, the iron oxide film was equilibrated for 24 hours with a 0.03 mM arsenate solution at the same pD value.

Competitive adsorption between arsenate and phosphate

Single adsorption of phosphate on iron oxide. In order to study the competitive adsorption of arsenate and phosphate, the single adsorption of phosphate at pD 4 and 8.5 was first studied. As already shown in Figure 9, IR absorption bands appeared in the 1200-950 cm\(^{-1}\) region of the spectrum stemming from phosphate adsorbed on the iron oxide film at both pD values, 4 and 8.5. The molar absorptivity of the different phosphate complexes adsorbed at the two pD values studied was considered to be very similar, as reported previously.\(^{35}\) The integrated area between 1200 cm\(^{-1}\) and 950 cm\(^{-1}\) was used to estimate the total amount of phosphate adsorbed on the iron oxide. Figure 15 shows pseudo-isotherms for phosphate adsorption at room temperature at pD 4 and 8.5, see Paper III for details. The amount of phosphate adsorbed on the iron oxide was higher at pD 4 than at pD 8.5 at each phosphate concentration in solution throughout the whole concentration range studied. Further, as for arsenate, the amount adsorbed on the iron oxide film increased with increasing concentration in solution throughout
the concentration range studied suggesting that complete monolayer coverage was not reached during the course of these experiments. These curves, indicate very similar adsorption behaviour for arsenate (Figure 12) and phosphate in analogous experiments, which is in concert with previous reports.\textsuperscript{16,18}

In a real soil amendment application it is very likely that phosphate is also present as nutrient to facilitate plant growth on the soil as discussed previously, and since the adsorption of arsenate and phosphate is similar, it is thus of utmost importance to study the competitive adsorption of phosphate and arsenate on iron oxides. Most of the competitive adsorption between arsenate and phosphate in the present work was performed at concentrations of 0.03 mM for both arsenate and phosphate in solution. At these concentrations the surface coverage of the iron oxide is low for both oxoanions, see Figures 12 and 15.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{image1.png}
\caption{Integrated area of the bands between 1200 and 950 cm\textsuperscript{-1} assigned to adsorbed phosphate on iron oxide plotted vs. the concentration of phosphate in solution at (\(\bar{z}\)) pD 4 and (\(\bar{z}\)) pD 8.5. At each concentration, the system was allowed to equilibrate for 5 hours before recording the spectra.}
\end{figure}

\textbf{Substitution of phosphate for arsenate at pD 4.} Figure 16 shows spectra (from a to c) recorded during the experiment in which phosphate was pre-adsorbed from a 0.03 mM solution at pD 4 on an iron oxide film for 5 hours. As stated earlier, five bands situated at 1124, 1084, 1035, 1014, 998 cm\textsuperscript{-1} appeared and became more intense with time, indicating adsorption of phosphate with time. The relative intensity of the most
intense bands at 1124, 1035 and 998 cm\(^{-1}\) were constant and were thus assigned to the same complex, viz. either the deuterated binuclear bidentate complex ((≡FeO)\(_2\)(OD)PO) or the monodentate doubly deuterated complex ((≡FeO)(OD)\(_2\)PO). On the other hand, the bands at 1084 and 1014 cm\(^{-1}\) were assigned to de-deuterated complexes, viz. either the non-deuterated binuclear bidentate complex ((≡FeO)\(_2\)PO\(_2\)) or the mono-deuterated monodentate complex ((≡FeO)(OH)PO\(_2\)), see Paper III for details. Since the intensity of the bands due to the deuterated phosphate complex (at 1124, 1035 and 998 cm\(^{-1}\)) was greater than the intensity of the bands caused by the de-deuterated complex (at 1084 and 1014 cm\(^{-1}\)), the concentration of adsorbed deuterated complex appeared higher than the concentration of de-deuterated complex throughout the single phosphate adsorption.

After 50 minutes of adsorption (spectrum b), only the bands at 1124, 1035 and 998 cm\(^{-1}\) were observed. Hence, the deuterated phosphate complex adsorbed mainly within the first hour of adsorption. On the other hand, spectrum e-b (shown in the lower part of Figure 16) which is the result of subtracting spectrum b (after 50 minutes of adsorption) from spectrum e (after 5 hours of adsorption), only shows bands evolving from species adsorbed between 50 minutes and 5 hours adsorption time. Only the two bands at 1084 and 1014 cm\(^{-1}\) were observed in spectrum e-b, indicating that only the de-deuterated phosphate complex adsorbed after the first hour of adsorption, thus showing a significantly slower kinetics of adsorption than the deuterated phosphate complex.

After these first 5 hours, arsenate was added to the solution achieving equimolar concentration of the two oxoanions in solution. The pH was kept constant during the whole experiment. Spectra in the central part of Figure 16 (from h to f) were recorded during this second stage of the experiment. Bands previously assigned to adsorbed arsenate, in the range 900-800 cm\(^{-1}\), immediately appeared as arsenate was added to the solution and their intensity increased with time. Simultaneously, the bands originating from phosphate complexes (at 1200-950 cm\(^{-1}\)) decreased in intensity with time as a result of desorption of phosphate species from the iron oxide. Furthermore, the bands assigned to the deuterated phosphate complex (at 1124, 1035 and 998 cm\(^{-1}\)) were reduced very fast whereas the bands assigned to the de-deuterated complex (at 1084
and 1014 cm$^{-1}$) remained almost unchanged, which indicates very different stability for the two types of complexes. To the best of our knowledge, this is the first report of different stabilities towards arsenate induced desorption for the two adsorbed phosphate complexes. Spectrum e-h (shown in the lower part of Figure 16), which is the result of subtracting spectrum h (recorded after 5 hours of phosphate desorption in the presence of arsenate in the system) from spectrum e (recorded after 5 hours of pure phosphate adsorption), highlights only the bands in which the intensity decreased during the competitive adsorption with arsenate. Only bands assigned to the deuterated complex (at 1124, 1035 and 998 cm$^{-1}$) appeared in spectrum e-h, which indicates that only this complex desorbed when arsenate was introduced in the system, and the results further implies that the de-deuterated complex was very stable under these conditions.
Figure 16. Spectra recorded as a 0.03 mM phosphate solution at pH 4 was flowing over an iron oxide film after (a) 7 min. (b) 50 min. (c) 122 min. (d) 200 min. and (e) 5 hours. After 5 hours, the solution was adjusted to be equimolar in phosphate and arsenate viz. 0.03 mM at pH 4 and spectra were recorded after (f) 320 min. (g) 360 min. and (h) 600 min. (e-b) spectrum calculated from the subtraction of spectrum (b) from spectrum (e). The (e-h) spectrum was calculated by subtracting spectrum (h) from spectrum (e). The continuous vertical lines represent the wavenumbers 1124 cm\(^{-1}\), 1035 cm\(^{-1}\) and 998 cm\(^{-1}\) whereas the discontinuous lines represent 1084 and 1014 cm\(^{-1}\).

Substitution of phosphate for arsenate at pH 8.5. Figure 17 shows data when the same experiment was repeated at pH 8.5 (see Paper III for experimental details). Spectra shown in the upper part of this Figure were recorded during phosphate adsorption at pH 8.5. Two main bands at 1064 and 1021 cm\(^{-1}\) (assigned to phosphate complexes
adsorbed on the iron oxide) appeared in the spectra and their intensity increased with time indicating adsorption of phosphate with time. The bands were assigned to either the non-deuterated binuclear bidentate complex \((\equiv\text{FeO})_2\text{PO}_4^-\) or to the mono-deuterated monodentate complex \((\equiv\text{FeO})(\text{OH})\text{PO}_4^-\), see Paper III for details on the band assignments. These are the same complexes as those assigned to the 1084 and 1014 cm\(^{-1}\) bands at pD 4. The shift in band position when the pD was changed from 4 to 8.5 might have been induced by e.g. changes in the adsorption sites caused by the change in pD, or due to different hydrogen bonding strength at the different pD values or possibly a change in the interactions with other phosphate complexes.

When arsenate was added to the system, the intensity of the bands at 1064 and 1021 cm\(^{-1}\) decreased with time as a consequence of phosphate desorption from the iron oxide film whereas the intensity of the bands assigned to arsenate species adsorbed on iron oxide (900-800 cm\(^{-1}\)) increased with time as a result of the adsorption of arsenate. It was thus concluded that arsenate species adsorbed on the iron oxide replacing the phosphate complexes previously adsorbed.

**Figure 17.** Spectra recorded as a 0.03 mM phosphate solution at pD 8.5 was flowing over an iron oxide. Spectra were recorded at (a) 7 min, (b) 27 min, (c) 50 min, (d) 175 min and (e) 300 minutes. After 5 hours adsorption time, an equimolar (0.03 mM) arsenate and phosphate solution at pD 8.5 was in contact with the iron oxide film and spectra at various recorded adsorption times, (f) 307 min, (g) 330 min, (h) 410 min and (i) 600 minutes.
Substitution of arsenate by phosphate at pH 4 and at pH 8.5. Figure 18 shows the spectra recorded during the competitive adsorption experiment in which arsenate was pre-adsorbed from a 0.03 mM solution on an iron oxide film for 5 hours at (A) pH 4 and (B) pH 8.5. This experiment was chosen as a simple simulation of a real application where arsenate contaminated soil is amended with iron oxide and where phosphates are subsequently added in small amounts as plant nutrient. In the upper part of Figure 18, the spectra recorded during the arsenate pre-adsorption stage at pH 4 (A) and 8.5 (B) are shown. The bands between 900 and 800 cm\(^{-1}\), previously (Figure 8) assigned to adsorbed arsenate species, increased with time for the whole 5 hours of adsorption, indicating adsorption of arsenate on the iron oxide. After pre-adsorption of arsenate, phosphate was added to the solution resulting in an equimolar concentration of the two oxoanions, and spectra were recorded with time. The spectra shown in the lower part of Figure 18 correspond to the second stage of the experiment when phosphate was added to the system. The bands assigned to adsorbed arsenate at 900-800 cm\(^{-1}\) decreased in intensity simultaneously as the bands assigned to phosphate adsorbed (1200-950 cm\(^{-1}\)) increased in intensity. The Figure thus shows that arsenate species pre-adsorbed at pH 4 could partially be desorbed due to competitive adsorption of phosphate. However, the decrease in intensity of the arsenate bands was only about 10%. Moreover, the spectroscopic bands assigned to adsorbed arsenate did not change in shape during the course of the experiment indicating that the structure of the adsorbed complexes did not change during the adsorption/desorption processes. The results obtained at pH 8.5 were similar to the results at pH 4, albeit at pH 8.5 seemingly more arsenate desorbed as phosphate was added to the system. This follows from the fact that at pH 8.5 the intensity of the arsenate band decreased with 20% as compared with 10% at pH 4.
Figure 18. (A) Spectra recorded when a 0.03 mM arsenate solution at pH 4 was in contact with an iron oxide film at (a) 7 min, (b) 20 min, (c) 45 min, (d) 70 min, (e) 145 min, (f) 165 min and (g) 300 min adsorption times. After 300 minutes adsorption time, an equimolar 0.03 mM arsenate and phosphate solution at pH 4 was in contact with the iron oxide film and spectra at the following recorded times, (h) 302 min, (i) 320 min, (j) 340 min, (k) 400 min, (l) 460 min and (m) 600 min. (B) Spectra recorded when a 0.03 mM arsenate solution adjusted at pH 8.5 was in contact with an iron oxide film at (a) 2 min, (b) 20 min, (c) 40 min, (d) 130 min, (e) 300 min adsorption times. After 300 minutes adsorption time, an equimolar 0.03 mM arsenate and phosphate solution at pH 8.5 was in contact with the iron oxide film and spectra at the following recorded adsorption times, (f) 307 min, (g) 330 min, (h) 380 min, (i) 450 min and (j) 600 min.

