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Non-Metabolic Reduction of Cr(VI) by Bacterial Surfaces under Nutrient-Absent Conditions

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Interactions between bacteria and aqueous chromium can control the valence state and speciation of chromium in the subsurface, and hence can control the fate of chromium in the environment. The fate of chromium in the environment is strongly dependent on its valence state. Under oxidising conditions, chromium exists as Cr(VI), and is readily bio-available due to the high solubility of Cr(VI)-bearing minerals. Conversely, Cr(III) minerals are extremely insoluble, and when chromium is present as Cr(III), its availability to organisms is limited. Therefore, in order to understand the response of natural systems to chromium contamination and to design bio-remediation strategies for such contaminated systems, it is imperative to understand each of the important bacterial mechanisms that affect chromium distribution. Virtually all previous experimental studies of bacterial Cr(VI) reduction have focused on metabolic enzymatic Cr(VI) reduction to Cr(III), using large excess concentrations of electron donors. The optimum pH for metabolic enzymatic Cr(VI) reduction by bacteria appears to be under pH 7 conditions. Reduction rates decrease significantly at both higher and lower pH conditions, with little or no metabolic enzymatic Cr(VI) reduction occurring under acidic conditions. In general, bacteria exist in the subsurface under nutrient-poor conditions. However, both surfaces and organic compounds can catalyse Cr(VI) reduction, so it is possible that bacterial surfaces may induce Cr(VI) reduction in and of themselves, independent of active bacterial metabolism and in the absence of high concentrations of electron donors. If such non-metabolic nutrient-absent Cr(VI) reduction occurs, then it could be the dominant reductive pathway in non-engineered geologic systems. Although metabolic enzymatic Cr(VI) reduction is well-documented, there are few studies examining non-metabolising cells in electron donor absent conditions. In this study, we measured the reduction capabilities of two bacterial species in the absence of external electron donors. The experiments utilise both resting state cells as well as irradiated cells to isolate non-metabolic reduction pathways. The objective of this study is to determine if a non-metabolic nutrient-absent reductive pathway exists involving bacterial cell walls, and if so to quantify the kinetics of, and controls on, the dominant reduction reaction. We conducted batch adsorption experiments, measuring Cr removal from solution after exposure to bacterial suspensions under constant ionic strength and initial Cr concentration conditions. Removal kinetics were determined by sampling as a function of time for up to 200 h, and experiments were conducted under fixed pH conditions, between pH 2 and 9, using both a gram positive *(Bacillus subtilis)* and a gram negative *(Shewanella putrefaciens)* species. The reversibility of the removal reactions was tested, and we also conducted parallel experiments using supernatant only from bacterial suspensions to test whether bacterial surfaces are required for Cr removal to occur. Cr concentrations in the aqueous samples were measured using an ICP-AES approach with matrix-matched standards. The valence state of the bacterially-bound Cr was constrained using EXAFS. Our results show that pH exerts a controlling effect on Cr removal in the presence of bacteria, but we observe a dramatically different pH trend than has been observed for metabolic enzymatic Cr(VI) reduction. In our experiments, the fastest Cr removal occurs under the most acidic conditions, with decreasing removal rates with increasing pH. The removal was not reversible when pH was increased, and the removal did not occur in bacteria-free solutions, even if those solutions had been in contact with bacteria for over 24h prior to separation and experimentation. The EXAFS of the Cr present on the bacteria indicates that the Cr is present at least partially as Cr(III). The experimental results indicate that the bacteria are responsible for non-metabolic reduction of Cr(VI) to Cr(III). Detailed interpretation of the kinetic data suggests that the reduction process is a two staged overall reaction, with an initial rapid mechanism followed by a slower reaction that follows a pH-dependent first-order rate law. This is the first observation of the potential for non-metabolising bacterial cells to reduce a metal, and presumably the reaction is driven by oxidation of one or more cell wall components. The fact that bacteria can reduce Cr(VI) even in the absence of external electron donors and without active metabolic function implies that such a process may be extremely important in affecting the environmental fate of Cr.