Probing Surface-Catalysed , Microbial Reduction of Hexavalent Chromium Using Synchrotron Infrared Spectroscopy

Bryne T. Ngwenya[1] and Fariba Bahrami[2].
[1]School of GeoSciences, University of Edinburgh, Grant Institute, West Mains Road, Edinburgh EH9 3JW, UK.
[2]CCLRC Daresbury Laboratory, Daresbury, Warrington, Cheshire WA4 4AD, UK.

The use of microbes for the electrochemical reduction (metabolic or non-metabolic) of Cr(VI) to Cr(III) is widely believed to provide a viable and sustainable strategy for remediation of Cr(VI) contaminated wastewaters. When reduction occurs through the non-metabolic pathway, the rate of Cr(VI) reduction is favoured at acidic pH and decreases almost linearly with increasing pH. It has been suggested that this behaviour is due to a decrease in adsorption of Cr(VI) to the microbial cells as the pH increases. We have conducted preliminary chromium reduction experiments in the presence of an Enterobacter sp. of bacteria to test the hypothesis that the reduction reaction is surface-catalysed and hence that adsorption of Cr(VI) onto the cells is a pre-requisite.

Because bacterial cell walls contain carboxyl functional groups which deprotonate at near-neutral pH values to render the cell negatively-charged, we reasoned that blocking these groups would maximise adsorption of Cr(VI) at near-neutral pH and accelerate the reduction reaction. We blocked carboxyl functional groups by esterification with methoxymethane (63°C, 30 minutes) in the presence of concentrated sulphuric acid. Chromium reduction experiments were conducted with the esterified biomass at pH 2.5 and 5.2.

These experiments showed that the reduction rate was first order with respect to Cr(VI) concentration. Moreover, there was no difference in reduction rate between esterified cells and heat-killed (65°C, 30 minutes) cells at low pH (2.5). However, the reduction rate for esterified biomass showed up to 3-fold increase over the rate for heat-killed controls at pH 5.2. This increase brings the reduction rate at pH 5.2 to within 0.5 times the rate at pH 2.5. However, the increase in reduction rate at pH 5.2 does not appear to be associated with significantly enhanced adsorption relative to heat-killed controls.

To further probe this paradoxical result, we characterised the biomass with both lab based and Synchrotron Fourier Transform Infrared Spectroscopy. Synchrotron Infrared Spectroscopy revealed a significant decrease in infrared absorption for the esterified biomass around the 1400-1350 cm^{-1} absorption region, where we expect carboxyl stretching. These changes were not resolvable using with thermal FTIR or acid-base titrations, presumably because the surface densities of the functional groups are rather low (~10^{-5} mol/g cells). Thus the high photon flux of the synchrotron source appears to be necessary to detect changes in surface speciation. Nonetheless, these observations suggest that the surface-catalysed reduction reaction is rather complex and that it's pH dependence cannot be explained fully by changes in adsorption of Cr(VI).