As discussed previously, adsorbed arsenate was more strongly bonded to the iron oxide surface than were adsorbed phosphate complexes at the pH values studied. However, the previous experiments were all carried out at equimolar concentrations of phosphate and arsenate. Therefore the experiments with arsenate pre-adsorbed were repeated but with a five times higher phosphate concentration i.e. 0.15 mM, see Paper III for further experimental details. The adsorption kinetics of phosphate at pH 4 and 8.5 followed by the desorption induced by the addition of phosphate at t=300 min. are shown in Figure 21. As expected, arsenate desorbed to a larger extent when the concentration of phosphate in the solution was higher. At pH 4, the final concentration of pre-adsorbed arsenate changed from 90% of the maximum surface concentration at equimolar concentrations of phosphate and arsenate to 70% of the maximum surface.
concentration. The change in the final relative amount adsorbed at pH 8.5 was from 80% at equimolar concentrations to 50% when the phosphate concentration was five times higher than the concentration of arsenate.

Figure 19. The peak height of the band at ~840 cm\(^{-1}\) assigned to arsenate adsorbed on iron oxide plotted as a function of time. The arsenate concentration was 0.03 mM and the pH was (■) 8.5 and (□) 4. At t=300 min, phosphate was added in appropriate amounts while keeping the arsenate concentration constant at 0.03 mM. At pH 4, the phosphate concentrations were (△) 0.03 mM and (○) 0.15 mM and at pH 8.5 (▲) 0.03 mM and (●) 0.15 mM.

In summary, the adsorption of arsenate on the iron oxide was relatively stable under the conditions studied. However, the arsenate complexes were less stable in the presence of phosphates and at higher pH. Therefore, in order to apply chemical amendments in order to decrease the mobility of arsenate in arsenic contaminated soils, parameters like pH and phosphate concentration in the soil must be controlled.
Conclusions

The ATR-FTIR spectroscopy technique was proven to be very useful for studying the adsorption and desorption of arsenate and phosphate species on iron oxide and both single component and binary systems could be studied in situ.

The adsorption of arsenate and phosphate on iron oxide was highly pD dependent with higher adsorption capacities at lower pD in the range studied.

Adsorption/desorption experiments suggested that arsenate to a great extent formed inner-sphere complexes on the iron oxide. Furthermore, a higher fraction of inner-sphere complexes, compared to outer-sphere complexes, was observed at pD 4 than at pD 8.5.

Arsenate showed stronger adsorption than phosphate on iron oxide under similar conditions.

Two different phosphate complexes adsorbed on iron oxide at pD 4, one deuterated and one de-deuterated. The two complexes showed distinct differences in their stabilities. The deuterated complex was easily desorbed due to competitive adsorption with arsenate species whereas the de-deuterated phosphate complex was more stable.

The relatively strong affinity of arsenate for the iron oxide 6-line ferrihydrite, indicate that iron oxide coated waveguides in combination with FTIR spectroscopy might be useful as a sensor for detecting arsenate in aqueous solutions.

Although the formed arsenate complexes were relatively stable under the conditions studied, the results clearly indicate that when applying iron oxides as a soil amendment, care should be taken to control pH and the phosphate content in the amended soil so as to minimize leaching of arsenate to the environment.
Future work

As the conditions in soils may vary a lot, more experiments should be performed to study the influence of e.g. ionic strength and redox potential on the adsorption of arsenate on iron oxides. Also, the competitive adsorption between arsenates and other compounds such as sulphate, chromate, carbonates (to a higher extent than in the present work), cations (Zn, Pb, Al, Cu), humic acids or other organic contaminants coexisting with arsenate in natural system should be studied.

Further, EXAFS measurements on the system studied might help in identifying which complexes were formed on the iron oxide.

An interesting track would also be to exploit the good adsorption properties of the iron oxides to develop an efficient adsorbent material for e.g. purification of drinking water.
References


[23] Lumsdon, D.G.; Fraser, A.R.; Russel, J.D.; Livesey, N.T., New infrared bands assignments for the arsenate ion adsorbed on synthetic goethite (α-FeOOH), Soil Sci. 35 (1984) 381-386.


A powerful method for studying the adsorption of As(V) on iron oxides in situ
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A powerful method for studying the adsorption of As(V) on iron oxides in situ

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Stabilization by iron oxides has been proposed as a remediation technique for arsenic contaminated soils in order to prevent leaching into the environment (Kumpiene, 2005). For this to be successful, studies are needed to establish under which conditions the complexes formed are stable. In the present study, we focus on the further development of a powerful technique, ATR-FTIR spectroscopy (Mirabella, 1993), for studying the adsorption of arsenate species on iron oxides. With this technique it is possible to, in situ, gain both quantitative (e.g. Langmuir adsorption parameters) and qualitative (e.g. structure of the complexes formed) data of adsorption. At the present, only few publications are available on the use of this technique for studying oxyanion sorption on iron oxides. (McComb et al., 2007; Roddick-Lanzilotta et al., 2001)

In the present work, ca 800 nm thick films of a Synthetic Iron Oxide (SIO) deposited on an ATR crystal was used as adsorbent. Arsenate adsorption on an SIO film at five different pH ranging between 4 and 12 and at an arsenate concentration of 0.03 mM in D2O solution was studied. Bands at ~ 835 and 870 cm⁻¹ emanate from arsenate adsorbed on SIO (Lumsdon et al., 1984). Negative bands in the range between 1020 and 1600 cm⁻¹ have previously been assigned to carbonate species (Bargar et al., 2005), suggesting that carbonates are desorbing from the SIO surface upon adsorption of arsenates. These species were probably formed from CO₂ absorption onto the SIO from ambient air. As expected, the amount of adsorbed arsenates decreases with increasing pH. The adsorption kinetics at pH 4 for a 0.03 mM arsenate solution and the simultaneous desorption of carbonate followed by the desorption kinetics of arsenates adsorbed when flushing with pure D₂O at pH 12 was also studied.

In conclusion, the technique has great potential as a tool both for assessing the stability of iron oxide-arsenate complexes and for identifying the different complexes formed.

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References

Adsorption of As(V) on iron oxide nanoparticle films studied by in situ ATR-FTIR spectroscopy

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Adsorption of As (V) on iron oxide nanoparticle films studied by in situ ATR-FTIR spectroscopy

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ABSTRACT

Stabilization of arsenic contaminated soils by iron oxides has been proposed as a remediation technique to prevent leaching of arsenate into the environment. Fundamental studies are needed to establish under which conditions the complexes formed are stable. In the present work, a powerful technique, viz. ATR-FTIR spectroscopy, is adapted to the studies of adsorption of arsenate species on iron oxides. This technique facilitates acquisition of both quantitative and qualitative in situ adsorption data.

In the present work, about 800 nm thick films of 6-line ferrihydrite were deposited on ZnSe ATR crystals. Arsenate adsorption on the ferrihydrite film was studied at pH values ranging from 4 to 12 and at an arsenate concentration of 0.03 mM in D2O solution. The amount of adsorbed arsenate decreased with increasing pH as a result of the more negatively charged iron oxide surface at higher pH values. The adsorption and desorption kinetics were also studied. Arsenate showed a higher adsorption rate within the first 70 min and a much lower adsorption rate from 70 to 300 min. The low adsorption rate at longer reaction times was partly due to a low desorption rate of already adsorbed carbonate species adsorbed at the surface. The desorption of carbonate species was evidenced by the appearance of negative absorption bands. The desorption of adsorbed arsenate complexes was examined by flushing with D2O and it was found that the complexes were very stable at pH 4 suggesting formation of mostly inner-sphere complexes whereas a fraction of the complexes at pH 8.5 were less stable than at pH 4, possibly due to the formation of outer-sphere complexes.

In summary, the ATR technique was shown to provide in situ information about the adsorption rate, desorption rate and the speciation of the complexes formed within a single experiment, which is very difficult to obtain using other techniques.

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1. Introduction

1.1. Background

Arsenic is an element known to cause several severe complications to the health. Long term exposure to low concentration may lead to cancer and skin diseases, whereas exposure to higher concentrations is lethal [1]. Still, arsenic is the 20th most abundant element in natural systems, the 14th most abundant element in seawater and the 12th in the human body [1]. Arsenic can be found in two different oxidation states, As(V) which dominates under oxidizing conditions, and As(III), which is the predominant species in reducing environments. The latter is considered more toxic and also presents a higher mobility than As(V) in natural systems [1-2].

Bangladesh and the West Bengal in India are the two areas in the world that shows the most severe arsenic ground water contamination. [1] However, there are contaminated areas all over the world: China, Chile, Argentina, Poland and Sweden are a few examples. The arsenic contamination occurs naturally in the environment, but it can also be a result of human activities like mining, coal combustion, and the use of arsenic based pesticides. [2] CCA wood preservative was used for timber treatment since the 1930s and is a mixture of copper, chromium, and arsenic oxides or salts. The wood was preserved from decomposition by fungi, insects, and marine borers. The preservative also improved weather-resistance and paint adherence. As a consequence of deficient industrial practice, most of the wood impregnation sites have become contaminated with high concentrations of arsenic, chromium and copper.

Remediation of contaminated sites by removing the soil is expensive and environmentally disruptive. The risk of a contaminated site for the environment and human health, however, can be minimized by reducing the mobility and bioavailability of trace elements in soil. This can be achieved by amending soils with contaminant-immobilizing additives, i.e. stabilize the soil chemically. [3] Arsenic has been shown to be strongly adsorbed onto iron oxides. [4] Thus, stabilization of arsenic contaminated soil...
by adsorption of iron oxide has been studied as a promising remediation technique,[1,6–8] Nevertheless, the technique is still under development and several factors e.g. pH, redox potential and presence of other ions may affect the adsorption and the stability of adsorbed arsenic species and further evaluation of these parameters are needed in order to develop a more reliable stabilization method.

The structure of arsenic (V) complexes adsorbed on iron oxide have been studied using the Extended X-ray Absorption Fine Structure (EXAFS) technique.[4,9–11] In all these studies, it is concluded that the bidentate binuclear inner-sphere complexes, see Fig. 1(b), are the most thermodynamically favored and thus the most abundant species found on the iron oxide surface. However, there are some contradictions in the conclusions regarding the formation of bidentate mononuclear and monodentate complexes, see Fig. 1(a) and (c) respectively, demonstrating that the adsorption of arsenate on iron oxides is not fully understood.

The formation of the bidentate binuclear complex has also been studied by Fourier Transform Infrared Spectroscopy (FTIR) on dry samples,[12,13] and it was demonstrated that the arsenic complexes were formed via the hydroxyl groups at the iron oxide surface.

