ARSENIC REMOVAL BY GOETHITE AND JAROSITE IN ACIDIC CONDITIONS AND ITS ENVIRONMENTAL IMPLICATIONS

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Abstract

Schwertmannite ($Fe_8O_8(OH)_{5.5}(SO_4)_{1.25}$), jarosite ($KFe_3(SO_4)_2(OH)_6$) and goethite (FeOOH) control natural attenuation of arsenic in acid mine drainage (AMD) impacted areas. Batch experiments were conducted to examine the sorption capacity of synthetic goethite and synthetic jarosite at highly acidic pH (1.5-2.5), at two ionic strengths (0.02-0.15 mol dm^{-3}, NaCl) and at sulphate concentrations in the range of $5 \cdot 10^{-3}$ to $2.8 \cdot 10^{-1}$ mol dm^{-3}. In the absence of competitive effects of other anions, K-jarosite presents better removal efficiency than goethite for As(V). The maximum sorption capacity is estimated to be $1.2 \cdot 10^{-4}$ and $7.0 \cdot 10^{-6}$ mol m^{-2} for jarosite and goethite, respectively, under similar experimental conditions. The variation of arsenic sorbed on goethite as a function of the equilibrium arsenic concentration in solution fits a non-competitive Langmuir isotherm. In the case of K-jarosite, sorption data could not fit a Langmuir or Freundlich isotherm since sulphate-arsenate anion exchange is probably the sorption mechanism. Ionic strength and pH has little effect on the sorption capacity of goethite and jarosite in the small range of pH studied. The presence of sulphate, which is the main anion in AMD natural systems, has a negative effect on arsenic removal since sulphate competes with arsenate for surface sorption sites. Moreover, mobilization of arsenic in the transformation of schwertmannite to jarosite or goethite at pH 2-3 is proposed since the sorption capacities of goethite and K-jarosite are considerably lower than those reported for schwertmannite.

Keywords: Arsenic removal, goethite, jarosite, Langmuir isotherm, AMD

1. Introduction

Acid mine drainage (AMD) due to sulfide oxidative dissolution is a major cause of water contamination world-wide [1]. Arsenic is one of the main AMD pollutants whose concentration can reach up to hundreds of mg L^{-1} as a result of the oxidation of As-rich sulphides such as arsenopyrite and As-rich pyrite [1]. The As(III) released from the dissolution of these minerals [2] is rapidly oxidized to As(V) [3], which is sorbed more strongly than As(III) to Fe(III) oxides and hydroxides [4].

Arsenic concentrations in AMD polluted areas are naturally attenuated by newly formed precipitates (schwertmannite ($Fe_8O_8(OH)_{5.5}(SO_4)_{1.25}$), K-jarosite ($KFe_3(SO_4)_2(OH)_6$) and goethite (FeOOH)) [5,6]. These minerals therefore play an important role in the removal of trace elements from solution by adsorption and co-precipitation [7].

These iron oxide precipitates are formed in acid waters and are initially poorly ordered minerals such as schwertmannite, which may transform with time into goethite and jarosite. This transformation has been observed under laboratory [5] and field [8] conditions. The instability of schwertmannite has a significant impact on the water chemistry because the progressive transformation of the As-bearing amorphous iron oxyhydroxides into more crystallized iron oxides leads to the release of arsenic to the water [9].

Given that inorganic aqueous arsenic is an environmental and human health concern world-wide, a number of studies have addressed the use of different adsorbents [10] including schwertmannite [11, 12], goethite [13-19], and jarosite [20-21] in an attempt to reduce its aqueous concentration. In the case of goethite, the effects of pH, initial arsenic concentration or the presence of other elements (silicic acid, dissolved organic carbon (DOC) or sulphate) on arsenic sorption capacity of goethite have been reported in the literature. As regards jarosite, there have been few studies on its sorption capacity

[20-21]. Likewise, there is little bibliography on arsenic sorption in highly acidic conditions with the result that the relative ability of jarosite and goethite to retain arsenic remains unclear [5]. Some studies claim that arsenic can remain immobilized in jarosite by replacing sulphur in sulphate tetrahedral [21], whereas other works show that arsenic is retained more in goethite than in jarosite [22].

The quantification of the arsenate sorption capacity of these precipitates at low pH is necessary to develop effective management strategies to remediate AMD impacted areas. This enables us to understand and predict arsenic behaviour in streams, rivers and pit lakes and to determine the potential risk of releasing sorbed arsenic under reductive conditions (e.g. pit and lake bottoms). The present paper seeks to quantify the As(V) removed by jarosite and goethite at low pH (1.5-2.5). To this end, synthetic jarosite and goethite were used separately to quantify the respective arsenic removal capacity. The effect of sulphate content was studied because sulphate is the main anion that competes with arsenate for surface sites. The effect of ionic strength was also studied given its seasonal variations.

2. Materials and Methods

2.1 Solid synthesis and characterization

Sorption experiments were conducted with synthetic goethite and synthetic jarosite. Goethite synthesis was carried out following the Schwertmann and Cornwell methodology [23]. According to this method, 180 mL of 5M KOH (Merck) and 100 mL of 1M $Fe(NO_3)_2$ (Merck) were mixed. The suspension was diluted to 2L with Milli-Q ultrapure water (18 $M\Omega$·cm) and aged for 60 h at 70ºC. Thereafter, the suspension was washed several times with Milli-Q ultrapure water and dried at 50ºC. K-Jarosite was synthesized according to Baron and Palmer [24], dissolving 5.6 g of KOH from Merck

and 17.2 g of $Fe_2(SO_4)_3 \cdot 5H_2O$ from Panreac in 100 mL of Milli-Q ultrapure water at 95ºC and 1 atm. The solution was placed in a covered beaker on a hot plate and stirred continuously. After 4 h, the precipitate settled and the supernatant solution was decanted. The precipitate was then washed several times with ultrapure water (18 *M*Ω·cm) and dried at 110ºC for 24 h. The synthesized solids were identified by means of X-ray diffraction (XRD) using a Bruker D5005 diffractometer with Cu Kα radiation and scanned from 0 to 60 degrees 2θ with a continuous scan at a rate of 0.025º/18s. The surface area was measured using a Micromeritics Gemini 2370 surface area analyzer. The BET-determined surface area of goethite and jarosite was 29.4±1.9 $m^2\ g^{-1}$ and 2.3±0.3 $m^2\ g^{-1}$, respectively, using 5-point N_2 adsorption isotherms.

