Phytoremediation Studies of Metal-hyperaccumulated Plants for the Contaminated Soils Using XANES/EXAFS Spectroscopy

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Heavy metal ions such as Cd^{2+} and Pb^{2+} are non-essential metals micronutrients for plant metabolism, but when present in excess can become extremely toxic. Thus, when these ions are not available to the roots, plants develop specific deficiency symptoms. At high concentrations, however, these metals can become extremely toxic, as do the non-essential metals, causing symptoms such as chlorosis and necrosis, stunting, leaf discolouration and inhibition of root growth.

The functional groups within the plant cell wall provide the amide, amine, hydroxyl, carboxylic, imidazole, sulfate, sulfydryl, phosphate, and thiol groups that can bind metals. The systems available for the acquisition of metal ions by the roots, transport and distribution around the plant, and regulation of their cytosolic concentrations are clearly integral to normal plant growth and development. By analyzing the energetics of these processes, in many cases we can see that transport proteins must play a vital role in heavy metal homeostasis. Throughout the entire plant kingdom from higher plants to eukaryotic microalgae, heavy metal-binding peptides, phytochelatins [PCs, (γ-Glu-Cys)n-Gly, where n = 2-11], are well known to play an important role in detoxification of toxic heavy metals.

The EXAFS and XANES spectra were collected at the TXR BL16A1 at the NSRRC of Taiwan. An electron storage ring was operated with an energy of 1.5 GeV and a current of 100-150 mA. A Si(111) DCM was used for providing highly monochromatized photon beams with energies of 0.9 to 9 keV and resolving power (E/ΔE) of up to 7000. Data were collected in fluorescence or transmission mode with a Lytle ionization detector for S (2472 eV) K edge experiments at room temperature. The EXAFS data will be analyzed by using the UWXAFS 3.0 program and FEFF 8.0 codes.

At the cellular level, toxicity may result from binding to sulhydryl groups in proteins thereby inhibiting enzyme activity or protein function, or by producing a deficiency of other essential ions. Especially, thiol or sulfate functional groups are more stronger sites bound with Cd and Pb ions and may form Cd- and Pb-SH or Cd- and $PbSO_4$ complex. The Cd and Pb atoms and S K-edge EXAFS spectra indicating the Cd-S and Pb-S species with bond distances of 2.21 and 2.80 Å respectively were found in Figure 1. Coordination numbers of Cd-S and Pb-S species were 3.9 and 4.2 respectively. These results may offer a further study on the hyperaccumulation mechanism and distribution of Cd or Pb ions in contaminated plant for the contaminated soils. Due to the heavy metals in contaminated soils may have strong relationships with organic matter concentration, but more significantly with their extractable forms. These data indicated the heavy metals in the soils could bond with humic or fulvic acid to form organometallic compounds that may be evaluated by EXAFS spectroscopy. The major routes of phytoremediation of plants include active metal efflux, synthesis of metal-binding peptides like metallothioneins, phytochelatins, and vacuolar sequestration. In addition, Strains or ecotypes in strongly metal-enriched environments have usually evolved exceptionally high levels of heavy metal tolerance.

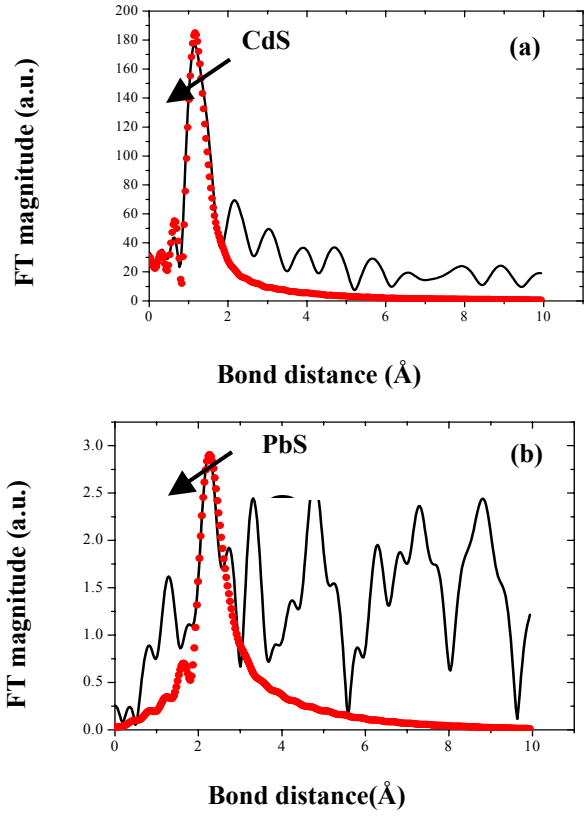

Figure 1. Fourier transform of (a) CdS and (b) PbS for sulfur K edges hyperaccumulated in the contaminated tissues of plants. The best fitting of the EXAFS spectra are expressed by the circle lines.