The kinetics of arsenate adsorption on goethite was studied using the Pressure-Jump Relaxation technique.[14] Two distinct adsorption regimes could be distinguished, first an adsorption regime with high adsorption rate followed by a second regime with low adsorption rate. The proposed mechanism consists of two steps, formation of an inner-sphere monodentate surface complex with a high rate of adsorption followed by a slow ligand exchange leading to the formation of inner-sphere bidentate complexes. The kinetics of adsorption of arsenate on goethite was also studied through batch experiments.[15] In this study, again two kinetic regimes were observed. The authors concluded that the first high adsorption rate corresponds to the adsorption of arsenate on the more accessible sites on external surface of the iron oxide, whereas the slow second adsorption rate is related to the slow diffusion of arsenate into the pores of the iron oxide particles and the subsequent adsorption on the internal surface.

The adsorption of carbonate species on metal oxide films like hematite[16] or zirconium dioxide[17] has been studied in situ using ATR-FTIR spectroscopy providing detailed information on the infrared absorption bands for the C-O bond in these species and describing their adsorption behavior. The effects of carbonate species in the adsorption of arsenic on iron oxides have also been studied, ex situ, using ICP-AES and ICP-MS as a quantitative method in batch adsorption experiments.[18,19] It was found that the final amount of arsenic adsorbed was not affected by the presence of carbonate species. Nevertheless the presence of carbonates reduced the adsorption rate during the early stage of the adsorption at pH 8, whereas it enhanced the rate at pHs 4 and 6.[18]

Currently, only very few publications are available on the use of the ATR-FTIR technique for studying As(V) oxyanion sorption on iron oxides.[2,20,21] In these studies, the technique was used in order to: decrease the Limit of Detection of arsenate in water, study the H2O2 catalyzed reduction of arsenic (V) adsorbed on ferrhydrite and the adsorption of As(V) on a natural soil sample.

In the present work, the focus was on arsenate adsorption on synthetic iron oxide and to further develop the ATR method. The use of D2O instead of H2O increased considerably the signal to noise ratio in the region of the spectra where the As–O stretching bands appear and thus the detectability of the As(V) species adsorbed on iron oxide.

1.2. The ATR-FTIR technique

ATR-FTIR (Attenuated Total Reflection–Fourier Transform Infrared) spectroscopy[22] has proved to be a powerful tool for adsorption studies[23] including adsorption on metal oxides,[20,24–27] transition metals,[28–30] metal sulphides[31–33] and zeolites.[34,35] The technique may give both quantitative and qualitative information on the adsorption i.e. it can give information from which kinetics and thermodynamics of adsorption can be inferred and in addition it may be used for identification of the complexes formed. In the ATR technique, the incident IR beam is totally reflected inside an ATR crystal, see Fig. 1. At each reflection the electric field of the IR radiation probes the vicinity of the crystal surface where the sample is placed. The depth of penetration (d95) which is a rough measure on the distance sampled by the electric field, depends on the refractive indices of both the ATR crystal and the sample as well as of the wavelength of the incident beam. Thus, the depth of penetration is increasing with decreasing wavelength. In the present work, the depth of penetration in the frequency range 1000–800 cm−1 is ∼1 μm. Since the technique only probes the vicinity of the crystal, it is a powerful tool for studying the properties of thin films and their surface chemistry.

As mentioned above, the focus here is on the development of the in situ ATR-FTIR method and its ability to reveal information about the stability in the adsorption of As(V) oxyanions on synthetic iron oxide films.

2. Experimental

2.1. Iron oxide synthesis and film preparation

An iron oxide suspension was synthesized following the method described by McQuillan.[26] 1 ml of a 0.7 M iron (III) chloride (FeCl3·6H2O; Riedel-de Haën, p.a. 99%) solution in distilled water was added drop-wise to 50 ml of boiling distilled water. The obtained solution was kept under vigorous stirring and boiling for 5 min. Subsequently, the dark brown-red suspension formed was retained and dialyzed for approximately 24 h using a dialysis membrane (MWCO 12–14000; Spectra/Por Dialysis membrane; Spectrum laboratories). The suspension was dialyzed against distilled water. Throughout the dialysis, the distilled water on the opposite side of the dialysis membrane was changed several times in order to eliminate all the ions (ferric and chloride) originating from the initial iron chloride solution. As a result of the dialysis, the pH of the suspension changed from approximately 1.5 to 5.
The dialyzed iron oxide suspension was subsequently diluted by mixing the sample suspension with equal weights of methanol (CH₃OH; Kebo lab, >99.8%) in order to obtain better wetting properties in the following step. A volume of 600 μl of the suspension was spread, with the help of a pipette’s tip, on the ATR crystal so that it covered about 5 cm² of the crystal. The volume of the suspension was dried in room air thus forming an even film. After drying, an identical film was prepared on the other side of the ATR crystal.

2.2. Characterization by scanning electron microscopy, X-ray diffraction, nitrogen adsorption and zeta potential measurements

The topography and thickness of the film was investigated using a scanning electron microscope (SEM, Philips XL 30) equipped with a LaB₆ filament as the electron source. The zeta potential of dilute iron oxide suspensions in 0.01 M KNO₃ at pH values from 4 to 11.5, was measured by electrophoresis (ZetaCompact) using the Smoluchowski equation.

A powder was obtained by freeze drying the iron oxide suspension after dialysis. The powder was characterized with X-ray Diffraction (XRD, Siemens D5000) using Bragg–Brentano geometry at a step size of 0.02 degrees. Nitrogen adsorption at liquid nitrogen temperature was measured using a Micrometrics ASAP 2010 instrument. The sample was degassed at a temperature of 140 °C for about 24 h prior to the measurements. The sample was degassed at this temperature in order to avoid phase transformation of the ferrihydrite to hematite. It has been reported that ferrihydrite powder was stable up to 170 °C after outgassing for 6 h whereas it transformed to hematite after 1 h exposed to an air atmosphere. [36]

2.3. ATR-FTIR measurements

A Bruker IFS 66 v/s equipped with a DTGS (Deuterated TriGlycine Sulphate) detector was used for the ATR-FTIR measurements. All spectra were recorded at a resolution of 4 cm⁻¹ by co-adding 200 scans. A stainless steel flow cell with two compartments for liquid of about 2.5 cm³ on each side of the ATR crystal, was used in the experiments. A trapezoidal ZnSe ATR crystal (Crystan) with a size of 52 mm × 20 mm × 2 mm and 45° cut edges was used and the cell/crystal interfaces were sealed by Viton gaskets. The arsenate solutions were prepared from sodium hydrogen–arsenate heptahydrate (Na₂AsO₄·7H₂O; Fluka; p.a. 98.5%) in deuterium oxide (D₂O, Aldrich, 99 atom % D). The solutions were fed to both compartments of the flow cell, which were connected in series.

The solution was pumped through the flow cell and recirculated to a vessel using a peristaltic pump (Fig. 3b). The pD in the vessel was controlled by adding solutions of either deuterium chloride (DCl; Aldrich; 99 atom % D) or sodium deuteroxide (NaOD; Aldrich; 99+ atom % D) in D₂O and argon gas (AGA, 99%) was bubbled through the liquid in the vessel to minimize the dissolution of atmospheric CO₂ into the solution. A single beam background spectrum of D₂O with the same pD value as used during the subsequent experiment was recorded before each experiment unless stated otherwise.

The total volume of the liquid in the system was about 50 ml and this solution thus contained about 1.5 × 10⁻⁶ mol As (V) species. The concentration of the iron oxide suspension was 10.75 g/l and as 1.2 μl of the iron oxide suspension was used to prepare the film, the weight of the iron oxide film was 1.3 × 10⁻⁵ g. The adsorption capacity of As (V) on ferrihydrite is about 650 mmol(As(V))/kg (ferrihydrite) [37] and the film thus had an adsorption capacity of about 8.4 × 10⁻⁹ mol As(V) species, i.e. there was about 180 times more As (V) species in solution compared to the adsorption capacity and the concentration in the solution will be constant during adsorption. The arsenate concentration was still analyzed before and after the experiment using Inductively Coupled Plasma–Optical Emission Spectroscopy (ICP-OES, PerkinElmer optima 2000 DV) in order to verify a negligible concentration change of the arsenates in solution during the adsorption process.

3. Results and discussion

3.1. Characterization of the iron oxide powder

The XRD pattern recorded from the freeze dried iron oxide powder showed very broad reflections, which indicates small crystal size as expected for ferrihydrite, see Fig. 4. The peak positions and relative intensities agreed well with those reported for 6-line ferrihydrite. [36]
Fig. 5. BJH pore size distribution curve derived from the N2 adsorption data on the 6-lineferrihydrite powder.

The surface area of the iron oxide powder, calculated by applying the BET equation on the nitrogen adsorption data, was 190 m²/g and from the BJH analysis, pores ranging between 2 and 10 nm was observed, see Fig. 5. These pores likely originate from inter-particle voids in the powder sample and it is probable that the inter-particle pore size distribution was similar in the film.

Another XRD pattern of the iron oxide powder was recorded after degassing at 140 °C for 24 h in order to confirm that no phase transformation occurred during the degassing. The obtained XRD pattern was identical to the one recorded before heating showing that the heating associated with the degassing did not cause any phase transformation.

The zeta potential as a function of pH was measured from pH 4 to 12 and the point of zero proton charge was estimated to about 7.5–8. These results are in line with previous reports for 6-lineferrihydrite. [36] The point of zero D⁺ charge is not known but was assumed not to be far from the point of zero proton charge and therefore the dominating surface sites at different pH values may be illustrated as follows:

≡ Fe–OD₂⁺ (dominating at pH 4) (I)
≡ Fe–OD⁻ (dominating at pD 8) (II)
≡ Fe–O⁻ (dominating at pD > 10) (III)

Fig. 6a shows a top view SEM image of the film, which illustrates that the film appears to be comprised of spherical grains with a diameter smaller than 30 nm. The sample was coated with a thin (ca 10 nm) gold layer prior to recording the SEM images to avoid sample charging, however, this also results in that the particles appear larger than in reality. Fig. 6b shows a SEM image of the cross-section of the iron oxide film on a ZnSe crystal. Cross-sectional images recorded at numerous other locations were very similar and illustrated that the thickness of the film was about 700–900 nm throughout the entire sample. Further it can again be seen that the film consists of small, densely packed particles.

3.2. Absorption bands for As(V) species in solution and for adsorbed species on iron oxide

Fig. 7 shows the infrared spectra recorded with FTIR-ATR spectroscopy using an uncoated ZnSe crystal in contact with a 13 mM arsenate solution (in D₂O), at different pD's. All spectra were recorded using the same solution, only the pD was adjusted in steps from pD 4 to 12. Each time the pD was changed, the corresponding changes in the spectra were very rapid reflecting the time to pump the solution from the beaker to the cell. After the initial pD induced change, the spectra did not change during the following 60 min showing that the species formed were stable. Subsequently, the reverse experiment was performed i.e. the pD of the solution was adjusted in steps from pD 12 to pD 4, and the process was proved to be completely reversible (not shown). Moreover, the intensity of the bands from spectra recorded at different arsenate concentrations fits into a straight line passing through the origin (not shown).

