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Biosorption Characteristics in the Mixed Heavy Metal Solution by Biosorbents of Marine Brown Algae

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Abstract−The biomass of nonliving, dried marine brown algae *U. pinnatifida*, *H. fusiformis*, and *S. fulvellum* harvested in the sea near Cheju Island, Korea were studied for their sorption ability of copper, zinc, and lead. The metal uptakes by biosorbent materials increased with increasing initial metal concentration and pH in the range of C_i 0.05-10 mM. The higher metal uptakes were obtained in the range of pHs 4.0-5.3, 4.0-6.0, and 3.0-6.0 for copper, lead, and zinc, respectively. The metal uptakes by biosorbent materials decreased in the following sequence: *U. pinnatifida*>*H. fusiformis*>*S. fulvellum*. The maximum metal uptake values of *U. pinnatifida* for Cu^{2+}, Pb^{2+}, and Zn^{2+} in the single metal solution are 2.58, 2.6, and 2.08 meq/g in the range of pHs 5.3-4.4, respectively. The metal uptakes by biosorbent materials in the mixed metal solution decreased greatly in comparison to each metal uptake in the single metal solution.

Key words: Biosorption, Heavy Metal, Mixed Metal Ions, Marine Brown Algae, Biomass, Biosorption Rate

INTRODUCTION

There has been an increasing concern over dangerous levels of heavy metals contaminating the aquatic environment and the sources of potable water. Environmental pollution by toxic heavy metals has been caused by many activities, largely industrial, although sources are agriculture wastes and sewage disposal [Yu and Matheickal, 1996]. The specific problem associated with heavy metals in the environment is their accumulation in the food chain and their persistence in nature. Conventional technologies for the removal of heavy metals such as chemical precipitation, membrane technology, electrolysis, ion exchange, evaporatory recovery, adsorption method, biological treatment method, and flotation method using surfactants [Thomas, 1989] are often inefficient and/or very expensive when used for the reduction of heavy metal ions to very low concentrations [Volesky, 1990]. This has led to a growing interest in the application of biosorption technology for reducing the levels and accumulation of toxic metals in the environment.

Algae are photosynthetic microorganisms comprising thousands of genera and species, many of which have novel metal-binding properties. A number of workers investigated the feasibility of using cheaply available marine or fresh water algae for heavy metal removal [Lee and Suh, 2001; Yu and Kaewsarn, 1999; Kim et al., 1998; Darnall et al., 1986; Holan et al., 1993]. These studies revealed an interesting potential associated with certain algal species and that biologically active (living) or inactive (nonliving) algal cells can reversibly bind significant quantities of metal ions from aqueous solutions [Yu and Matheickal, 1996; Darnall et al., 1988; Kuyucak and Volesky, 1988; Volesky, 1987; Greene et al., 1987; Ferguson and Bubela, 1974]. However, the use of living algal culture in heavy-metal-recovery operations give some great difficulties for the control and maintenance of algal growth in polluted waters. Some studies have indicated that the nonliving algal biomass may be even more effective in sequestering and accumulating metallic elements than the living cells and tissues [Harssal, 1963; Rice, 1956] The major advantage of the use of nonliving algae is that binding and recovery of the metal ions can occur under conditions that are normally toxic to living cells. Increased heavy metal selectivity of biosorbent materials would be undoubtedly result in higher efficiency of heavy metal concentration processes, which in turn, would positively affect the economics of the overall process [Kim, 1996].

Marine brown algae contain multiple binding sites for metals such as phosphate, carboxyl and sulphydryl groups, none of which are likely to be specific for one type of metal [Hunt, 1986]. This has important consequences for any industrial process based on sorption of metals to biomass. Industrial effluents are likely to contain several different metals and metal binding components which may interfere with recovery of the metal of interest. However, many biosorption studies are carried out on metal solutions containing a single type of metals. Conclusions drawn from such studies may not be valid when application of this technology to an actual industrial effluent is considered.

The present work focuses on the sorption performance and selectivity of several heavy metals (copper, zinc, and lead) of three biosorbents of nonliving, dried marine brown algae *U. pinnatifida, H. fusiformis,* and *S. fulvellum.* These biosorbents are abundantly available ubiquitous marine brown algae in the sea near Cheju Island, Korea. Heavy metal uptake properties in the single and mixed heavy metal solution were examined. The effects of co-existing cations on biosorption were also investigated. The biosorption performances as functions of initial metal ion concentration and pH of the solutions, biosorption isotherms, biosorption rate were also investigated.

EXPERIMENTAL

1. Biomass

The marine brown algae (*Phaeophyta*) *Undaria pinnatifida, Hiz-*

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ikia fusiformis, and *Sargassum fulvellum* harvested in the sea near Cheju Island. These materials were washed with distilled water several time to remove excess salt. It was freeze-dried and stored in 4 °C refrigerator for further study.