In addition, the saturation indexes (SI) of reacted solution were calculated employing the PHREEQC code [25] and thermodynamic database WATEQ4F [26].

2.2 Experimental methodology

Stock As(V) solutions with concentrations from $3 \cdot 10^{-5}$ to $1 \cdot 10^{-2}$ mol dm^{-3} were prepared by dissolving sodium hydrogen arsenate ($Na_2HAsO_4 \cdot 7H_2O$ (Sigma) of reagent grade in Milli-Q ultrapure water. H_2SO_4 (95-97%) and HCl (32%) from Merck were used to acidify the experiments with and without sulphate, respectively. To determine the effect of sulphate on As(V) sorption, stock As(V) solutions ($1 \cdot 10^{-3}$ mol dm^{-3}) were prepared by adding Na_2SO_4 (Merck). NaCl (Merck) was added to adjust the background ionic strength of 0.02 and 0.15 mol dm^{-3}.

Batch experiments were carried out by reacting 20 cm^3 of metal solution in stoppered polyethylene bottles with 0.05 g of solid. The experiments were conducted at room temperature (22±1˚C) and the bottles were stirred continuously for 50 h. After a predetermined contact time, the aqueous samples in each bottle were decanted and

74 filtered through 0.20 μm pore size filters. The supernatant was analyzed for total iron,
75 arsenic, potassium and sulphur by Inductively Coupled Plasma Atomic Emission
76 Spectrometry (ICP-AES, Thermo Jarrel-Ash with CID detector and a Perkin Elmer
77 Optima 3200 RL). Detection limits for Fe, As, K and sulphur were $3 \cdot 10^{-7}$, $1.3 \cdot 10^{-6}$,
78 $1.3 \cdot 10^{-5}$ and $3.1 \cdot 10^{-6}$ mol·dm^{-3}, respectively. The accuracy of the ICP-AES
79 measurements was estimated to be around 3%. In the analyses of ICP-AES, calibration
80 with sets of standards was performed and the regression coefficients exceeded 0.999.
81 Three laboratory standards were analyzed every 15 samples to check the accuracy of the
82 results. Blanks and duplicates were also analyzed with each batch of samples. Dilutions
83 from 1:6 to 1:8 were performed to ensure that the concentration of the samples was
84 within the concentration range of the standards.
85 At lower arsenic concentrations than the ICP detection limit, total arsenic concentration
86 was determined using Varian 3000 Zeeman graphite furnace atomic absorption
87 spectrometer (GF-AAS) at a wavelength of 193.7 nm. The spectrometer was equipped
88 with a graphite tube atomizer and programmable sample dispenser. The detection limit
89 for As was $1.33 \cdot 10^{-8}$ mol·dm^{-3}. Calibration with sets of standards was performed and the
90 regression coefficients exceeded 0.999. Three laboratory standards were analyzed every
91 10 samples to check the accuracy of the results. Dilutions from 1:2 to 1:4 were
92 performed to ensure that the concentration of the samples was within the concentration
93 range of the standards. All sample analyses were conducted in triplicate.
94 The pH of the solutions was measured at equilibrium (pH_{eq}) using a Crison pH-meter
95 combination electrode with temperature compensation. The calibration of the pH was
96 carried out with standard buffer solutions of pH 2 and pH 4. The accuracy was ±0.02 pH
97 units (±4.5% in H^+ activity).

Different series of batch experiments were conducted to quantify the arsenic removal by goethite and jarosite in accordance with this experimental methodology: (i) Sorption kinetics were evaluated at pH 1.5, 2 and 2.5 and initial As(V) concentrations of $1 \cdot 10^{-3}$, $2 \cdot 10^{-3}$, $3 \cdot 10^{-3}$, $4 \cdot 10^{-3}$, $5 \cdot 10^{-3}$, $6 \cdot 10^{-3}$, $1 \cdot 10^{-2}$ mol dm^{-3}; (ii) Sorption capacity by goethite and jarosite were examined as a function of pH (1.5-2.5) at initial As(V) concentrations of $3 \cdot 10^{-5}$, $5 \cdot 10^{-5}$, $1 \cdot 10^{-4}$, $3 \cdot 10^{-4}$, $5 \cdot 10^{-4}$, $1 \cdot 10^{-3}$, $2 \cdot 10^{-3}$, $3 \cdot 10^{-3}$, $4 \cdot 10^{-3}$, $5 \cdot 10^{-3}$, $6 \cdot 10^{-3}$, $1 \cdot 10^{-2}$ mol dm^{-3} and two constant ionic strengths (0.02 and 0.15 mol dm^{-3} NaCl), and (iii) competitive effect of sulphate was studied at pH 2 in background solutions of $5 \cdot 10^{-3}$, $1.5 \cdot 10^{-2}$, $2 \cdot 10^{-2}$ and $2.8 \cdot 10^{-1}$ mol dm^{-3} of sulphate.

The concentration attached to the solid, $\{As\}_S$ in mol m^{-2}, was calculated by the difference between the initial concentration of arsenic in the solution, $[As]_0$, and the equilibrium concentration, $[As]_{eq}$, and normalized with the surface area (SA, in m^2) to volume (V, in dm^3) according to the equation:

(1) $$\{As\}_s = \left([As]_0 - [As]_{eq}\right) \times \frac{V}{SA}$$

Concentrations of potassium, sulphur and total iron were used to determine the amount of solid dissolved. The results were normalized with respect to the final mass.

3. Results and discussion

3.1 Solid phases

Solid phases were characterized before and after reacting with the solutions at the different pH values. XRD patterns (see Fig. 1) demonstrate that the solids were goethite and jarosite, respectively.

