



ChromiumVI and Humic acids interaction

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Even it is assumed that, due to thermodynamic constraints, hexavalent chromium do not occur in natural soils and water, there are evidences that it can enter either from several natural processes or from human activities. For instance, natural outstanding amounts of hexavalent chromium have been found in soils of Paradise Valley (Arizona), and chromate/dichromate mineral phases have been found in the Atacama Desert (Chile). Actually, there is a growing concern about chromium containing fertilizers and wood preservatives such as Chromate-Copper Arseniates (CCA) that represent the greater exogenous input of Cr into the soil. Most forms of CrIII present or added to soils are kinetically inert, but under chemically favourable circumstances, such as the lowered pH, the interaction with oxides/superoxides of Mn, the microbial biomass size and activity, can be oxidated to soluble and reactive Cr VI. As the soil dynamics of CrVI is similar to nitrate, water and groundwater samples can be thus contaminated. At the same time, Cr VI in soil would be expected to become reduced by organic matter in the natural soil environment. Humic acids (HAs) are natural carbon-rich biopolymers ubiquitous in terrestrial and aquatic environments, whose multiple properties seem to be purpose-built for many life-sustaining functions, from agriculture to industry, environment and biomedicine. Due to the polyfunctionality together with the zwitterionic character, HAs are one of the powerful chelating agents among natural substances. Infact, one of the most significant properties of humic acids is their ability to interact with xenobiotics to form complexes of different solubility and chemical and biochemical stability. In this work we investigated the interaction between CrVI and humic acids by using Differential Pulse Stripping (DPS) voltammetry, Uv-visible (UV-Vis) spectroscopy, and Extended X-ray Absorption Fine Structure (EXAFS) spectrometry. Humic acids (HAs) were extracted from an air died soil sample taken from the surface horizon of an Haplumbrept soil (USDA) by following the IHSS protocol for their purification. Standard solution of 0.20mM of K-

dichromate was used. The experiments were carried out at pH 6. EXAFS experiments on CrVI standard solution without or with HAs were performed at Hamburg Synchrotronstrahlungslabor (HASYLAB) - Deutsche Elektronen-Synchrotron DESY. Electrochemical and spectroscopic responses were studied after stepwise addition of HAs at CrVI standard solution. Results obtained from voltammetric and UV-Vis analyses indicated that interaction between CrVI and HAs probably occurred via supramolecular process, leading to the formation of CrVI-HAs micelles. According to EXAFS analyses, the interaction did not imply significant changes in the original tetrahedral structure of CrVI, thus suggesting that HAs, at pH6, did not exerted any chemical reduction CrVI-CrIII and that micelles might act as carriers of CrVI throughout the soil profile to the groundwater.