2. Experimental Methods

Analytical grades of $Cu(NO_3)_2 \cdot 3H_2O$, $Pb(NO_3)_2$, $Zn(NO_3)_2 \cdot 6H_2O$, and $Cr(NO_3)_3 \cdot 9H_2O$, Na_2CO_3, HNO_3, and NaOH were used and the solutions were prepared with deionized distilled water. The stock solutions of metal ions were prepared as 1,000 mg/L and diluted as desired concentrations with water, respectively.

In the biosorption kinetics experiments in the solution containing single metal ion, 500 mL of metal solution prepared as 50 mg/L (Cu 0.787 mM, Zn 0.765 mM and Pb 0.241 mM) and 0.2 g of biomass were added to 1 L Erlenmeyer flask, and then batch experiments were performed stirring with magnetic stirrer. The uptake capacity of biomass was determined by measuring the concentration of the metal ion in the aqueous phase before and after contact with the biomass.

The biosorption experiments in the solutions containing mixed metal ions, were performed by the same method as the biosorption kinetics experiments in the solutions containing single metal ion using the concentrations of metal ions prepared as each metal ion concentration of 50 mg/L (Cu 0.787 mM, Zn 0.765 mM and Pb 0.241 mM), respectively.

In order to investigate the effect of pH on the biosorptive capacity of metal ions by biosorbent materials, pHs 2, 3, 4, 5, and 6 were controlled with sodium carbonate (10^{-4} N) and HNO_3 or NaOH and performed as above.

The concentrations of metals in solution with air-acetylene (copper, zinc, and lead) by an atomic absorption spectrophotometer (GBC 904AA). The detection limit and wavelength for copper, zinc, and lead were 25 µg/L and 324.7 nm, and 9 µg/L and 228.8 nm, and 60 µg/L and 217 nm, respectively.

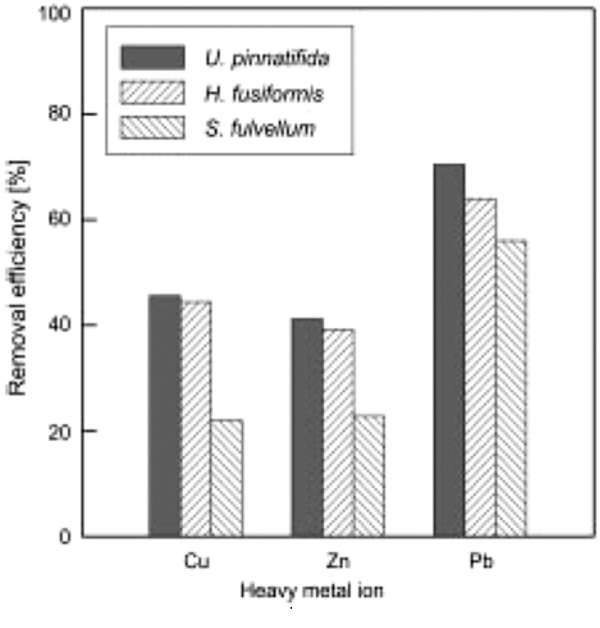

Fig. 1. Comparison of removal efficiency for biomass of nonadjusted pH in single metal ion solution (initial metal ion concentration: Cu 0.787 mM, Zn 0.765 mM, Pb 0.241 mM).

RESULTS AND DISCUSSION

1. Metal Uptake in the Single Metal Solution

1-1. Comparison of Metal Uptake Abilities for Biosorbents

Fig. 1 compares each metal ion removal performance of the biosorbents of nonliving, dried marine brown algae *U. pinnatifida*, *H. fusiformis*, and *S. fulvellum*. 0.2 g of each biosorbent were used in the 50 mg/L metal ion concentration in 500 mL solution at 20 °C.

This figure shows that Cu, Zn, Pb and Cr metal ion removal performance were 46, 41, 70, and 50% in the case of *U. pinnatifida*; 44, 39, 64, and 41% in the case of *H. fusiformis*; 22, 23, 56, and 36% in the case of *S. fulvellum*, respectively. This finding demonstrates that different algal species exhibit different metal binding capacities at a given pH and is similar to the result of Greene et al. [1987] and Gardea-Torresdey [1988]. Among the biosorbent materials the metal biosorption capacity by each biosorbent decreased in the following sequence: *U. pinnatifida*>*H. fusiformis*>*S. fulvellum*.

Fig. 2 shows the variation of the metal ion uptake with time. As shown in Fig. 2, the experimental results show that the higher metal biosorption capacity as initial concentration was higher, and that about 90% of the total uptake occurred in 30 minutes, irrespective of metal concentration. This feature are caused by the increase of driving force of mass transfer as the initial metal ion concentrations rise. This is considered because all the metal ion is adsorbed to the surface of biosorbent, similarly to the inorganic biosorbent but differently from living microorganism.

