Arsenic sorption onto disordered mackinawite as a control on the mobility of arsenic in the ambient sulphidic environment

M. Wolthers, L. Charlet[1] and C.H. van der Weijden

Department of Geochemistry, Faculty of Earth Sciences, Utrecht University, P.O. Box 80021, 3508 Utrecht, The Netherlands
[1] *OSUG, Université Grenoble I, CNRS, LGIT, BP. 53, 38041 Grenoble cedex 9, France*

Abstract: Arsenate, As(V), sorption onto synthetic disordered mackinawite (FeS_{am}) follows Langmuir-type behaviour. As(V) is not reduced prior to or during sorption. Arsenite, As(III) sorption can be expressed by a Freundlich isotherm. Comparison of the experimental sorption isotherms to field data describing the mobility of arsenic in a Bangladesh aquifer shows that arsenic mobility may be controlled by As(V) sorption onto FeS_{am} in the aquifer sediment.

1. INTRODUCTION

A crucial control on the mobility and immobilisation of arsenic is sorption onto particulate phases [1], since arsenic is relatively soluble, and thus mobile, at pH values higher than 5.5 over a wide range of redox conditions. In anoxic sulphidic settings, iron(II) sulphides are ubiquitous and are likely to play such a crucial role. Disordered mackinawite, or FeS_{am}, is thought to be a major component of the acid volatile sulphide (AVS) fraction of sediments [2]. Scavenging of trace elements by FeS_{am} is an important pathway for removal of these elements from solution in anoxic environments (e.g., [3]). However, arsenic sorption onto Fe(II) sulphides has not been extensively investigated.

In reducing waters with low sulphide, S(–II), concentrations, arsenic occurs in solutions predominantly as oxyanions of As(V) or As(III). In the present study, experimentally determined sorption behaviour of As(V) and As(III) onto FeS_{am} is reported. Synthetic FeS_{am}, which was previously characterised [4,5], was used as a model solid for studying the interaction between aqueous arsenic species and FeS_{am}. The sorption isotherms of As(V) and As(III) were measured and the results were compared to field data from Harvey *et al.* [6] for a Bangladesh aquifer.

2. MATERIALS AND METHODS

Experiments were run under O_2-free conditions by directly flushing the reaction vessel with N_2 gas, which was purified by bubbling through a succession of two 15 wt.% pyrogallol in 50 wt.% KOH solutions to remove O_2, a Chrompack™ oxygen and sulphide scrubber for additional cleaning and Milli-Q™ water to saturate the N_2 with water vapour. The O_2 concentration in the reaction vessels was below 1 $\times$ 10^{-6} M (0.03 ppm), which is the detection limit of the Orion™ O_2 probe (850).

Solutions were prepared from Milli-Q™ water and purged for at least 30 minutes with O_2-free N_2 before use. The background ionic medium was 3–morpholinopropanesulphonic acid (MOPS, Merck™) pH buffer. All solutions were freshly prepared before each experiment. Stock solutions of As(III) and As(V) were prepared by dissolving $NaAsO_2$ (Fisher Chemicals™) and $Na_2HAsO_4 \cdot 7H_2O$ (Fisher Chemicals™) in Milli-Q™ water. S(–II) and Fe(II) solutions were prepared by dissolving $Na_2S \cdot 9H_2O$ (Fisher Chemicals™) or Mohr's salt ($Fe(NH_4)_2(SO_4)_2 \cdot 4H_2O$; Merck™) in the MOPS solution. Fresh

FeS$_{am}$ was synthesised *in situ* by adding 200 mL 1 × 10^{-3} M S(–II) solution to a 1 × 10^{-3} M Fe(II) solution in the reaction vessel while constantly flushing with N$_2$. Disordered mackinawite formed immediately and was left to age in the reaction vessel for one hour before experimentation started. The concentration of the *in situ* prepared FeS$_{am}$ was 0.5 × 10^{-3} M, that is ~0.044 g L^{-1}. The sorption isotherms for As(III) and As(V) were measured at in a 0.05 M MOPS buffer solution set to pH ~7.5. Known amounts of As(III) or As(V) were added to the FeS$_{am}$ suspension and left for half an hour, a time sufficient for the arsenic concentration to stabilise [4]. Aliquots were taken before the next arsenic addition and immediately filtered (0.45 μm pore diameter). The filter membrane was washed with 5 mL 6 M HCl to extract FeS$_{am}$.
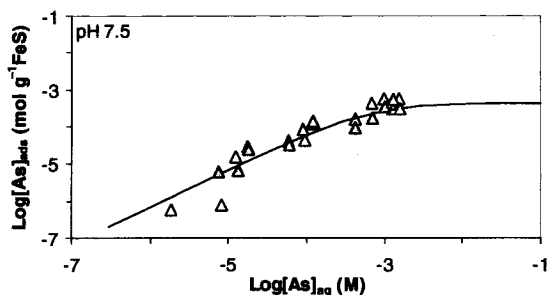

