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As(V) retention mechanisms onto iron oxides: from the laboratory to the field

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Arsenic is a toxic element originating from both natural and anthropogenic sources. Under surficial conditions, arsenic behaviour is mostly driven by precipitation, metabolic reactions within living organisms and surface reactions on minerals, especially iron oxides. Although several studies have addressed the local environment of As in synthetic As-doped iron oxides a controversy still remains concerning the nature of the As-Fe-oxides complexes and their reactivity, as a function of the oxidation state of arsenic and the nature of the mineral surface. These information are particularly important to understand and predict the mobility of As in contaminated soils and sediments.

In order to improve our knowledge of these complex reactions and to check for their relevancy towards natural systems, a set of natural soil samples have been compared with synthetic model compounds, including As(V) sorbed onto - and co-precipitated with -2Lines-ferrihydrite with various Fe/As ratios. EXAFS analysis revealed that the second neighbour contribution around As(V) is fitted by a dominant As-Fe contribution at 3.30 Å and a minor As-Fe at 2.90 Å. These distances correspond to arsenates linked to iron octaetra by double-corner sharing and edge-sharing respectively. Similar As-Fe contributions have been observed in several soil samples collected on heavily contaminated sites and geochemical anomalies from the Massif Central (France) [1]. These spectroscopic data attest for the importance of As sorption/co-precipitation processes in limiting As mobility in soil surface horizons provided the persistence of slightly acidic and oxidizing soil conditions.

References

- [1] Morin G., Lecoq D., Juillot F., Calas G. and Ildefonse P. (2002) EXAFS evidence of sorbed arsenic(V) and pharmacosiderite in a soil overlying the Echassieres geochemical anomaly, Allier, France. *Bulletin de la Société Géologique de France* **173**, 281-291.

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Catalyzed oxidation of arsenic(III) by hydrogen peroxide on the surface of ferrihydrite

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Knowledge of the redox kinetics of arsenic is crucial for understanding the impact and fate of As in the environment or for optimizing As removal from drinking water. Rapid oxidation of As(III) adsorbed to ferrihydrite (FH) in the presence of hydrogen peroxide (H₂O₂) might be expected for two reasons: Firstly, adsorbed As(III) is assumed to be oxidized more readily than the undissociated species in solution. Secondly, catalyzed decomposition of H₂O₂ on the FH surface might also lead to As(III) oxidation. In this study, attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) was used to monitor the oxidation of adsorbed As(III) on the FH surface in situ [1].

ATR-FTIR allowed to clearly distinguish between adsorbed As(III) and As(V). Upon adsorption of As(III) onto FH, no oxidation within minutes to hours was observed prior to the addition of H₂O₂. After H₂O₂ addition, the appearance of adsorbed As(V) on the FH surface could be followed in situ. Initial pseudo-first-order oxidation rate coefficients for adsorbed As(III), determined at H₂O₂ concentrations from 8.4 μM to 8.4 mM and pH values from 4 to 8, increased with the H₂O₂ concentration according to $\log k_{ox} (\text{min}^{-1}) = 0.17 + 0.50 \log [\text{H}_2\text{O}_2] (\text{mol/L})$ (n=21, r²=0.87).

Only a weak pH-dependence of the $\log k_{ox}$ was found (~0.04 log units increase per pH-unit). ATR-FTIR experiments with As(III) adsorbed onto amorphous Al hydroxide showed that Fe was necessary to induce the As(III) oxidation by catalytic H₂O₂ decomposition.

The results from this study indicate that the catalyzed oxidation of As(III) by H₂O₂ on the surface of iron (hydr)oxides may be a relevant reaction pathway in environmental systems such as surface waters as well as in engineered systems for As removal from water.

Reference

- [1] Voegelin A. and Hug S. J. (2003) *ES&T* **37**, 972-978.