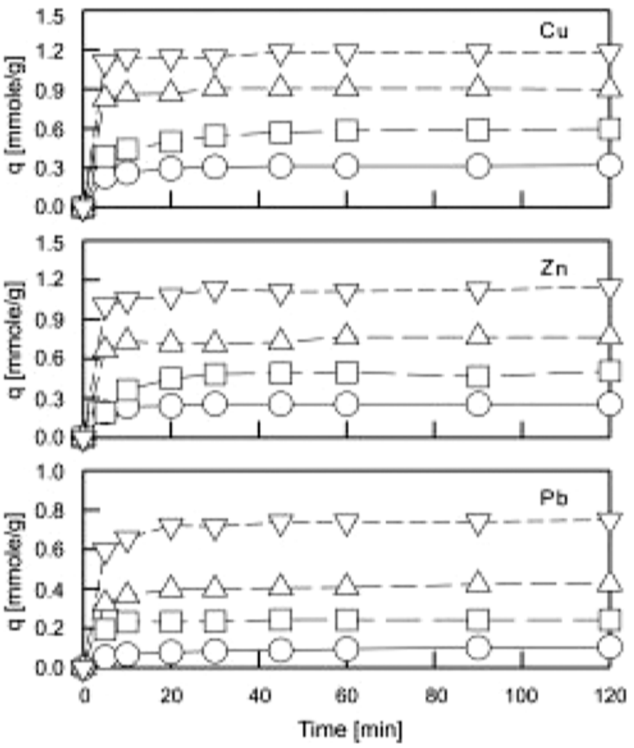

Fig. 2. Uptake profiles of each metal ion biosorption by biomass of *U. pinnatifida* at nonadjusted pH (biosorbent dry mass: 0.2 g, initial metal concentration: Cu (○: 0.157 mM, □: 0.393 mM, △: 0.787 mM, ▽: 1.574 mM), Zn (○: 0.153 mM, □: 0.382 mM, △: 0.765 mM, ▽: 1.530 mM), Cu (○: 0.048 mM, □: 0.121 mM, △: 0.241 mM, ▽: 0.483 mM).

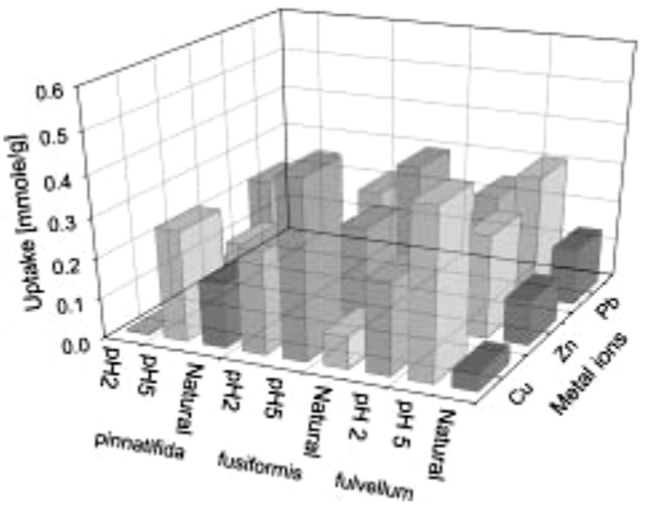

Fig. 3. Comparison of each metal ion uptake by each biomass at pH 2, pH 5, and nonadjusted pH.

Fig. 3 compares each heavy metal ion uptake of the biosorbents of nonliving, dried marine brown algae. As shown in this figure, a higher uptake was obtained in the pH 5 and it was observed that the metal ion uptakes are highly affected by pH of solution.

1-2. Effect of pH on Heavy Metal Uptake

It is known that the pH of the solution is more sensitive than temperature and heavy metal biosorption increases as pH approaches to neutral [Norberg and Persson, 1984] or the optimum pH is present according to the biosorbents used [Haug et al., 1974; Strandberg, 1981].

