

Biosorption of lead by *Laminaria japonica*

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Characteristics of biosorption of lead by marine algae, *Laminaria japonica*, were examined. The biosorption capacity of lead by *L. japonica* was achieved up to 30% of its own weight and proportional to the initial lead concentration. However, the opposite result was shown in different initial weight of biomass. Ion exchange reaction between lead ions and calcium ions was observed on lead biosorption with Ca-loaded biomass. Stoichiometric coefficient, which can represent the exchange ratio between metal ions and protons during elution process, was determined as 1.39. Therefore, it was concluded that the reaction between lead ions already attached in biomass and protons in bulk solution was not fully stoichiometric ion exchange relation at elution process.

Key words: *Laminaria japonica*, Lead Ions, Biosorption, Ca-loaded Biomass, Ion Exchange

1. Introduction

Heavy metals contaminated wastewaters are originated from mining, metal plate, dyestuff, electronic, and petroleum industries¹. Although conventional heavy metal treatment processes such as chemical precipitation, chemical oxidation and reduction, electrochemical treatment, evaporative recovery, filtration, ion exchange, and reverse osmosis can remove heavy metals from wastewater easily in its high concentration condition, it is difficult to be an attractive alternative in low concentration condition, especially below 10 mg/L of heavy metal.

To remove low concentration heavy metal ions from the water solution effectively, biosorption process has been proposed recently^{2,3}. Biosorption is a removal and/or recovery method, which is based on the metal-sequestering properties of certain natural materials of biological origin. The mechanisms of biosorption for sequestering heavy metals by biomaterial origins have been known as adsorption, inorganic

precipitation, complexation, ion exchange⁴, active transport⁵, and passive uptake⁶.

Lead could be called as "big one" because three important and severely toxic heavy metals, lead, cadmium, and mercury, have been notoriously called as "big three". Many researchers have developed a lot of biosorbents to remove lead, such as bacteria⁷, fungi⁸, and algae⁹. Among these biosorbents, especially, marine brown algae was known as a good biosorbent for removing lead ions in aqueous solution¹⁰, and it contains extracellular polymeric substances (EPS) such as alginate in cell surface above 30% of the cells in weight¹¹, which offers biosorption site for sequestering heavy metal ions. The main advantages of the biosorption process are as follows¹²; (1) metals at low concentration can be selectively removed (2) biosorbent has very low affinity for calcium and magnesium ions (3) effluent concentrations meet the regulations (4) the system operates over the broad pH range (pH 3 to 9) (5) the system is effective over a temperature range of 4 to 90 degree (6) the system offers low capital investment and low operation costs (7) the cost and liability of toxic sludge disposal are eliminated by converting pollutant metals to a metal product.

In this study, the availability of *Laminaria japonica* as a biosorbent for removing lead ions in aqueous solution was examined, which is grown and collected in Korean beach. The effects of pH, initial lead and biomass concentrations, and

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biosorption isotherm were investigated. Also, the biosorption isotherm for lead was fitted to Langmuir and Freundlich models. To examine the elution capacity of biomass and relationship between lead ions and protons as a eluent, distribution coefficient and stoichiometric coefficient were introduced.

2. Materials and Methods

2.1 Marine brown algae and Lead ion solution

Raw *Laminaria japonica* used in this experiment was collected and sun-dried on the beach near Kijang, east coast of Korea. Dried raw biomass was washed with distilled water. 5 g of raw biomass was added to 1L of 0.5M $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (100 rpm shaking overnight at room temperature). Biomass was filtered off and washed with the same volume of distilled water and then, dried overnight at 60. Lead ion solutions of desired concentration were prepared by dissolving analytical grade of $\text{Pb}(\text{NO}_3)_2$ in distilled and deionized water.

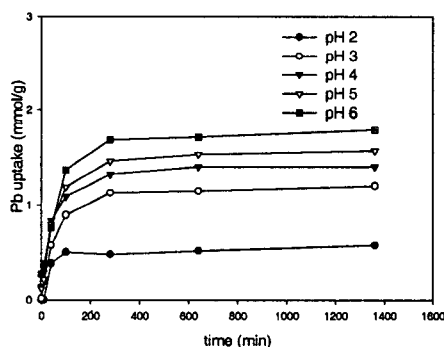


Fig. 1. pH effects on the biosorption capacity of lead by *L. japonica*.

