

Report as of FY2006 for 2006KY70B: "Nitrate and Nitrite Transformation by Fe(II) adsorbed on Kaolinite"

Publications

- Dissertations:
 - Rakshit, Sudipta, 2006, Abiotic Interactions of Iron (II) Species with Nitrate and Nitrite, Ph.D. Dissertation, Plant and Soil Science Department, University of Kentucky, Lexington, Kentucky, 73 p.
- Conference Proceedings:
 - Rakshit, Supdipta and Christopher J, Mothocha, 2007, Nitrite Reductions by Fe (II) Associated with Kaolinite, in Proceedings of the Kentucky Water Resources Annual Symposium, Kentucky Water Resources Research Institute, Lexington, Kentucky, p 89-90.

Report Follows

Problem and Research Objectives

The microbial reduction of solid Fe(III) hydr(oxide) minerals by iron reducing bacteria is an important process in biogeochemical cycling of nutrients and trace metal contaminants. The presence of nitrate (NO_3^-) can inhibit the net Fe(III) reduction to Fe(II) under anoxic conditions. There are several mechanisms proposed to explain such phenomena.¹ One proposed mechanism involves simultaneous NO_3^- and Fe(III) reduction coupled to chemical reoxidation of Fe(II) to Fe(III) by nitrite (NO_2^-), the intermediate of NO_3^- reduction. Several researchers hypothesized this pathway both in agricultural soil slurries and pure cultures.²⁻⁴ A majority of the Fe(II) produced during microbial Fe(III) reduction exists in precipitated or sorbed forms.^{5,6} In fact, Kukkadapu et al. (2001) reported that in Fe(III) oxide-rich subsoils with mixed mineralogy, dissolved biogenic Fe(II) adsorbed strongly to kaolinite. Accordingly, the objective of this study was to investigate the role of Fe(II) associated with kaolinite in the reduction of NO_2^- .

Methodology

Reference Georgia kaolinite (KGa-1b, Clay Minerals Repository, University of Missouri) was purchased and sieved to $<45 \mu\text{m}$ fraction size. The mineral was characterized by x-ray diffraction, total surface area, surface charge, optical spectroscopy (UV-VIS-NIR), and chemical extractions. The chemical extractions were performed using 0.5 and 6.0 mol/L HCl. Stirred-batch experiments were conducted in an anaerobic chamber under argon to simulate Fe(III)-reducing conditions. The following treatments were implemented: 1) Solution Fe(II)- NO_2^- , 2) Fe(II)-kaolinite- NO_2^- , 3) Control (kaolinite- NO_2^-), and 4) Blank (NO_2^- alone). All experiments contained 120 m^2 kaolinite L^{-1} , initial NO_2^- level of 0.45 mmol L^{-1} , Fe(II) concentration of $25 \mu\text{mol L}^{-1}$, and pH 6. Parallel experiments were conducted where nitrous oxide (N_2O) gas was measured in the headspace of Fe(II)-kaolinite- NO_2^- slurries. Gas chromatography was employed to quantify N_2O using a thermal conductivity detector. At pre-selected time points, suspensions were filtered through a $0.2 \mu\text{m}$ membrane filter paper. Solution NO_2^- and Fe(II) concentrations were measured by ion chromatography and optical spectroscopy, respectively. Total Fe was quantified by flame atomic absorption spectrophotometry.

Principal Findings and Significance

Nitrite was reduced rapidly by Fe(II) associated with kaolinite when compared with solutions devoid of kaolinite. The NO_2^- reduction rate was roughly sixteen-fold greater by Fe(II)-kaolinite when compared to solution Fe(II). One of the major products of NO_2^- reduction was N_2O , an important greenhouse gas. In the process, Fe(II) was reoxidized to Fe(III). In addition, it was found that NO_2^- was reduced by the control (kaolinite-alone) with no added Fe(II). Further experiments revealed the presence of Fe(II) and Fe(III) impurities in kaolinite which participated in NO_2^- reduction. This supports the chemical reoxidation pathway of Fe(II) by NO_2^- in contributing to the inhibition of Fe(III) reduction. Further experiments will be conducted to better understand the mechanism of the electron transfer process between NO_2^- and adsorbed Fe(II). Stimulating Fe(III) reduction to produce reactive Fe(II) species may be a useful

strategy to remove NO_3^- from water supplies. This research is timely given the desire to protect water resources from elevated NO_3^- levels.

References

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