

## Speciation study of hexavalent chromium reduced by Humic acid

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### Introduction

A reduction of Cr(VI) by organic materials in soil such as Humic and Fulvic acid (HA and FA) is a very interesting phenomenon for environmental problems because pollutant Cr(VI) disappears in a field system easily [1, 2]. Recently, it was also found that the Cr(VI) in soil is reduced even in dry condition [3]. So far, the reduction study of Cr(VI) by HA and FA have targeted for the reduction kinetics. However, there is little speciation examinations of Cr(VI) after a reduction process. The main purpose of this study is to elucidate the speciation of Cr(VI) reduced by HA and distinguish the Cr(III) originated from pollutant Cr(VI) and the Cr(III) in a natural state.

### Methods

The  $K_2Cr_2O_7$  and  $Cr(NO_3)_3 \cdot 9H_2O$  were used as reactant Cr(VI) and Cr(III), respectively. Two kinds of HA purchased from Aldrich Chemical Co. and Wako Co. were selected for a reducing compound. The 2.5  $\mu$ g, 25  $\mu$ g, and 250  $\mu$ g of Cr(VI) and 50  $\mu$ g of Cr(III) were reacted with 1mg HA in a 10ml solution at pH 2.0 for 7 days. The reactants were filtrated by a 0.1  $\mu$ m PTFE membrane filter and dried in under vacuum. The Cr(VI) remaining unreactive was removed from HA by filtration.

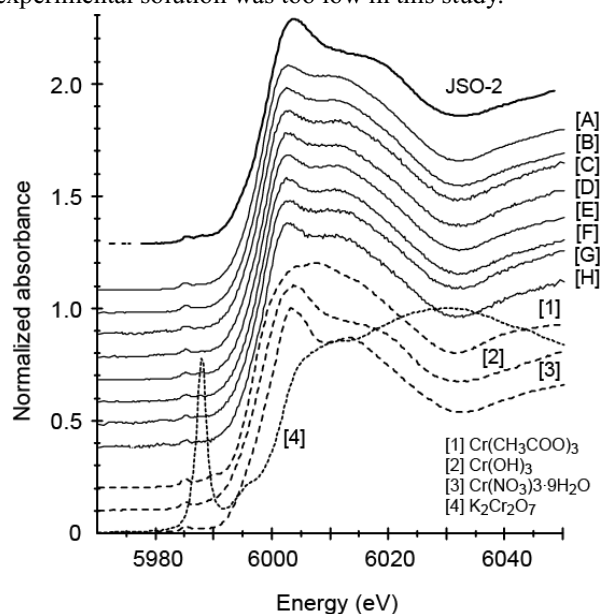
### Experiment

The Cr K-edge XANES spectra were recorded in a fluoresce mode at the BL-12C of KEK-PF under an atmosphere and at room temperature. The fluorescence X-ray was measured by a 19 element pure-Ge SSD. For comparison, several kinds of chromium compounds ( $K_2Cr_2O_7$ ,  $Cr(OH)_3$ ,  $Cr(NO_3)_3 \cdot 9H_2O$ , and  $Cr(CH_3COO)_3$ ) and JSO-2 that is a geochemical reference material and contains  $K_2Cr_2O_7$  were measured in a fluorescence mode.

### Results and Discussion

Figure 1 shows the Cr k-edge XANES spectra of HA reacting with Cr(VI) and Cr(III). There are little differences of Cr XANES spectra between two kinds of reactant HA. Types and proportions of functional groups that bind Cr(III) may be common to each other. Interestingly, the HA reacting with Cr(VI) has the same spectra as those with Cr(III). The Cr(III) produced by reduction process binds with HA like Cr(III). Also the Cr XANES spectra have no significant change with the increasing amount of Cr(VI). In the range of experimental conditions, the types and proportions of functional groups

that bind Cr(III) do not change. The comparison of Cr XANES spectra of HA reacting with Cr(VI) and Cr(III) to those of chromium compounds suggests that 40% of Cr(III) just adsorbed on HA electrostatically and the rest of Cr(III) binds to a  $CH_3COO$ -like functional group of HA. Finally, the Cr XANES spectra of JSO-2 was compared with the above materials. Tsuno et al. [3] reported that the Cr(VI) added to JSO-2 totally reduced to Cr(III). However, the spectra is resemble not to those of HA reacting Cr(VI) and Cr(III) but to those of  $Cr(OH)_3$ . The results suggest 1) that Cr(VI) in JSO-2 was reduced by Fe(II) and precipitated as  $Cr(OH)_3$  or 2) that the pH of experimental solution was too low in this study.



**Figure 1.** The Cr K-edge XANES spectra. [A], [B], [C], and [D] shows Aldrich HA reacting with 2.5  $\mu$ g, 25  $\mu$ g, and 250  $\mu$ g of Cr(VI) and 50  $\mu$ g of Cr(III), respectively. [E], [F], [G], and [H] shows Wako HA reacting with 2.5  $\mu$ g, 25  $\mu$ g, and 250  $\mu$ g of Cr(VI) and 50  $\mu$ g of Cr(III), respectively.

### References

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