

## 게껍질 표면에서의 납의 침전

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### MICROPRECIPITATION OF LEAD ON THE SURFACE OF CRAB SHELL

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#### **Introduction**

The presence of heavy metals in the environment can be detrimental to a variety of living species. Unlike organic pollutants susceptible to biological degradation, heavy metals will not be degraded into harmless products. Therefore, a treatment of ground waters and wastewaters containing soluble heavy metals is important for public health. Various treatment methods have been employed to remove heavy metals from industrial wastewaters : precipitation, adsorption, ion exchange, reverse osmosis, electrolysis, etc. However, because of its certain limitations, attention has centered on new ways of removing heavy metals from aqueous and solid wastes. Biologically based processes for metal removal are effective under various conditions as alternatives where conventional treatment methods are failed. The adsorption by biosorbents is very effective for the removal of trace quantities of metals from wastewater. A non-protein polymer such as chitin and chitosan have been well known as biosorbents for metal removal among other biopolymers. Chitin is a natural polysaccharide consisting of (1-4)-2-acetamido-2-deoxy-D-glucose units, some of which are deacetylated. Acetamido groups are known as nonspecific chelators and they form hydrogen bonds with heavy metals. It is obtained from fungi, insect, lobsters, shrimp, krill and so on but the most important commercial sources are the exoskeletons of crabs. *Protunus trituberculatus* is a kind of crab of which shell is consisted of 58% calcium carbonate, 17% chitin, 10% protein, 13% moisture, and 2% others, which is based on weight percentage, approximately. Herein, calcium carbonate, a major component of crab shell, may be useful in the metal-bearing wastewater treatment because calcium carbonate forms strong metal-carbonate precipitates and complexes with chelating agents. So far as, chitin or chitosan has been widely studied for removal of heavy metals from wastewater. However raw crab shell was not conducted.

In this paper, we performed series of batch tests using crab shells to treat lead-bearing wastewaters. Removal of the lead by crab shells was investigated for the various pH values in the synthetic wastewater. To search a major mechanism of lead removal, surface compositions and functional groups that are effective to the lead removal were studied and solid structure was also studied by X-ray diffraction method.

### **Materials and Methods**

**Materials** *Protunus trituberculatus* is a kind of crab commonly captured on the coast of Korea. The crab shells were powdered and sieved to 200 mesh, which were used in the experiments. Lead nitrate(Junsei Chemical Co., Ltd., Japan) solution was diluted with de-ionized water. All chemicals used were of reagent grade.

**Experimental Methods** Experiments were performed at room temperature and samples were prepared in duplicate. Crab shell about 0.5g/L was added to each set of 200mL flasks. Lead solutions without crab shells were used as a control. Ionic strength was adjusted with NaNO<sub>3</sub> to 0.05M. The pH in the flasks was adjusted with 1M/6M NaOH and 1M/6M HNO<sub>3</sub> to cover the pH range from 2.0 to 11.0. Supernatants were collected for the analysis of residual lead contents in capped test tubes and centrifuged during 5 minutes at 3000 rpm.

**Analytical Methods** Atomic Absorption Spectrophotometer(AAS, Perkin-Elmer model 3100) equipped with hollow cathode lamps was used to analyze the total metal concentrations in the supernatants. The wavelength for lead was 283.3nm. If necessary, samples were diluted with de-ionized water prior to analysis. Electron Spectroscopy for Chemical Analysis(ESCA, Leybold LHS-10 ESCA, Germany) ; it is also termed X-ray Photoelectron Spectroscopy(XPS), was used to analyze the surface compositions of crab shell. The crab shell used in the experiments was dried, pressed firmly onto tantalum stub, and transferred to the spectrometer under high vacuum about 10<sup>-9</sup> torr. Spectra were obtained using an Al(10keV, 30mA) source. Selected samples were observed with a Scanning Electron Microscope(SEM ; Philips 535M ) equipped with Energy Dispersive Spectroscopy(EDS ; EDAX international Co. PV 9900) at 15kV of the acceleration voltage. The samples were mounted on a stainless steel stub using double-stick tape and then coated with a thin layer of gold. Fourier Transform Infrared Spectrometer(FTIR ; Bomem MB-100) were used to identify the functional groups of crab shell. The solids formed in the solution with the addition of crab shell were examined by X-ray diffraction(XRD) methods. All XRD analyses were conducted with RIGAKU D/MAX-III X-ray diffractometer(Japan) using CuK- $\alpha$  radiation at 30kV and 40mA. Measurements were made using continuous scanning technique from 10 to 70 of 2 $\theta$ .

### **Results and Discussion**

**Equilibrium isotherm of lead uptake** The results of lead uptake isotherm, plot for solid-phase concentration of lead (crab shell uptake  $q$ , mg/g) against the residual equilibrium lead concentration( $C_{eq}$ , in mg/L), were used to evaluate the capacity of lead by crab shell. To avoid the lead-carbonate precipitates formed, the experiments were conducted at initial pH 5.0. The equilibrium isotherms showed that crab shell took up lead from aqueous solutions to the extent of 1300mg Pb/g crab shell. A shell of *Protunus trituberculatus* was mainly composed of calcium carbonate and chitin, which seemed to significantly affect the lead removal. Compared with other biosorbent, crab shell could be a suitable material to remove lead in the solution.

To search a major mechanism of lead removal by crab shell, we analyzed surface compositions and function groups that seemed to effective to the lead removal, and solid structure after reacting crab shell with PbNO<sub>3</sub> solution.

