

***In situ* Immobilization of Redox Sensitive Contaminants**

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¹Abstract: Laboratory column experiments were conducted to determine microbiological reduction of Cr(VI) with a facultative anaerobe *Shewanella alga* Simidu (BrY-MT), and included both columns packed with pyrolusite (β -MnO₂) coated-sand, and uncoated-sand. In concurrence with these experiments, a mathematical model has been developed to quantitatively identify coupled processes that control chromium transport and geochemical-microbiological reactions. Calculations of this model were also compared to data collected from the column experiments. Results obtained from the column experiments with Cr(VI)-containing influent solutions demonstrate that BrY-MT effectively reduces Cr(VI) to less toxic Cr(III) even in presence of strong oxidizing agent, β -MnO₂-coated sand. The experimental results show that Cr(VI) reduction by BrY-MT is strongly influenced by the presence of β -MnO₂-coated sand. Reduction of Cr(VI) is faster in pure quartz sand than in quartz sand coated with β -MnO₂.

Contamination of groundwater and soil by redox-sensitive contaminants has gained importance in recent studies (Saiers et al. 2000, Guha et al. 2001a and b). Many redox sensitive contaminants like chromium (Cr), cobaltEDTA (CoEDTA), and uranium (U) transport in the subsurface is dependent on the pH of the pore water and soil chemistry. The transport of Cr in the subsurface at many of the U.S. Department of Energy facilities is influenced by hydrological, geochemical, and microbiological processes. No studies to date have focused on coupled hydrological, geochemical, and microbiological processes affecting Cr transport, either in laboratory column or in field-scale experiment. The successful use of microorganisms for *in situ* stabilization of contaminants requires an understanding of coupled flow, transport, and reaction processes that control their growth and distribution in porous media. In order to better understand these hydrobiogeochemical systems attempts have been made to simulate subsurface conditions in laboratory column experiments.

Results of the experiments conducted with columns packed with pure quartz sand (Figure 1) indicate a relatively instantaneous reduction of Cr(VI) within a time interval of 2 hours, as compared to columns packed with β -MnO₂-coated sand (Figure 2) where delayed reduction of Cr(VI) occurred after 57 hours. This delayed reduction of Cr(VI) by BrY-MT is due to the strong oxidizing agent β -MnO₂. Separate column experiments

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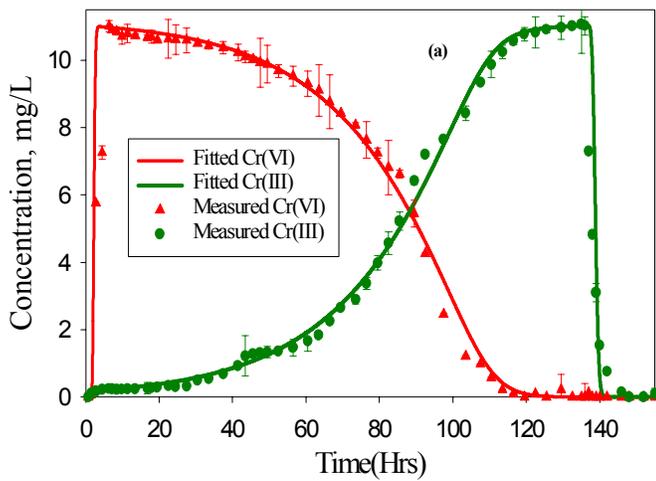


Figure 1: Chromium (VI) reduction by BrY in **absence** of Mn-oxides.

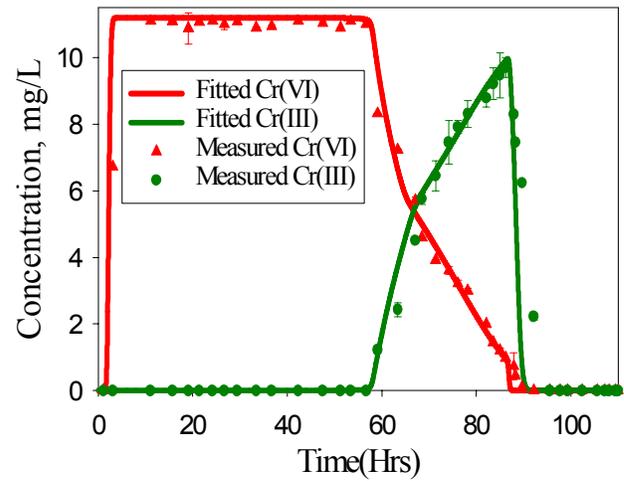


Figure 2: Chromium (VI) reduction by BrY in **presence** of Mn-oxides

conducted under anaerobic conditions with column packed with β -MnO₂-coated sand and in absence of BrY-MT showed sustained oxidation of Cr(III) by the Mn(IV)-oxides.