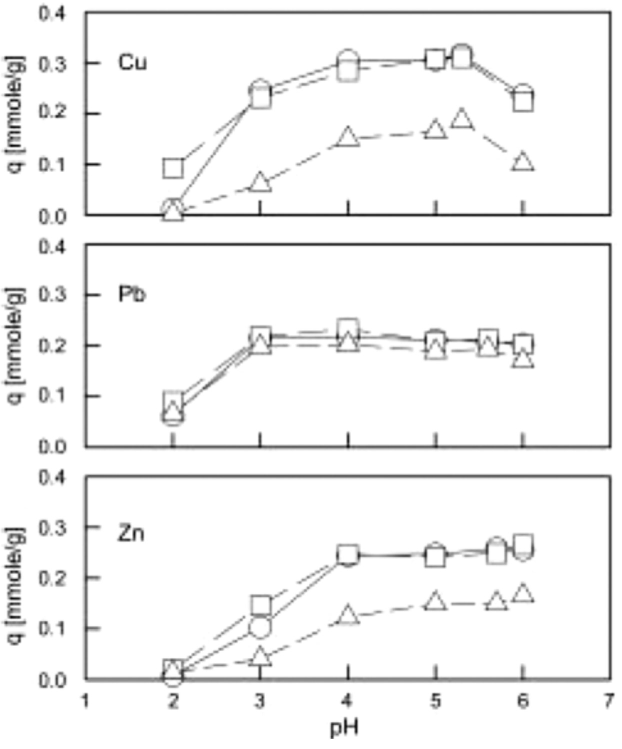

Fig. 4. Effect of pH on each metal ion uptake (Biosorbent: *U. pinnatifida* (○), *H. fusiformis* (□), *S. fulvellum* (△); Biosorbent amount: 0.2 g; Initial metal ion concentration: Cu 0.787 mM, Zn 0.765 mM, Pb 0.241 mM).

Fig. 4 shows the effect of pH on the heavy metal ion uptake by biosorbent materials in a solution containing each heavy metal ion of 50 mg/L (Cu 0.787 mM, Zn 0.765 mM and Pb 0.241 mM). The adsorption of heavy metals increased with rising pH of solution. As shown in Fig. 4, a low pH of 2 resulted in a markedly lower metal biosorption. A higher uptake was obtained in the pH range of 4.0-5.3, 4.0-6.0, 3.0-6.0, and 4.0-5.0 for copper, zinc, and lead, respectively. These results show the suitability of the biosorbent even for treatment of acidic waste waters, and were compared to those of Aksu and Kutsal [1987] who also studied the heavy metal ions uptake and found that pH 4.2, 2.2, and 3.9 were the optimum values for copper, iron, and zinc uptake by *Chlorella*, respectively.

The pH dependence of metal uptake could be largely related to the various functional groups on the algal cell surfaces and also on the metal solution chemistry [Yu and Matheickal, 1996]. Crist et al. [1981] demonstrated that mechanism of metal-ion binding to nonliving algal cells may depend on the species of metal ion, the algal organism, and the solution conditions. They presented evidence that metallic cation binding to *Vaucheria* sp. occurred at least in part by an ion-exchange mechanism and suggested that electrostatic attraction plays an important role in metal uptake process. It is considered that the pH dependence of metal-cation binding generally occurs when the active metal-binding sites (such as carboxylate or amine groups) can also bind protons. At lower pH values, the concentration of protons is so high that many metal-adsorbent bonds are made labile and the protons effectively compete with metal ions for the binding sites, thus resulting in a reduced metal uptake. At higher pH, the metal ions become more competitive with hydrogen ions resulting in an increased metal uptake.

Experiments were not conducted beyond pH 6.0 to avoid heavy metal precipitation because insoluble metal hydroxides start precipitating from the solutions at higher pH values and making the true sorption studies impossible.

1-3. Adsorption Equilibrium

The adsorption isotherms for each ions are shown in Fig. 5. Adsorption from aqueous solution at equilibrium is usually correlated by one of the two following adsorption isotherm relationships, the

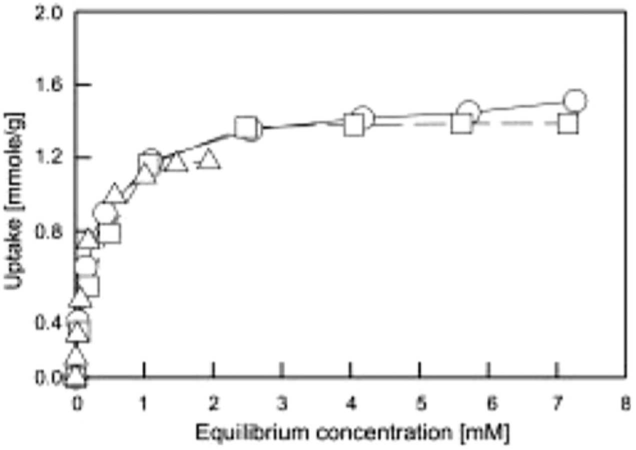

Fig. 5. Metal biosorption isotherms for *U. pinnatifida* at nonadjusted pH (○: Cu, □: Zn, △: Pb).

Langmuir isotherm and the Freundlich isotherm [Kam et al., 1997; Lee et al., 1997].

