

## Reduction of toxic Cr(VI)-humic acid in an ionic liquid



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### ABSTRACT

Remediation of soil contaminated by toxic hexavalent chromium species associated with humic acid (Cr(VI)-HA) and adsorbed Cr(VI) in pores frequently experiences technical difficulties. In the present work, a feasibility study for extraction of the Cr(VI) species from a molecular sieve MCM-41 (Mobil Composition of Matter No. 41) that was used to simulate the pore system of soil, with a green solvent (ionic liquid), 1-butyl-3-methylimidazolium chloride ([C<sub>4</sub>mim][Cl]), was carried out. After a 30-min extraction, approximately 70% of the Cr(VI) species can be extracted. By component fitted X-ray absorption near edge structure (XANES) spectroscopy, about 48% of the Cr(VI)-HA are reduced to form less toxic species (Cr(III)-HA) during extraction with [C<sub>4</sub>mim][Cl]. Note that the Cr-O in the [C<sub>4</sub>mim][Cl] phase has a slightly greater bond distance (BD) (0.162 nm) possibly due to the fact of that the fraction of Cr(III) is increased in the extraction process. The non-extractable chromium remaining in MCM-41 has a much greater fraction of Cr(III) (78%) and its BD is further increased to 0.195 nm. The coordination numbers of chromium for the 1st shell Cr-O in the Cr(VI) and Cr(III) species are in the range of 2.4–2.9, suggesting that chromium is chelated with HA and adsorbed in MCM-41. The <sup>1</sup>H NMR data also suggest that the enhanced reduction of the Cr(VI) species may be related to interactions between chromium species and electron-rich imidazole ring of the [C<sub>4</sub>mim]<sup>+</sup>. This work also exemplifies that the fate of toxic chromium species in the complicated remediation of contaminated soils can be revealed in a molecule-scale study by synchrotron X-ray absorption spectroscopy.

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### 1. Introduction

Humic substances (85–90%) being the main organic matters in soil have active functional groups that may undergo various biological or chemical reactions. For example, hydroxyl and carboxyl groups of humic substances may adsorb metal ions, causing contamination in soil [1–3]. Soil generally contains pore systems associated with a high surface area, and that increases the absorptive capacity of metal ions therein [4]. Heavy metals such as chromium, zinc, arsenic frequently found in industrial wastewaters may contaminate soil and underground water when illegally discharged [5–8].

Trivalent chromium (Cr(III)) is one of the essential elements for animals and humans, on the contrary, hexavalent chromium (Cr(VI)) has been considered hazardous [9]. Oxidation states of chromium are highly dependent on the redox reactions engaged in its environment. The main Cr(VI) species in soil are hydrochromate (HCrO<sub>4</sub><sup>-</sup>), dichromate (Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>), and chromate (CrO<sub>4</sub><sup>2-</sup>) [10]. The Cr(VI) containing compounds may cause cardiovascular, kidney, liver, and skin diseases [11–13]. Concentrations of chromium in contaminated soils may be decreased by conventional methods such as water washing or extraction with acid and surfactant solutions. However, they have disadvantages of low efficiency, less

reutilization ability (due to soil ruined during extraction), and discharging secondary wastewater for additional treatments.

Ionic liquids (ILs) are considered as one of the green solvents applied in catalysis, extraction, purification, and environmental pollution controls [14–17]. It is worth noting that cations and anions of an IL can be selectively matched to obtain tunable and desirable physical and chemical applications [18,19]. ILs having a high thermal stability and negligible vapor pressure can be used at a wide temperature range [20,21]. Thus ILs can replace the conventional organic solvents, especially in extraction of heavy metal ions with a relatively high selectivity from wastewaters or contaminated soils. For example, the extraction efficiencies of Zn<sup>2+</sup>, Cd<sup>2+</sup> and Fe<sup>3+</sup> from a wastewater using the IL (methyltrioctylammonium chloride ([MTOA][Cl])) were greater than 94% [22]. Similar extraction efficiencies for Zn<sup>2+</sup> and Cd<sup>2+</sup> by [omim][BF<sub>4</sub>] (1-methyl-3-octylimidazolium tetrafluoroborate) were also observed [22]. Note that organic matters were found to dissolve in ILs. Cellulose and lignin may also be extracted using an IL, i.e., 1-butyl-3-methylimidazolium chloride ([C<sub>4</sub>mim][Cl]) [23–25]. Humic acid (HA) in soil could also be extracted by [C<sub>4</sub>mim][Cl] [26,27].

