SHORT COMMUNICATION

Continuous Biosorption of Heavy Metal Ions by Ca-loaded *Laminaria japonica* in Fixed Bed Column

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Abstract—Continuous biosorption process for removal of lead and copper by laboratory scale fixed-bed reactor was carried out using Ca-loaded *Laminaria japonica*. All biosorption processes were observed as cation exchange such as Pb^{2+} vs. Ca^{2+}, Cu^{2+} vs. Ca^{2+}, and Pb^{2+} vs. Cu^{2+}. The affinity of lead ions towards *L. japonica* was stronger than that of copper ions because the initial amount of desorbed Cu^{2+} in Cu-Pb system was higher than that of eluted Pb^{2+} in Pb-Cu system.

Key words: Biosorption, Fixed Bed Column, Lead Ions, *Laminaria japonica*, Ion Exchange

INTRODUCTION

Waste heavy metal ions, which have a reputation of negative effect on the environment through the food chain, are generated from mining, dyestuff, electric, and petroleum industries. Conventional methods for removing heavy metal ions from wastewaters include chemical precipitation, oxidation or reduction, ion exchange, filtration, electrochemical treatment, membrane technologies and evaporation recovery [EPA, 1991]. These processes are ineffective or extremely expensive, especially when the heavy metals are in solutions containing in the order of 1 to 10 mg/L of dissolved state [Volesky, 1990].

In recent years, the removal of heavy metal ions by biomass materials, has received great attention because of its potential application in environmental protection. Some mechanisms such as purely physico-chemical interaction, metabolism and extracellular precipitation have been suggested for the removal of heavy metal ions from solutions by biomaterials [Suh et al., 1998a, b].

Among the huge diversity of biomass available, marine algae have already proved to be promising for heavy metal removal/recovery [Lee, 1996; Leusch et al., 1995]. The brown seaweed of the genus *Sargassum* has been studied for its capacity to selectively bind gold at low pH [Kuyucak and Volesky, 1989a] and chemically modified cells of *Undaria pinnatifida* showed the sorption capacity of 350 mg lead/g biomass, which is comparable to the capacity of ion-exchange resin [Kim, 1996].

Biosorption experiments of batch type in one-metal system have been mainly carried out. Although new biosorbents were developed and used in the pilot test on the basis of the results of the laboratory experiments, it did not put to practical use yet, because most heavy metal ions did not exist in water and wastewater as only one component.

In this study, in an attempt to investigate the possibility for the direct use of Ca-loaded *Laminaria japonica* packed in a fixed column, the relationship between heavy metal ions biosorbed and calcium ions desorbed was examined.

MATERIALS AND METHODS

1. Biomass (Ca-loaded *L. japonica*) and Heavy Metals

Raw *L. japonica* 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 1 L of 0.5 M $Ca(NO_3)_2 4H_2O$ (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 50 °C. Heavy metal solutions of desired concentration were prepared by dissolving analytical grade of $Pb(NO_3)_2$ and $Cu(NO_3)_2$ in distilled and deionized water. pH of the solutions in the feed tank were adjusted to 4.5 with pH controller.

2. Biosorption Experiments in the Column

A chromatography column of 2.5 cm I.D. and 50 cm length (Canlab) was used with an adjustable plunger and the initial height of the packing equal to L=27 cm. Concentrations of solutions used in these experiments were 100 mg/L (0.48 mmol) of lead and 31 mg/L (0.48 mmol) of copper, respectively. Continuous biosorption experiments were consisted of two steps. In the case of Pb-Cu system, at first, a single solution of lead was fed to the fixed-bed and the amount of biosorbed lead was compared with the desorbed calcium to investigate the mechanism of biosorption. Secondly, after continuous biosorption experiment of lead ion in the column was conducted, copper solution was fed to the column directly. Then, the concentrations of biosorbed copper, desorbed lead, and residual calcium were analyzed. In the case of Cu-Pb system, the order of feeding to the column was reversed. The superficial velocity of lead and copper solutions was 2 cm/min and controlled using a peristaltic pump. The samples of the effluent were collected by means of a fraction collector, and the concentrations of Pb^{2+}, Cu^{2+}, and Ca^{2+} in the samples were determined by atomic absorption spectrometer.

