

XANES/EXAFS Characterization of Heavy Metal Bioaccumulated in Contaminated Oysters (*Crassostrea gigas*) on P or S Ligand-Binding Sites

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Generally, pacific oysters (*Crassostrea gigas*) have been cultivated by using a bottom-layer method in bays or gulfs. In Taiwan, due to rapid industrialization, urbanization, or various development projects along its coastline and catchment basin, the bays receive toxic discharges from polluted streams and water courses. Recently, toxic heavy metals in the streams across the steel, metallurgy, coating industries or semiconductor manufacturing, especially in Keh-Yea stream, are found. Thus, water quality in the bays has been deteriorated and local production of oyster has been significantly reduced. The functional groups within the cell wall of oysters provide the amide, amine, hydroxyl, carboxylic, imidazole, sulfate, phosphate, and thiol (mercaptan) or sulfhydryl (mercapto, R-SH) groups that can bind metals. Especially, thiol, sulfate or phosphate functional groups are more stronger sites bound with heavy metal ions and may form M-SH, MSO₄ or MPO₄ complex. The uptake of metal ions can take place by entrapment in the cellular structure and subsequent biosorption onto the binding sites present in the cellular structure of oysters.

EXAFS spectroscopy can investigate the information on the atomic arrangement of bioaccumulated Cu metals in terms of bond distance, number and kind of near neighbors, thermal and static disorder. The mechanisms of Cu biosorption or bioaccumulation in the soft tissues of oysters may be easy to imagine but have not been clearly identified for the fine structures of Cu bonding in the tissues of oysters up to now. Thus, the main objective of the present study was further investigate the fine structures and oxidation states of S species bound with Cu ions bioadsorbed or bioaccumulated in the soft tissues of oysters by EXAFS spectroscopy.

The EXAFS 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 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. The EXAFS data will be analyzed by using the UWXAFS 3.0 program and FEFF 8.0 codes.

High-resolution camera was used primarily for examination of the microstructure and morphology of the soft tissues of contaminated oysters shown in Figure 1. Colorful morphology and structure of metal-

contaminated oyster with its soft tissue were observed by photos in the oyster breed area. The green-like color of soft tissue may indicate that the oyster was contaminated by organometallics especially for copper ions. The cell surface of the tissues for contaminated oysters consists of biopolymer such as polysaccharides, proteins, and lipids, which act as a basic binding site of copper ions. The functional groups within the cell wall of contaminated oysters provided the sulfate, thiol or sulfhydryl groups that can bind copper ions. Especially, thiol or sulfate functional groups are much stronger sites bound with copper ions and may form Cu-SH or CuSO₄ complex. The S EXAFS spectra indicating the Cu-S species with bond distance of 2.05 Å was found in Figure 2. Coordination numbers of the Cu-S species from S EXAFS spectra was 2.5. The uptake of copper ions can take place by entrapment in the cellular structure and subsequent sorption onto the binding sites present in the cellular structure of the tissues for contaminated oysters.

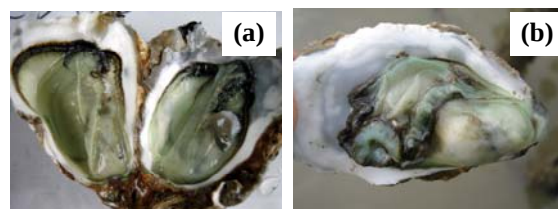


Figure 1. (a) Colorful morphology and (b) structure of metal-contaminated oyster with its soft tissue. The green-like color of soft tissue may indicate that the oyster was contaminated by organometallics especially for Cu ions.

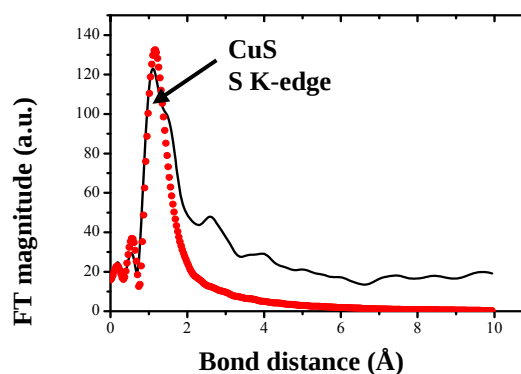


Figure 2. Fourier transform of CuS for sulfur K edges EXAFS that the Cu species bonded with sulfur in the tissue of contaminated oyster sample. The best fitting of the EXAFS spectra are expressed by the circle lines