

Speciation of As in the blackfoot disease endemic area

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Speciation of arsenic (As) in well water and contaminated soil in the blackfoot disease endemic area has been studied by extended X-ray absorption fine structural (EXAFS) spectroscopy in the present work. Experimentally, we found that arsenic in the well water possessed an As-O bond distance of 1.72 Å with a coordination number (CN) of 4.3. In the blackfoot disease area, arsenic with a high oxidation state (As(V)) was also observed in the contaminated soil. In the early stage (after 90 minutes) of the electrokinetic remediation (EKR) of the contaminated soil, the in-situ EXAFS data indicated that the CN of As-O (1st shell) decreased slightly, that may be due to the perturbation of the incompact As atoms in the outer shells by EKR.

Keywords: Blackfoot disease; As; EXAFS; electrokinetic remediation

1. Introduction

Unexpected high levels of arsenic (As) can be present in underground water as a result of mineral weathering and dissolution (Manning, et al., 1998). Arsenic is of environmental concern due to its toxic properties. The most prevalent species of dissolved As in the environment are arsenate and arsenite, and both species are known to exist in natural waters. Due to the lack of understanding of As speciation in the blackfoot disease endemic area in Taiwan, in the past 20 years, a controversy between As and humic substances as the cause of blackfoot disease has not been resolved.

Electrokinetic remediation (EKR) is one of the feasible technologies for in-situ soil decontamination (Probstein & Hicks, 1993; Lageman, 1993; Trombly, 1994; Acar & Alshawabkeh, 1993). EKR is economically attractive and environmentally acceptable. EKR has been demonstrated successfully to remove more than 90% of heavy metals from soil, clay, and sand (Hicks & Tondorf, 1994; Acar & Alshawabkeh, 1993).

Although EKR has been proven to be feasible in laboratory or bench-scale experiments and small-scale field tests (Lageman, 1993), an understanding of the complex transport phenomena and electrochemistry involved in the EKR process is not well understood. X-ray absorption spectroscopy can be used in identification of local structure of elements in a complex matrix. Structural information such as coordination number, bond distance and oxidation state elements can be determined by EXAFS spectroscopy. Thus, the main objective of the present work was to

investigate the speciation of As present in the well water and the As-contaminated soil in the black-foot disease area by EXAFS. In addition, an in-situ EXAFS cell was used to reveal the speciation of As during the EKR process.

2. Experimental

Arsenic in the four sample well waters from the blackfoot disease area was reacted (30 L of each well water) with two grams of high purity γ -Al₂O₃ (As/Al₂O₃) for spectroscopic studies. Concentrations of As in the well waters were 120-280 ppb. In order to preserve the chemical properties of the humic substance and As in the water, the adsorption process was conducted carefully with a minimum exposure to air (nitrogen sealed) in adsorption columns at 298 K for at least 50 hours. About 40-50% of As in the water were adsorbed on γ -Al₂O₃.

An As-contaminated soil obtained from the blackfoot disease was also packed in a home-made in-situ EXAFS cell (Liu, et al., 2001) that was filled with 0.01 M potassium nitrate as conductive solution for the EKR experiments. A DC voltage of 100 volts was constantly applied to the electrodes.

The XANES and EXAFS spectra of the As/Al₂O₃ and the As-contaminated soil were examined on the Wiggler SL-3B beamline at the Taiwan Synchrotron Radiation Research Center (SRRC). The electron storage ring operated at an energy of 1.3 GeV (current of 80-200 mA). The standard deviation calculated from the averaged spectra was used to estimate the statistical noise and error associated with each structural parameter. Each EXAFS spectrum was recorded at least twice.

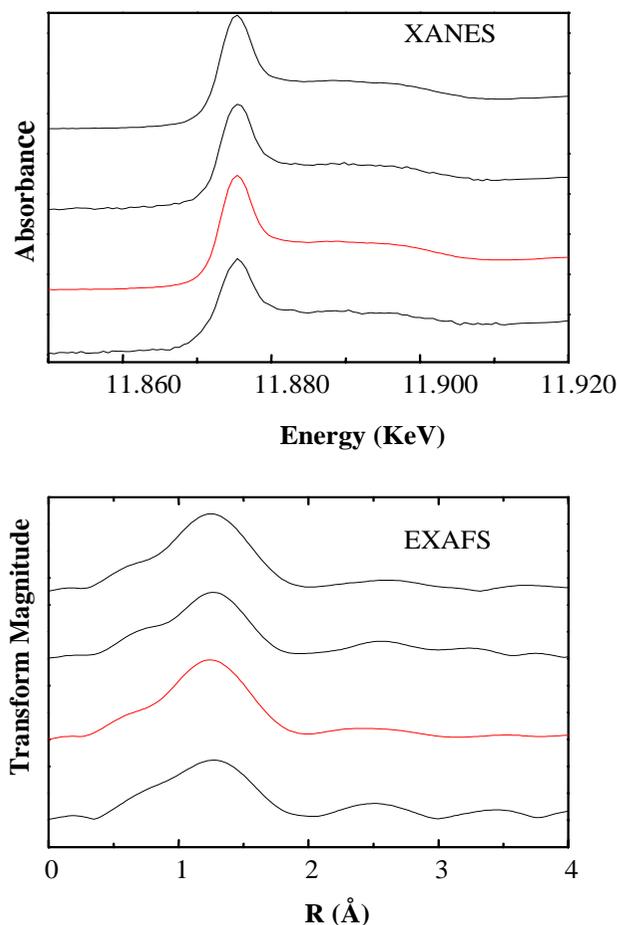
The EXAFS data were analyzed using the UWXAFS 3.0 and FEFF 7.0 programs (Stern et al., 1995). The absorption edge was determined at the half-height (precisely determined by the derivative) of the XANES (X-ray absorption near edge structure) spectroscopy after pre-edge baseline subtraction and normalization to the maximum above-edge intensity. The isolated EXAFS data was normalized to the edge jump and converted to the wavenumber scale.