Therefore, we concluded that the signal mostly emanates from species in the solution and not from species adsorbed on the surface of the uncoated ATR crystal. The pKₐ values of the arsenate species are 2.2, 6.7 and 11.2 for pKₐ₁, pKₐ₂ and pKₐ₃, respectively. [1] Therefore the predominant specie at pD 4 is H₂AsO₄⁻, whereas HAsO₄²⁻ is dominating at pD 8.5 and AsO₄³⁻ together with HAsO₄²⁻ at pD 11.8. Upon changing pD, the corresponding changes in spectra were immediate and did not change with time. Thus, the absorption bands illustrated in Fig. 7 originate from the different arsenate species present in solution. Consequently, the different species of arsenate in D₂O solution can be distinguished. From the spectrum at
pD 4, the bands appearing at 908, 875 and 730 cm$^{-1}$ originate from H$_2$AsO$_4^-$ in D$_2$O. The spectrum recorded at pD 8.5 shows only one band in the As–O stretching area. This absorbance band is located at 856 cm$^{-1}$ and stems from the As–O stretching vibration of the HAsO$_4^{2–}$ entity. [20] The spectrum recorded at pD 11.8 shows both the HAsO$_4^{2–}$ band at 856 cm$^{-1}$ and a band at 806 cm$^{-1}$ originating from AsO$_4^{3–}$.

Fig. 8 illustrates spectra obtained with an uncoated ATR crystal and with an ATR crystal coated with an iron oxide film. The spectra shown in Fig. 8 were all recorded during different experiments. Spectrum (a) was recorded when a 1 mM arsenate solution in D$_2$O at pD 4 was flowing over a ZnSe crystal. Spectrum (c) was recorded using an ATR crystal coated with an iron oxide film in contact with a 0.03 mM arsenate solution in D$_2$O at pD 4 after 300 min over a ZnSe crystal. Five background spectra of D$_2$O flowing over an uncoated ZnSe crystal were recorded previous to the adsorption experiment. The adsorption from a 0.03 mM arsenate solution using an iron oxide coated ATR element at the same five different pD values, were recorded during the adsorption experiment. The adsorption experiments were performed on the same iron oxide and after 70 min of contact with a 0.03 mM arsenate solution. During the course of the experiment the pD was adjusted from the highest pD value, 12, to the lowest, 4. In the pD range 4–10, absorption bands are observed at 875 and 840 cm$^{-1}$ as a result of adsorption of arsenate on the iron oxide. These bands are shifted to slightly lower wavenumbers compared to the bands observed for arsenate in solution. These shifts are caused by a change in the As–O vibrational mode of the As(V) species adsorbed on the iron oxide surface. For the whole pD range, the arsenate species are negatively charged whereas the iron oxide surface is positively charged at low pD and negatively charged at high pD as discussed above. This will of course influence the amount of arsenate species adsorbed as well as the strength of the surface complex formed, as generally accepted for anions adsorbed on iron oxides. [36]

Fig. 9a shows spectra recorded at different pD after 70 min of adsorption from a 0.03 mM arsenate solution using an iron oxide coated ZnSe crystal. Five background spectra of D$_2$O flowing over an iron oxide coated ATR element at the same five different pD values, were recorded previous to the adsorption experiment. The adsorption experiments were performed on the same iron oxide and after 70 min of contact with a 0.03 mM arsenate solution. During the course of the experiment the pD was adjusted from the highest pD value, 12, to the lowest, 4. In the pD range 4–10, absorption bands are observed at 875 and 840 cm$^{-1}$ as a result of adsorption of arsenate on the iron oxide. These bands are shifted to slightly lower wavenumbers compared to the bands observed for arsenate in solution. These shifts are caused by a change in the As–O vibrational mode of the As(V) species adsorbed on the iron oxide surface. For the whole pD range, the arsenate species are negatively charged whereas the iron oxide surface is positively charged at low pD and negatively charged at high pD as discussed above. This will of course influence the amount of arsenate species adsorbed as well as the strength of the surface complex formed, as generally accepted for anions adsorbed on iron oxides. [36]

Fig. 9b shows the absorbance at about 840 cm$^{-1}$ versus pD. As expected, the absorbance decreases with pD, as a result of the decreasing amount adsorbed, which in turn probably is a result of that the surface becomes less positively charged and eventually negatively charged (surface complexes I–III above). The surface complexes I and II above admit two types of bonding between iron oxide and arsenate. Either OD or OD$_2$ is expelled from the surface during reaction with the anion implying an inner-sphere complex or the arsenate species are D-bonded to the surface sites. [20] In the latter case an outer-sphere complex is formed. To distinguish...
between these two possibilities is however not straightforward, especially since both types of bonding may be simultaneously represented at the metal oxide surface. However, D-bonded outer-sphere complexes are expected to be less strongly attached to the surface as compared to inner-sphere complexes, and desorption experiments should at least give a hint to which type of complex dominates (see the discussion under the next subsection).

The absorption bands shifted slightly to lower wavenumber at higher pD values. The most intense band was shifted from 840 to 830 cm\(^{-1}\) (10 cm\(^{-1}\)) when the pD value was changed from 4 to 8, whereas the shoulder of the peak shifts from 875 to 855 cm\(^{-1}\) (20 cm\(^{-1}\)). The shift produced in the bands could be due to the deprotonation of the arsenic (V) species adsorbed on the iron oxide particles at higher pD values. The configuration of the complexes formed on the iron oxide seems to be the same at pD 4 and 8.5 since the same number of bands stems from both arsenic complexes which indicates that the complexes have the same symmetry, \(C_{2v}\) or lower.

The band at 949 cm\(^{-1}\) has been assigned to the \(\text{Fe-O-D}\) bending vibration. [16] In the present work, a negative band at 949 cm\(^{-1}\) appeared simultaneously as the positive band emerged from the arsenate adsorbed on the iron oxide film. The intensity of the negative band at 949 cm\(^{-1}\) stemming from \(\text{Fe-O-D}\) follows the same trend as the intensity of the positive band at 840 cm\(^{-1}\) assigned to the arsenate species. This result indicates that arsenate is adsorbed on Fe-\(\text{OD}_{2}^{+}\) sites, as has been reported previously.[12] Nevertheless, this (negative) band would also appear if some particles had been expelled constantly from the iron oxide film during the experiment.

In addition, some negative bands in the 1500–1000 cm\(^{-1}\) range appeared. These bands were assigned to carbonate species desorbing from the iron oxide film. [16] Hence, in addition to the adsorption sites I–III above, the surface is also characterized by Fe-carbonate sites. The carbonate species may have formed during synthesis of the iron oxide particles or during deposition of these particles on the ATR crystal, since contact with air is hardly avoidable. In these measurements, background spectra were recorded at each pD after equilibrium had been established between pD adjusted \(\text{D}_{2}\text{O}\) and iron oxide. Hence, the carbonate species adsorbed on the iron oxide film were equilibrated before the starting arsenate adsorption. Therefore, the negative bands assigned to carbonate species indicate that these species were substituted for arsenate during the adsorption reaction and they may compete for the same adsorption sites.

Fig. 10 shows spectra recorded at different times (from 1.5 to 300 min) during the adsorption on an iron oxide film from a 0.03 mM arsenate solution at pD 4. Previous to the experiment the iron oxide film was in contact with \(\text{D}_{2}\text{O}\) at pD 4 and a background spectrum was recorded. At \(t = 0\) the arsenate concentration in the \(\text{D}_{2}\text{O}\) was set to 0.03 mM while keeping the pD constant at 4 and the adsorption experiment started. After 1.5 min of adsorption, weak bands at 875 and 840 cm\(^{-1}\) were observed. These bands, caused by adsorbed arsenate species, increased in intensity with increasing time of adsorption. Simultaneously, negative absorption bands emerged at 1701, 1657, 1585, 1559, 1534 1464, 1409, 1359, 1068, 1022 and 949 cm\(^{-1}\). The negative band at 949 cm\(^{-1}\) has been assigned to the iron oxide \(\text{Fe-O-D}\) as stated previously. The bands at 1585, 1559, 1534, 1464, 1409 and 1359 cm\(^{-1}\) have been assigned to both asymmetric and symmetric \(\text{C=O}\) stretching of carbonate species,[16] whilst the bands observed at 1068 and 1022 cm\(^{-1}\) have been assigned to totally symmetric \(\text{C=O}\) stretching modes.[16]

Fig. 11 shows the intensity (band height) of the absorption band for arsenate at 840 cm\(^{-1}\) and the band emerging from carbonate at 1409 cm\(^{-1}\) as a function of time. The data was retrieved from the same experiment as the spectra presented in Fig. 10, however for the sake of clarity, not all spectra recorded are shown in Fig. 10. Both adsorption of arsenates and desorption of carbonates are relatively fast within the first 70 min, followed by a slow adsorption as well as desorption process. After 300 min, none of the two processes had reached equilibrium. The declining reaction rates might be due to two different steps. Firstly, desorption of carbonates from the iron oxide surface might be a rate limiting step for the adsorption of arsenate. Secondly, slow diffusion of the arsenate species from solution to the less accessible adsorption sites in the mesoporous iron oxide film as reported earlier.[15]

### 3.4. Desorption of As (V) from iron oxide

To study the stability of the adsorbed As(V) complexes, in situ FTIR spectra were used for monitoring the stability of the complexes formed as the pD changed. Two different pD’s were tested viz. 8.5 or 12. Arsenate was first adsorbed on the iron oxide by exposing the film to a 0.03 mM solution of As (V) at pD 4 for 300 min. Thereafter, the pD was changed to either 8.5 or 12, keeping the As (V) concentration constant at 0.03 mM. The experiment was performed with two different iron oxide films, one for the experiment where the pD was changed to pD 8.5 and the other one when the pD was changed to 12. Only one adsorption curve from a 0.03 mM arsenate solution at pD 4 is shown in Fig. 12, since the two curves obtained were very similar. The peak height of the 840 cm\(^{-1}\) band originating from adsorbed arsenate, was then followed as a function of time after the pD change, see Fig. 12. At both pD’s, the desorption processes was faster during the first 40 min, followed by a slower process at times >40 min. From the decrease in peak height, it was estimated that approximately 20% of the adsorbed arsenate on the film had desorbed after 200 min at pD 8.5 whilst 65% was desorbed after...
200 min at pH 12. The observed decrease in the amount adsorbed was expected since the iron oxide surface is more positively charged at pH 4 than at pH 8.5 and 12. In addition, at higher pHs the concentration of OD groups in solution is higher and these ions might also compete with the arsenate species for the iron oxide surface sites.\textsuperscript{[5,38]}

To investigate the stability of the surface complexes formed, a simple rinsing experiment was performed. Two iron oxide films were prepared and a background spectrum of each film was recorded under the flow of D$_2$O adjusted to pH 4 and pH 8.5 respectively. The two films were subsequently dismounted from the flow cell and equilibrated during 24 h with 0.03 mM arsenate in aqueous solution, one at pH 4 and the other one at pH 8.5. Subsequently, the two films were rinsed with water at pH 4 and pH 8.5, respectively, to remove the arsenate in solution and finally the films were dried. The ATR crystals with the films treated at pH 4 and pH 8.5 were then mounted in the spectrometer and in situ FTIR spectra were recorded while the films were flushed with pure D$_2$O at pH 4 and pH 8.5, respectively. The results obtained from the rinsing experiment at pH 4 are shown in Fig. 13. The arsenate barely desorbed from the film during the first 100 min and no desorption was observed between 100 and 200 min. Approximately 90% of the arsenate previously adsorbed on the iron oxide film was still adsorbed on the iron oxide film after 200 min of flushing at pH 4. These desorption experiments thus suggest a very strong bond of the arsenate to the iron oxide surface at pH 4. These, in turn, indicate a reaction of arsenate–iron oxide complexes. Evidently, a fraction of the surface complexes formed at the higher pH values represent more weakly bonded species. It is therefore suggested here that these species could be D-bonded to the iron oxide surface (outer-sphere).

