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Biosorption of Chromium by Ca-loaded *Laminaria Japonica* Biomass

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1. Introduction

Biosorption, the passive non-metabolically mediated process of metal ion binding by living or dead biomass, may serve as a means for purifying industrial wastewaters that contain toxic heavy metal ions. Compared to other technologies, the advantages of biosorption are the high purity of the treated wastewater and the cheap raw material: waste products from other industries (e.g., fermentation byproducts) or naturally abundant biomass (e.g., marine algae) may be used as biosorbents(1).

The metal ion binding mechanism in biosorption may involve different processes such as complexation, coordination, electrostatic attraction, or microprecipitation whereby ion exchange plays a major role in the binding of metal ions by algal biomass(2). In the case of biosorption of heavy metals by brown algal biomass, the mechanisms can be viewed as being extracellular or occurring discretely at the cell wall(3).

The order Laminaries are the most important groups of algae to the field of biosorption because of the abundance of their cell wall matrix polysaccharides and extracellular polymers. The alginate polysaccharides is mainly responsible for the natural ion-exchange capacity of the brown algae. Its unique macromolecular structure gives rise to selective metal binding whose mechanism is commonly represented as "egg-box" model. The "egg-box" model have been supported by X-ray diffraction(4).

Although *L. Japonica* reveals a high adsorption capacity of heavy metals and almost 99% of heavy metal elution by means of acids, the percentage of Cr ion desorption is very low.

The main objectives of this study were to analyse the sorption capacity of *L. Japonica* and try to determinate the reasons of low Cr ion desorption.

2. Materials and methods

2.1. Biomass treatment

Previous investigations(5) showed that Ca-loaded biomass is more suitable for Cr ion sorption. Raw *L. japonica* was collected and sun-dried on the beach near Kijang, East Coast of Korea. Dry raw biomass was treated by soaking in 1 N $CaCl_2$ solution in flask

shaken gently on an orbital shaker. Five grams of raw biomass was added to 500 ml of 1 N $CaCl_2$ (100 rpm shaking for 8 hours at room temperature) then the biomass was filtered off and washedwith the same volume of distilled water and then dried for 24 hours at 60℃. The weight loss of biomass throughout pretreatment was approximately 37%.

2.2. Sorption experiments

The Chromium solutions of desired concentrations were prepared by dissolving $Cr(NO_3)_3$ in distilled deionized water to desired initial concentrations. All sorption experiments were performed by suspending 100 mg of biomass in 100 ml of the metal-bearing solution and shaking on an orbital shaker for 8 hours. 0.1 N HCl and 0.1 N NaOH were used for pH 4.5 adjustment. At the end of experiment each sample was filtered by 0.18 μm Millipore membrane and the filtrate was analyzed by atomic adsorption flame emission spectrophotometer (Shimadzu AA 6200) for the equilibrium metal content. The reaction is commonly monitored by measuring the amount of metal remaining in solution until it becomes time invariant. The filtered biomass was washed with distilled water and dried for 24 hours at 60℃ and weighted for desorption experiments.

The metal uptake was calculated as q(mg/g) (Eq. 1)

$$q = \frac{V \cdot (C_i - C_e)}{M}, \tag{1}$$

where C_i and C_e are the initial and final (equilibrium) metal concentration in the solution, respectively (mg/L), V is the solution volume (L), and M is the initial mass of the used biosorbent (g).

Desorption experiments were performed by: (a) suspending 50 mg of metal-loaded biomass in 50 ml 0.1 N HNO_3 (b) heating under 700 oC in electric furnace for 5 hours. At the end of each desorption experiment the samples were filtered using Whatman No. 1 and the filtrate was analyzed by AAS. The filtered biomass was washed with distilled water, dried for 24 hours at 60℃ and then weighted. The metal uptake was calculated from the desorption experiments results as q (mg/g) (Eq. 2)

$$q = \frac{V \cdot C_f}{M}, \tag{2}$$

where Cf is the final eluted metal concentration in solution (mg/L), V is the solution volume (L), and M is the initial mass of the used biosorbent (g).

At the end of experiment all biomass samples were analysed by Scanning Electron Microscope (Hitachi S-3000N).

3. Results and discussion

The adsorption of metals by different types of algae was observed to be a reversible phenomenon and could be represented by Langmuir adsorption isotherm. Langmuir isotherm equation is based on monolayer sorption onto a surface with finite number of identical sites, which are homogeneously distributed over the sorbent surface and is given by Eq. 3

$$\frac{C_e}{q} = \frac{C_e}{q_{max}} + \frac{1}{(K \cdot q_{max})}, \quad (3)$$

where q_{max} and K are Langmuir constants denoting maximum adsorption capacity and the affinity of binding sites ($k_{adsorption}/k_{desorption}$), respectively. These constants can be determinated from the $1/C_e$ versus 1/q.