Concentrations of potassium, sulphur and total iron were used to calculate the amount of solid dissolved. As for goethite, the iron concentration corresponded to an amount of

121 solid dissolved less than 1 %. As regards jarosite, the aqueous potassium concentration
122 indicated that the amount of dissolved jarosite ranged from 20-35%.
123 Given the possibility of precipitation of new phases under the experimental conditions,
124 the saturation indexes of the reacted solution with respect to As and Fe-bearing phases
125 were determined using the PHREEQC code [25] and the WATEQ4F thermodynamic
126 database [26], which was enlarged with data from Bigham et al. [27] and Yu et al. [28]
127 to account for the schwertmannite solubility (Table 1). It is observed that all the reacted
128 solutions were undersaturated with respect to all As-bearing phases, including scorodite
129 ($FeAsO_4{:}2H_2O$). Although the solubility product of amorphous Fe(III)-arsenate is
130 unknown, the solubility of the amorphous phase is generally greater than that of the
131 crystalline phase [29]. Therefore, precipitation of As and Fe-As bearing phases during
132 the experiments is discarded. As regards the Fe-phases, some solutions appear to be
133 supersaturated with respect to hematite. However, hematite is only formed at high
134 temperatures (150-200ºC) in the pH range 0-3 [30]. It is worth noting that PHREEQC
135 calculations do not consider kinetic aspects, and the formation of goethite in Fe(III)
136 systems is very slow (weeks to months at room temperature) [23]. Moreover, after
137 reaction, XRD patterns of samples only show the presence of goethite and jarosite,
138 discarding the precipitation of any new solid phase.

139 *3.2 Sorption Kinetics*

140 Suspensions were stirred continuously. In the case of goethite, equilibrium was reached
141 after 18 h (Fig. 2a). Jarosite-sorption kinetics showed an increase in As sorption even
142 after 53 h, and equilibrium was not attained (Fig. 2b). Iron concentration in the goethite
143 solutions was always lower than $3 \cdot 10^{-4}$ mol dm^{-1}, indicating that less than 1% of initial
144 goethite was dissolved. Concentration of sulphur, potassium and iron increased over the
145 jarosite experimental runs. This increase in metal concentration accounted for around

35±5 and 22±3 % of dissolved solid at pH 1.5 and 2, respectively. Therefore, goethite scarcely dissolved and sorption was the only process that occurred in this pH range. By contrast, jarosite dissolution occurred together with arsenic sorption.

3.3 As(V) uptake from solution. Effect of arsenic concentration

As(V) removal from aqueous solution was investigated at initial As(V) concentrations of $3 \cdot 10^{-5}$ to $1 \cdot 10^{-2}$ mol dm^{-3} at pH_{eq} of 1.5-2.5.

The variation of the As(V) sorbed onto goethite with the equilibrium arsenic concentration in solution is shown in Fig. 3. The experimental data fit a non-competitive Langmuir isotherm that is expressed as:

$$(2)\quad \Gamma = \Gamma_{max} \frac{K_L \cdot [As]_{eq}}{1 + K_L \cdot [As]_{eq}}$$

where Γ is the quantity of arsenic sorbed on the solid, Γ_{max} is the maximum arsenic sorption, K_L is the Langmuir constant and $[As]_{eq}$ is the arsenic concentration in solution in equilibrium.

The maximum sorption capacity (Γ_{max}) obtained for goethite is $7.0 \cdot 10^{-6}$ mol m^{-2}. The good fit of the experimental data to the Langmuir isotherm (Fig. 3) indicates that the coverage of the sorption sites was in the form of a monolayer, and all surface sites had nearly the same sorption energies. The parameters obtained from the fit are listed in Table 2.

Earlier spectroscopic studies [15, 31, 32] have shown that arsenate is sorbed onto iron hydroxides, such as goethite, forming inner sphere surface complexes by ligand exchange with hydroxyl groups at the mineral surface. Waychunas et al. [31], Fendorf et al. [32] and Sherman and Randall [33] reported the formation of bidentate complexes, resulting from corner sharing with AsO_4 tetrahedra and edge-sharing pairs of FeO_6 octahedra.

The sorption capacity of jarosite was compared with that of goethite at the same initial As(V) concentrations and under the same experimental conditions (Fig.4).

It is not easy to interpret arsenic sorption on jarosite given jarosite dissolution in this low pH range. The sorption data obtained could not fit a Langmuir or a Freundlich isotherm. Nonetheless, useful quantification was possible. Jarosite sorption kinetics showed that sorption occurred, and that the amount of arsenic sorbed was the maximum in all experiments after 53 h. Thus, the highest amount of arsenic removed, calculated by eq. 1, was around $1.2\pm0.2\cdot10^{-4}$ mol m^{-2} according to the maximum sorption capacity values of jarosite at the end of the experiments. Hence, jarosite appears to be significantly more effective in sequestering As(V) than goethite (Fig. 4). This result is in good agreement with Gräfe et al. [21], who observed that the As(V) sorption mechanism on jarosite was substantially different from that on goethite. These authors reported significantly larger surface coverage of As(V) on jarosite with respect to As(V) on goethite. According to these authors, jarosite was more effective in removing As(V) than goethite because of the presence of structural sulphate groups that could be replaced by As(V).

The As(V) removal capacities obtained in this study for goethite and jarosite were compared with earlier results obtained with natural and synthetic phases (Table 3). This comparison was made by normalizing the results with respect to the surface area. Our results indicate that the maximum capacity of goethite is between 6 and $7\cdot10^{-6}$ mol m^{-2} at pH 1.5-2.5. These values are very similar to the findings reported by Lehmann et al. [13] at pH 3 for natural goethite. At pH 3-7, sorption capacities ranged approximately from $3\cdot10^{-6}$ mol m^{-2} to $4.6\cdot10^{-6}$ mol m^{-2} on both natural and synthetic goethite according to Matis et al. [16], Dixit and Hering [14] and Giménez et al. [17].

3.4 Effect of pH on As(V) removal

195 Sorption of As(V) onto iron (oxy)hydroxides depends on pH given that both aqueous
196 arsenate species and the iron (oxy)hydroxide surface charge are pH-dependent. Under
197 acidic conditions, sorbed protons on the functional groups of the surface cause an
198 overall positive surface charge with the result that anions can be sorbed. The aqueous
199 arsenate species present in the pH range studied are H_3AsO_4 and $H_2AsO_4^-$. Although
200 [H_3AsO_4] predominates over [$H_2AsO_4^-$] at pH < 2.3, [$H_2AsO_4^-$] can be preferentially
201 sorbed in this low pH range. Table 2 shows that arsenate sorption on goethite decreases
202 slightly with increasing pH. A similar trend has been observed in earlier studies at pH
203 higher than 4.5 [14, 17]. According to Hsia et al. [36], this behaviour is reasonable since
204 surface protonation increases the number of positively charged sites as the pH
205 decreases. This enhances the attraction force between arsenic anions and the iron oxide
206 surface, thereby increasing the amount of arsenate sorbed on the solid surface.
207 Jarosite showed no significant differences in the As(V) removal capacity in the short
208 range of pH studied. The sorption mechanism via exchange sulphate-arsenate suggested
209 by Gräfe et al. [21] could account for the negligible pH effect on the jarosite As(V)
210 removal capacity.

