



Speciation of chromium compounds from humic acid-zeolite Y to an ionic liquid during extraction

Hsin-Liang Huang*, Yu Jhe Wei

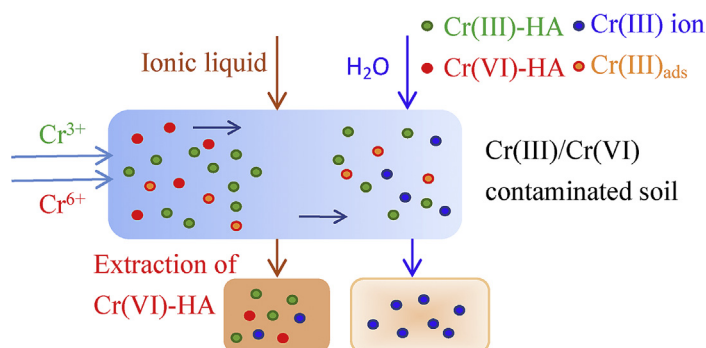
Department of Safety, Health and Environmental Engineering, National United University, Miao-Li 36003, Taiwan



HIGHLIGHTS

- The reduction and desorption of Cr compounds in an ionic liquid (IL) increased the mobility of Cr(III) in simulated soil for remediation.
- Interaction between IL anions and Cr compounds occurred in IL.
- The remediation of contaminated soils is revealed in molecular-scale understandings.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Available online 28 November 2017

Keywords:

Chromium
Humic acid
Microporous system
Ionic liquid
EXAFS
XANES

By synchrotron X-ray absorption spectroscopy, chemical structures of hexavalent chromium (Cr(VI))/trivalent chromium (Cr(III)) adsorbed on humic acid (HA)-zeolite Y and extracted in an ionic liquid (1-butyl-3-methylimidazolium tetrafluoroborate ([C₄mim][BF₄])) have been studied. By combining the competitive adsorption results and reduction of Cr(VI)-HA with the carboxyl groups of HA, Cr(III)-HA (58%) was shown to be the major compound in HA-zeolite Y using synchrotron X-ray absorption near-edge structure (XANES) spectroscopy. In an ionic liquid phase, the reduction of Cr(VI)-HA to Cr(III)-HA and the desorption of Cr(III) from HA were caused by [C₄mim][BF₄]. The ⁹F nuclear magnetic resonance (NMR) spectra show that the perturbation of the [C₄mim][BF₄] anion was affected by the extractable chromium species. The formation of a Cr(III) ion affected the increase in the bond distance for the 1st shell Cr–O of the chromium species in [C₄mim][BF₄] using extended X-ray absorption fine structure (EXAFS) spectroscopy. The changes in the non-extractable chromium species remaining in HA-zeolite Y were also caused by [C₄mim][BF₄] during extraction. The desorption of the adsorbed Cr(III) on HA and zeolite Y was observed to form Cr(III) ions. As the percentage of Cr(III) ions remaining in HA-zeolite Y increased, a slightly greater bond distance for Cr–O was found at 2.01 Å. The enhanced reduction of Cr(VI)-HA and desorption of Cr(III) adsorbed on the HA and zeolite Y to form Cr(III) ions were affected by [C₄mim][BF₄]. Increased mobility of Cr(III) in the simulated soil can promote the migration of Cr(III) ions into the H₂O during soil washing for remediation.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Chromium (Cr) compounds used in industry processes may cause pollution in the environment. The organic matter in soil

* Corresponding author.

E-mail address: hlhuang@nuu.edu.tw (H.-L. Huang).

contains 70–80% humic acid (HA) [Schinitzer, 1986]. HA can form complexes with metals and is regarded as an adsorbent of organic and inorganic pollutants [Livens, 1991; Ghabbour et al., 1997; Lu and Zhu, 2012; Leone et al., 2014; Shuang et al., 2015; Feng et al., 2008; Bibak 1994; Seki and Suzuki, 1995]. The chromium compounds adsorb onto the HA of the soil, causing pollution which retards the self-purification capacity of the soil [Bradl, 2004]. The hexavalent chromium (Cr(VI)) containing compounds may cause kidney, liver, cardiovascular and skin diseases [Dayan and Paine, 2001; Felter and Dourson, 1997; Liu et al., 1997]. Another stable chromium form in nature is trivalent chromium (Cr(III)). Cr(III) is one of the essential nutrients, and the toxicity of Cr(III) is lower than that of Cr(VI). However, the concentration of Cr(III) in wastewater is still limited by effluent standards [Environmental Protection Administration, 2011; Ministry of the Environment, 2015]. The Cr(III) ions can chelate with HA (Cr(III)-HA) more easily than Cr(VI) ions. Therefore, accumulation and low mobility of Cr(III) occur in the soil. Furthermore, metals adsorb in the micropores of the soil. The high concentration of chromium compounds is adsorbed in microporous activated carbons [Kantarli and Yanik, 2010]. Natural zeolite, which is microporous, is suitable for the removal of metal contaminants; it is also a soil pollutant which causes metals in the soil to adsorb in the micropores. Zeolite Y has a three-dimensional channel structure with a 7.4 Å pore opening; it is composed of a tetrahedral structure of SiO₄ and AlO₄. The properties of zeolite Y include high thermal stability and high adsorption capacity; therefore, the high adsorption efficiency of metal ions from water to zeolite Y have been observed [Lin et al., 2010]. The low mobility of chromium compounds adsorbed on HA and the microporous system in the soil decrease the extractable efficiency of soil washing for remediation.