A general form of the Langmuir model equation is

$$q=\frac{q_{max}bC}{1+bC} \tag{1}$$

The Freundlich isotherm, which is an empirical formulation, frequently will represent the adsorption equilibrium over a limited range in solute concentration. One form of the equation is

$$q=KC^{1/n} \tag{2}$$

The informative values for the Langmuir isotherm and the Freundlich isotherm, which were obtained from experimental data, are also summarized in Table 1. From r^2 value in Table 1, it was found that the metal ion biosorption by the biosorbent materials followed the Langmuir isotherm better than the Freundlich isotherm. The adsorption of metals by microorganisms was observed to be a reversible phenomenon and could be represented by the Langmuir adsorption isotherm [Kuyucak and Volesky, 1987; Khummongkol et al., 1982].

The Langmuir parameter b reflects quantitatively the affinity between the sorbent and the sorbate. The maximum adsorption capacities (q_{max}) were obtained by using the nonlinear regression method of both adsorption equation. The q_{max} values for *U. pinnatifida* for Cu^{2+}, Pb^{2+}, and Zn^{2+} are 2.58, 2.6, and 2.08 /g, respectively. The corresponding values for *H. fusiformis* are 2.29, 2.30, and 1.92 meq/g, respectively.

The comparison of the q_{max} values of dried marine brown algae *U. pinnatifida*, *H. fusiformis*, and *S. fulvellum* with those of other adsorbents is given in Table 2. Many of these adsorbents such as activated carbon, natural zeolite and ion exchange resins have been used in many practical metal recovery applications [Blanchard et al., 1984; Arulanantham et al., 1989]. It is seen from the table that the heavy metal uptake capacities of dried marine brown algae *U. pinnatifida*, *H. fusiformis*, and *S. fulvellum* exceed the uptake capacities of activated carbon, natural zeolite, and other biosorbents

Table 1. Removal efficiency and uptake of each metal ions by biosorbent materials in the single metal solution

Biosorbent materials	Langmuir parameters					Freundlich parameters				
	Weight basis		Mole basis			Weight basis		Mole basis		
	q_{max} (mg/g)	b	q_{max} (mmol/g)	b	r^2	K	n	K	n	r^2
Cu										
U. pinnatifida										
pH 3.0	65	0.044	1.023	2.796	0.992	8.65	2.833	0.818	3.198	0.926
pH 4.0	77	0.079	1.212	5.019	0.982	14.18	3.205	0.993	3.304	0.92
Nonadjusted pH^a	82	0.105	1.291	6.672	0.981	18	3.311	0.589	2.833	0.928
H. fusiformis										
Nonadjusted pH^b	72	0.1	1.133	6.354	0.983	17.48	3.425	0.926	3.407	0.926
S. fulvellum										
Nonadjusted pH^c	47	0.035	0.74	2.224	0.999	5.96	2.809	0.411	2.811	0.9
Zn										
U. pinnatifida										
Nonadjusted pH^a	68	0.068	1.04	4.445	0.989	13.56	2.994	0.837	2.996	0.922
H. fusiformis										
pH 3.0	50	0.053	0.765	3.465	0.985	8.1	3.096	0.478	3.094	0.904
pH 4.0	61	0.054	0.93	3.526	0.992	10.55	2.899	0.684	2.896	0.933
Nonadjusted pH^b	63	0.076	0.96	4.968	0.984	13.37	3.096	0.793	3.115	0.936
S. fulvellum										
Nonadjusted pH^c	44	0.043	0.673	2.811	0.987	5.73	2.762	0.397	2.766	0.89
Pb										
U. pinnatifida										
Nonadjusted pH^a	269	0.102	1.299	21.126	0.998	35.25	2.688	1.234	2.692	0.919
H. fusiformis										
pH 3.0	189	0.08	0.913	16.57	0.994	22.94	2.656	0.787	2.72	0.94
pH 4.0	213	0.093	1.028	19.262	0.994	27.31	2.717	0.939	2.717	0.918
Nonadjusted pH^b	238	0.992	1.15	20.298	0.992	30.89	2.591	1.04	2.747	0.918
S. fulvellum										
Nonadjusted pH^c	147	0.062	0.71	12.841	0.996	18.43	2.591	0.696	2.593	0.933

Cu^a: The starting pH of the solution with no pH adjustments was in the range of 5.3-4.8 and the final pH of those was in the range of 5.3-4.4, 5.3-4.4, and 5.3-4.6 for *U. pinnatifida*, *H. fusiformis*, and *S. fulvellum*, respectively.

Zn^a: The starting and final pH of the solution with no pH adjustments was in the range of 5.7-5.4.

Pb^a: The starting and final pH of the solution with no pH adjustments was in the range of 5.6-4.8 and 5.9-4.5, respectively.