211 *3.5 Effect of ionic strength on As(V) removal*

212 The effect of ionic strength on the As(V) sorption was studied by means of experiments
213 carried out at 0.02 mol·dm^{-3} and 0.15 mol dm^{-3} NaCl solutions. The results plotted in
214 Fig. 5 show that As(V) sorption is independent of ionic strength. The results suggest
215 that As(V) adsorption on goethite could proceed via the formation of inner-sphere
216 surface as indicated in earlier studies [15, 31, 32].

217 *3.6 Effect of sulphate on As(V) removal*

AMD waters are characterized by exceptionally high sulphate concentrations. These values usually exceed 0.01 mol dm^{-3} [5, 6, 37], and are possibly higher than 0.2 mol dm^{-3} in tailing pore waters [38]. Competitive effects of co-occurring solutes such as sulphate have been demonstrated in earlier works [39].

Table 4 shows that the quantity of arsenate sorbed onto both solids decreased as sulphate concentration increased. This decrease is very marked in the case of jarosite even at low sulphate concentrations (e.g. percentage sorbed is around 1-4% in the presence of sulphate and 38% in the sulphate free solution; Table 4).

The inhibition of arsenate sorption on goethite was much lower than in jarosite in sulphate rich solutions (Table 4). The effect of sulphate was significant when sulphate concentrations exceeded $2.8 \cdot 10^{-1}$ mol dm^{-3} in the pH range studied. A similar decrease in sorption of As(V) in the presence of sulphate was obtained by Wilkie and Hering [39], who studied the competitive effects of sulphate and arsenic sorption on hydrous ferric oxide (HFO).

Our results are consistent with the different sorption mechanisms reported in earlier studies that indicate that sorption capacity of goethite is slightly affected by sulphate, whereas jarosite, which exchanges sulphate groups for arsenate groups, decreases its exchange capacity as sulphate increases in solution.

3.7 Importance of goethite and jarosite sorption in AMD

Our findings show that goethite and jarosite are effective As(V) sorbents in highly acidic, pH favouring the natural attenuation of arsenic in AMD environments. These sorption capacities are in the wide range of that of low-cost adsorbents or activated carbons at very low pH (see Table 5 in Mohan and Pittman [10]).

In the absence of sulphate, the As(V) maximum sorption capacities of goethite and jarosite were 15 mg g^{-1} and 21 mg g^{-1}, respectively, under experimental conditions

243 similar to those of this study. These values are considerably lower than those reported
244 by Fukushi et al. [11, 12, 40] for As(V) sorption capacity of schwertmannite (80 mg g^{-1}
245 for synthetic and 60 mg g^{-1} for natural schwertmannite in AMD). This suggests that a
246 net release of As(V) to the water could occur during schwertmannite transformation into
247 jarosite or into goethite. Moreover, if these solids were dragged to reductive
248 environments (e.g. pit bottoms), the potential risk of arsenic release would be higher in
249 the case of schwertmannite.

250 **4. Conclusions**

251 Goethite and jarosite effectively remove As(V) from water at pH ≤ 2.5. In the absence
252 of the competitive effects of sulphate, jarosite eliminates aqueous arsenate more
253 efficiently than goethite in extremely acidic AMD water. pH has little effect on arsenate
254 removal and ionic strength has no substantial effect on the arsenic sorption on jarosite
255 and goethite. The competitive effect of sulphate, which is the main anion in AMD
256 impacted waters, is greater on the As(V) sorption capacity of jarosite than on that of
257 goethite.

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Figures:

