

Experimental study of arsenite adsorption to goethite

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The present report is part of a series of adsorption studies of various As compounds to the iron(III) oxyhydroxide goethite. The goal of these studies was to obtain a consistent set of experimental data covering a range of conditions (such as As/goethite ratio or ionic strength at variable pH), which should be apt to testing surface complexation models. Arsenite is interesting in this respect because over a wide range of pH it exists as H_3AsO_3 . Modelling often requires a range of surface species, but such a range is difficult to justify in cases such as arsenite, i.e. protonation of H_3AsO_3 is not expected. The prospective modelling is also constrained by the use of different experimental methods (see Experimental section): in particular uptake data were obtained for As and H over a range of As/goethite ratios, whereas most conventional studies involve uptake data only.

Experimental section

Goethite was prepared as described in detail elsewhere (1). Arsenite adsorption to goethite was studied by potentiometric titrations, pH-stat measurements and in batch uptake experiments. The arsenite stock solution was standardized by potentiometric titration. The concentrations of proton active sites of goethite was determined by titration with excess acid as described previously (1). Since it has been reported that arsenite stock solutions can be (partly) oxidized to arsenate, special care was taken to avoid

such reactions. The stock solution was always filled up with a layer of argon (purged through appropriate washing bottles). The stock solution was also titrated in regular intervals over the whole period it was used. During the whole period no oxidation of arsenite could be detected in the titrations. All measurements were done in NaCl media (usually 0.1 M but also in 0.6 M). The free proton concentration (i.e. $pH = -\log[H^+]$) is given in all the results, since calibration was always done on the concentration scale. Arsenite was measured by ICP-AES. The arsenite to goethite ratio is symbolized by R, which is the ratio between total concentration of arsenite and the total concentration of proton active surface sites. The proton uptake data obtained from acid-base titrations and the pH stat experiments are given as Z curves, where Z is defined as the amount of protons reacted per proton active surface site.

Results and discussion

Figure 1 shows the uptake of arsenite at three different values of R. Even below $R = 1$, <100 % arsenite uptake is observed, indicating that the affinity of arsenite to (proton active sites of) goethite is lower compared to arsenate, which behaves in a similar fashion to phosphate (Lützenkirchen and Lövgren, unpublished results). The uptake curves are compatible with previous reports in that decrease

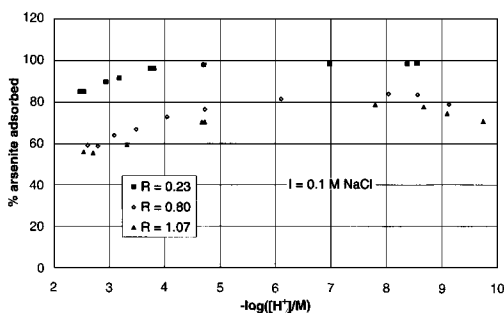


FIG. 1. Adsorption of Arsenite to goethite as a function of Ph at different values of R (=TOTAs/sites).

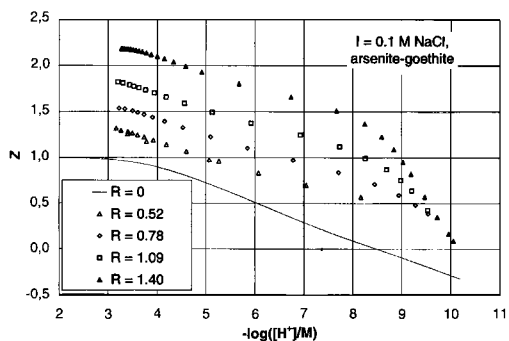


FIG. 2. Z as a function of Ph at different values of R for the arsenite/goethite system.

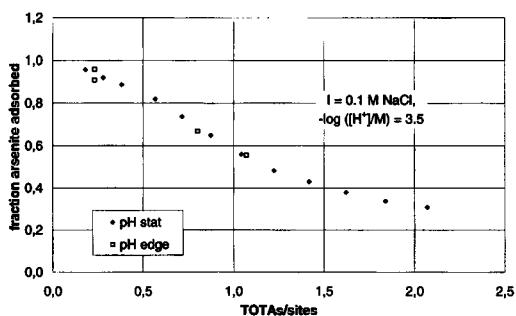


FIG 3a. Adsorption of arsenite to goethite at Ph = 3.5 as a function of R. Data labelled pH edge correspond to those reported in Fig. 1.

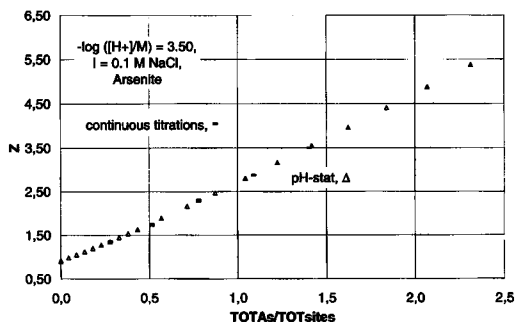


FIG. 3b. Z as a function of R for the arsenite/goethite system at Ph = 3.5. Data labelled continuous titrations correspond to those reported in Fig. 2.

at low pH and high pH occurs.

Figure 2 shows titration curves of goethite in the absence and presence of arsenite. The titrations were fully reversible. The results of the different titrations appear to coincide at high pH, where desorption of arsenite is expected. It was somewhat surprising that at low pH the equilibration criteria were very quickly fulfilled, although in this region desorption of arsenite occurs (Fig. 1). This might indicate either that arsenite adsorption takes part (partly) on sites that are not proton active or that arsenite is not very tightly bound to goethite. Both arguments can in principle be supported by the results presented in Fig. 1.

Figure 3a shows a comparison between arsenite uptake obtained in a pH stat experiment (at pH 3.5) and the results from Fig. 1. Figure 3b shows a similar comparison for the Z values obtained in the pH stat measurements and the results obtained in the continuous titrations. It is obvious that there is a very good agreement between the independent measurements, indicating that the obtained data can

hardly be questioned and can be used for modelling exercises using some surface complexation model.

Figure 4 shows the uptake of arsenite for similar values of R at different values of ionic strength. It is apparent that in the way data are treated in this case, a lower value of R at higher ionic strength results in decreased uptake. This is an indication for relatively weak bonding for arsenite to goethite.

Summary

The experimental results presented indicate that a reliable data set for arsenite adsorption to goethite has been obtained. The data show that arsenite is relatively weakly bound to goethite, when compared, e.g. to arsenate, which is manifested by <100% uptake of arsenite for cases where the arsenite to proton active site ration is <1 and through a decrease in arsenite adsorption on increase in ionic strength. The first point could also be explained by the adsorption of arsenite to surface sites that are not proton active.

References

- Lövgren, L., Sjöberg, S. and Schindler, P.W. (1990) *Geochim. Cosmochim. Acta*, **54**, 1301–6.

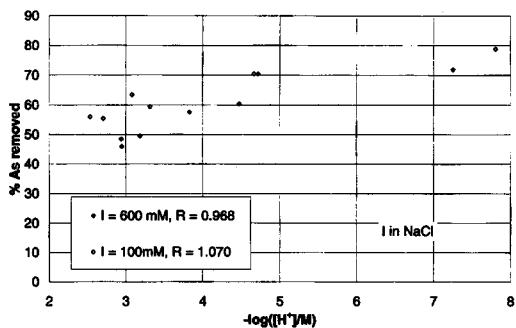


FIG. 4. Adsorption of arsenite to goethite as a function of Ph for different values at similar values for R.