RESULTS AND DISCUSSION

In continuous fixed-bed biosorption column, the concentration

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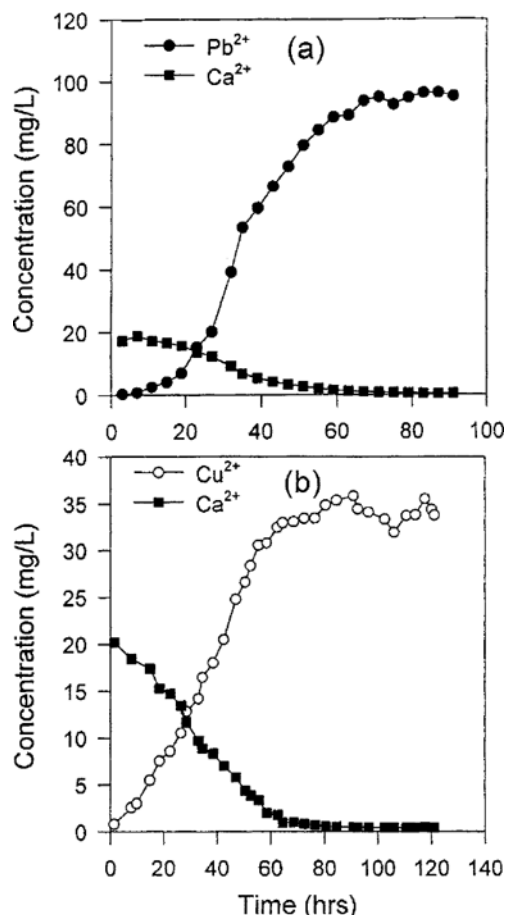E-mail: hslee@uou.ulsan.ac.kr

Fig. 1. Variances of Pb^{2+} and Ca^{2+} concentration (a) and Cu^{2+} and Ca^{2+} concentration (b) in effluent solution when Pb^{2+} and Cu^{2+} were biosorbed to Ca-loaded biomass in fixed bed column, respectively. Superficial velocity was 2 cm/min.
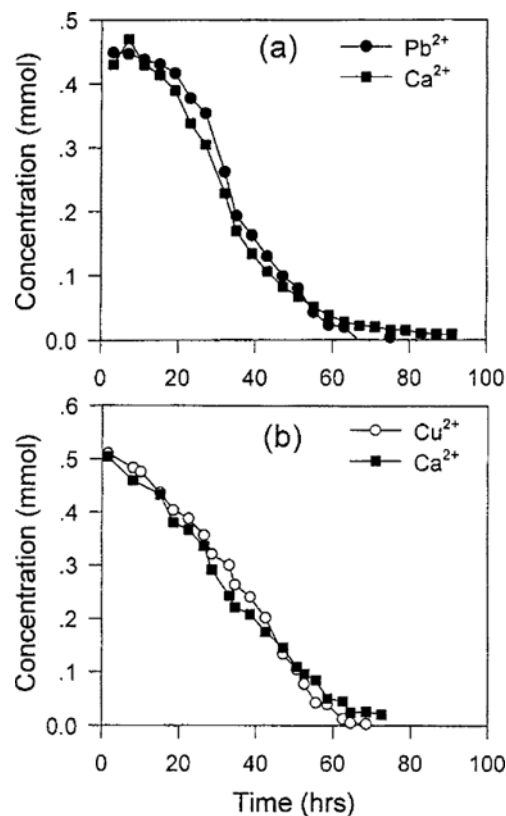

Fig. 2. Comparison of the amounts between biosorbed heavy metal ions and desorbed Ca^{2+}. (a) biosorbed Pb^{2+} and desorbed Ca^{2+}; (b) biosorbed Cu^{2+} and desorbed Ca^{2+}.

variance of effluent Pb^{2+} and Cu^{2+} with time was shown in Fig. 1. As shown in Fig. 1(a), about 60 hours were required to reach an equilibrium state for biosorption of Pb^{2+}. Ca^{2+} was eluted until 60 hours during the biosorption of Pb^{2+}. After 20 hours, both breakthrough of Pb^{2+} and desorption curve of Ca^{2+} were changed sharply. In the case of Cu^{2+} biosorption [Fig. 1(b)], the required time to reach an equilibrium state was similar to that of Pb^{2+}, but the breakthrough of initial effluent was different from that of Pb^{2+}. This means that the affinity of copper ions at the beginning period was slower than that of lead ions. The total biosorption amounts of lead and copper for 60 hours were about 252.78 mg/g and 68.63 mg/g, respectively. Molecular weight of lead and copper is 207.19 g and 63.55 g. Changing to mole basis, biosorption amounts of lead and copper became 1.22 mmol/g and 1.08 mmol/g, respectively. If there were same binding (may be ion exchange) sites in used Ca-loaded *Laminaria japonica*, it was considered that the difference of maximum biosorption amount between two metals was caused by the affinity to calcium ions and size difference of the two metals.