3. Results and Discussion

Figure 1 shows the XANES spectra of As (As/Al₂O₃) in the well water from the black foot disease area. Mainly As(V) was found, as shown of a feature at 11876 eV in the XANES spectra. A small amount of As(III) was also observed. Least-squares fits to the XANES spectra in Figure 1 indicated that As(V) was the main As species in the well waters. In Figure 1, the EXAFS data also show that the feature centered at 1.72 Å arisen from As atoms in the first coordination shell with about 4.3 nearest oxygen atoms while a small feature at about 3.2 Å represented scattering from atoms in the second coordination shell.

The in-situ As K-edge XANES spectrum of the As-contaminated soil is shown in Figure 2. The derivative of XANES spectrum revealed the existence of As(III) and As(V) in the contaminated soil. About 40% of As(V) was observed in the contaminated soil in the electrolyte (with no electric field). In the EKR process for 90 minutes, the relative amount of As(V) increased slightly.

The in-situ EXAFS spectra of the soil in the electrolyte and during EKR process were also recorded. An over 99% reliability of the in-situ EXAFS data fits for As in the EKR process was obtained. The As-O bond distance of the contaminated soil was


Figure 1

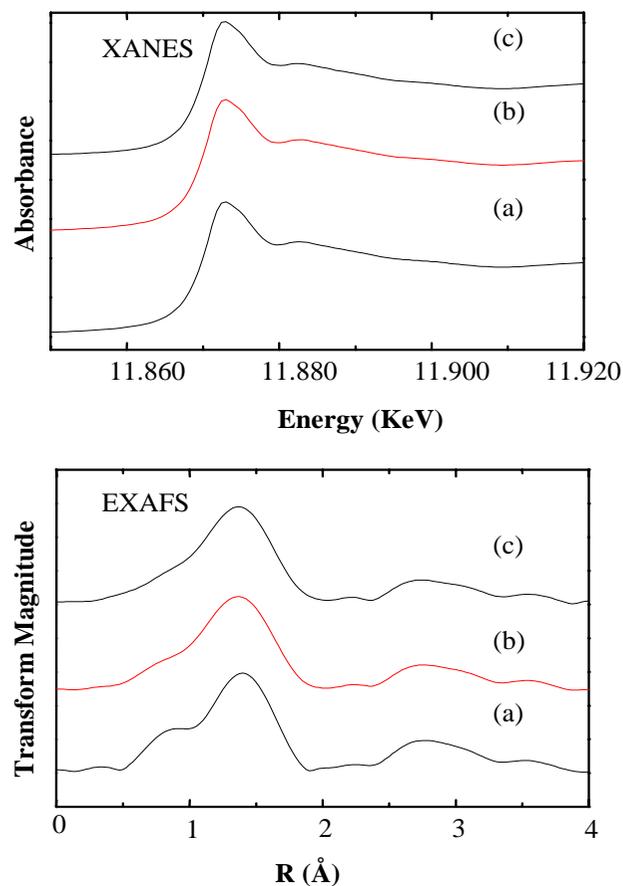
XANES and EXAFS spectra of As in the four well waters in the blackfoot disease endemic area. As from the water was adsorbed to Al_2O_3 substrate before data collection.

1.81 Å with a coordination number (CN) of 3.8. Prolonging the EKR to about 90 minutes, the CN of As-O (1st shell) decreased slightly, that may be due to the perturbation of the incompact As atoms in the outer shells by EKR.

4. Conclusions

Arsenic in the well water in the blackfoot disease endemic area is mainly As(V). The As-O bond distance was 1.72 Å with about 4.3 nearest oxygen atoms. Remediation of the As-contaminated soil by EKR for 90 minutes did not lead to a significant change of the speciation of As. However, a slight reduction of the CN of As was observed that might be due to the fact that the incompact As atoms in the outer shells were perturbed by EKR. The work illustrates the utility of the in-situ EXAFS cell for studying the speciation of As in natural water and in the EKR process.

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Figure 2

XANES and EXAFS spectra of As in the (a) contaminated soil, (b) in electrolyte and (c) in the EKR process for 90 minutes.

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