**FTIR spectra of crab shell for molecular characterization** The FTIR, a instrument of element analysis was used to identify the chemical and physical characteristics of the crab shell. From the result of chemical analyses by FTIR, some functional groups of the crab shell were observed. Comparing the spectrum of raw crab shell with the spectra of acid-rinsed and Pb-treated crab shell, the adsorption band at the range of  $1700\text{-}800\text{cm}^{-1}$  wavenumbers was significantly different. The reduced intensities of the two carbonate band centered at  $1443$  and  $873\text{cm}^{-1}$  were attributed to the dissolution of calcium carbonate in acidic reaction condition. The amine nitrogen on each chitin monomer unit has been suggested as the active site for metal ion coordination. The effect of metal coordination on the frequency of the amide ( $1658\text{cm}^{-1}$ ) was not observed as the difference of expected. The shifts in these bands have been reported in the literature, but for these systems was not significantly changed in this pH ranges. Consequently, FTIR spectra confirmed that  $\text{NHCOCH}_3^-$  and  $\text{CO}_3^{2-}$  were effective to the lead removal comparing before and after reaction with lead. From these results, we assumed that  $\text{Pb}^{2+}$  removal by crab shell was mainly through  $\text{CaCO}_3$  dissolution followed by lead-carbonate precipitation on the surface of crab shell.

**XRD patterns of crab shell for structural characterization** The X-ray diffraction patterns of the samples that were studied in pH 6.0 matched those of  $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2(\text{s})$  and  $\text{PbCO}_3(\text{s})$ . These solids seemed to be in equilibrium with  $\text{Pb}_2(\text{CO}_3)_2(\text{OH})_2$  and  $\text{PbCO}_3(\text{s})$ . The equilibrium speciations would suggest that  $\text{PbHCO}_3^+$  and  $\text{Pb}_3(\text{OH})_4^{2+}$  were the predominant Pb species in this pH region, which seemed to form strong  $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$  and  $\text{PbCO}_3$  solids. These observations suggested that below pH 10.3, the dissolved lead was in equilibrium with  $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2(\text{s})$  and  $\text{PbCO}_3(\text{s})$ . In this pH region where the crystalline of basic carbonates [ $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ ] formed, total dissolved Pb concentrations were below those expected from equilibrium.

Consequently from results of FTIR and XRD, we assumed that  $\text{Pb}^{2+}$  removal by crab shell was mainly through  $\text{CaCO}_3$  dissolution followed by  $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$  and  $\text{PbCO}_3$  precipitation near the surface of crab shell and then lead crystals formed are adsorbed to the chitin on the crab shell. The major mechanisms are hypothesized as follow.

**SEM micrographs of crab shell** The SEM micrographs equipped with EDAX displayed the surface of crab shell and structure of lead precipitates. A strong Ca EDAX signal was obtained for the crab shell samples which was rinsed with weak acid and then collected. However, none at all was observed for the samples which was equilibrated with lead in the acidic conditions. After equilibration with  $\text{Pb}^{2+}$ , the SEM micrographs shown in figure were obtained. Small flake-like particles were noted on the surface of crab shell. EDAX indicated that the particles were high in lead. At higher concentration, small nodules were observed on the surface of crab shell and these also showed Pb content by EDAX analysis. Much change occurred on the surface of crab shell after equilibration with lead in acidic conditions. Nitrate which was used to adjust ionic strength was not included in the above reactions, since no solid containing  $\text{NO}_3^-$  was formed. SEM micrographs equipped with EDAX show that lead crystals were a separate phase formed near the surface of crab shell. It appeared that most of the precipitation occurred near the crab shell surface where the solubility constants of lead carbonates were probably exceeded due to locally high carbonate [ $\text{CO}_3^{2-}$ ] concentrations.

### **Conclusions**

The characteristics of lead removal by crab shells were investigated for the various pH values in the synthetic wastewater. To search a major mechanism of lead removal, surface compositions and functional groups that are effective to the lead removal were studied by ESCA and FTIR. XRD and SEM analyses were also conducted to obtain the structural information of crystals on the surface of crab shell. Based on the present study, the following conclusions can be drawn :

1. Maximum uptake of lead by crab shell was 1300mg Pb/g crab shell in the equilibrium experiments. Crab shells can be a suitable biosorbent to remove lead in aqueous solutions.
2. Removal efficiency of lead by crab shell was pH dependent, but was less sensitive than that of control without crab shell. The optimum pH range for the maximum lead removal by precipitation and adsorption on the surface of crab shells was expanded to 5.5-11.0, whereas that of controls was from 8.5 to 11.0.
3. FTIR spectra confirmed that  $\text{NHCOCH}_3^-$  and  $\text{CO}_3^{2-}$  were effective to the lead removal comparing before and after reaction with lead. Surface compositions(e.g. O and N) and specific functional groups(e.g.  $\text{NHCOCH}_3^-$ ) seemed to act as nonspecific chelators and formed hydrogen bonds with heavy metals at lower pH values than those of 5.5.
4. As a results of XRD and SEM micrographs equipped with EDAX,  $\text{Pb}^{2+}$  removal by crab shell seemed to occur mainly through  $\text{CaCO}_3$  dissolution followed by  $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$  and  $\text{PbCO}_3$  precipitation near the surface of crab shell and then lead crystals formed were adsorbed to the chitin.

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