Figure 1. As(V) sorption isotherm at pH 7.5, experimental data (open and filled triangles are duplicate experiments) and model curve according to reaction (1) (full line); [FeS$_{am}$] = 5 × 10^{-4} M and [As]$_{tot}$ ≈ 3 × 10^{-5} M.
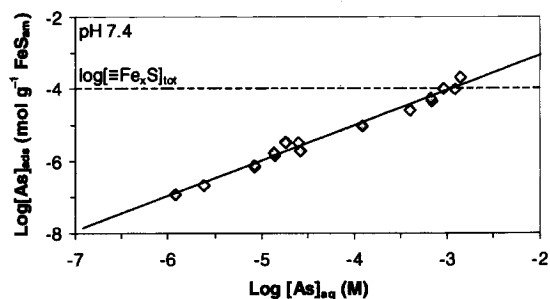
Figure 2. As(III) sorption isotherm at pH 7.4, experimental data (open and filled diamonds are duplicates), the Freundlich isotherm fit according to equation (2) (solid line) and the total concentration of surface sites [≡Fe$_x$S]$_{tot}$ (horizontal dashed line); [FeS$_{am}$] = 5 × 10^{-4} M and [As]$_{tot}$ ≈ 3 × 10^{-5} M.

Total dissolved iron in the filtrates was measured by UV-VIS [7]. Total dissolved arsenic and dissolved As(III) concentrations were determined by hydride generation AAS [4,8]. The concentration of As(V) was calculated from the difference between the total As and As(III) concentrations. Additionally, samples were routinely analysed for a range of elements including Fe and As concentrations by ICP-OES.

3. RESULTS AND DISCUSSION

3.1. As(V)

The sorption isotherm for As(V), measured at pH 7.5, is depicted as triangles in Figure 1. Initially, the slope of the isotherm is ~1, however, at higher dissolved As(V) concentrations it levels off. The isotherm can be described as a Langmuir isotherm, implying a constant sorption affinity until site-saturation is approached and one dominant type of binding site controlling As(V) sorption. The isotherm starts to level off at high As(V) concentrations, indicating saturation of the specific binding site. If sorption is monodentate and all specific sites are occupied, then the saturation concentration should indicate the concentration of the specific binding site at the surface. In fitting the Langmuir isotherm, the ≡FeSH$_2$,$^+$ concentration at pH 7.5 from the surface model proposed by Wolthers [4] was used as input. As can be seen in Figure 1, the sorption isotherm data tend to level off at this predicted site concentration. This suggests that the ≡FeSH$_2$,$^+$ site is the specific binding site for monodentate As(V) sorption, in agreement with XAS data for As(V) sorbed in crystalline mackinawite [9]. No reduction to As(III) prior to or during sorption was observed. From these observations, the following overall sorption reaction can

be proposed:

K_{ads},* $\equiv FeSH_2,^+ + AsO_3(OH)^{2-} \leftrightarrow \equiv FeS-O-As(OH)_3,^-$ (1)
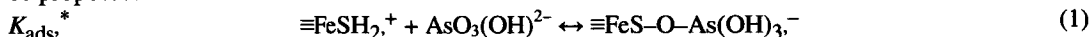
The best fit to the Langmuir sorption isotherm at pH 7.5 is acquired with a log $K_{ads},^* = +3.2 \pm 0.1$ for reaction (1).
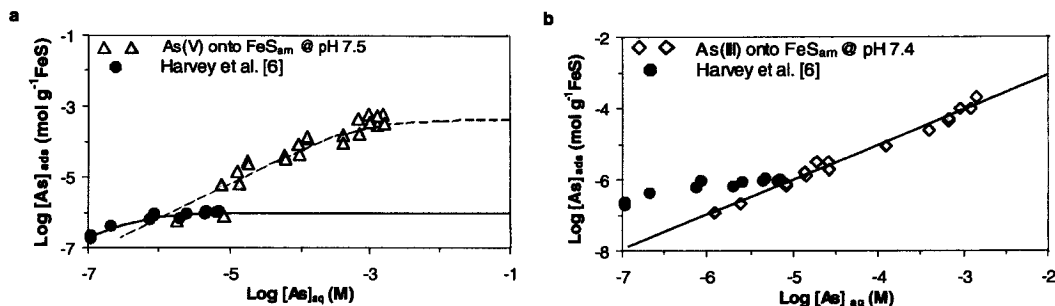