Table 2. Comparison of heavy metal uptake capacities of various adsorbents [Yu and Matheickal, 1996]

Adsorbents	q_{max} (meq/g)		References
	Pb^{2+}	Cu^{2+}	
Natural zeolite	0.16		Matheickal and Yu [1995]
Powdered activated carbon	0.20		Matheickal and Yu [1995]
Saccharomyces cerevisae (yeast)		0.163	Volesky [1990a]
Rhizopus arrhizus (fungus)	1.00	0.50	Volesky [1990a]
Granular activated carbon, F-400	0.30	0.06	Muraleedharan et al. [1995]
Ion exchange resin (Duolite GT-73)	2.74		Volesky [1994]
U. pinnatifida (marine algae based)	2.6	2.58	This study
H. fusiformis (marine algae based)	2.30	2.26	This study
S. fulvellum (marine algae based)	1.4	1.5	This study

and are however comparable with those of the commercial ion exchange resin.

1-4. Biosorption Rate

For biosorption, the biosorption rate should be considered as well as the biosorption isotherms. Although it provides useful data on the maximum metal uptake capacity and biosorbent affinity for the metal, the biosorption isotherm cannot provide the information on the metal uptake of the biosorbent per unit time necessary for determining the contact time, which directly affects the design of equipment and operating costs when a biosorption process is used for water and wastewater treatments.

The biosorption rate was obtained from the results in Fig. 4 which showed the biosorption kinetics for each metal ion with initial concentration (C_o). Each initial biosorption rate (r_{ad}) at C_o was obtained from initial rate method [Fogler, 1992]. The initial biosorption rates on initial metal concentration for each metal ion were plotted in Fig. 5. As shown in this figure, the adsorption rate increased with the increase of initial metal ion concentration. The relationship between the initial biosorption rate and the initial concentration of metal ion can be expressed as follows:

$$r_{ad}=kC_o \tag{3}$$

The values of k were found by applying the values of r_{ad} and C_o to Eq. (3) using linear regression method. Data during the first 5 min of rate experiment was used for determination of biorption rate. The biosorption rate of each metal ion for *U. pinnatifida* could be expressed as shown in Table 3.

Khummongkol et al. [1982] developed a model for metal uptake by microorganisms based on surface adsorption and then applied it to the uptake of cadmium by *C. vulgaris*. They assumed a linear equilibrium relationship between the metal in the solution and that adsorbed on the cell surface. However, this was confirmed for low concentrations in short-term cadmium uptake experiments.

Although the metal biosorption can be expressed relatively well by the above rate equation in the range of this experiment as shown in Fig. 6, it is considered that more experiments, such as those on the biosorption rate with biosorbent amount, should be performed and verified in order to obtain more exact biosorption rate equation.

Table 3. Adsorption rate of each heavy metal ion as a function of initial concentration

Heavy metal	Adsorption rate, r_{ad} [mmole/g·min]
Cu	$0.157C_o$
Pb	$0.254C_o$
Zn	$0.139C_o$

2. Metal Uptake in the Mixed Metal Solution

Industrial effluents are likely to contain several different metals and metal binding components which may interfere with recovery of the metal of interest [Yu and Matheickal, 1996]. However, many biosorption studies are carried out on metal solutions containing a single type of metal. Conclusions drawn from such studies may not be valid when application of this technology to an actual industrial effluent is considered.

Crist et al. [1981] revealed that metal ions could not only displace protons, both other already bound molecules, for instance, strontium could displace zinc even though it was securely bound to the wall in studies with the alga *Vaucheria.*

It was investigated that the selectivity of the metals by biosorbents materials in the mixed metal solution. The biosorbents materials were added to the solution containing 50 mg/L of copper, zinc, and lead (Cu 0.787 mM, Zn 0.765 mM and Pb 0.241 mM) at different pH values, respectively and the respective metal uptake was examined. The biomass-metal system attained the final equilibrium

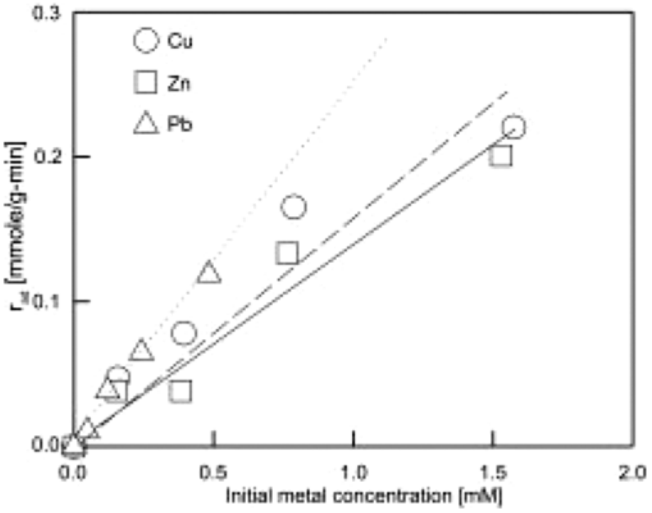

Fig. 6. Comparison of each metal biosorption rate for *U. pinnatifida* at nonadjusted pH.