To compare the amounts of biosorbed Pb^{2+} and Cu^{2+} with that of desorbed Ca^{2+}, the concentrations of Pb^{2+}, Cu^{2+}, and Ca^{2+} in effluent solutions with time were shown in Fig. 2. They were represented all as unit of mmol. As shown in Fig. 2, the amounts of biosorbed Pb^{2+} and Cu^{2+}, and desorbed Ca^{2+} were almost coinci-

dental. Therefore, it was considered that the biosorption of Pb^{2+} and Cu^{2+} to *L. japonica* was an ion exchange process and Ca^{2+} ions bound to the biomass of *L. japonica* were replaced by Pb^{2+} and Cu^{2+} in the binding site of the cell. It was probable that all Ca-loaded biomass were changed to Pb-loaded one due to ion exchange. Kuyucak and Volesky [1989b] observed that the alginic acid, one of the cellular components, played a major role in biosorption of cobalt as a support material for ion exchange. In the case of Lee [1997], however, although the content of alginate could be changed by physical and chemical pretreatment, the maximum uptake of Cu, Cr, and Al was independent of the alginate content. This implies that other cellular components besides alginic acid can be considered for heavy metal biosorption of the biomass by ion exchange.

After a continuous Pb^{2+} biosorption in fixed-bed had been conducted, Cu^{2+} solution was fed to the column packed with Pb-loaded biomass. At this case, the amounts of biosorbed Cu^{2+} and eluted Pb^{2+} with time were shown in Fig. 3(a), and the reverse case was shown in Fig. 3(b). In the case of Pb-Cu system [Fig. 3(a)], the amounts of ion exchange for Pb^{2+} and Cu^{2+} were almost equal with time. But the amount of eluted Pb^{2+} was approximately 0.43 mmol/g biomass and about 40% of biosorbed lead ion were eluted by copper ion. In the reverse case, about 90% of biosorbed copper ion were eluted by lead ion. As shown in Fig. 3(b), the results of the Cu-Pb system were slightly different. The concentration of initial effluent for Cu-Pb system (0.5 mmol) was much higher than that of Pb-Cu system (0.3 mmol). This means that the displacement of
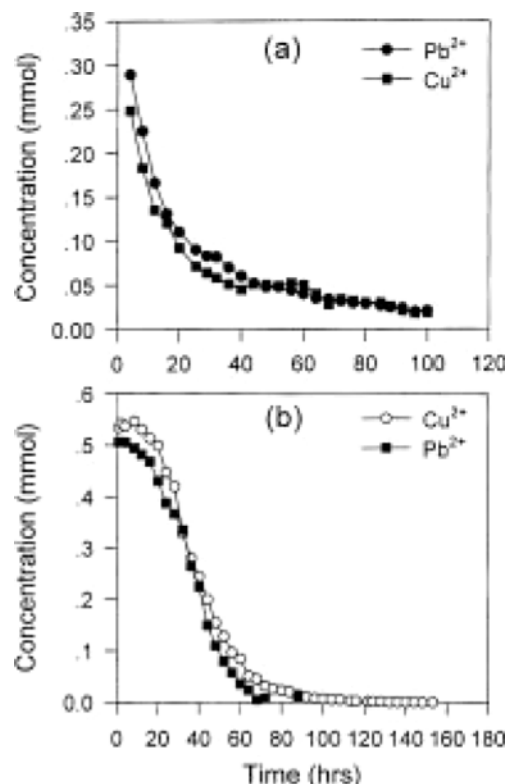
Fig. 3. The amounts of biosorbed Cu^{2+} and desorbed Pb^{2+} (a), and biosorbed Pb^{2+} and desorbed Cu^{2+} (b) in Pb-Cu and Cu-Pb continuous biosorption systems, respectively.

copper ion by lead ion easily proceeded, while the reverse case did not. Total uptakes of heavy metals for each case were approximately 1.12 mmol/g biomass. Therefore, the affinity towards biomass of Pb^{2+} was higher than that of Cu^{2+}. And the difference of the time to reach an equilibrium state between two systems was remarkable. Consequently, the difference of affinity between heavy metal ions and biomass in continuous two-metal systems has an important effect on the elution efficiency and the time to reach an equilibrium state of heavy metal ions.

CONCLUSIONS

The metal uptake of copper and lead in one-metal system was

approximately 1.22 mmol/g and 1.08 mmol/g, respectively. In both Pb-Cu and Cu-Pb systems, all biosorption processes by Ca-loaded *L. japonica* in continuous fixed-bed column were observed as cation exchange because the amounts of sorbed Pb^{2+}, Cu^{2+}, and eluted Ca^{2+} were almost coincidental. The affinity of lead towards biomass was stronger than that of copper.

ACKNOWLEDGMENT

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