Figure 3. Data extracted from Harvey *et al.* [6] (their Figure 2c) and plotted as black circles in comparison to the experimental sorption isotherms reported here (Figures 1 and 2).

3.2. As(III)

The sorption isotherm for As(III) (diamonds in Figure 2) at pH 7.4 shows linear sorption with a slope of ~1.25. The sorption isotherm (Figure 2) can be interpreted in terms of a Freundlich isotherm. It shows no surface site saturation at high As(III) concentrations. Any of the predicted specific surface sites [4] would be saturated before the highest levels of sorbed As(III) in the experiment were reached. This implies sorption at different site types with different sorption affinities. At the highest As(III) concentrations, all sites are saturated (dashed line in Figure 2), while As(III) sorption does not tend to level off, indicating a continuum from sorption to coprecipitation, which is in agreement with the observations of Farquhar *et al.* [9].

The association of As(III) with FeS_{am} can be expressed in terms of a Freundlich isotherm, describing the relation between the As(III) concentration at the surface, $[As(III)]_{ads}$, and in solution, $[As(III)]_{aq}$:

$$[As(III)]_{ads} = 0.074[As(III)]_{aq}^{0.97}$$ (2)

This conditional Freundlich isotherm (pH 7.4) fits the sorption isotherm data with $R^2 = 0.98$ (Figure 2).

4. ARSENIC MOBILITY IN A BANGLADESH AQUIFER

Harvey *et al.* [6] studied the mobility of arsenic in relation to groundwater extraction in Bangladesh. They showed that arsenic mobilisation is associated with recent inflow of carbon into the aquifers through either organic carbon-driven reduction or displacement by carbonate. The aquifer sediment contains little, if any, purely Fe(III) oxyhydroxide. Thus, if ferric oxyhydroxides control arsenic mobility, they do so in small quantities. Despite this paucity of ferric oxyhydroxides (< 5%), they modelled the mobility of arsenic in this aquifer as a release of sorbed arsenic from ferric oxyhydroxides, induced by reduction. An alternative explanation for the mobility of arsenic in this aquifer may be found in the control by iron(II) sulphides, which form 10 to 70% of the total solid iron fraction in the sediment.

As discussed by Harvey *et al.* [6], the observed inverse relation of dissolved sulphate with arsenic in the natural groundwater, and the presence of AVS in the sediment near the dissolved As peak, suggest that arsenic is not liberated by oxidative dissolution of pyrite. However, this observation does show a correlation between arsenic mobility and the presence of iron(II) sulphides. The most reactive of the

iron(II)-sulphide fraction is AVS (e.g. [3]), the bulk of which is thought to be FeS_{am} [2]. To test a possible control of FeS_{am} on arsenic mobility in the aquifer studied by Harvey *et al.* [6], their Langmuir isotherm, derived from experimental field data (Figure 2c in [6]), is compared to the Langmuir isotherms for As(V) and As(III) sorption onto FeS_{am} reported in the present study (Figure 3). The field isotherm overlaps with the sorption isotherm for As(V) onto FeS_{am} (Figure 3a), suggesting that the total dissolved-arsenic concentration in the aquifer is controlled by As(V) sorption onto FeS_{am}. In contrast, the field isotherm does not overlap with the sorption isotherm for As(III) onto FeS_{am} (Figure 3b). In the field, more arsenic is sorbed than predicted by the As(III) isotherm. More than 90% of the dissolved arsenic in the aquifer is As(III). Possibly, the recent input of fresh, labile, organic carbon and the consequently stronger reducing conditions enhanced the otherwise slow reduction of As(V) to As(III) (cf. [10]). From the above comparison, it may be concluded that if arsenic mobility is controlled fully by sorption onto the FeS_{am}-surface, as suggested in Figure 3a, then a complete reduction of As(V) to As(III) would cause a weaker sorption and, hence, even higher concentrations of dissolved arsenic in the aquifer.

Acknowledgements

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