![Fig. 13. Spectra recorded after (a) 1.5 min. (b) 20 min. (c) 50 min. (d) 100 min. (e) 200 min of desorption in D$_2$O at pH 4. Before desorption the iron oxide film was equilibrated for 24 h with a 0.03 mM arsenate solution at the same pH value.](image1)

![Fig. 14. Spectra recorded after (a) 1.5 min. (b) 75 min. (c) 130 min. (d) 200 min of desorption in D$_2$O at pH 8.5. Before desorption the iron oxide film was equilibrated for 24 h with a 0.03 mM arsenate solution at the same pH value.](image2)

was still adsorbed on the iron oxide film after 200 min of flushing. Evidently, a fraction of the surface complexes formed at the higher pH value represent more weakly bonded species. It is therefore suggested here that these species could be D-bonded to the iron oxide surface (outer-sphere).

4. Conclusions

In situ ATR-FTIR spectroscopy was proven to be a powerful technique to study the adsorption/desorption of arsenate on an iron oxide films. It was possible to monitor the adsorption/desorption in situ as a function of time as the technique is very sensitive to small amounts of arsenate adsorbed. Moreover, the technique permits simultaneous monitoring of other adsorbed species, e.g. carbonate species, which may interact with the arsenate–ferricydrate–D$_2$O system. As the measurements are made in situ, no further sample preparations are needed, thus avoiding any transformation of the sample during preparation.

The desorption experiments indicated that inner-sphere complexes are formed between the iron oxide surface and the arsenate at pH values ranging from 4 and 8.5. Nevertheless, a higher fraction of D-bonded (outer-sphere) complexes seemed to be present at pH 8.5 than at pH 4. It was also shown that already adsorbed carbonate species desorbed from the iron oxide surface upon arsenate desorption.

The technique will be an important tool in forthcoming investigations on how different factors, such as, ionic strength and competitive adsorption with other adsorbates affect the stability of arsenate–iron oxide complexes.

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References

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In Situ ATR-FTIR Studies of Competitive Adsorption of Arsenate and Phosphate on Ferrihydrite

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In Situ ATR-FTIR Studies of Competitive Adsorption of Arsenate and Phosphate on Ferrihydrite

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Abstract

The competitive adsorption of arsenate and phosphate on iron oxides is important from an environmental perspective. A thorough understanding of this simple system may aid the understanding of the mobility of these oxoanions in more complex and relevant systems such as in soils. Such understanding may also aid the development of new methods to amend arsenic contaminated soils or the development of adsorbents for removing arsenate from drinking water. In the present study, in-situ ATR-FTIR spectroscopy was used for the first time to study competitive adsorption of phosphate and arsenate on ferrihydrite.

It was found that the adsorption of both oxoanions at pD 4 was reduced to approximately the same extent when the other oxyanion was adsorbed from solution with the same concentration simultaneously, whereas phosphate adsorption was reduced to a slightly higher extent at pD 8.5. Moreover, the desorption of pre-adsorbed arsenate when phosphate was added to the system was significantly lower than in the reverse experiment where pre-adsorbed phosphate desorbed substantially as arsenate was added to the system. At pD 4, two phosphate complexes adsorbed on the iron oxide, one deuterated and one de-deuterated. When phosphate was pre-adsorbed and arsenate later added to the system, the deuterated phosphate complex desorbed rapidly while the de-deuterated phosphate complex was quite stable. To the best of our knowledge, this is the first time this difference in stability of the different phosphate
complexes is reported, and shows the power of employing in-situ spectroscopy for this kind of studies.

1. Introduction

Arsenic is a toxic element which may cause blackfoot disease and skin-, lung-, bladder- and kidney cancer etc.\textsuperscript{1} The routes of exposure to humans are basically by air, drinking-water or food.\textsuperscript{1} High arsenic concentration in drinking water can be found in drinking well-water in many countries, such as; New Zealand, Romania, the Russian federation, Taiwan, Argentina, Bangladesh and India but also in mine drainage areas in e.g. Poland or Sweden.\textsuperscript{2} The concentration of arsenic in ground water is controlled by the arsenic content in the rock soil.\textsuperscript{1} Inorganic arsenic occurs either as As(V) with the main species being arsenic pentoxide, arsenic acid and arsenates whereas the main species of As(III) are arsenic trioxide, sodium arsenite and arsenic trichloride.\textsuperscript{2} The As(V) species shows a lower toxicity and mobility in soil than the As (III) species.\textsuperscript{1, 2}

In nature, arsenic is frequently associated with metal sulfides e.g. lead, silver, copper, cobalt or iron sulfides.\textsuperscript{1} However, arsenic may also be of anthropogenic sources e.g. in mining tailings, in agricultural chemicals or in antifungal wood preservatives.\textsuperscript{1, 3} The use of arsenic compounds in combination with chromate and copper in antifungal wood preservatives, CCA (Copper, Chromate, Arsenate), has been widely used since the 1930’s. As a consequence of deficient impregnation methods, many impregnation sites today show high levels of arsenic in the soil.

In most of the contaminated sites, the aim of soil remediation is to recover the ecosystem and soil functionality. For this reason, contaminant mobility and bioavailability should be minimized so as to reduce the toxicity to organisms and improve vegetation establishment. To reduce risks related to arsenic spreading in the environment, the mobility and bioavailability of As in soil can be reduced by the addition of iron.\textsuperscript{4, 5} Iron is interesting as amendment for stabilizing arsenic
contaminated soil because of its high affinity for arsenic oxyanions in combination with a low cost. However in soil amendments, fertilizer addition is often necessary to improve plant growth on nutrient deficient soils. Phosphate is one of the principal soil nutrients, making it an important component of many fertilizers. Due to the similar behaviour of arsenates and phosphates, the presence of phosphorus compounds in fertilizers added to iron oxide stabilized soils may lead to a significantly increased As leaching in the environment as phosphate species compete with arsenate species for sites on the iron oxide surface.\textsuperscript{6-8}

The adsorption of arsenic on various iron oxides/oxyhydroxides, for simplicity hereafter referred to as just iron oxides, has been widely studied.\textsuperscript{9-11} The adsorption of arsenate anions on iron oxide has been shown to be pH dependent with maximum adsorption at moderately low pH, i.e. pH 3-5. The arsenate complexes formed on iron oxide surface have been extensively studied using EXAFS (Extended X-ray Absorption Fine Structure).\textsuperscript{11-15} These studies concluded that bidentate binuclear complexes are the predominant complexes. Nevertheless contradictory information is found in the literature reporting both formations of monodentate as well as mononuclear bidentate complexes on the iron oxide adsorption sites. Loring et al. (2008) used ATR-FTIR (Attenuated Total Reflection – Fourier Transform Infrared) and EXAFS measurements and concluded that arsenate formed monodentate complexes on the goethite surface instead of bidentate binuclear complexes. The adsorption of arsenate complexes on iron oxides and their structure are thus not fully understood yet.

Arsenic adsorption on iron oxide at the D\textsubscript{2}O-iron oxide interface has been studied recently using ATR-FTIR spectroscopy.\textsuperscript{9, 13} In these studies it was concluded that very similar complexes were formed at pD 4 and pD 8.5 and the possible difference between the complexes adsorbed on the iron oxide at pD 4 and 8.5 is the deuteration at lower pD. The hydroxyl sites of the iron oxide were shown to be the active sites through which arsenate complexes were adsorbed.\textsuperscript{16}
The adsorption of phosphate on iron oxides have been previously studied using ATR-FTIR spectroscopy.\textsuperscript{17-19} It was reported that phosphate adsorption on iron oxide showed a pH dependence similar to that of arsenate with higher adsorption at lower pH.\textsuperscript{17} Based on FTIR data, the authors concluded that deuterated binuclear bidentate complexes were the predominant species adsorbed on iron oxides at pH between 3-6 whereas the non-deuterated binuclear bidentate complexes were the predominant complexes at pH > 7.5.

Antelo et al and Liu et al studied the single component adsorption of arsenate and phosphate anions on iron oxides and concluded that the adsorption behaviour was very similar.\textsuperscript{20, 21} Both oxoanions adsorbed in very similar amounts on goethite at pH 3.0 to 8.5. Nevertheless, phosphate desorption from goethite was higher than arsenate desorption in the presence of oxalate ions indicating that arsenate might be stronger bonded to the iron oxide than phosphate.

The competitive adsorption of phosphate on iron oxides like goethite and ferrihydrite has been studied using batch adsorption experiments.\textsuperscript{20-24} When goethite was exposed to a solution of equal molar concentrations of arsenate and phosphate, equal amounts of arsenate and phosphate complexes were adsorbed on the iron oxide at pH > 6, whereas slightly higher adsorption of arsenate was observed at pH < 6. When arsenate was pre-adsorbed on goethite, the adsorption of phosphate was shown to be highly inhibited by the presence of arsenate, however for the reverse experiment, with phosphate pre-adsorbed, the inhibiting effect of phosphate for arsenic adsorption was much weaker.\textsuperscript{21}

ATR-FTIR spectroscopy has proved to be a powerful tool for adsorption studies on synthetic and natural mineral surfaces.\textsuperscript{25-29} The incident IR beam is totally reflected inside an ATR crystal, see Figure 1. At each reflection, the electric field of the IR radiation probes the outer-side of the crystal to a distance of about 1 \( \mu \text{m} \) from the surface.\textsuperscript{30} Since the sample is placed at the surface of the crystals and only the vicinity
of the crystal is probed, it is a powerful tool for studying the properties of thin films and their surface chemistry.

