

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231374627>

Biosorption of Heavy Metal Ions (Pb, Cu, and Cd) from Aqueous Solutions by the Marine Alga *Sargassum* sp. in Single- and Multiple-Metal Systems

ARTICLE *in* INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH · MARCH 2007

Impact Factor: 2.59 · DOI: 10.1021/ie0615786

CITATIONS

69

READS

132

3 AUTHORS, INCLUDING:



Yen-Peng Ting

National University of Singapore

131 PUBLICATIONS 4,208 CITATIONS

SEE PROFILE



Jiaping Paul Chen

National University of Singapore

130 PUBLICATIONS 4,303 CITATIONS

SEE PROFILE

Biosorption of Heavy Metal Ions (Pb, Cu, and Cd) from Aqueous Solutions by the Marine Alga *Sargassum sp.* in Single- and Multiple-Metal Systems

Ping Xin Sheng, Yen-Peng Ting,* and J. Paul Chen

Department of Chemical & Biomolecular Engineering, National University of Singapore, Kent Ridge Crescent, Singapore 117576

The sorption of heavy metals (lead, copper, and cadmium) by a marine algal biomass *Sargassum sp.* was studied in single and multiple metal-ion systems. Kinetic experiments in the single-metal system revealed very rapid removal rates of metal ions, with ~90% of the total adsorption occurring within 10–60 min. Biosorption performance for each single metal ion showed an increase in specific metal uptake with an increase in pH. Experimental data for each metal ion were well-described by the Langmuir adsorption isotherm. Generally, the algal biomass demonstrated the highest uptake for lead, followed by copper and cadmium, with this uptake trend correlating with the electronegativities and stability constants of the metal-ion hydroxides. The effect of the presence of multiple metal ions on the biosorption performance has been investigated, and the results have been evaluated using the modified competitive Langmuir model and modified Jain–Snoeyink model, both of which fit the data well. The metals with the highest uptake capacity in single-metal systems showed a greater inhibitory effect on the biosorption of other metal ions in the multiple-component systems. The study showed the good performance of metal uptake by *Sargassum* in both single- and multiple-metal systems.

1. Introduction

Biosorption is a process that utilizes inexpensive biomass to sequester toxic heavy metals and is particularly useful for the removal of trace levels of contaminants from industrial effluents.¹ Compared with conventional methods (such as chemical oxidation or reduction, precipitation, and membrane separation), biosorption processes offer several advantages, such as low operating cost, minimization of the volume of chemical and/or biological sludge to be disposed of, high efficiency in detoxifying very dilute effluents, and no nutrient requirements.^{1,2}

Much has been reported on the use of different biosorbents for single-metal-ion solutions, and studies have provided insight into the identification of several microbial biomass types that are effective in concentrating metals. It has been noted that, although single toxic metallic species rarely exist in natural and wastewaters, and that the presence of multiple metal ions often causes an interactive effect, insufficient attention seems to have been given to this problem.^{3–5} Biosorption of a single species of heavy-metal ion is affected by several factors, which include the specific surface properties of the microorganism and the physicochemical parameters of the solution, such as temperature, pH, initial metal-ion concentration, and biomass concentration. The combined effects of two or more metal ions in the solution also are dependent on the number of metal-ion species competing for binding sites, as well as the metal-ion concentration of each species.

The Langmuir isotherm is commonly used to describe the adsorption phenomena for single-component metal biosorption, and take the form

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad (1)$$

where q_{\max} (expressed in units of mmol/g) and b (expressed in

units of L/mmol) are constants that reflect, respectively, the maximum metal adsorption capacity and the affinity between the metal ion and the biosorbent. The extension of the basic Langmuir model to account for competitive adsorption in multiple-metal systems can be formulated as follows:

$$q_{e,i} = \frac{q_{\max,i} b_i C_{e,i}}{1 + \sum_{i=1}^n b_i C_{e,i}} \quad (2)$$

where the terms $q_{\max,i}$ and b_i are derived from the corresponding individual Langmuir isotherm equations; $q_{e,i}$ and $C_{e,i}$ are, respectively, the uptake and final concentration when adsorption equilibrium is reached; and n is the number of metal ions in solutions. The Langmuir model assumes that each component is adsorbed onto the surface according to ideal solute behaviors, where there is no interaction or competition between molecules involved under homogeneous conditions. To account for non-ideal systems using the Langmuir theory, Jain and Snoeyink⁶ introduced an additional term into eq 2 for binary metal systems:

$$q_{e,1} = \frac{(q_{\max,1} - q_{\max,2}) b_1 C_{e,1}}{1 + b_1 C_{e,1}} + \frac{q_{\max,2} b_1 C_{e,1}}{1 + b_1 C_{e,1} + b_2 C_{e,2}} \quad (3)$$

where $q_{\max,1} > q_{\max,2}$. The additional term on the right-hand side of eq 3 (proportional to the quantity $q_{\max,1} - q_{\max,2}$) is the Langmuir expression for the amount of solute 1 adsorbed onto the surface without competition. The second term on the right-hand side represents the amount of solute 1 adsorbed onto the surface in competition with solute 2. The amount of solute 2 adsorbed onto the sorbent surface can be calculated from eq 2.