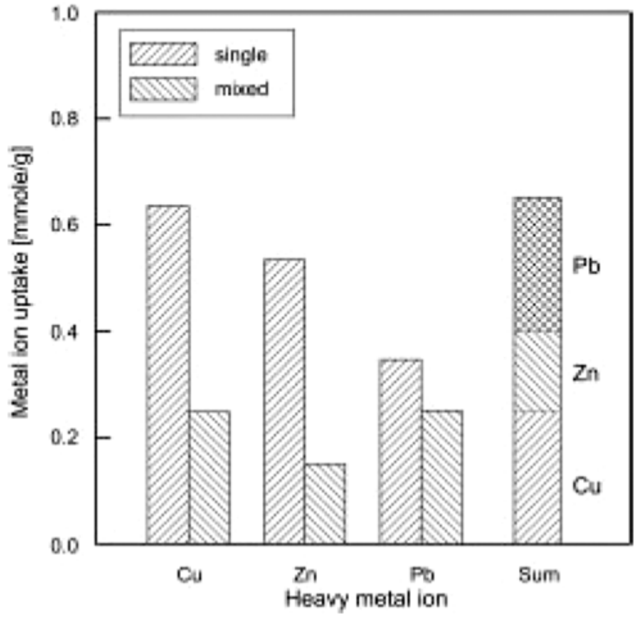

Fig. 7. Comparison of each ion uptake in the single and mixed metal solution for each biomass (initial solution concentration: 1.8 mM, each ion concentration in the mixed metal solution: Cu 0.787 mM, Zn 0.765 mM, Pb 0.241 mM).

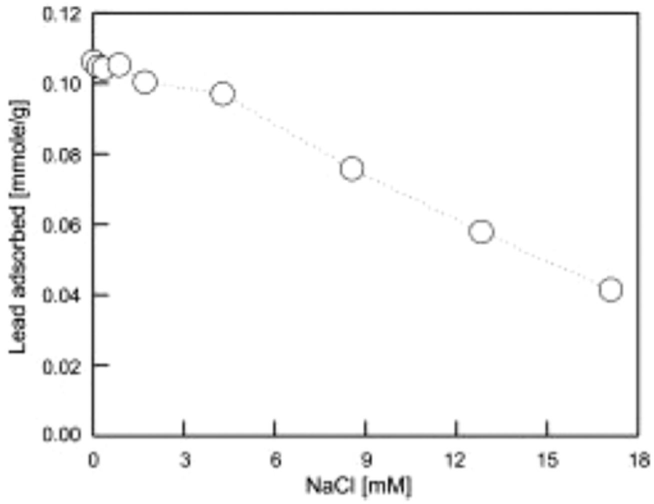

Fig. 8. Effect of ionic strength on the lead uptake by *U. pinnatifida* (Initial lead concentration: 0.048 mM, biosorbent amount: 0.2 g).

plateau at a contact time within 30 min. The starting pH of mixed metal solution without pH adjustments was 3.4 and changed little as biomass was added and after 2 hours of contact. The respective metal uptake in the mixed metal solution at different pH values was obtained and the results are shown in Table 4, together with the values obtained at C_i of 50 mg/L from the biosorption isotherm. As shown in Table 4, the metal uptakes except for lead in the mixed metal solution, decreased greatly compared to those in the mixed metal solution irrespective of biosorbent materials. However, the sum of each metal ion uptake in the mixed metal solution was higher than that in the single solution. This feature is caused by the increase of driving force of mass transfer as the initial total ion concentration increase. The metal uptakes by biosorbents decreased in the following sequence: *U. pinnatifida*>*H. fusiformis*>*S. fulvellum*. These results are identical to those in the single metal solution.

3. Effect of Ionic Strength

Industrial effluents contain large amounts of light metal ions such as calcium, magnesium, sodium and potassium along with the heavy metal ions. These metal ions often reduce the binding capacity of adsorbents such as commercial ion exchange resins. This effect can be smaller in biosorption systems. Thus, the effect of ionic strength

Table 4. Comparison of the uptakes of heavy metals in the mixed metal solution and those in the single metal solution at initial concentration of 50 mg/L (Cu 0.787 mM, Zn 0.765 mM and Pb 0.241 mM)

