

A bio-nanotechnological approach to the remediation of alkaline Cr(VI) containing leachate from chromite processing ore residue

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Interactions at the microbe-mineral interface are known to produce reactive nano-scale mineral phases. These nanoparticles (NPs) can be harnessed in an innovative “bio-nanoremediation” approach to various contaminated land problems. The purpose of this study was to develop a novel treatment strategy for the redox active metal, chromium via reduction of mobile toxic Cr(VI) to the relatively insoluble and non-toxic Cr(III). Hyperalkaline (pH≈12) Cr(VI) leachates associated with chromite processing ore residue (COPR) have led to significant environmental Cr(VI) contamination. Over the last century up to 1.5 million m³ of COPR were produced and landfilled in the urbanised area of Glasgow, UK, alone [1]. This has led to sustained leaching of residual Cr(VI) contaminating groundwaters and tributary streams flowing in to the River Clyde.

Cr(VI) removal from COPR related waters was assessed for a nano-engineered magnetite (BnM) biomineral. This nanoparticle, exhibiting reducing properties due to its high surface Fe(II) content, was synthesised via reduction of amorphous ferrihydrite by the Fe(III)-reducing bacterium *Geobacter sulfurreducens* [2]. The biogenic magnetite was then subjected to a one-step functionalization process, to generate nanoscale Pd(0) on its surface giving a novel magnetically recoverable bio-nanocatalyst (Pd-BnM) [3]. These biogenic NPs were then compared to a synthetic alternative, nano Zero Valent Iron (nZVI), for remediation applications.

Using pure Cr(VI) solutions at environmentally relevant alkaline pH values, an approximate 50% loss in efficiency (compared to performance in acidic conditions) was observed in both the BnM and nZVI NP treatments, with the nZVI demonstrating a greater capacity for removal. The Pd-BnM performed best, with sustained Cr(VI) removal when supplied with hydrogen gas, removing 240 mg Cr(VI) per g of NP within 50 hours reaction time (reaching over 450 mg after 290 hours) in comparison to a maximum of 29 mg removal when supplied with formate as an electron donor for metal reduction. The fate of the Cr was investigated using TEM and XPS analysis.

Following application of the NP treatments to the COPR leachate slurry, complete removal of the 1.6 mM Cr(VI) in solution was achievable with comparable removals to those observed from pure Cr(VI) solutions. This study therefore demonstrates the ability of both biogenic and synthetic NPs for removal of Cr(VI) from alkaline leachates from COPR.

[1] Farmer, J.G., et al (2002) *Journal of Environmental Monitoring*, **4**, 235-243.

[2] Cutting, R. S., et al (2009) *Geochimica et Cosmochimica Acta*, **73**, 4004-4022.

[3] Coker, V. S., et al (2010) *ACS Nano*, **4**, 2577-2584.

Ethanol binding, orientation and bilayer structure on R-plane corundum surfaces

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Introduction

The interaction and binding of organic species with mineral surfaces is a large frontier in geochemistry. Mineral surfaces may sequester, sort, or contribute to breakdown reactions of organic molecules, but much of the details of these processes are poorly informed.

Compared to inorganic sorbates, which interact with a surface by forming covalent and hydrogen bonds, and couple strongly to surface water molecules; organic structures may have partial or dominant hydrophobic interactions and reduced interaction with waters, multiple charges on a single molecule (e.g. zwitterion), and complex multi-site interactions with surface functional groups. In addition, a range of conformations may be possible, allowing adaptation to a surface, but differing from the solvated water-borne entity. These considerations have limited both the scope and utility of many past studies, with the vast majority involving measurement of uptake without information on the actual binding geometry or reaction mechanisms. The topic is one of profound interest given enormous numbers of industrial organic pollutants, natural biological agents, and pharmaceutical breakdown products entering the environment.

Results

We are developing a program to couple sum-frequency vibrational spectroscopy (SFVS), surface x-ray scattering methods, and computer simulations to characterize organic species interactions with well-known mineral surfaces. The first work involves ethanol as a single monolayer, and as a bulk liquid, on the corundum R-plane (1-102) surface [1]. SFVS spectra in the C-H range show that the monolayer has a well-defined anisotropic arrangement consistent with the R-plane termination. Specific molecular orientations and anisotropy can be explained by the formation of two hydrogen bonds between the ethanol molecules and the hydroxyls on the surface [2]. When bulk ethanol is present, the first layer is similarly anisotropic, but the second is apically opposite with a nearly isotropic distribution.

[1] Sung et al. (2011) *J. Phys. Chem. C* **115**, 13887-13893., Sung et al. (2011) *J. Amer. Chem. Soc.* **133**, 3846-3853. [2] Sung et al. (2011) *J. Phys. Chem. Lett.* **2**, 1831-1835.