Microbial arsenate reduction *vs* arsenate sorption: Experiments with ferrihydrite suspensions

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The mobility of inorganic arsenic species in contaminated sediments and aquifers is mainly governed by sorption and redox processes. These processes also play an important role when judging bioavailability and toxicity of As. Numerous publications have disclosed the sorption reactions of arsenate (As(V)) and arsenite (As(III)) on ferric hydr(oxides) and its surface chemistry (e.g. Fuller *et al.*, 1993: Raven *et al.*, 1998; and ref. in both). Recent studies also have characterized several strains of bacteria which accomplish dissimilatory reduction of As(V) to As(III) (Laverman *et al.*, 1995 and ref. therein) and have documented its importance in the biogeochemical cycle of dissolved arsenic occurring in anoxic sediments (Ahmann *et al.*, 1997 and ref. therein).

However, the question remains to whether arsenate bound to solid phases (sorbed, co-precipitated) is also available for dissimilatory activities of these bacteria. The present laboratory study addresses this question and the reaction mechanism of the overall reduction.

Material and methods

2-line ferrihydrite (Fehy) and ferrihydrite co-precipitated with As(V) was synthesized and aged according to Fuller *et al.* (1993) using ferric chloride instead of ferric nitrate. Washed cell suspensions of *Sulfurospirillum barnesii* strain SES-3 (bac) were prepared according to Laverman *et al.* (1995).

The reaction mixture of 70 ml in a serum bottle consisted of: Ferrihydrite suspension (5 mM as Fe), washed cell suspension of SES-3 (~ 10^9 cells/ml), sodium arsenate either dissolved (1 mM, As(V) start) or presorbed on Fehy (As(V) pres, 0.8 mM) or co-precipitated with Fehy (As(V) copr, 1.0 mM), sodium lactate (lac, 1 mM), HEPES pH buffer 7.3 (5 mM), calcium, magnesium and sodium chloride (0.5, 0.5, 5 mM, respectively). No phosphate or other nutrients were added. All manipulations were performed in an anoxic glove box. Bottles were continuously shaken (250 rpm) at 25°C. Aliquots were sampled in progressively longer time intervals and analysed for: Dissolved (filtered 0.2 μm) As(V) and As(III), in some experiments, also As(V) and As(III) bound to Fehy (centrifuged pellet dissolved in 5 M HCl), lac and acetate (ac) as the degradation product of lac, all by HPLC; Fe(II) (desorbed in 0.5 M HCl) by colorimetry (ferrozine); Partly, total As and Fe sorbed by ICP-AES. In addition microbial and chemical control experiments were run, also in duplicates.
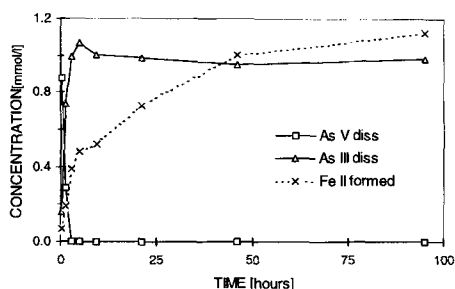

FIG. 1. Changes in concentrations during the bacterial reduction of dissolved arsenate and particulate ferrihydrite in separate experiments.
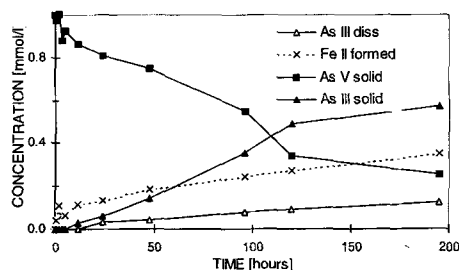

FIG. 2. Changes of concentrations in the suspension of arsenate co-precipitated with ferrihydrite caused by bacterial reduction.
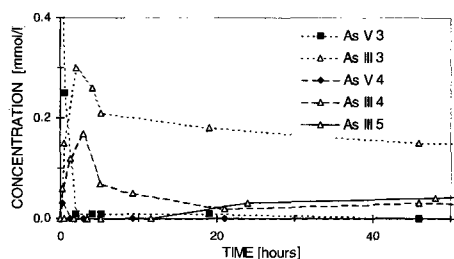
FIG. 3. Concentration changes of dissolved Arsenic species during bacterial reduction of arsenate bound to ferrihydrite. 3: As(V) sorbed (added at the start), 4: As(V) presorbed 1 day, 5: As(V) co-precipitated.

