# 인산기로 화학변형된 조류를 이용한 중금속제거

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# Removal of Heavy Metals from Wastewater using Phosphorylated Marine Alga *Undaria pinnatifida*

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## Introduction

Many industries discharge heavy metals such as lead, cadmium and mercury in their waste-water. The presence of lead in drinking water is known to cause various types of serious health problems leading to death in extreme exposure cases[1]. The requirement for economical and efficient method for lead removal from waste-water or ground water has stimulated the investigation of unconventional method. These days many research results using biomass such fungi, bacteria and algae for removal of heavy metals have been reported.

But simple biomass including living or dead one cannot be directly adapted to real process for removal of heavy metals because its uptake capacity for heavy metals is still low compared to that of commercial ion-exchange resin. If its uptake capacity could increase dramatically by simple chemical modification of cell wall, chemically modified biomass could be used efficiently in real waste-water process.

Macaskie, L.E. et al[2] has reported that liberated phosphate ion from glycerol 2-phosphate by phosphatase enzyme could form precipitates with lead and cadmium on *Citrobacter* cell surface. Metal accumulation may be limited by column blockage by the precipitates formation of metal phosphate, while the need for a phosphate donor involves an additional economic consideration.

This problem may be detoured by introducing phosphate groups onto the cell wall. In this report, the cell wall of brown marine alga, *Undaria pinnatifida,* was chemically modified by making a phosphate ester linkage between phosphoric acid and hydroxyl group of the cell wall. *Undaria pinnatifida* having phosphate groups could remove various heavy metals and showed much higher uptake capacity for lead.

# Material and Methods

## Phosphorylation of Undaria pinnatifida

The phosphorylation reaction of biomass was accomplished as follows: 10 g of powdered Undaria pinnatifida biomass, 100 g of urea and 5 g of various forms of phosphate including orthophosphoric acid, disodium phosphate, and monosodium phosphate were added into 100 ml of dimethylformamide. The mixture was reacted at 100 ℃ for 5 hours. After cooling, the reaction mixture was filtered. The residue on filter paper was washed throughly with deionized water and dried in drying oven at 60 ℃. The yield were different depending on the forms of phosphate.

## Sorption experiments

The uptake capacity of biomass was determined by measuring the concentration of the lead ion in the aqueous phase before and after contact with the biomass and expressed according to; $q = \frac{V*(C_i - C_f)}{1000*M}$, where q is the uptake capacity(mg lead/ g biomass) and $C_i$ and $C_f$ are the initial and final lead ion concentrations(mg/l), respectively. V is the volume of sample solution(ml), and M is the dry weight of the biomass added(g).

# Results and Discussion

## The lead uptake by phosphorylated biomass

The effect of phosphorylation and its eventual biosorption performance is of primary interest. Figure 1 shows the isothermal uptake capacity of Undaria pinnatifida and phosphorylated biomass. The maximum uptake capacity of phosphorylated biomass increased about two times than that of natural biomass. Furthermore, affinity constant of phosphorylated one was much higher than that of natural one. The complex constant between phosphate and lead ion is known to be higher compared to that of lead and carboxyl group which is regarded as a major group for removal of lead in Undaria pinnatifida biomass.

The hydrogen ion concentration of the heavy metal solution was a very crucial factor in the lead uptake by phosphorylated Undaria pinnatifida biomass as shown in Figure 1. There is a competition between hydrogen ion

and lead ion to the binding site of the cell. Although affinity constant of phosphorylated biomass decreased at low pH values, its value still maintained higher values than that of natural biomass at high pH values.

As a result, the phosphorylated biomass could adsorb much heavy metal ions even in low pH solution and it may open the door to application for acidic waste-water.

