Adsorption and oxidation of Cr(III) on the surface of MnO_2

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Genesis of Cr(VI) from natural sources in soil and ground water has been reported widely in the world. It was found that Cr(III) within ultramafic- and serpentinaite-derived soils/sediments can be oxidized and dissolved through natural processes, leading hazardous levels of aqueous Cr(VI) in surface and groundwater [1]. In this process, adsorption and oxidation of Cr(III) on the surface of MnO_2 are the key reactions. In order to elucidate the relationship between "adsorption" and "oxidation" at the solid surface, we performed batch adsorption experiment in the air using various type Mn oxides and $CrCl_3 \cdot 6H_2O$ solution. Aliquotes of suspension were collected with adequate time interval. The samples were filterd by membrane filter with pore size of 0.22 μm and concentrations of total Cr and Mn in the liquid phase were measured by ICP-AES, while concentration of Cr(VI) was obtained by colorimetry using diphenylcarbazide. During the adsorption experiment, pH, ORP and DO were monitored continuously by using electrodes.

The results showed that the series of reactions generally started by adsorption of Cr(III) onto the solid surface followed by oxidation to Cr(VI), desorption of Cr(VI) and dissolution of Mn. The occurrence of each reaction was affected significantly by experimental conditions, especially the concentrations of Cr(III) and MnO_2, particle size and crystal form of MnO_2 and temperature. When the concentration of Cr(III) is more than 10^{-6} M and δ-MnO_2 is used at 25°C, these processes took place almost simultaneously. On the other hand, when the concetration of Cr(III) is 10^{-7} M and β-MnO_2 is used at 0°C, Cr(III) was adsorbed but was not desorbed from the solid surface. XANES spetrrum of Cr for this sample didn't show the existance of Cr(VI), suggesting that the Cr(III) adsorbed was not oxidized to Cr(VI). From these results, it was suggested that adsorption of Cr(III) onto MnO_2 is necessary to its oxidation, but some condition is required in order to oxidize the adsorbed Cr(III) to Cr(VI).

Reference

[1] Oze *et al.*, (2007) PNAS **104**, 6544-6549.