MCM-41 (Mobil Composition of Matter No. 41) having a well-defined hexagonal structure is a mesoporous molecular sieve with a high thermal stability and surface area [28–31]. The openings of the uniform tubular channel in MCM-41 are in the range of 1.5–3.0 nm, allowing large organic molecules diffused in and out. In the present work, a better

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understanding of how the toxicity of Cr(VI) species in soil could be reduced was studied by synchrotron X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy. Specifically, the simulation system containing Cr(VI) chelated with HA (Cr(VI)-HA) in MCM-41 was used to represent the complicated metal ion-organic matters contaminated soil for the extraction studies with an IL, i.e., [C<sub>4</sub>mim][Cl].

## 2. Experimental

Detailed procedures for the preparation of MCM-41 were described previously [32]. The IL ([C<sub>4</sub>mim][Cl]) was prepared with equal moles of 1-methylimidazole (99%, ACROS, USA) and 1-chlorobutane (99%, Alfa-Aesar, USA) which were mixed and refluxed at 343–353 K for 2 days. After cooling, 30 mL of ethyl acetate (99.9%, J. T. Baker, USA) was added to remove the unreacted 1-methylimidazole. About 2 g of MCM-41, 1.5 g of humic acid (HA) (Aldrich, USA), and 50 mL of deionized water were stirred for 24 h and dried at 343 K for 4 h. For the simulation of the Cr(VI) associating with HA contaminated soil for X-ray absorption spectroscopic studies, Cr(VI) chelated with HA (Cr(VI)-HA) in MCM-41 ((Cr(VI)-HA)/MCM-41) was prepared by mixing 15 mL of 0.07 M K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (99%, Showa, Japan), 0.5 mL of H<sub>2</sub>SO<sub>4</sub> (95–98%, Panreac, USA), and 3.5 g of HA-MCM-41 at 298 K for 1.5 h. The (Cr(III)-HA)/MCM-41 samples for X-ray absorption spectroscopic studies were also prepared in the similar way. CrCl<sub>3</sub>·6H<sub>2</sub>O (93%, Showa, Japan) was used as the Cr(III) species. About 0.4 g of (Cr(VI)-HA)/MCM-41 and (Cr(III)-HA)/MCM-41 was extracted by 1.5 g of [C<sub>4</sub>mim][Cl] at 378 K for 30 min.

Chemical structure of the samples before and after extraction with [C<sub>4</sub>mim][Cl] was determined by EXAFS and XANES that were recorded on the Wiggler beam line (16A1) at the Taiwan National Synchrotron Radiation Research Center in an electron storage ring with an energy of 1.5 GeV and a current of 300 mA. A Si(111) double-crystal monochromator was used for energy selection with an energy resolution ( $\Delta E/E$ ) of  $1.5 \times 10^{-4}$ – $2.1 \times 10^{-4}$  (eV/eV). The photon energy was calibrated using a chromium foil absorption edge at 5989 eV. The standard deviation calculated noise and error associated with each structural parameter. The raw absorption data in the region of 50–200 eV were fit to a straight line using the least-squares algorithms. The fitted pre-edge background was extrapolated throughout the whole data range and subtracted and normalized to reduce effects of the sample thickness. The near-edge spectra were ranged between the threshold and the point at which the EXAFS began. The XANES spectra extend to an energy of 50 eV above the edge.

The spectra were collected at the energy of 5789–5969 and 5969–6029 eV with the energy step sizes of 4 and 0.25 eV, respectively. At the energy of 6029–6989 eV, the spectra were recorded with the energy step size of 0.005 nm. The Cr K-edge absorption spectra were collected in the fluorescence mode with a Lytle detector. The XANES spectra of chromium model compounds such as CrCl<sub>3</sub>·6H<sub>2</sub>O, K<sub>2</sub>CrO<sub>7</sub>, Cr(NO<sub>3</sub>)<sub>3</sub>, Cr(OH)<sub>3</sub>, Na<sub>2</sub>CrO<sub>4</sub>, Cr<sub>2</sub>O<sub>3</sub>, CrO<sub>3</sub>, Cr(VI)-HA, Cr(III)-HA, Cr(VI)<sub>(ads)</sub> (by impregnation of K<sub>2</sub>CrO<sub>7</sub> (3 wt%) on MCM-41), Cr(VI)<sub>(ads)</sub> (by impregnation of CrCl<sub>3</sub>·6H<sub>2</sub>O (3 wt%) on MCM-41), and Cr foil were also measured. The XANES spectra of the chromium model compounds are shown in Fig. 1.