The experimental results also suggest that there is an initial reduction of Cr(VI) by BrY-MT, even in β -MnO₂-coated sand, but the Cr(VI) reduced is instantaneously oxidized by the presence of β -MnO₂. Furthermore, this implies that the rate of oxidation was faster compared to the rate of reduction, and the initial amount of biomass attached to the β -MnO₂-coated sand was not sufficient to optimize bacterial reduction of Cr(VI) over geochemical oxidation by β -MnO₂. This is evident from: (1) the longer time period of reduction (i.e. 57 hours), (2) that the biomass observed in the eluant was same as that in the uncoated sand (quartz sand). With time, the bacterial population dramatically increased, which was sufficient for sustained bacterial reduction.

The microbiological parameters (specific growth rate (μ) and yield coefficient (Y)) were independently estimated from separate batch experiments with quartz sand and β -MnO₂ coated sand; the standard errors of the parameter estimates were less than 15% of the mean value of the parameters. The attachment/detachment rates as well as the dispersivity rates of the bacteria in quartz sand and β -MnO₂-coated sand were also independently estimated from separate column experiments. Similar independent column experiments were conducted to estimate the adsorption/desorption and dispersivity rates of lactate in both quartz sand and β -MnO₂-coated sand. Likewise, the model closely simulated the data obtained from the batch and column experiments. The microbiological parameters, μ and Y , were both slightly larger in batch experiments conducted with β -MnO₂ coated sand than those obtained with pure quartz sand.

The hypothesis on which the model was based closely mimicked the experimental results, which confirm that non-linear reactions control Cr(III) oxidation, while dual-monod kinetic approach for bacteria controls the reduction of Cr(VI). Thus, the resulting appropriate mathematical model that has been developed takes into consideration the

relevant geochemical and microbiological kinetic processes that control the transport of Cr, bacteria, and the lactate (electron donor) in the subsurface. Cr(III) oxidation is very rapid, i.e. within a minute, but the reaction rate decreases once MnOOH precipitate covers the β -MnO₂ coated surface. The insoluble MnOOH acts as a blocking agent preventing further Cr(III) oxidation. The dependence of Cr(III) oxidation rates on MnOOH concentrations has also been quantified in terms of a Langmuir-type blocking function, which describe the linear decline in Cr(III) reaction rates with increasing MnOOH concentrations. The microbiological mathematical model was based on an appropriate assumption suitable for the subsurface conditions, where bacterial colonies were randomly attached to the solid surface with some bacteria freely floating in the bulk liquid.

Data obtained from laboratory investigations demonstrated that the interaction of Cr(III) with the subsurface soil and aquifer materials results in the oxidation of Cr(III) species to the highly stable and mobile Cr(VI). The dynamic column experiments of the present work explicitly demonstrate that dissimilatory metal reducing bacteria can be effective in reducing redox-sensitive metals. Such is the case with the bacterial strain BrY-MT, which is effective in reducing Cr(VI) to less toxic and immobile Cr(III), even in the presence of a strong oxidant like β -MnO₂. As demonstrated in the experimental results of the present work, understanding of these interactions is crucial to successful prediction of redox-sensitive metal transport through geologic media, which will require development of a mathematical model such that it accounts for the coupled hydrological and biogeochemical processes.

The results of this work supplement the severely limited database on the transport of Cr, and provide a means for quantifying the coupled hydrological, geochemical, and microbiological processes that contribute to the phenomenon. The outcome of this research will be directly applicable at various DOE sites, where *in situ* stabilization of redox sensitive contaminants is of priority concern.

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