

Hydrous ferric oxide nanoparticles – Structural reordering in response to surface sorption of Al-hydroxy species

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To explore the influence of a sorbate on the structural evolution of freshly precipitated ferrihydrite in the aqueous environment, experiments were conducted in a Fe/Al oxyhydroxy system. Al-hydroxyde coated ferrihydrite nuclei were prepared by forced hydrolysis of acid solutions containing varying ratios of Fe- and Al- nitrates. Equivalence points of the titration curves showed that pure Fe- respectively Al-(oxy)hydroxides formed, indicating that no significant Fe by Al substitution had taken place initially. The dried products, analysed by Raman spectroscopy showed indeed the presence of Fe- and Al-oxyhydroxides in all samples, but they also showed that the Fe phase evolves from a 2-line ferrihydrite in the absence of Al to a disordered akaganetite when Al increases in the synthesis system. These observations were confirmed by EXAFS spectra at the Fe K-edge. The change in structure seems to be caused by increasing amounts of Al substituting for Fe, as is suggested by a concomitant decrease of Fe atoms in the local environment around Fe. The XANES spectra at the Al K-edge also varied with Al concentrations, and supported the substitution hypothesis. To reconcile the results from titration experiments with those of the spectroscopic analyses, it must be concluded that Al substitution occurred after precipitation of ferrihydrite, most probably during a 15 hours period of equilibration at neutral pH allowed after hydrolysis. The results high light the dynamic interactions that may occur between sorbates and weakly ordered nano-size particles.

Nanoparticle facilitated transport of organic contaminants

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Naturally occurring nanoparticles (NP) are capable to enhance the transport of hydrophobic organic contaminants (HOCs) in porous media. Since HOC bind strongly to carbonaceous ENP the recent debate on the environmental impact of engineered nanoparticles (ENP) has become increasingly important. Carbonaceous ENP may act as carriers for contaminant transport and might be important when compared to existing transport processes. ENP bound transport is strongly linked to the sorption behavior, and other carbonaceous ENP-specific properties. In our analysis the HOC-ENP sorption mechanism, as well as ENP size and ENP residence time, were of major importance. Our results show that depending on ENP size, sorption kinetics and residence time in the system, the ENP bound transport can be estimated either as (1) negligible, (2) enhancing contaminant transport, or (3) should be assessed by reactive transport modeling.

The obtained results allow us to conclude that the importance of ENP mobility for contaminant transport in soils and aquifers is scaled according to two parameters, the affinity of the HOC to the ENP and the desorption kinetics of the HOC from the ENP. These parameters can be determined by standardized laboratory experiments and should be included in risk assessment frameworks. To obtain a realistic estimate of ENP carrier properties for HOC it is important to know if the system reacts under equilibrium conditions or if the desorption is extremely slow due to high affinity sites or trapping into aggregates. The model results show that under equilibrium conditions the contribution of ENP to the transport process is negligible. It is also shown that in instances where desorption is very slow or inexistent the ENP mobility and apparent concentration becomes increasingly important. A worst-case scenario, using an unrestricted ENP mobility and high ENP concentrations, may produce too high estimates for the ENP contribution to the HOC transport. In these cases, ENP mobility in the porous media should be investigated under the local hydrochemical conditions on a case-by-case basis.