Ionic liquids (ILs) have special physical and chemical properties. Because of their low volatility, which will reduce the overflow of steam, environmental pollution can be reduced to a minimum; therefore, traditional volatile organic compounds were replaced by ILs. In the extractable application of ILs, hydrophilic and hydrophobic ILs were used to extract Cu²⁺, Cr⁶⁺ and Zn²⁺ in aqueous solutions [Vidal et al., 2004]. The extractable efficiency of Cr⁶⁺ in a pH 2 solution can be increased using polymer ILs as the adsorbents [Ferreria et al., 2017]. Copper-HA (copper chelated with HA) complexes in the zeolite Y and nanoporous sorbent were also extracted with the hydrophobic IL [Huang and Chen, 2013; Huang, 2017]. Furthermore, Cr(VI) chelated with HA (Cr(VI)-HA) in the soil's simulated mesoporous system was extracted into the hydrophilic IL, enhancing reduction to a low toxicity Cr(III)-HA during extraction [Huang et al., 2017]. Therefore, IL can be used as an extractable solvent to extract the metal ion and complex. In this study, HA with a high cation exchange capacity (CEC) and zeolite Y with a high surface area were used to simulate the soil's microporous system. The main objective of this work was to study the speciation of adsorbed chromium (Cr(VI) and Cr(III)) in a simulated microporous system of the soil and extractable chromium in the hydrophilic IL (1-butyl-3-methylimidazolium tetrafluoroborate ([C₄mim][BF₄]) using synchrotron X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy. The influences of the chromium species by [C₄mim][BF₄] were also revealed.

2. Materials and methods

2.1. Characterization of humic acid and zeolite Y

The pH and CEC of humic acid (HA) (Aldrich, USA) and zeolite Y (PQ Corporation) were mixed with a 0.01 M CaCl₂ (96%, Sigma-Aldrich) solution and extracted using a 1 M CH₃CO₂NH₄ (98%,

Sigma) solution [Rayment and Higginson, 1992]. The surface area and pore size of zeolite Y were measured with a specific surface area and pore size distribution analyzer using the Gas adsorption method (Micromeritics ASAP, 2020). Table 1 shows the properties of HA and zeolite Y.

2.2. Preparation of the simulated chromium-contaminated soil

Zeolite Y, with a pore size of 7.4 Å, was used to simulate the microporous system of the soil. The pH of HA solution was adjusted to 7 before mixing with zeolite Y. The mixture contained 2 g of zeolite Y, 1.5 g of HA and 50 mL of deionized water stirred for 24 h and dried at 343 K to remove the H₂O. The solid used was HA-zeolite Y for the simulated soil. For the simulated chromium-contaminated soil in the X-ray absorption spectroscopic studies, Cr(VI) and Cr(III) adsorbed on HA-zeolite Y were prepared by mixing 30 mL of 0.03 M K₂Cr₂O₇ (99%, Showa, Japan), 0.03 M CrCl₃·6H₂O (93%, Showa, Japan) and 3.5 g of HA-zeolite Y at 298 K for 1.5 h and then filtering it with a 10 μm filter paper. The solid sample was dried at 343 K. The pH of the chromium solution was adjusted to 3–4 before mixing with HA-zeolite Y. 1 M HNO₃ (60–70%, J.T. Baker) and 1 M NaOH (98%, J.T. Baker) were used to adjust the pH levels of the solutions. Similar experimental methods have been described previously [Aris et al., 2002; Zhu et al., 2017].

2.3. Synthesis of the hydrophilic IL

To synthesize the IL ([C₄mim][BF₄]), 0.3 mol [C₄mim][Cl] and 0.3 mol potassium tetrafluoroborate (99.5%, ACROS) were mixed and stirred with 200 mL acetone (UST/NP grade, Pharmca) for 24 h. Detailed procedures for the preparation of [C₄mim][Cl] were described previously [Huang et al., 2017]. Precipitates in the solution were filtered with 10 μm filter paper.

2.4. Extractable process with the IL

About 0.4 g of chromium compounds in HA-zeolite Y was extracted by 1.5 g of [C₄mim][BF₄] at 378 K for 30 min. The solution was centrifuged at 3000 rpm for 10 min and then was filtered with 10 μm filter paper.

2.5. The concentrations of chromium adsorbed on HA-zeolite Y and extracted in the IL

One g of chromium adsorbed on HA-zeolite Y and extracted in the IL were digested with an appropriate amount of HNO₃ at 358 K for 3 h without boiling, respectively. After cooling, solutions were added 3 mL of H₂O₂ (35%, Sigma-Aldrich) and then heat to start the peroxide reaction for 15–20 min [US EPA, 1996]. The final total volume was brought to 50 mL.

2.6. Instrumental techniques

The morphologies of HA and zeolite Y were measured by scanning electron microscope (JSM-560, JEOL) (see Fig. 1). Atomic absorption spectrometer (Hitachi Z-5000) was applied to

Table 1
Properties of humic acid (HA), zeolite Y, and HA-zeolite Y.

	HA	Zeolite Y	HA-zeolite Y
pH	9.8	10.5	8.6
Cation exchange capacity (cmol/kg)	650	3.9	–
Surface area (m ² /g)	–	850	–
Pore size (Å)	–	7.4	–

Download English Version:

<https://daneshyari.com/en/article/8852522>

Download Persian Version:

<https://daneshyari.com/article/8852522>

[Daneshyari.com](https://daneshyari.com)