The main focus of this work was to study the competitive adsorption between arsenate and phosphate on iron oxide using in situ ATR-FTIR measurements. To the best of our knowledge, this is the first report on the competitive adsorption of arsenate and phosphate on iron oxide using in-situ ATR-FTIR spectroscopy. The aim is to gain new insights on the stability of different arsenate and phosphate complexes adsorbed on the iron oxide surface. This information is important in order to obtain a better understanding on the mobility of these oxoanions in natural soils and especially for arsenic contaminated soils treated with iron. In the latter case, the arsenic contaminated soil is remediated by addition of iron compounds and subsequently plants are grown in the soil, and often phosphates are added to increase plant growth. Therefore the desorption experiments of preadsorbed arsenate species in the presence of phosphate anions are especially important in order to understand these processes. This study will also provide fundamental knowledge regarding arsenic depuration from water since iron oxides have also been proposed as adsorbents for this kind of processes.2

2. Experimental

2.1 Iron oxide synthesis and film preparation

An iron oxide hydroxide viz. 6-line ferrihydrite suspension was synthesized using the same synthesis method as previously reported by the authors.9 In short, 50 ml of distilled water was heated to boiling, thereafter 1 ml. of a 0.7 M iron (III) chloride (FeCl₃•6H₂O; Riedel- de Haën, p.a. 99%) solution was added drop-wise to the boiling solution. After 5 minutes of boiling, the solution changed colour from yellow to a dark brown-red. The resulting iron oxide suspension was allowed to cool down and subsequently dialysed against distilled water for approximately 24 hours using a dialysis membrane (MWCO 12-14000; Spectra/Por Dialysis membrane; Spectrum
laboratories) in order to eliminate impurities from the synthesis suspension. As a result of the dialysis, the pH of the suspension changed from approximately 1.5 to 5.

The dialyzed suspension was subsequently diluted in equals weights of methanol (CH₃OH; Kebo lab, >99.8 %) resulting in an iron oxide content in the suspension of about 2 g/l. To coat the ATR crystal (Crystan, ZnSe, 52×20×2 mm and 45º cut edges), 500 µl of the iron oxide suspension was spread on the ATR crystal so that it covered about 5 cm² of the crystal. The suspension was then allowed to dry under ambient conditions thus forming an even film on the ATR crystal surface. After drying, a similar film was prepared on the other side of the ATR crystal.

2.2. General characterisation of the film and iron oxide particles

An FEI Magellan 400 field emission XHR-SEM was used to investigate the films. Cross sections of the samples were mounted on a holder and investigated using an accelerating voltage of 1 kV without applying any coating on the samples.

Freeze-dried powder of the synthesized iron oxide was characterized with X-Ray Diffraction (XRD, Siemens D5000) running in Bragg-Brentano geometry using a step size of 0.02 degrees 2 theta.

Nitrogen adsorption at liquid nitrogen temperature was measured on the freeze dried powder using a Micrometrics ASAP 2010 instrument. The powder was degassed at a temperature of 140º C for about 24h.

The zeta potential of the iron oxide particles suspended in 0.01M KNO₃ at different pH, from 4 to 12, was measured with electrophoresis (ZetaCompact).

2.3 ATR-FTIR measurements
All spectra were recorded at room temperature using a Bruker IFS 66v/s spectrometer equipped with a DTGS (Deuterated TriGlycine Sulphate) detector at a resolution of 4 cm\(^{-1}\) by co-adding 200 scans.

All experiments were performed using deuterium oxide (D\(_2\)O, Aldrich, 99 atom % D) as solvent. Prior to each measurement, a background spectrum was recorded of a 0.1M sodium chloride (NaCl, Merck; 99.5%) solution adjusted to the same pD as in the forthcoming experiment, i.e. pD 4 or 8.5. Before recording the background, the system was allowed to equilibrate for 5 hours. After recording the background an appropriate amount of a stock solution of sodium hydrogen-arsenate hepta-hydrate (NaH\(_2\)AsO\(_4\)•7H\(_2\)O; Fluka; p.a. 98.5%) or sodium phosphate monobasic monohydrate (NaH\(_2\)PO\(_4\)•H\(_2\)O; Sigma-Aldrich; 98-102%) was added to the 0.1 M sodium chloride solution and the adsorption experiment was started. The change in the total ionic strength upon addition of arsenate and phosphate was only 0.06 %, which is negligible.

Figure 1 shows a sketch of the experimental set-up. The pD of the solution was controlled with an automatic equipment (Metler Toledo, T70 pH-stat), which added a X M solution of either deuterium chloride (DCl; Aldrich; 99 atom % D) or sodium deuteroxide (NaOD; Aldrich; 99+ atom % D). The solution was pumped by a peristaltic pump, 10 ml/min., from the solution vessel into the stainless steel flow cell. The flow cell was mounted in the spectrometer and contained the iron oxide coated ATR crystal. After passing both sides of the ATR crystal, the solution was recirculated back to the solution vessel. The solutions were continuously bubbled with argon gas (AGA, 99%) in order to minimize absorption of CO\(_2\) from room air.

To verify that the concentration of arsenate and phosphate in the solution did not change during the experiment, the concentrations were analyzed before and after the experiments using Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES, Perkin Elmer optima 2000 DV).
2.4 Adsorption measurements

Measurement of adsorption of arsenate and phosphate oxoanions on the iron oxide film was performed at pH 4 and pH 8.5. The same iron oxide film was used for both pH values. The iron oxide film was in contact with pure D₂O adjusted to the same pH as in the subsequent adsorption experiment and a background spectrum was recorded after 5 hours of contact. The appropriate amount of either arsenate or phosphate was then added in order to successively increase the oxoanion concentration to 0.003, 0.012, 0.03, 0.12, 0.3, 0.6 and 1.2 mM. At each concentration, spectra were recorded every 5 minutes during 5 hours.

Competitive adsorption experiments between arsenate and phosphate were also performed at pH values of 4 and 8.5. A background spectrum of D₂O was recorded as described above. The concentration of both oxoanions was set to 0.03 mM by the addition the proper amount of arsenate and phosphate from stock solutions and spectra were recorded every 5 minutes during 5 hours.

Competitive adsorption experiments in which the oxoanions were added at different times were also performed at pH 4 and 8.5. Again a background spectrum was recorded as described above. The concentration of one of the oxoanions was then set to 0.03 mM and in situ ATR-FTIR spectra were continuously recorded for 5 hours.
After this period of time, the other oxoanion was added to the solution resulting in a solution equimolar in arsenate and phosphate (0.03 mM). In situ ATR-FTIR spectra were recorded during the following 5 hours.

3. Results and discussion

3.1 General characterization of the film

XRD data showed that the iron oxide particles consisted of pure 6-line-ferrihydrite. The point of zero charge was determined to be in the pH range 7.5-8.5, which is in line with previous reported results for 6-line-ferrihydrite. Figure 2 shows an SEM image of the cross section of an iron oxide film. It illustrates that the film was comprised of particles that were less than 10 nm in diameter. The specific surface area of the iron oxide was determined by nitrogen adsorption at liquid nitrogen temperature to 190 m$^2$/g. By assuming spherical particles, this corresponds to a particle diameter of 8 nm, in agreement with SEM observations. This particle size is typical for 6-line-ferrihydrite. The film thickness of the iron oxide film was measured at several points of the sample and varied between between 300 and 500 nm.

Figure 2. SEM image of the cross section of the iron oxide film on the ATR crystal. An arrow indicates the film thickness.
3.2 Adsorption of arsenate on iron oxide

Figure 3 shows the absorbance of the infrared band at ~840 cm\(^{-1}\), assigned to arsenate adsorbed on iron oxide,\(^9\) at different arsenate concentrations and after 5 hours of equilibration time at each concentration. The absorption bands were clearly distinguishable from the absorption bands from arsenate species in solution.\(^9\) It was previously concluded that the same adsorbed arsenate complex structure was formed at the two pD’s studied.\(^9\) The intensity of the band is proportional to the concentration of arsenate species adsorbed on the iron oxide film according to Beer’s law.\(^30\) Further, by assuming that the molar absorptivities are the same for the adsorbed species at both pD’s, it may be concluded that the amount of arsenate complexes adsorbed on the iron oxide film at a certain concentration is somewhat higher at pD 4 than at pD 8.5 in agreement with data obtained by quantitative methods.\(^9, 32\) A greater amount of adsorbed species is expected at lower pD since the iron oxide surface is more positively charged at lower pD and the electrostatic attraction between the surface and the oxoanion may thus be favourable for the adsorption.\(^9, 31\) The amount of arsenate adsorbed increased with increasing arsenate concentration in solution in the whole concentration range studied, suggesting that complete monolayer coverage was not achieved in these experiments. The adsorption isotherms of As(V) on 2-line-ferricydrite previously published in the literature are similar to the one observed in the present work indicating that complete monolayer coverage is only reached at bulk arsenate concentration of >2 mM both at pH 4.6 and 9.2.\(^32\) However, it should be noted that equilibrium was not reached even after 5 hours of equilibration time in the present work. Kinetic data will be discussed below (see Figure 8). Nevertheless, from the shape of the kinetic curve most of the adsorption seemed to have occurred after 5 hours of equilibration time and Figure 3 thus illustrates pseudo equilibrium data. Similar slow kinetics has been reported in earlier work.\(^33\)
3.3 Adsorption of phosphate onto iron oxide

Figures 4a and 4b show spectra for a 60 mM phosphate solution at pH 4 and 8.5 recorded using an uncoated ZnSe crystal, thus showing mainly species in solution. Based on the pKa values for phosphate reported in the literature viz. 2.2, 7.2 and 12.3, the dominating species in solution at pH 4 and 8.5 would be $\text{D}_2\text{PO}_4^-$ and $\text{DPO}_4^{2-}$, respectively.\textsuperscript{19} The pKa values are assumed to be nearly the same for deuterated species. At pH 4, three bands at 1180, 1084 and 940 cm$^{-1}$ were observed in the spectrum. These bands were assigned to the PO stretching modes of the $\text{D}_2\text{PO}_4^-$ species.\textsuperscript{19} In the spectrum recorded at pH 8.5, two bands at 1084 and 988 cm$^{-1}$ assigned to the PO stretching modes of $\text{DPO}_4^{2-}$ were observed. First the spectrum at pH 4 was recorded. Thereafter the pH was changed to 8.5 and as the pH changed, the spectrum changed immediately reflecting the de-deuteration of $\text{D}_2\text{PO}_4^-$ to $\text{DPO}_4^{2-}$. During the following hour, spectra were recorded regularly to check the stability. However no changes in the spectra were observed, showing that the formed species in solution are stable. Any adsorption of phosphate on the ZnSe crystal was assumed to be negligible since the intensity of the bands were constant with time and it was thus concluded that virtually all of the signal in spectra a and b originated from phosphate species in solution.
Figure 4 also shows spectra of phosphate adsorbed on iron oxide from a 0.03 mM phosphate solution at pH 4 c) or 8.5 d). The bands originating from adsorbed phosphate at pH 4 appeared at different positions as compared to the bands from phosphate in solution at the same pH. Since the predominant phosphate species in solution at pH 4 is $D_2PO_4^-$, the bands appearing in spectrum 4c were not stemming from phosphate species in solution, but from phosphate complexes adsorbed on iron oxide. Moreover, the bands observed when using the crystal coated with iron oxide are approximately three times more intense (spectrum 4c) than when a non coated crystal was used (spectrum 4a) despite the fact that the phosphate concentration in solution was 2000 times lower when spectrum 4c was recorded.

Similar results were obtained at pH 8.5, compare spectra b and d in Figure 4.