Results and discussion

The stoichiometric reduction of dissolved As(V) to As(III) by SES-3 in absence of Fehy proceeded within a few hours (Fig. 1). The rate of formation for Fe(II), the product of reduction of particulate ferrihydrite alone, was distinctly slower than that observed for As(V) reduction, probably caused by the limited bioavailability of Fe(III) in the Fehy matrix. The stoichiometric relationship in the As(V) reduction also implies that no further reduction of As(III) to As (0) or As(-III) occurred.

Bacterial reduction of coprecipitated As(V) was evident (Fig. 2), although its rate was about 100- fold slower than for dissolved As(V) alone. After 8 days about 2/3 of the added As(V) bound to Fehy was reduced to As(III), of which about 20% was dissolved and the remainder was bound to the solid phase. During the experiment dissolved As(V) was not detectable (<0.04 mM) and the sum of all As species remained constant within the analytical deviation. The Fe(II) evolved by microbial reduction of Fehy amounted to about half of the quantity of As(V) co-precipitated reduced.

In an experiment with As(V) presorbed (0.8 mM) onto Fehy about 80% of the As(V) was reduced to As(III) of which most was sorbed to Fehy (data not shown). In this incubation Fe(II) evolved at a similar rate and amount as shown in Fig. 1.

The kind of the As(V) bound to Fehy, either sorbed after start, 1 day presorbed or co-precipitated influences the evolution of dissolved As(III) (Fig. 3). In the cases with dissolved As(V) added initially and As(V) presorbed onto Fehy a distinct peak of dissolved As(III) was observed within few hours followed by a slow decrease. A similar decrease was also observed in the As(III) sorption control experiment without bacteria, see below. However, in the experiment with As(V) co-precipitated,

dissolved As(III) only evolves slowly and increases steadily over several days. This change in sorption behaviour of As(III) could indicate that surface properties of Fehy have altered in this experiment, especially with respect to its ability to sorb As(III).

In a sterile control experiment, in which dissolved Fe(II) and As(V) were added to Fehy co-precipitated with As(V), no As(III) was detected (< 0.02 mM) either in solution or on the solid phase over the 8 days and all As(V) remained bound to the Fehy (not shown). This result indicates clearly that under the prevailing experimental conditions and in the pH range of 7, no measurable abiotic (e.g. chemical) reduction of As(V) by Fe(II) occurred, even though Fe(II) sorbed onto Fehy represents a strong reducing agent.

When As(III) (1 mM) was added to Fehy with As(V) already presorbed or co-precipitated, nearly half of the amount added still sorbs onto Fehy, although at a much slower rate than reported by Raven et al. (1998). The concentration of dissolved As(V) did not change. Therefore these control experiments (data not shown) indicated that there were still sorption sites available on the surface of Fehy.

Conclusion

The results of this study clearly reveal, that as an overall process, arsenate bound to ferrihydrite can only be reduced by bacterial activity. However, reduction of As(V) bound to Fe(III) hydr(oxides) proceeds at a much slower rate than does that for dissolved As(V). Concerning the reaction mechanism, it could mean, that it is not necessary for arsenate to be first detached from ferrihydrite in order to be available for microbial reduction. Not so clear is the role of the concurrent reduction of ferrihydrite. It may be an independent process which does not directly influence As(V) reduction. Although it could be argued that surface groups of ferrihydrite must be reduced first before arsenate detaches into solution where it is subsequently reduced by bacteria. However, in the case of As(V) co-precipitated, the Fe(II) released only amounted to half of the As(V) reduced, which suggests that a hypothetically preceding reduction step of Fe(II) cannot account for all the As(V) reduced. Further work addressing the reaction mechanism question is needed.

References

Ahmann, D., Krumholz, L.R., Hemond, H.F., Lovley, D.R. and Morel, F.M.M. (1997) Environ. Sci. Technol., 31, 2923–30.