All the model parameters in these competitive isotherms for multiple-metal systems may be derived from single-component isotherms. Indeed, better accuracy may be achieved by extracting additional coefficients from the multiple-metal isotherms. For instance, an interaction term η , which is a characteristic of each species and is dependent on the sorption properties of the

* To whom correspondence should be addressed. Fax: (65) 6779-1936. E-mail: chetyp@nus.edu.sg.

sorbents, has been defined in the modified competitive isotherms. The modified competitive Langmuir model takes the form⁷

$$q_{e,i} = \frac{q_{\max,i} b_i (C_{e,i}/\eta_i)}{1 + \sum_{i=1}^n b_i (C_{e,i}/\eta_i)} \quad (4)$$

For a binary system, the modified Jain–Snoeyink model becomes⁶

$$q_{e,1} = \frac{(q_{\max,1} - q_{\max,2}) b_1 (C_{e,1}/\eta_1)}{1 + b_1 (C_{e,1}/\eta_1)} + \frac{q_{\max,2} b_1 (C_{e,1}/\eta_1)}{1 + b_1 (C_{e,1}/\eta_1) + b_2 (C_{e,2}/\eta_2)} \quad (5)$$

$$q_{e,2} = \frac{q_{\max,2} b_2 (C_{e,2}/\eta_2)}{1 + b_1 (C_{e,1}/\eta_1) + b_2 (C_{e,2}/\eta_2)} \quad (6)$$

The root-mean-square error (RMSE), which relates the measured and the calculated metal uptakes, may be defined for each component as

$$\text{RMSE} = \sum_{i=1}^N \left(\frac{q_{\text{exp}} - q_{\text{fit}}}{q_{\text{exp}}} \right)^2 \quad (7)$$

where q_{exp} and q_{fit} are the measured and the calculated results of metal uptake, respectively, and N is the number of measurements.

In this study, the biosorption of lead, copper, and cadmium by *Sargassum sp.* was investigated and compared in systems with both single and multiple metal ions. The metal binding capacity of *Sargassum*, as a function of pH, as well as the type and concentration of coexisting metal ions, was investigated. The single-component biosorption data have been analyzed using the Langmuir isotherm. The modified competitive Langmuir model and the Jain–Snoeyink model were used to characterize the simultaneous biosorption of Pb, Cu, and Cd ions by *Sargassum sp.* in multicomponent systems. A range of interaction coefficients (η) were selected and evaluated, and the specific values of each interaction coefficient (which provided the minimum residual defined by eq 7) were determined.

2. Materials and Methods

2.1. Materials. The raw biomass of *Sargassum sp.* was harvested from the coasts in Singapore. The biomass were washed with deionized water to remove extraneous materials and dried at 60 °C overnight. The dried biomass was then ground to various particle sizes, from which particles 500–800 μm in size were used in this work.

The stock metal solutions at various concentrations were prepared by dissolving lead nitrate, copper nitrate, cadmium nitrate, nickel nitrate, and zinc nitrate, respectively, which were all reagent grade (Merck, Germany). Hydrochloric acid (0.1 mol/L) and sodium hydroxide (0.1 mol/L) were prepared for use in pH adjustments.

2.2. Batch Experiments for Single-Metal Systems. The pH of single metal ions (Pb, Cd, and Cu) in 100-mL solutions in Erlenmeyer flasks was first adjusted to the desired values using 0.1 mol/L HNO_3 or 0.1 mol/L NaOH. A small amount (0.1 g) of biomass was then added into the solutions while stirring at

150 rpm at room temperature (22 ± 1 °C). The pH was measured at intervals of 20–30 min and adjusted accordingly. The samples for kinetics experiments were taken at periodic time intervals. For pH effect and isotherm experiments, the flasks were agitated for 6 h. The samples obtained was acidified and filtered (using 0.45- μm filters) before analysis, using inductively coupled plasma–optical emission spectrometry (ICP–OES) (Perkin–Elmer Optima 3000).

2.3. Batch Experiments for Multiple-Metal Systems. To determine the adsorption characteristics of a selected metal in binary metal mixtures, the initial concentrations of the selected metal were varied over a range of 0–3.0 mmol/L while the competing metal-ion concentration in each biosorption medium was held constant at 0.5, 1.0, or 1.5 mmol/L. To fully observe any competitive effect, the equilibrium experiments were conducted for binary and ternary metal mixtures with the equivalent concentration of each metal ion in the range of 0–3.0 mmol/L. Table 4 (presented later in this paper) shows the concentration of the metals in the single, binary, and ternary systems that have been investigated. All the experiments for the multiple-metal systems were conducted at pH 5.0 for 9.0 h.