**Figure 4.** Spectra of a 60 mM phosphate solution at (a) pH 4 and (b) pH 8.5 recorded using a non coated ATR crystal. Spectra of phosphate complexes adsorbed on iron oxide from a 0.03 mM phosphate solution at (c) pH 4 and (d) pH 8.5 recorded using a ATR crystal coated with iron oxide.
Figure 5 shows the integrated area (between 1200 and 950 cm⁻¹) of the infrared bands generated by phosphate complexes adsorbed on iron oxide at pH 4 and at pH 8.5 plotted versus phosphate concentration in solution. Following the assumption that the molar absorptivity coefficient of the different phosphate complexes are very similar,¹⁸ it follows that the amount of phosphate adsorbed was higher at pH 4 than at pH 8.5. This would be expected since the surface of the iron oxide is more positively charged at pH 4 than at pH 8.5 and thus the adsorption of oxoanions on iron oxide is favoured at lower pH values.

3.4 Competitive adsorption of arsenate and phosphate on iron oxide

3.4.1 Substitution of phosphate for arsenate at pH 4

Spectra shown in figure 6 (a to e) indicate an increase in the amount of phosphate adsorbed with time. At t=5 hours, arsenate was also introduced to the solution, resulting in a solution equimolar (0.03 mM) in arsenate and phosphate and the pH was kept constant at 4. The spectra recorded after arsenate addition are shown in figure 6 (f to h). Bands in the range 900-800 cm⁻¹ appeared immediately and became more intense with time as arsenate adsorbed on the iron oxide surface. At the same time, the intensity of the bands assigned to adsorbed phosphate (in the 1200-950 cm⁻¹ range)
decreased in intensity gradually, indicating desorption of phosphate from the iron oxide caused by the adsorption of arsenate.

The IR absorption bands at \( \sim 1124, \sim 1035 \) and \( \sim 998 \text{ cm}^{-1} \) that were observed in the first part of the experiment when only phosphate was adsorbed (spectrum 6a to 6e) seem to keep their relative intensities with time. The band at \( \sim 1124 \text{ cm}^{-1} \) has previously been assigned to the P=O stretching vibration of phosphate species.\(^{19}\) Since this band is observed, it indicates that the phosphate complex formed on the iron oxide surface did not have a resonance structure involving the P=O bond. Moreover, from the number of absorption bands due to adsorbed phosphate, it may be concluded that the symmetry of the molecule should be C\(_{2v}\) or lower. Therefore the most probable complexes generating these IR absorption bands would be the deuterated binuclear bidentate complex \( ([FeO])_2(OD)PO \) or the monodentate doubly deuterated complex \( ([FeO](OD)_2PO) \) as was suggested previously.\(^{18, 19}\) Complementary techniques, such as EXAFS, should be used in order to conclusively identify the complex. However, this is beyond the scope of this work. In the spectra recorded after the addition of arsenate (6f to 6h), the intensity of the band at \( \sim 1124 \text{ cm}^{-1} \) decreased rapidly, indicating low stability or fast desorption (exchange) of this complex. Upon phosphate desorption, the two bands at \( \sim 1084 \) and \( \sim 1014 \text{ cm}^{-1} \), also assigned to phosphate complexes, appeared more distinct in the spectra. The intensity of these bands were almost constant, suggesting that this complex was relatively stable and that it did not desorb to any great extent. The phosphate complex generating these IR absorption bands have lost their P=O stretching mode due to the formation of a resonance structure since P=O stretching bands appear at higher wavenumbers than 1100 cm\(^{-1}\).\(^{19}\) The dedeuteration of the complexes proposed previously,\(^{19}\) resulting in either a non-deutered binuclear bidentate complex \( ([FeO])_2PO_2^- \) or a monodentate monodeuterated complex \( ([FeO](OD)PO_2^-) \) could both give rise to these bands. Similarly as for the deuterated complexes discussed above, complementary techniques would be needed for an unambiguous assignment. Spectrum e-h in Figure 6 is the result of subtracting the spectrum recorded 5 hours after adding arsenate to the system (Figure 6h) from the spectrum recorded immediately before arsenate was added, i.e. spectrum e. The resulting spectrum shows that mostly the bands at \( \sim 1124, \sim 1035 \) and \( \sim 998 \text{ cm}^{-1} \)
decreased in intensity with time, and thus the phosphate complexes assigned to these bands desorbed. On the other hand, the absence of strong bands at \(~1084\) and \(~1014\) cm\(^{-1}\) in spectrum e-h means that these bands were relatively stable. Moreover, these bands had also been present in all spectra recorded during the phosphate adsorption; however hidden by the more intense bands reported before and thus were not clearly distinguished. Spectrum 6e-b was calculated by subtracting the spectrum recorded after 50 minutes of phosphate adsorption (Figure 6b) from the spectrum recorded after 5 hours (Figure 6e). The resulting spectrum shows that after approximately 50 minutes of phosphate adsorption, almost only the bands at \(~1084\) and \(~1014\) cm\(^{-1}\) increased their intensity. On the other hand, the bands at \(~1124\), \(~1035\) and \(~998\) cm\(^{-1}\) did not appear in the resulting spectrum, indicating that the deuterated complex was in equilibrium already after 50 minutes of adsorption. The opposite phenomenon was reported earlier,\(^{18}\) i.e. bands assigned to deuterated phosphate complexes (at 1123 and 1006 cm\(^{-1}\)) were weak, whereas the bands (at 1084 cm\(^{-1}\) and 1044 cm\(^{-1}\)) assigned to de-deuterated complexes were more intense. However there was a slight difference in the conditions for that experiment as compared to this work. In the experiments carried out by Luengo et al.,\(^{18}\) phosphate was adsorbed on goethite at pH 4.5 (i.e. slightly higher pH than in the present work) and from a 0.06 mM phosphate solution. The slight difference in pH may be the explanation for the difference in results since the pKa of phosphate complexes adsorbed on the surface of goethite was estimated to about 4.5 by titration experiments.\(^{19}\) It is thus possible that in the adsorption experiment performed by Luengo et al.,\(^{18}\) at pH 4.5 and using goethite as adsorbent material, the system was slightly above this pKa value, whereas in the experiments reported here, performed at pD 4 and using ferrihydrite as adsorbent, the system was slightly below the pKa value.

To summarize, two different phosphate complexes adsorbed on the iron oxide at pD 4. A hypothesis is that the difference between them was the deuteration of one of the oxygen atoms in the phosphate group. The deuterated complex showed a very fast adsorption within the first 50 minutes, whereas the de-deuterated complex was adsorbing during the 5 hours of adsorption time. When arsenate species was introduced in the system, the deuterated complex showed a very low stability on the
iron oxide film, desorbing almost completely whereas the de-deuterated complex was more stable. Even though the adsorption strength of each complex plays an important role in order to explain the stability/desorption behaviour for different complexes, an electrostatic effect can also play an important role. The structures proposed for the deuterated complexes adsorbed on the iron oxide, \(((\equiv FeO)_{2}(OD)PO)\) or \(((\equiv FeO)(OD)_{2}PO)\), have a neutral charge whereas the structures proposed for the de-deuterated complexes, either \(((\equiv FeO)_{2}PO_{2}^{-})\) or \(((\equiv FeO)(OD)PO_{2}^{-})\) have a negative charge. The predominant arsenate species in solution at this pH is the negatively charged \(D_{2}ASO_{4}^{-}\) ion, therefore the arsenate species may be electrostatically repelled by the negatively charged de-deuterated phosphate complexes adsorbed at the surface of the iron oxide thus being difficult to remove whereas the arsenate species in solution may approach to the deuterated phosphate complexes (no electrostatic repulsion) and replace them. It should be noticed here that the point of zero proton charged for this iron oxide was measured to be between pH 7.5 and 8.5.
Figure 6. Spectra of phosphate adsorbed onto iron oxide from a 0.03 mM phosphate solution at pH 4 after (a) 7 min. (b) 50 min. (c) 122 min. (d) 200 min. and (e) 5 hours of adsorption. After 5 hours, the solution was adjusted to be equimolar in phosphate and arsenate viz. 0.03 mM. Spectra were recorded after (f) 320 min. (g) 360 min. and (h) 600 min. Spectrum (e-b) calculated from the subtraction of spectrum (b) from spectrum (e). The (e-h) spectrum was calculated by subtracting spectrum (h) from spectrum (e). The continuous lines in the spectra represent the wavenumbers 1124 cm\(^{-1}\), 1035 cm\(^{-1}\) and 998 cm\(^{-1}\) whereas the discontinuous lines represent 1084 and 1014 cm\(^{-1}\).

3.4.2 Substitution of phosphate for arsenate at pH 8.5

Identical experiments as under subsection 3.4.1 were also performed at pH 8.5 and the results are shown in Figure 7. The figure shows that the amount of phosphate adsorbed increased with time similarly as at pH 4, although the amount adsorbed after 5 hours was significantly smaller at pH 8.5. Addition of arsenate to the solution again caused
Figure 7. Spectra recorded when a 0.03 mM phosphate from D₂O solution at pD 8.5 was adsorbed on iron oxide. Spectra were recorded after (a) 7 min, (b) 27 min, (c) 50 min, (d) 175 min and (e) 300 min. of adsorption. After 5 hours of adsorption, an equimolar (0.03 mM) arsenate and phosphate solution at pD 8.5 was brought in contact with the iron oxide film and spectra at different adsorption times, (f) 307 min, (g) 330 min, (h) 410 min and (i) 600 min were recorded.

The desorption of phosphate from the surface of the iron oxide. The major difference between pD 4 and pD 8.5 was the band shape and the frequency position of the absorption bands due to phosphate complexation (1200-950 cm⁻¹) and a shift of the band due to adsorbed arsenate (900-750 cm⁻¹) to lower frequency (~15 cm⁻¹). The infrared bands due to phosphate adsorption appeared at ~1064 cm⁻¹, ~1021 cm⁻¹. Weaker IR-absorption bands appeared below 1000 cm⁻¹ as well. The absorption at ~1064 cm⁻¹ and ~1021 cm⁻¹ have previously been assigned to non-deuterated deuterated bidentate binuclear complexes on iron oxide ((=FeO)₂PO₂)¹⁷-¹⁹ or mono-deuterated mononuclear complex ((=FeO)(OD)PO₂⁻).¹⁹ The peak position of the bands at ~1021 and ~1064 cm⁻¹ shifted to higher wave numbers with reaction time during the whole course of the experiment. The most intense band in the spectra shifted from 1021 cm⁻¹ to 1027 cm⁻¹ after 600 minutes of adsorption. In the spectrum recorded after 7 minutes of adsorption, the peak frequency was at 1064 cm⁻¹, this band was shifted to 1072 cm⁻¹ after 5 hours of adsorption, at this point arsenate was added to the system, however the band continued to shift to higher wavenumber to 1081 cm⁻¹ during the following 5 hour, despite the fact that phosphate desorbed during this time.
These shifts could be caused by a change in the interaction between the phosphate species or in the interaction between phosphate and arsenate adsorbed species.

