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Colloid generation from ferrihydrite macroaggregates by organic compounds enhances microbial reduction rates

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Microbial iron reduction is a major process in groundwater ecosystems and often associated with the degradation of organic contaminants. Yet, the high crystallinity and low solubility of iron oxides imposes only slow reduction rates. In contrast, natural iron oxide colloids are highly reactive due to the large specific surface area and their association with natural organic matter.

The objective of this work was to assess the reactivity of natural ferrihydrite colloids, and to quantify the influence of organic molecules on their stability and reactivity. As reference, abiotic experiments with synthetic ferrihydrite nano- and macroaggregates and different concentrations of humic acids or Na-citrate were performed. By this, the impact of steric repulsion on colloid stability and generation was evaluated. Additionally, the reactivity of the natural colloids was compared with synthetic ferrihydrite colloids and macroaggregates in anaerobic reduction experiments with G. sulfurreducens.

The rate of microbial reduction of natural colloids (50.9 μM h-1) was two orders of magnitude higher than compared to pure synthetic ferrihydrite colloids (0.8 μM h-1). When synthetic colloidal ferrihydrite was coprecipitated with citrate during synthesis, the iron reduction was accelerated to rates in the range of natural colloids (12.1 μM h-1). Low reduction rates of pure ferrihydrite colloids were attributed to the fast aggregation and loss of colloidal properties. Adsorption of natural humic acids (HAs) on the ferrihydrite surface with an Fe:HA (m/m) ratio of 5.6 stabilized colloids against aggregation. Furthermore, abiotic incubation with ferrihydrite macroaggregates and Na-citrate proved the partial disintegration of ferrihydrite due to the chelation of ferric iron. The production of colloids from the macroaggregates was also confirmed by intensities from dynamic light scattering. We explain this observation with the steric repulsion between the organic molecules. This colloid generation and chelation of ferric iron led to a 7-fold increase of microbial reduction rates.

We conclude that steric stabilization of colloidal ferrihydrite by organic acids and a possible colloid production from corresponding macroaggregates strongly enhances microbial iron oxide reduction. Chelation of iron and steric stabilization of ferrihydrite nanoaggregates might play a significant role in electron transfer processes in anoxic ecosystems.