Heavy metals	q (mg/g)						q (mmole/g)					
	U. pinnatifida		*H. fusiformis*		*S. fulvellum*		*U. pinnatifida*		*H. fusiformis*		*S. fulvellum*	
	Single	Mixed	Single	Mixed	Single	Mixed	Single	Mixed	Single	Mixed	Single	Mixed
Cu												
pH 2.0	-	4.5	-	1.5	-	1.0	-	0.071	-	0.0234	-	0.016
Nonadjusted pH[a]	40.4	15.8	-	13.8	-	10.5	0.636	0.249	-	0.217	-	0.165
pH 5.0[b]	57.0	24.6	55.5	22.8	27.4	18.5	0.897	0.387	0.873	0.359	0.431	0.291
Zn												
pH 2.0	-	6.6	-	5.8	-	5.5	-	0.101	-	0.076	-	0.084
Nonadjusted pH[a]	35	9.9	38.9	7.1	-	6.9	0.535	0.151	0.595	0.109	-	0.106
pH 5.0[b]	51.4	12.8	49.1	12.7	28.6	9.3	0.786	0.196	0.751	0.194	0.437	0.142
Pb												
pH 2.0	-	27.5	-	30.0	-	14.5	-	0.133	-	0.145	-	0.070
Nonadjusted pH[a]	72	52.0	75.6	53.0	-	42.0	0.347	0.251	0.365	0.256	-	0.203
pH 5.0[b]	88.0	75.7	80.0	68.5	70.0	54.5	0.425	0.365	0.386	0.331	0.338	0.263

[a] The uptakes of heavy metals at nonadjusted pH in the mixed metal solution was compared with the average values of those at pH 3 and pH 4 in the single metal solution, because pH value of the former was 3.6.

[b] The uptakes of heavy metals at pH 5 in the mixed metal solution was compared with those at nonadjusted pH 4 in the single metal solution, because pH value of the latter was around 5.

on the metal uptakes by biosorbent materials, the lead uptake by *U. pinnatifida* was examined in the presence of NaCl (0-17 mM). The pH of the solution was kept constant at 5.0 during this study. As shown in Fig. 8, the lead uptake decreased at higher ionic strengths over 1.68 mM. This result can be explained by considering the competitive effect of Na^+ ions for lead binding [Lee et al., 1998]. The ion exchanger tends to prefer the counter ion of higher valance and Cu^{2+} ion is selective than Na^+ ion for cation exchangers. Therefore *U. pinnatifida* may prefer Cu^{2+} ion to Na^+ ion for lead removal by lead removal by *U. pinnatifida* will be low, especially at low ionic strength.

CONCLUSIONS

Using the biomass of nonliving, dried marine brown algae *U. pinnatifida*, *H. fusiformis*, and *S. fulvellum* harvested in the sea near Cheju, their sorption performance of copper, zinc, and lead have been investigated.

The biomass-metal system attained the final equilibrium plateau within 30 min. The metal uptakes by biosorbent materials increased with increasing initial metal concentration and pH in the range of C_i 0.05-10 mM, although the higher and similar metal uptakes were obtained in the range of 4.0-5.3, 4.0-6.0, and 3.0-6.0 for copper, zinc, and lead, respectively, at a low C_i. Among the biosorbent materials the decreasing order was as follows: *U. pinnatifida*>*H. fusiformis*> *S. fulvellum* for copper and zinc; *U. pinnatifida*>*H. fusiformis*>*S. fulvellum* for lead. It was found that the metal uptakes by biosorbent materials follow the Langmuir isotherm equation. The maximum metal uptake values for *U. pinnatifida* for Cu^{2+}, Pb^{2+}, and Zn^{2+} in the single metal solution are 2.58, 2.6, and 2.08 meq/g, respectively. These heavy metal uptake capacities of dried marine brown algae *U. pinnatifida*, *H. fusiformis*, and *S. fulvellum* exceed the uptake capacities of activated carbon, natural zeolite, and other biosorbents and are comparable with those of the commercial ion exchange resin.

Each metal biosorption rate equation could be expressed as follows:

Copper: $r_{ad}=0.157C_o$, Lead: $r_{ad}=0.254C_o$, Zinc: $r_{ad}=0.139C_o$.

The metal uptakes by biosorbent materials in the mixed metal solution, decreased greatly in comparison to those in the single metal solution.

Comparing each capability among the biosorbent materials in this study using biosorption isotherms and biosorption rate model, it was considered that *U. pinnatifida* and *H. fusiformis* are effective in removing heavy metal ion from aqueous solution, applicable to the practical biosorption process.

NOMENCLATURE

b : Langmuir constant (related to energy of adsorption)
C : concentration of heavy metal ion in the solution [mM]
C_e : equilibrium concentration of heavy metal ion in the solution [mM]
C_o : initial concentration of heavy metal ion in the solution [mM]
k : biosorption rate constant
K : Freundlich constant
M : biosorbent weight [g]
n : Freundlich constant
q : heavy metal ion uptake (amount of heavy metal ion adsorbed per unit weight of adsorbent) [mmole/g]
q_{max} : maximum heavy metal uptake (amount of heavy metal ion adsorbed per unit weight of adsorbent) [mmole/g]
r_{ad} : initial biosorption rate of heavy metal [mmole/g-min]
V : volume of the solution [mL]

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