2.2 Biosorption and elution experiments

Biosorption experiments were performed by suspending 100 mg of biomass in 100 mL of lead solution and shaking on a gyratory shaker. 0.1N HCl or 0.1N NaOH were used for pH adjustments. During the experiment, samples were taken and filtered using 0.45 Millipore membrane, and the filtrates were analyzed by AAS (Shimatsu AA 680, Japan) for the analysis of metal content. The filtered biomass was washed with distilled water,

dried overnight at 60C, and weighed for elution experiments. Metal uptake was calculated as $q \text{ (mmol/g)} = V(C_i - C_e)/M$ where: C_i and C_e are the initial and equilibrium lead concentrations in the solution, respectively (mM), V is the solution volume (L), and M is the initial mass of the biosorbent used (g).

Suspending 100 mg of lead-loaded biomass in 100 mL of 0.1N HNO_3 solution and shaking on a gyratory shaker for 8 hours performed elution experiments. At the end of the experiment, samples were filtered and the filtrate was analyzed by AAS. The filtered biomass was washed with distilled water, and dried overnight at 60C. The amount of desorbed lead was calculated as $q \text{ (mmol/g)} = V \times C_f / M$ where: C_f is the final eluted lead concentration in the solution, V is the solution volume, and M is the initial mass of the biosorbent used.

3. Results and Discussion

Fig. 1 shows the pH dependence on the biosorption capacity of lead by *L. japonica*. As shown in Fig. 1, the biosorption capacity was higher at higher pH than that at lower pH because of the competition effect with hydrogen ions in the solution [8].

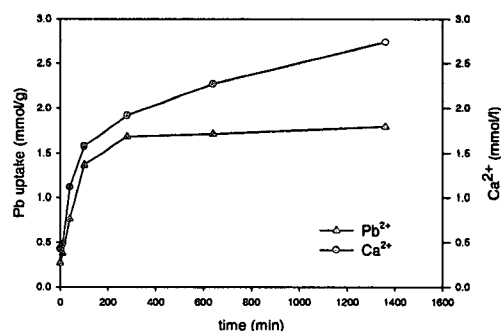


Fig. 2. Relationship between biosorbed Pb^{2+} and eluted Ca^{2+} during the biosorption of lead by *L. japonica*.

When the biosorption process proceeded at pH 6, relationship between the biosorbed lead ions and eluted calcium ions from biomass was shown in fig. 2. The amount of eluted calcium ions was higher than that of biosorbed lead ions, especially after 600 minutes of operation. It can be considered that stoichiometric ion exchange reaction between biosorbed lead ions and eluted

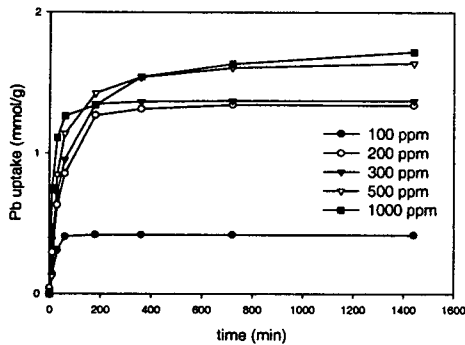


Fig. 3. Effect of initial lead concentration on its adsorption to *L. japonica*.

calcium ions was occurred in the beginning period, however, there was no stoichiometric ion exchange between those two metal ions after 600 minutes because of competition with protons in solution.

Fig. 3 shows the effect of initial lead concentration on the biosorption capacity by *L. japonica*. The biosorption capacity of lead at high initial concentration was higher than that at low initial concentration. However, in case of 300 and 500 mg/L, biosorption capacity showed almost equal, and similar tendency was shown at initial concentrations of 700 and 1,000 mg/L.