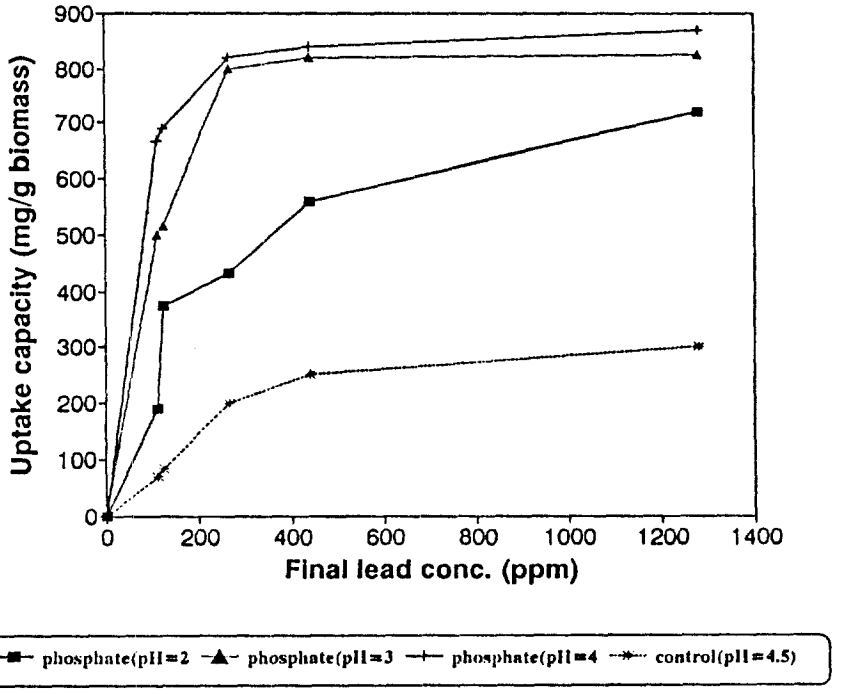


**Figure 1. pH effects on the uptake of lead by phosphorylated biomass**

## The instrumental analysis of lead-phosphorylated biomass complex

Since the phosphorylated Undaria pinnatifida accumulated the lead on its out layer, there is some possibility that the adsorbed lead could be eluted and recovered from the cell without any serious effects on the cell structure.

EDX was employed to confirm whether the electron dense part on the cell wall is made up of lead. The EDX probe connected to a scanning electron microscope was focused on the electron dense part observed on the TEM pictures. Typical EDX spectra of virgin biomass and lead-ladened is presented in Figure 2. EDX spectra proved the existence of lead on the cell

wall. Beverigee and Murray[3] have reported in the research for determination of metal deposit site that there are possible two-step mechanism : i.e., the initial binding reaction occurred between stoichiometric amounts of soluble metal and reactive sites within the wall. This metal then nucleated an inorganic deposition, which accumulated nonstoichiometric amounts. We adapted the XRD to determine whether the electron dense parts were composed of phosphate binding complex. In the case of simple metal hydroxides precipitate, XRD reveals amorphous structure. The spectra of XRD indicated the crystalline structure of metal-phosphate complex(Figure 3). So it means that there is the binding reaction between lead ions and binding sites on the cell wall.

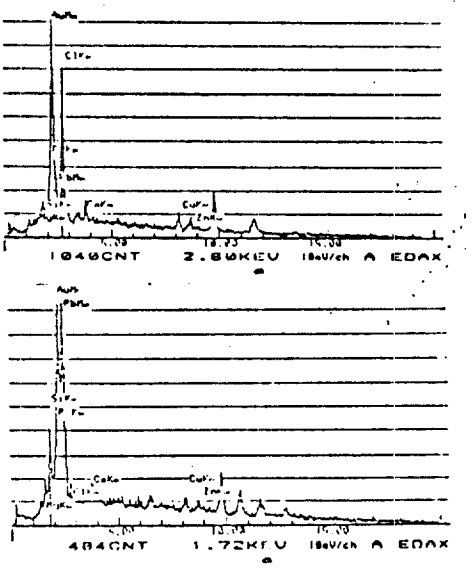

Figure 2. EDAX spectroscopy peak pattern
(a) before contact
(b) after contact lead

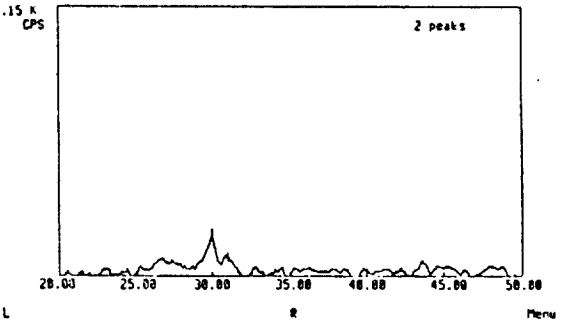


Figure 3. XRD peak pattern of biomas (two peaks detected)

# References

[1] Volesky, B.(ed.) 1990. Biosorption and biosorbents,. pp3-6. In: B. Volesky(ed), Biosorption of heavy metals, CRC Press Boca Raton, FL.

[2] Macaskie, L.E. 1990. An immobilized cell bioprocess for the removal of heavy metals from aquous flows. J. Chem. Tech. Biotechnol. 49 : 357-379

[3] Beveridge, T.J., Murray, R.G.E. 1980. Sites of metal deposition in the cell wall of *Bacillus subtilis*. J. Bacteriol. 141 : 876-887