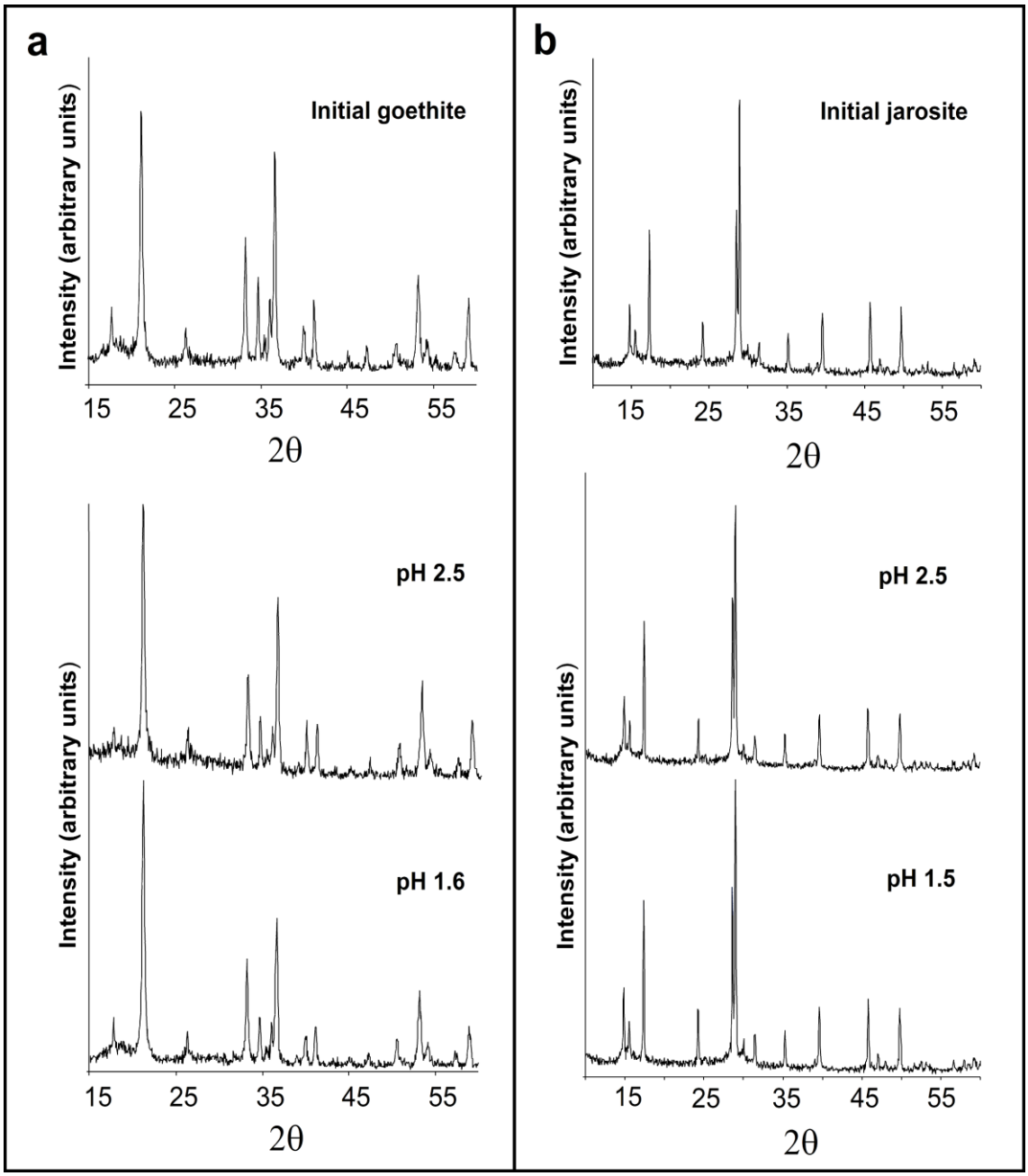

Figure 1. Powder X-ray diffraction patterns of initial and residual solids after reaction: (a) at pH 1.6 and 2.5 and at 0.15 mol dm^{-3} of ionic strength; (b) at pH 1.5 and 2.5, and at ionic strength 0.15 mol·dm^{-3}.

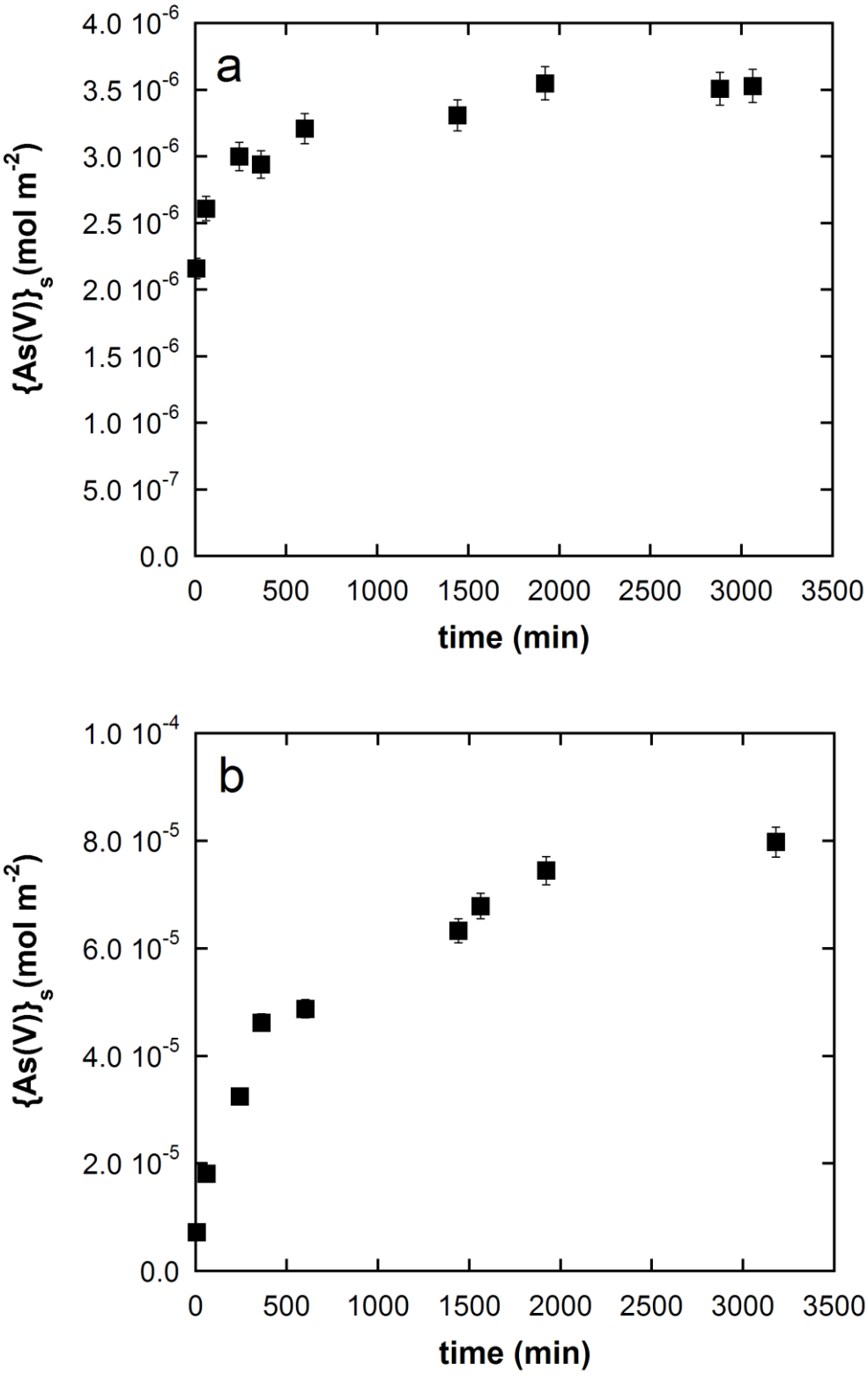

Figure 2. Kinetics of As(V) sorption on goethite (a) and jarosite (b). pH_{eq} was 1.6 and 1.5 for goethite and jarosite respectively, and $[As(V)]_0=1\cdot10^{-3}$ mol·dm^{-3} and initial solid was 0.05 g. Error bars correspond to the analytical error.