In Fig. 4, biosorption capacity of lead per unit mass of biomass was oppositely proportional to

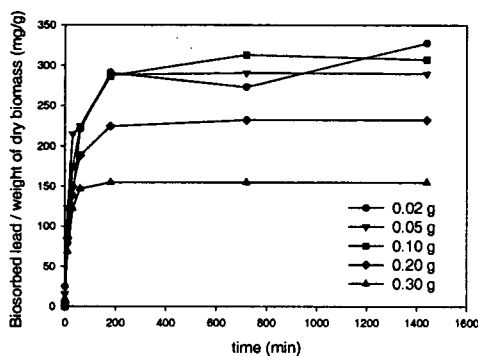


Fig. 4. Effect of biomass dry weight on lead biosorption to *L. japonica* at initial lead concentration of 500 mg/L.

the amount of biomass used. However, there was no difference of biosorption capacity at biomass weight of 0.10, 0.20, and 0.30 mg/L. This means

that the maximum biosorption amount was appeared at 0.10 mg/L biomass, thus, there was no need to feed more biosorbents in this experimental condition.

Fig. 5 shows the biosorption isotherms of lead by *L. japonica*. The experimental data was almost exactly accorded with both Langmuir and Freundlich isotherms within the concentration range used in this experiment. Therefore, the biosorption of lead by *L. japonica* was considered as a complex adsorption containing physical and chemical sorption mechanism. However, considering the result of fig. 2, the biosorption mechanism would be explained as a chemical adsorption such as ion exchange.

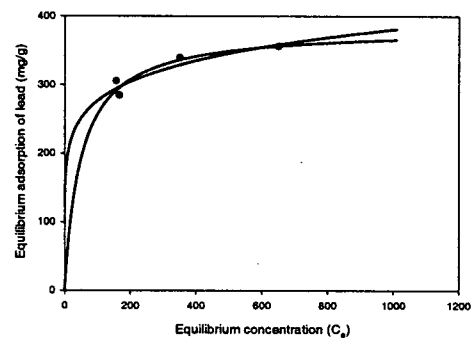
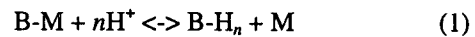


Fig. 5. Equilibrium isotherm of lead for *L. japonica*.

As shown in Fig. 6, the elution capacity of lead by HCl was higher at low final pH condition than that at high pH. At pH 1.0, the elution capacity was almost reached to 100%. Ion exchange between heavy metal ions and proton can be expressed as follows¹³;



Equilibrium constant from eq.(1) is

$$K = \frac{[B-H_n][M]}{[B-M][H]^n} \quad (2)$$

Therefore, eq.(2) can be transferred with logarithmic form.

$$\text{Log} \left(\frac{[B-M]}{[M]} \right) = \text{Log} D = n\text{pH} + \text{pK} + \text{Log}[B-H_n] \quad (3)$$

Where, M = heavy metal concentration in solution

D = distribution coefficient
 B-M = biosorbent-metal complex
 n = stoichiometric coefficient
 $B-H_n$ = protonated metal-binding sites

The stoichiometric coefficient, n , is dependent with protonated sites in biosorbent and pH, which represent the exchange ratio between metal ions and protons during elution process. In this experiment, the value of n was observed as 1.39. Therefore, it was concluded that the reaction between lead ions already attached in biomass and protons in bulk solution was not fully stoichiometric ion exchange relation at elution process.

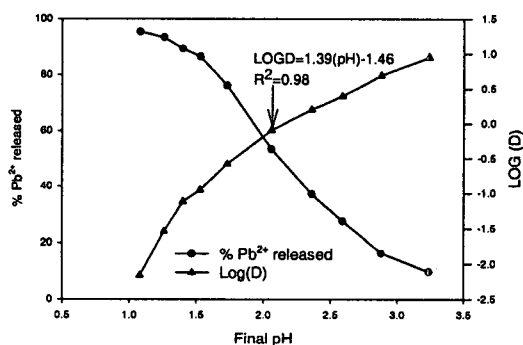


Fig. 6. Influence of pH on lead elution from *L. japonica* using HCl.

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