The EXAFS data were analyzed using the UWXAFS 3.0 and FEFF 8.0 simulation programs [33–38]. The isolated EXAFS data were normalized to the edge jump and converted to a wavenumber scale. To diminish the residual and Debye-Waller factors of analysis, the Fourier transform was performed on *k*<sup>3</sup>-weighted EXAFS oscillations in the range of  $25 \pm 5$  to  $120 \pm 5$  nm<sup>-1</sup>.

<sup>1</sup>H NMR (nuclear magnetic resonance) shifts of the samples were determined on a Bruker Advance 300 spectrometer with tetramethyl silane (TSM) as an internal standard (acquisition, time = 1.373 s, actual pulse repetition time = 2 s, number of scans = 32 and

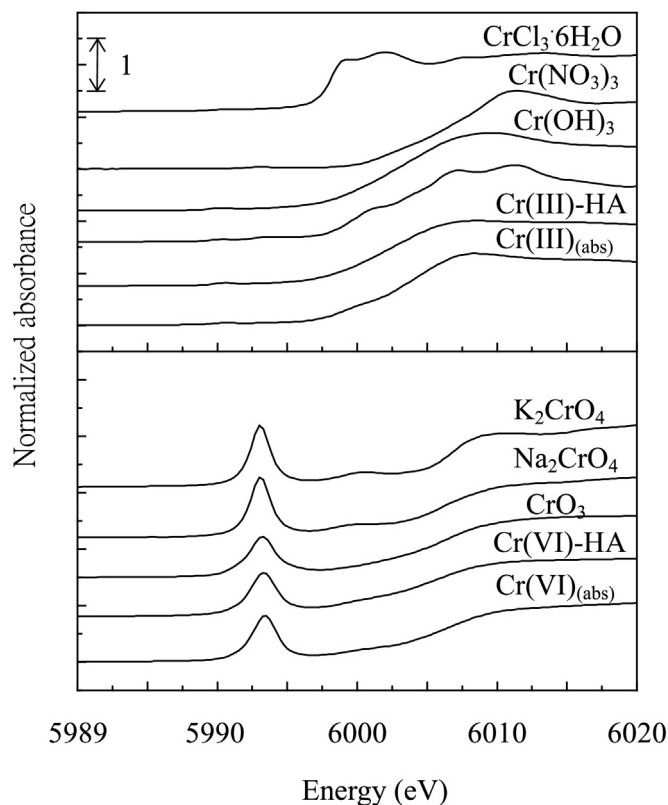


Fig. 1. Normalized Cr K-edge XANES spectra of chromium model compounds.

excitation pulse angle = 30°). The functional groups of HA which was chelated with chromium species in the MCM-41 before and after extractions with [C<sub>4</sub>mim][Cl] were recorded on the Fourier transform infrared (FTIR) spectrometer (Nicolet 6700). For all spectra reported, a 64-scan data accumulation was conducted at a resolution of 4 cm<sup>-1</sup>.

## 3. Results and discussion

The chemical structure changes of chromium in the (Cr(VI)-HA)/MCM-41 in the course of extraction with the IL ([C<sub>4</sub>mim][Cl]) are shown in Fig. 2. The pre-edge intensity of 3d elements with the *T<sub>d</sub>* symmetry is greater than those with the *O<sub>h</sub>* symmetry. The intense pre-edge peaks for the tetrahedral species of 3d transition metals are associated with the p component in the d-p hybridized orbital. The height of pre-edge peak is depended on the number of d-electrons of tetrahedral species [39,40]. The existence of Cr(VI) and Cr(III) in MCM-41 and [C<sub>4</sub>mim][Cl] can be revealed by the pre-edge feature centered at 5993–5994 eV in the XANES spectra (see Fig. 2) and that are distinctive for deconvolution in the component fitting. The XANES spectra analyzed with the linearly-combined XANES fit vectors for the component fits between 5969 and 6029 eV. In Fig. 2(a), it is clear that about 8% of Cr(VI) was reduced to form the relatively low toxic Cr(III). The interactions between Cr(VI) and carboxyl groups of HA leading to a reduction of Cr(VI) have been reported [41,42]. Additional observations of the interactions between HA and Cr(VI)/Cr(III) by FTIR are shown in Fig. 3. The red shifts of the feature at 1409 cm<sup>-1</sup> for HA related to its stretching of C=C to 1394–1384 cm<sup>-1</sup> are seen as the Cr(III) and Cr(VI) are chelated with HA. In addition, the red shifts (1101 → 1078 cm<sup>-1</sup> and 914 → 879 cm<sup>-1</sup>) for the C—O stretching in HA associated with the Cr(III) and Cr(VI) species are also found.

Note that Cr(VI) may be reduced and formed Cr(III) ( $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}$ ,  $E^\circ = +1.33\text{ V}$ ) during

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