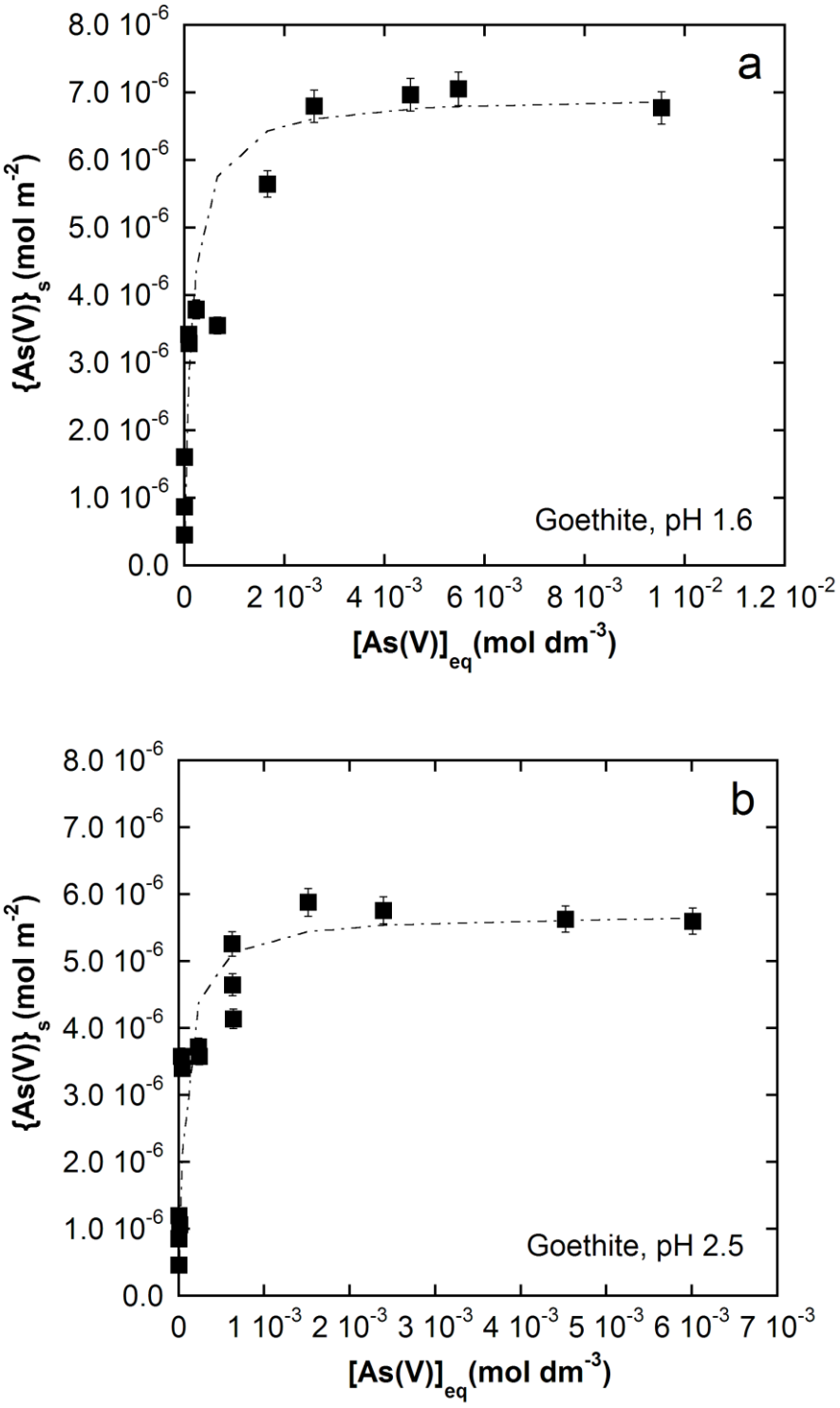

Figure 3. As(V) sorption isotherms for goethite. 0.05 g of solid at 0.15 mol·dm^{-3} ionic strength and pH_{eq} 1.6 (a) and 2.5 (b). Dotted lines correspond to the best fit data by using a Langmuir isotherm (see text). Error bars correspond to the analytical error.

