Arsenic speciation and mobility in contaminated soils: Comparison of column and batch extraction experiments

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Aims

The chemical behavior of arsenic (As) in soils is dependant on a variety factors. These involve soil characteristics as well as its chemistry (e.g. pH, Eh, phosphate concentration, etc). The aims of this study are to understand the behaviour of As and the precise mechanisms involve in its mobility within two historically polluted industrial sites. To this end, an overall methodological approach was constructed: (1) a highly detailed characterization in arsenic pollution determined by an arsenic speciation made by a variety of techniques (2) mobility tests with static studies (single batch extractions) and dynamic studies (columns experiments). These leaching experiments were done by varying the pH and phosphate concentrations. The remobilization kinetics of As, inherent to column experiments, were also investigated in a series of single batch tests with varying extraction times.

Results and discussion

In the three soils studied, As was mainly present as arsenate (between 92 to 100% of total As) and arsenite was the other As species detected. No arsenic crystalline phases were identified. SEM-EDS investigations showed an arsenic/iron association; this was confirmed by the sequential extractions experiments which also suggested an As association with amorphous iron oxides. This pollution characterization shows As as being potentially labile by reductive dissolution of iron oxides.

Concerning mobility tests; despite the given extraction conditions (pH or phosphates concentrations), dynamic tests led to an arsenic remobilization which was much more important than the semi-equilibrium leaching test batches; this remobilization could reach, in the alkaline medium (pH 11), 78% of total As, by the end of the experimentation. These mobility experiments also provided information about As release mechanisms in such specific conditions.

Improved thermodynamic equilibrium constants of phosphate adsorption onto HFO

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Phosphate released via fertilizer overuse and sewage disposal causes widespread eutrofication of freshwater systems and may promote desorption and release of other oxyanions (arsenate, chromate) adsorbed onto sedimentary hydrous ferric oxide (HFO) and other minerals. Understanding these processes requires accurate data that quantify the pertinent equilibrium surface complexation reactions.

In this study we have carried out batch experiments measuring phosphate adsorption onto HFO as a function of pH, phosphate concentration, ambient CO_2 and ionic strength in $NaNO_3$ electrolyte at 25° C. The results were used to constrain mass law and mass action parameters for PO_4^{3-}, HPO_4^{2-}, and $H_2PO_4^-$ adsorption onto HFO according to a double-layer model formulation. Our optimal values for equilibrium constants of the following reactions,

K1: $XOH + H_2PO_4^- + H^+ <==> X\text{-}H_2PO_4 + H_2O$
K2: $XOH + H_2PO_4^- <==> X\text{-}HPO_4^- + H_2O$
K3: $XOH + H_2PO_4^- <==> X\text{-}PO_4^{-2} + H_2O + H^+$

where XOH denotes the hydroxyl group on HFO, are listed below:

	DM90	1 σ unc.	This study	1 σ unc.
Log K1	18.981	-	19.0	0.33
Log K2	13.081	0.044	14.1	0.75
Log K3	5.411	0.101	8.3	0.39

These improved values principally differ from those of DM90 in the K3 reaction, which our results constrain as three orders of magnitude more stable. Our values were constrained using a larger dataset than that used by DM90 and therefore should better describe phosphate-HFO adsorption over a wider range of systems compositions.

Reference

DM90: Dzombak D. A. and Morel F. M. M. (1990) Surface Complexation Modeling: Hydrous Ferric Oxide, Wiley-Interscience, New York.