Results calculating by eq. 3 are represented in Fig. 1. Langmuir constants q_{max} and K are calculating from the linear type of Langmuir isotherm and are 0.993 mmol/g and 0.003, respectively.

When the heavy metal concentration was increased, little pH increase was observed and this was attributed to the fact that the maximum binding capacity of the biomass had been reached and all exchangeable sites were occupied by the heavy metal.

It is well known that Cr^{3+} cations in water can undergo hydrolysis and complexation reactions, the extent of which depend primarily on the total Cr(III) concentration, on the pH, and on the type of anions present in solutions. The simple hydrolysis of Cr^{3+} can be written as follows:

$$Cr^{3+} + H_2O \rightleftarrows Cr(OH)^{2+} + H^+ \quad (4)$$

This reaction generates divalent cations Cr(OH)2+and protons which contribute to the increased acidity of Cr(III) solutions. If Cr^{3+} is being taken up by the biomass, reaction (4) proceeds to the left, leading to the depletion of protons and hence a rise in pH. In contrast, if Cr(OH)2+ sorbs onto the biomass, the reaction (4) naturally proceeds to the right and the solution becomes more acidic. The value of the equilibrium constant of reaction (4) has been reported by Hunt (1965) to be $K_h = 10^{-3.82}$ yielding a pK_h of 3.82. This means that at pH=3.8, approximately 50% of the overall Cr(III) content of the system will be in the $Cr(OH)^{2+}$ form.

Desorption experimental results are shown at Fig. 2.

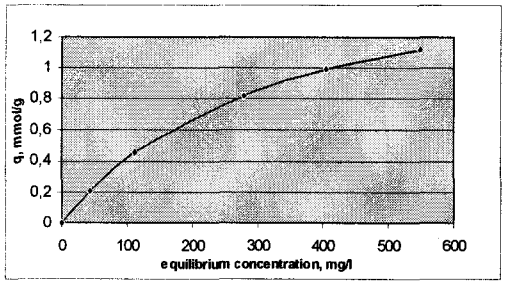

Fig. 1. Chromium uptake for Ca-loaded *L Japonica* biomass at pH 4.5.

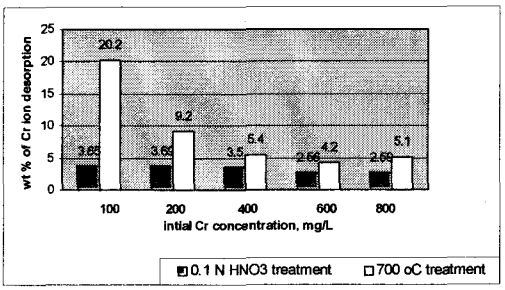

Fig. 2. Weight percentage of Cr ion desorption using 0.1 N HNO_3 and 700℃ treatment.

It seems to be obvious that under 700℃ all bonds in biomass should be broken and Cr ion should release, but AAS still detects very low desorption degree.

Scanning Electron Microscope (Hitachi S-3000N) was used for analysing the biomass structure and composition. The results are shown at Tables 1-3.

Table 1. The biomass composition after Cr sorption

Element	C	O	Ca	Cr
Weight %	30.54	49.71	0.16	19.59
Atomic %	42.19	51.50	0.06	6.25

Table 2. The biomass composition after 0.1 N HNO_3 treatment

Element	C	O	Ca	Cr
Weight %	43.03	47.71	0.25	9.01
Atomic %	53.15	44.20	0.09	2.56

Table 3. The biomass composition after burning at 700℃

Element	C	O	Ca	Cr
Weight %	10.59	44.14	1.22	44.05
Atomic %	19.53	61.04	0.69	18.74

Comparing the data get from AAS analyzing and Scanning Electron Microscope analyzing there reveals a difference between the amount of Cr ion in biomass detected (Table 4).

Table 4. The biomass composition detected by AAs and SEM

Detector	Cr ion amount, wt %		
	sorption	desorption by 0.1 N HNO_3	burning at 700℃
AAs	11.3	14.7	18.65
SEM	19.59	9.01	44.05

Analyzing gathered results one can come to the conclusion that the difference between adsorbed and eluted amounts of Cr and the difference between detected amount of Cr ion in biomass and in the solution may be caused by the formation of insoluble chromium oxide Cr_2O_3 in sorption solution. Due to this insoluble form Cr ion can not be detected to a high degree of accuracy.

More detailed analysis is needed to confirm the molecular structure of biomass for choosing the proper method of Cr ion desorption.

4. Summary

Biosorption can be used to eliminate heavy metals from industrial effluents or to recover precious metals from processing solutions. Scanning Electron Microscopedetected a high Cr sorption capacity of L. Japonica biomass almost 45% of its dry weight at pH 4.5. It should be mentioned that adjusting the pH influences on sorption capacity of biomass.

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