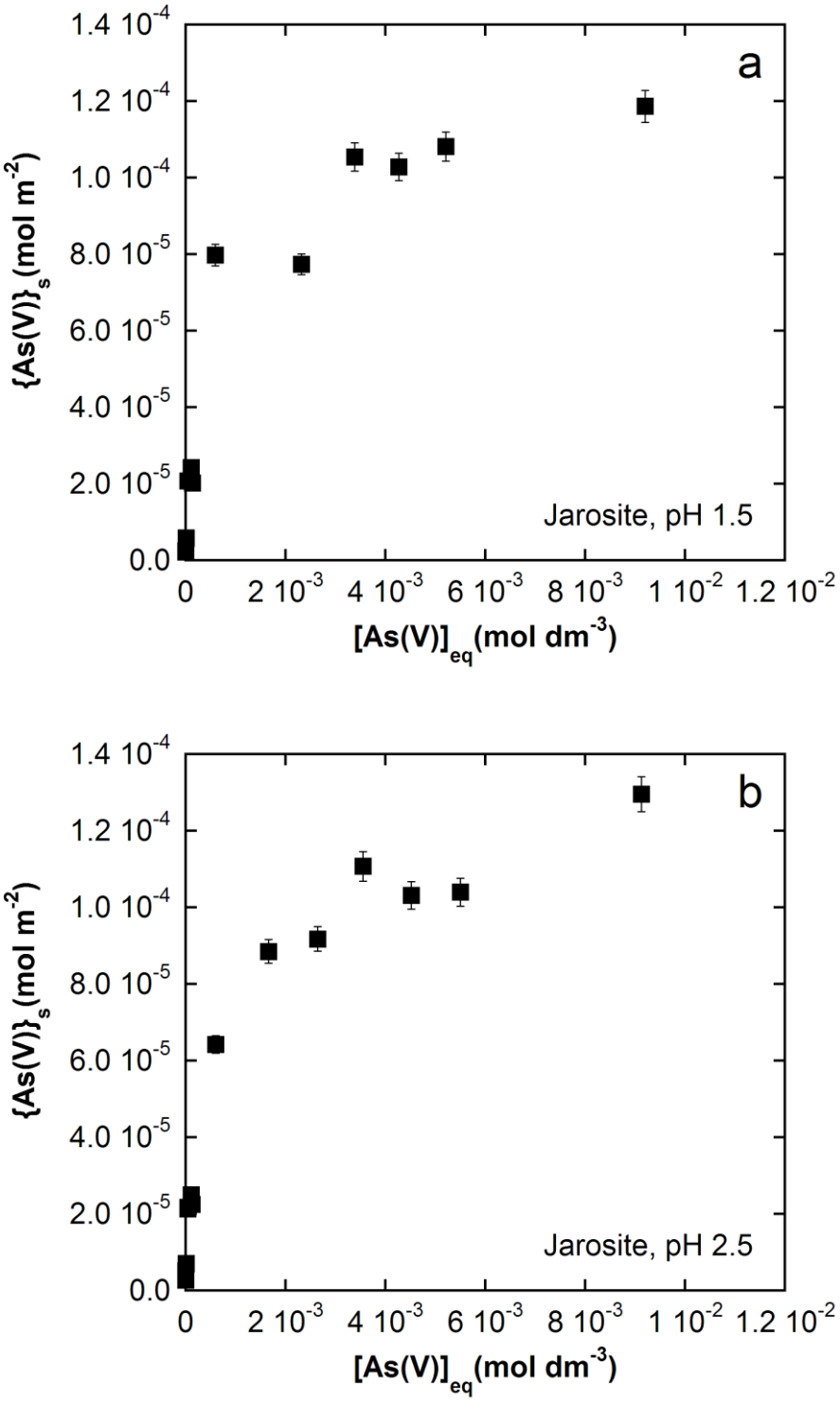

Figure 4. As(V) removed by jarosite at pH_{eq} 1.5 (a) and 2.5 (b) and 0.15 mol·dm^{-3} ionic strength. Initial solid was 0.05 g. Error bars correspond to the analytical error.

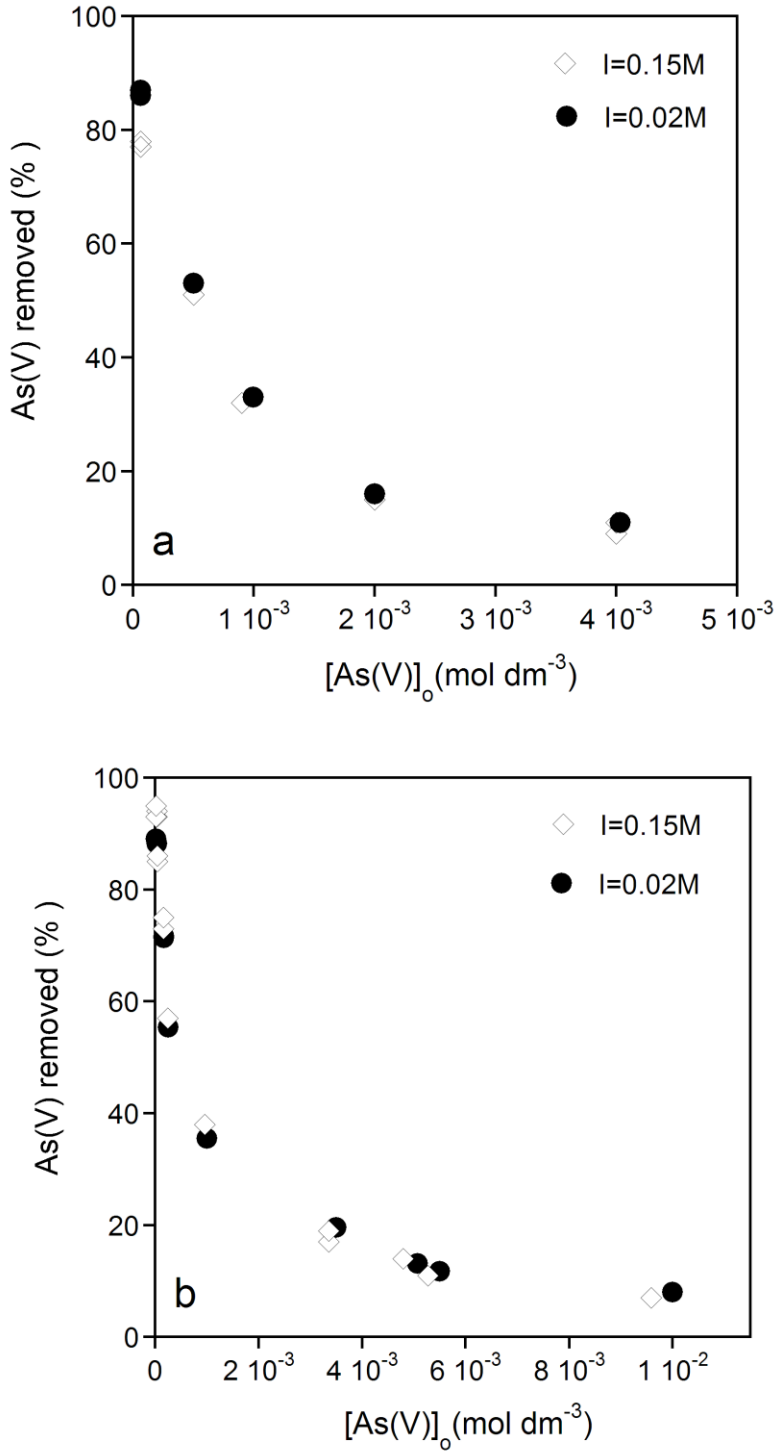

Figure 5. Variation of the As(V) sorption onto (a) goethite and (b) jarosite with ionic strength (0.15 and 0.02 mol dm^{-3} NaCl) at pH_{eq} 2 and different arsenic (V) concentrations in solution.

Tables:

Table 1. Calculated saturation index (SI) for Fe-As mineral phases of reacted solutions using the PHREEQC code and the WATEQ4F database with the exception of schwertmannite: logK=10.15 (Yu et al. [51]) and logK=18.0 (Bigham et al. [20]).

