Chromium in Sludges Used as Soil Ameliorants

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Introduction

Various solid organic wastes can be added to soil both as an effective means of disposal and for soil amelioration. While the practice can improve soil fertility and physical and chemical properties such as organic content and pH, there is some concern that toxic heavy metals may also be introduced into the soil environment, and subsequently into the food chain. Bulk analysis may exaggerate the risk, as metals may be present but may not be bioavailable or may be in a relatively benign form. Chromium is a good example, since Cr^{3+} is comparatively harmless and relatively insoluble, while Cr^{6+} is generally believed to be toxic and is highly soluble and hence mobile.[1]

In this work two Indian sludges used in a major soil improvement project were selected for study. The first was low in chromium; the second had high chromium concentrations. Both samples were subjected to x-ray absorption near-edge structure (XANES) analysis to establish both the levels at which chromium might be detected in the soil samples and the oxidation state of the chromium.

Methods

One author (M. A. Powell) supplied the Indian soil samples. The soils were spread thinly on clear tape to make the XANES measurements. The Cr K-edge XANES were taken at ther PNC-CAT 20-BM-B beamline at the Advanced Photon Source (APS) at Argonne National Laboratory. The soils were measured in fluorescence yield mode using an Oxford Instruments NaI scintillation detector.

The standards $CrCl_3 \bullet 6H_2O$ and K_3CrO_4 were obtained from Fisher Scientific Co. and used as is. Samples were spread thinly on tape and the XANES were measured in transmission mode.

Results and Discussion

As the oxidation state of an atom increases, the core electronic states become more tightly bound, producing a measurable shift in the XANES spectra to higher photon energies. The local geometry around the absorbing atom also affects the XANES spectra. The spectra of four coordinate transition metal ions (such as Cr^{6+}) exhibit an intense pre-edge peak due to $3d$-$4p$ mixing.[2,3,4] The XANES spectra of Cr^{3+} compounds do not have this sharp feature. Thus, the differences between the two oxidations states of Cr can be clearly seen (Fig. 1).

The XANES of the two soil samples are shown in Fig. 2. The spectra have been scaled for clarity. Clearly, neither spectrum exhibits a pre-edge peak from the presence of Cr^{6+} species. Therefore, both soil samples contain mostly Cr^{3+} species.

Conclusions

We used XANES to examine two Indian soils that were used as soil ameliorants. It was found that the Cr contained in the soils was predominantly in the relatively benign Cr^{3+} oxidation state. We would like to continue this work by investigating the kinetics of Cr oxidation/reduction in soils.

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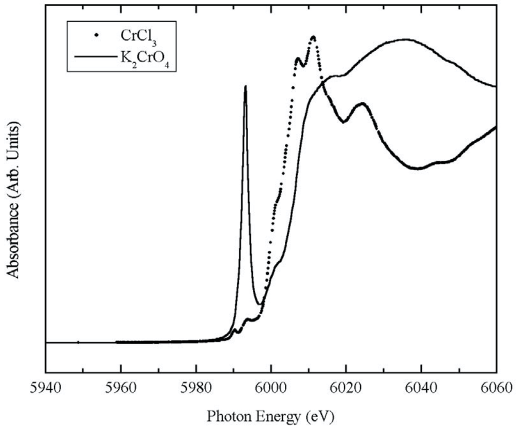

FIG. 1. Cr K-edge XANES spectra of $CrCl_3$ [Cr^{3+}] and K_2CrO_4 [Cr^{6+}].

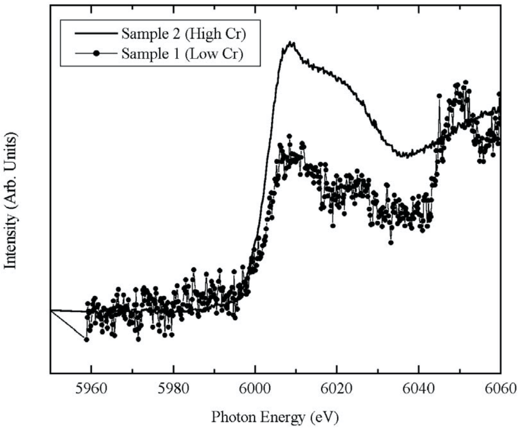

FIG. 2. Cr K-edge XANES spectra of the two soil samples.

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