Figure 8 shows the adsorption kinetics obtained from the same experiment as shown in Figures 6 and 7. The integrated area of the bands appearing between 1200 and 950 cm\(^{-1}\) were plotted vs. time, giving two kinetic curves for phosphate at pH 8.5 and pH 4. The intensity of the bands assigned to phosphate complexes increased with time at both pH’s indicating that the concentration of phosphate complexes on the iron oxide film increased with time. The higher slope of the curve determined at pH 8.5 below ca 70 minutes indicates that the initial adsorption rate was higher at pH 8.5 than at pH 4. After ca 70 minutes of adsorption, the curves leveled out, in particular the curve determined at pH 8.5, which might indicate adsorption of different species or adsorption on different sites. As already discussed, the amount of phosphate complexes adsorbed seemed to be higher at pH 4 than at pH 8, which has been reported before.\(^3\) When arsenate was added to the solutions the phosphate desorbed from the iron oxide. The peak height of the band at ~840 cm\(^{-1}\) assigned to arsenate adsorbed on iron oxide increased in intensity simultaneously as the amount of adsorbed phosphate decreased due to desorption from the iron oxide.

The results thus show that arsenate species replaced some of the phosphate complexes pre-adsorbed on the iron oxide films at both pH 4 and pH 8.5. The observed exchange occurred despite the low surface coverage, indicating that both oxyanions preferentially adsorb on certain high–energy sites which are the ones preferentially occupied at low surface coverage in order to lower the surface energy.
Figure 8. Integrated area of the absorption bands between 1200 and 950 cm<sup>-1</sup>, assigned to adsorbed phosphates (from a 0.03 mM solution) at (■) pD 8.5 and (○) pD 4. At t=5 hours, arsenate was added in an appropriate amount, yielding a solution equimolar (0.03 mM) in phosphate and arsenate. The kinetics after arsenate addition was monitored by the integrated area of the bands between 1200 and 950 cm<sup>-1</sup> at (Ŷ) pD 8.5 and (Ƒ) pD 4. For arsenate, the peak height of the band at ~840 cm<sup>-1</sup> was used to monitor the kinetics at (Ɣ) pD 8.5 and (ż) pD 4.

3.4.3 Substitution of arsenate for phosphate at pD 4 and pD 8.5

Representative spectra recorded during adsorption of arsenate (0.03 mM in D<sub>2</sub>O) at pD 4 are shown in Figure 9A. Spectra in the upper part of the figure correspond to the adsorption of arsenate during the first 5 hours. The lower part of the same Figure shows spectra of adsorbed phosphate after pre-adsorption of arsenate. As phosphate was introduced in the system, bands in the region 1200-950 cm<sup>-1</sup> appeared and their intensity increased with time indicating the adsorption of phosphate species on the iron oxide. At the same time, the bands assigned to arsenate did not undergo any major change in their intensity except for a slight decrease. Hence, phosphate in solution could only replace arsenate pre-adsorbed on the iron oxide to a small extent, indicating that arsenate was more strongly adsorbed than was phosphate. This agrees well with the results discussed in the previous subsection (3.4.1) where pre-adsorbed phosphate were readily exchanged for the more strongly adsorbing arsenate. Spectra of arsenate species adsorbed on iron oxide showed two main bands at ~875 cm<sup>-1</sup> and ~840 cm<sup>-1</sup>. 
Their relative intensities and peak positions remained constant during the course of the experiment, indicating that the arsenate complex formed on the iron oxide surface was the same during both adsorption and desorption. Regarding the bands associated with phosphate (1200-950 cm\(^{-1}\)), the appearance of the bands was very similar to the ones obtained for phosphate adsorbed at the same pD, albeit the band intensities were significantly lower.

Spectra recorded when the same experiment was repeated at pD 8.5 are shown in Figure 9B. The spectra shown in the upper part of this figure were recorded during the first part of the experiment when only arsenate species were present in the system and the spectra shown in the lower part of the figure were recorded after phosphate was added to the system. Two main broad bands appeared at ~855 cm\(^{-1}\) and ~830 cm\(^{-1}\) in all spectra recorded during the first 5 hours. The intensity of these bands increased with time as a result of an increase in the amount of arsenate species adsorbed on the iron oxide film. In the second part of the experiment the presence of phosphate led to the appearance of bands at 1200-950 cm\(^{-1}\) assigned to phosphate complexes adsorbed on the iron oxide film. These bands increased in intensity with time indicating the adsorption of phosphate on the iron oxide. At the same time, the bands assigned to arsenate species decreased slightly in intensity as expected due to some replacement of pre-adsorbed arsenate by phosphate species. However, again pre-adsorbed arsenate species were relatively stable against exchange for phosphate. The position of the bands assigned to adsorbed arsenate complexes remained constant during the whole experiment as did their relative intensities indicating that the structure of the arsenate complexes on the iron oxide surface did not change upon desorption, suggesting that arsenate adsorbs as a single complex or, in the case of different complexes being formed, the relative number of each complex was constant. The different band positions at pD 4 and 8.5 observed for arsenate are most likely a result of de-deuteration of the arsenate species at higher pD.\(^9\)

Figure 9C illustrates the adsorption/desorption kinetics of both phosphate and arsenate at both pD’s. As previously, the peak height of the 840 cm\(^{-1}\) band was used to indicate arsenate surface concentration whereas for phosphates the integrated area of the bands
at 1200-950 cm\(^{-1}\) was used. Similarly as observed for the adsorption of phosphates, the adsorption of arsenate was faster at pH 8.5 than at pH 4 during the first 45 minutes. Thereafter the amount of arsenate adsorbed on the iron oxide seemingly levelled out (very low adsorption rate) at pH 8.5 whereas the amount of arsenate on the iron oxide kept increasing with time at pH 4. Assuming that the arsenate complexes at pH 4 and pH 8.5 have similar molar absorptivities, the concentration of the complexes adsorbed on the iron oxides after 5 hours was approximately 25% higher at pH 4 than at pH 8.5. The higher adsorption at low pH is most probable an effect from surface charge where the more negatively charged surface at high pH reduces the adsorption of the negatively charged anions. The point of zero charge for this iron oxide was previously determined to be between 7.5-8.5, consequently at pH 4 the iron oxide surface is positively charge whereas it is neutral-negative at pH 8.5. As phosphate was introduced into the system, arsenate desorbed from the surface at both pH 8.5 and pH 4 but only to a minor degree.
Figure 9. (A) Spectra recorded for a 0.03 mM arsenate solution adjusted at pH 4 and in contact with an iron oxide film at (a) 7 min, (b) 20 min, (c) 45 min, (d) 70 min, (e) 145 min, (f) 165 min and (g) 300 min of adsorption. After 300 minutes of adsorption, an equimolar 0.03 mM arsenate and phosphate solution at pH 4 was brought in contact with the iron oxide film and spectra after (h) 302 min, (i) 320 min, (j) 340 min, (k) 400 min, (l) 460 min and (m) 600 min were recorded. (B) Spectra recorded when a 0.03 mM arsenate solution adjusted at pH 8.5 was in contact with an iron oxide film at (a) 2 min, (b) 20 min, (c) 40 min, (d) 130 min, (e) 300 min. Adsorption times. After 300 minutes adsorption time, an equimolar 0.03 mM arsenate and phosphate solution at pH 8.5 was in contact with the iron oxide film and spectra at different adsorption times, (f) 307 min, (g) 330 min, (h) 380 min, (i) 450 min and (j) 600 min, were recorded. (C) The peak height of the band at ~840 cm⁻¹ which was assigned to adsorbed arsenate (from a 0.03 mM solution) at (Ŷ) pH 8.5 and (Ƒ) pH 4. At t=5 hours, phosphate was added in an appropriate amount, yielding a solution equimolar (0.03 mM) in phosphate and arsenate. The kinetics after phosphate addition was monitored by the peak height of the band at ~840 cm⁻¹ assigned to adsorbed arsenate at (_FUNCION_ ) pH 8.5 and ( Đo ) pH 4. For phosphate, the integrated area of the bands between 1200 and 950 cm⁻¹ was used for monitoring the kinetics at (●) pH 8.5 and (○) pH 4.
As concluded above, arsenate complexes adsorbed on iron oxide were more stable than the adsorbed phosphate complexes at the two pD values studied. Therefore another exchange experiment was performed in order to assess the stability of arsenate complexes at significantly higher phosphate concentrations, which may be more realistic from a soil stabilization perspective.

First arsenate was pre-adsorbed on the iron oxide film from a 0.03 mM D$_2$O solution for 5 hours as in the previous experiments. Subsequently, phosphate was added to the solution yielding a phosphate concentration of 0.15 mM i.e. five times higher than in the previous experiment. Figure 10 shows the intensity of the band at ~840 cm$^{-1}$ assigned to arsenate species plotted vs. time and in the presence of phosphate at a concentration of 0.15 mM at pD 4 and 8.5. After the addition of phosphate, the intensity of the arsenate band decreased with time at both pD’s, indicating that the concentration of arsenate complexes adsorbed on the iron oxide was decreasing with time upon phosphate adsorption. For comparison, the desorption kinetics obtained at a phosphate concentration of 0.03 mM during desorption is also shown in the Figure. As expected, arsenate desorbed to a larger extent when the concentration of phosphate in the solution was higher. At pD 4, the final concentration of arsenate complexes adsorbed on the iron oxide was ~ 70% of the initial value whereas at pD 8.5 only about 50% of the initial value remained after 5 hours. As a comparison, the corresponding values at a phosphate concentration of 0.03 mM were 90% and 80 % at pD 4 and 8.5, respectively. These results supports the previous findings that arsenate was much more strongly adsorbed than phosphate at both pD’s since the desorbed fraction was in the same range even though the concentration of phosphate in solution varied a factor five.
Figure 10. The peak height of the band at ~840 cm\textsuperscript{-1} assigned to arsenate adsorbed on iron oxide plotted as a function of time. The arsenate concentration was 0.03 mM and the pD’s were (■) 8.5 and (○) 4. At t=300 min., phosphate was added in appropriate amounts while keeping the arsenate concentration constant at 0.03 mM. At pD 4, the phosphate concentrations were (△) 0.03 mM and (○) 0.15 mM and at pD 8.5 (▲) 0.03 mM and (●) 0.15 mM.

To the best of our knowledge, these are the first experiments using the in-situ ATR-FTIR technique for studies of the competitive adsorption of arsenate and phosphate on synthetic iron oxide. The technique was proven to be a powerful tool for these kinds of studies. At both pD values studied, arsenate complexes were shown to be more strongly bonded to the iron oxide surface than the phosphate complexes. At pD 8.5, it was necessary with a phosphate concentration as high as 0.15 mM, in order to reduce the concentration of arsenate complexes on the surface within 300 minutes to half of that before phosphates were added. At pD 4 still only about 30 % of the arsenate desorbed during 300 minutes showing that arsenate adsors even stronger at this pD.

In order to prevent leaching of arsenic to the environment from pre-adsorbed arsenic on iron oxide, as could be an expected situation in soil remediation or in water purification applications using iron oxide adsorbents, the pD (pH in a natural system) and the phosphate concentration in the natural system needs to be controlled. A weakly acidic pD (pH) would be ideal both due to a higher adsorption capacity at this lower pD and since the arsenate seems to be much more strongly adsorbed than phosphate at weakly acidic pD values.
References

[16] Lumsdon, D.G.; Fraser, A.R.; Russel, J.D.; Livesey, N.T., New infrared bands assignments for the arsenate ion adsorbed on synthetic goethite (α-FeOOH), Soil Sci. 35 (1984) 381-386.
