Role of humic substances in metal compexation, reduction and reoxidation processes

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Humic substances are known to be complex in nature with varying structural and functional characteristics, and their effect on biological reduction and oxidation of metals such as uranium(VI) and Fe(III) is not fully understood.. In this study, various humic materials and/or subfractions were charatcterized by both wet-chemical and spectroscopic analyses such as ¹³C-nuclear magnetic resonance (NMR) and Fourier-transform infrared (FTIR) spectroscopy. The role of humic materials in enhancing the biological reduction of Fe(III) and U(VI) was evalauted in both laboratory batch kinetic studies and field push-pull tests. Results indicate that, in the presence of the dissimilatory metal reducing bacterium Shewanella putrefaciens CN32, all humic mateirals were able to enhance the reduction of Fe(III) and U(VI) under anaerobic, circumneutral pH conditions. The presence of humic materials enhanced the U(VI) reduction rates (up to ~10 fold) and alleviate the toxicity effect of Ni²⁺ to microorganisms. Such an enhancement effect is attributed to the ability of these humics in facilitating electron transfer reactions and in complexing toxic Ni²⁺ ions. Among various humic materials, soil humic acid was found to be particularly effective in mediating the biological reduction of Fe(III) and U(VI) as compared with the fulvic acid and other humic fractions with relatively low aromatic contents. These results suggest that, depending on chemical and structural properties, different NOM components may play different roles in enhancing the biological reduction of Fe(III) and U(VI). Polycondensed aromatic humic acids may be particularly useful in mediating the biological reduction of these metals in soil.

Of particular interest of these findings is the possibility that humic-mediated bioreduction of contaminants such as U(VI) can lead to immobilization or remediation of the contaminated site because reduced forms of U(IV) are sparingly soluble and can thus be strongly retained in soil. However, further studies indicate that humics also formed complexes with reduced U(IV) and prevented it from precipitation. In addition, humics increased the re-oxidation of reduced U(IV) (when exposed to oxygen) with a re-oxidation half-life on the order of a few minutes. Both of these processes render uranium soluble and potentially mobile in soil. These observations point out important challenges on the use of the bioreduction technology for immobilizing uranium thereby remediating contaminated sites in the field because of the wide occurrence of humic substances in soil and groundwater. Therefore, future studies must address the stability and retention of reduced or immobilized U(IV) as a means of longterm stewardship of contaminated sites.

Reduction of inorganic arsenic with humic materials

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In natural systems, arsenate (As-V) can be reduced to arsenite (As-III) by a number of different processes. The goal of the present research is to study the abiotic reduction of arsenate through the intervention of different humic materials. Results indicate that arsenate can be reduced to varying degrees depending on the humic composition, concentration and solution pH. The reduction potentials of several humic acids were studied, and these materials were used as reducing agents for inorganic arsenic. A novel ion chromatographic method of monitoring arsenate reduction by humate solutions was developed. Reduction of arsenate to arsenite was found to proceed in the 20 to 50% range. The kinetics appeared to be quite slow, with the reactions often taking up to 48 hours to reach completion.