Mineral phase	Formula	Solutions reacted with goethite		Solutions reacted with jarosite		
		pH 1.5	pH 2.5	pH 1.5	pH 2	pH 2.7
				No sulphate		
Arsenolite	As_2O_3	-47.02	-47.76	-47.02	-47.29	-48.11
As native	As	-73.56	-73.92	-73.55	-73.69	-74.10
$As_2O_{5(cr)}$	As_2O_5	-12.81	-13.55	-12.81	-13.08	-13.90
$As_2S_{3(am)}$	As_2S_3	-	-	-418.10	-420.75	-425.43
Claudetite	As_2O_3	-47.06	-47.80	-47.06	-47.33	-48.15
$Fe(OH)_{3(a)}$	$Fe(OH)_3$	-5.07	-4.34	-5.69	-4.23	-2.33
$Fe_2(SO_4)_3$	$Fe_2(SO_4)_3$	-	-	-25.41	-24.97	-25.17
Goethite	FeOOH	0.82	1.55	0.21	1.66	3.56
Hematite	Fe_2O_3	3.65	5.10	2.42	5.33	9.13
JarositeH	$(H_3O)Fe_3(SO_4)_2(OH)_6$	-	-	-10.73	-7.95	-4.83
Jarosite-K	$KFe_3(SO_4)_2(OH)_6$	-	-	-8.52	-5.24	-1.42
Jarosite-Na	$NaFe_3(SO_4)_2(OH)_6$	-	-	-10.27	-6.99	-3.16
Maghemite	Fe_2O_3	-6.74	-5.29	-7.97	-5.07	-1.27
Schwertmannite (logK=10)	$Fe_8O_8(OH)_{4.5}(SO4)_{1.75}$	-	-	-28.37	-18.13	-5.19
Schwertmannite (logK=18)	$Fe_8O_8(OH)_{4.5}(SO_4)_{1.75}$	-	-	-36.37	-26.13	-13.19
Scorodite	$FeAsO_4{\cdot}2H_2O$	-3.33	-2.97	-3.95	-2.63	-1.14
				Sulphate		
Arsenolite	As_2O_3	-47.02	-47.76	-47.02	-47.27	-48.06
As native	As	-73.55	-73.93	-73.56	-73.68	-74.08
$As_2O_{5(cr)}$	As_2O_5	-12.81	-13.55	-12.81	-13.06	-13.85
$As_2S_{3(am)}$	As_2S_3	-415.25	-420.81	-414.86	-417.25	-421.75
Claudetite	As_2O_3	-47.06	-47.80	-47.06	-47.31	-48.10
$Fe(OH)_{3(a)}$	$Fe(OH)_3$	-5.58	-4.93	-6.08	-4.80	-2.88
$Fe_2(SO_4)_3$	$Fe_2(SO_4)_3$	-15.32	-18.97	-15.93	-15.58	-15.55
Goethite	FeOOH	0.32	0.96	-0.19	1.09	3.01
Hematite	Fe_2O_3	2.64	3.92	1.63	4.19	8.03
JarositeH	$(H_3O)Fe_3(SO_4)_2(OH)_6$	-8.50	-9.78	-9.75	-7.34	-4.06
Jarosite-K	$KFe_3(SO_4)_2(OH)_6$	-	-	-7.50	-4.59	-0.61
Jarosite-Na	$NaFe_3(SO_4)_2(OH)_6$	-8.04	-8.37	-9.61	-6.56	-2.55
Maghemite	Fe_2O_3	-7.75	-6.47	-8.76	-6.20	-2.37
Schwertmannite (logK=10)	$Fe_8O_8(OH)_{4.5}(SO4)_{1.75}$	-25.82	-23.50	-29.63	-20.65	-7.46
Schwertmannite (logK=18)	$Fe_8O_8(OH)_{4.5}(SO_4)_{1.75}$	-33.82	-31.50	-37.63	-28.65	-15.46
Scorodite	$FeAsO_4{\cdot}2H_2O$	-3.84	-3.57	-4.34	-3.19	-1.66

Table 2. Parameters of the Langmuir isotherms obtained for As(V) sorption onto goethite as a function of pH and ionic strength.

Experimental conditions		Results		
pH_{eq}	Ionic Strength (mol dm^{-3})	K_L (dm^3 mol^{-1})	Γ_{max} (mol m^{-2})	R^2
2.30±0.15	0.02	$(9.9\pm0.4)\cdot10^{3}$	$(6.2\pm0.4)\cdot10^{-6}$	0.991
2.45±0.20	0.15	$(1.4\pm0.01)\cdot10^{4}$	$(5.7\pm0.3)\cdot10^{-6}$	0.998
1.59±0.10	0.15	$(7.3\pm0.1)\cdot10^{3}$	$(7.0\pm0.4)\cdot10^{-6}$	0.995

Table 3. Summary of experimental conditions and of As(V) removal capacities of goethite and jarosite obtained in this study and in earlier works.

	Mineral	Synthesis method	Solid concentration (gL^{-1})	[As] initial ($molL^{-1}$)	Contact time (h)	BET (m^2g^{-1})	pH	As(V) removed (mol m^{-2})
Lehmann *et al*. [13]	Goethite	*Natural*	1	$1.3\cdot10^{-4}$ to $1.3\cdot10^{-3}$	24	96	3**	$6.3\cdot10^{-6}$
Matis *et al*. [16]	Goethite	Wells [34]	1	$1.3\cdot10^{-4}$ to $1.3\cdot10^{-3}$	0.5	132	3-3.3†	$4.6\cdot10^{-6}$
Dixit and Hearing [14]	Goethite	Schwertmann&Cornwell [23]	0.5	$1\cdot10^{-5}$ to $1\cdot10^{-4}$	24	54	4†	$3.2\cdot10^{-6}$
Giménez *et al*. [17]	Goethite	*Natural*	5	$1\cdot10^{-6}$ to $3\cdot10^{-3}$	48	2	7.5†	$3.0\cdot10^{-6}$
This study	*Goethite*	Schwertmann&Cornwell [23]	2.5	$3\cdot10^{-5}$ to $1\cdot10^{-2}$	48	29	1.6†	$7.0\cdot10^{-6}$
This study	*Goethite*	Schwertmann&Cornwell [23]	2.5	$3\cdot10^{-5}$ to $1\cdot10^{-2}$	48	29	2.3†	$6.2\cdot10^{-6}$
This study	*Goethite*	Schwertmann&Cornwell [23]	2.5	$3\cdot10^{-5}$ to $1\cdot10^{-2}$	48	29	2.5†	$5.7\cdot10^{-6}$
Gräfe *et al*. [21]	Jarosite*	Sondi et al. [35]	-	$2.5\cdot10^{-4}$	336	3	5.6†	$1.4\cdot10^{-5}$
This study	*Jarosite*	Baron&Palmer [24]	2.5	$3\cdot10^{-5}$ to $1\cdot10^{-2}$	48	2	1.5-2.5†	$1.2\cdot10^{-4}$

*Na-Jarosite
** initial pH
† equilibrium pH

Table 4. Comparison of the % As(V) sorbed in the presence and absence of sulphate at pH 2 and $[As(V)]_0=1\cdot10^{-3}$ mol dm^{-3}.

	$[SO_4^{2-}]$ (mol dm^{-3})	% As sorbed
Jarosite	-	38
	0.005	4
	0.020	1
	0.280	0
Goethite	-	32
	0.005	31
	0.015	28
	0.020	25
	0.280	0