All experiments in this work were conducted in duplicate, and the average results were presented. Biosorption metal uptake q was calculated from the sorption system mass balance:

$$q \text{ (mmol/g)} = \frac{V(C_i - C_f)}{W} \quad (8)$$

where V is the volume of the solution (given in liters), W is the amount of biomass (given in grams), and C_i and C_f are, respectively, the initial and final metal concentrations (each given in units of mmol/L).

3. Results and Discussion

3.1. Determination of Equilibrium Time. Kinetic experiments were performed to determine the equilibrium time for the uptake of Pb, Cu, and Cd ions by *Sargassum sp.* in single-metal systems. The results show that, generally, similar kinetic behaviors were observed for all experiments at pH 5.0, 4.0, and 3.0: a very rapid initial sorption over a few minutes, followed by a long period of a much slower uptake. It was noted that, with decreasing pH, the time needed to reach an equilibrium decreased for all three metals (data not shown). Because of the fact that lower pH results in a higher concentration of (the competing) H^+ ions (and, hence, lower availability of the binding sites), less time was needed for the sorption of metal ions. However, all adsorption equilibrium was attained within 3 h, with 90% of the total adsorbed metal ions occurring within 10–60 min. Therefore, a period of 6 h was sufficient for the equilibrium experiments.

A rapid two-stage kinetics of biosorption has been reported for many biosorption systems. For instance, Çeribas and Yetis⁸ observed that a large amount of nickel and lead was removed by *Phanerochaete chrysosporium* within the first 5 min of contact time, followed by a relatively slower uptake rate, with equilibrium being attained after 3 h. Matheickal et al.⁹ reported that 90% of the total soluble cadmium was removed from solution by *Durvillaea potatorum* within 30 min of agitation; there was negligible decrease in the cadmium concentration over the next 5 h. High sorption rates are clearly desired, because a shorter contact time eventually translates to a smaller contact equipment, which, in turn, directly affects both the capacity and operation cost of the process.

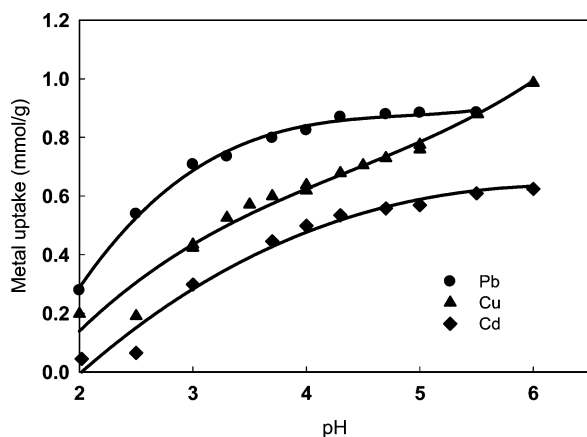


Figure 1. Uptake capacities by *Sargassum sp.* as a function of pH. (Conditions: $m = 1.0$ g/L; $C_0 = 1.0$ mmol/L.)

Various functional groups (e.g., carboxyl, sulfhydryl, amine etc.) may serve as metal binding sites on the cell wall.¹ These functional groups differ, with respect to both the strength of the metal sorptive bond and the rate of adsorption on these sites. This results in the fast and slow uptake stages for the same metal ion. Diffusion-controlled models have been used to describe the kinetics of metal biosorption from aqueous solutions. It was assumed that the reaction time for sorption (i.e., binding to the functional group) was much shorter than that for diffusion of the ions through the biomass, and that intraparticle diffusion was the most important mass-transfer resistance during the sorption process.^{10,11} Our recent work showed that ion exchange had an important role in the removal of heavy metals by the alga used in this work.¹²

3.2. Effect of Solution pH. Altering the pH changes the solution chemistry of aqueous systems and significantly affects biosorption performance.^{1,9} The effect of pH on the sorption of lead, copper, and cadmium by *Sargassum sp.* is shown in Figure 1. The uptake of heavy-metal ions increased sharply when the pH was increased from 2.0 to 4.5, but was less pronounced at higher pH. In the case of copper, where an increasing uptake occurred at pH > 5.5, this phenomenon may be attributed to the precipitation of insoluble copper species. These findings are consistent with those reported by other researchers.⁹

At pH < 4.5, the metal ions Pb, Cu, and Cd are present in their free ionic form, and, hence, the sharp increase in metal adsorption from pH 2 to 4.5 is not due to the change in metal speciation. Instead, it is likely that the type and ionic state of the functional groups on the cell wall at these pH values determine the extent of sorption. In addition, H^+ ions may compete with metal ions for the cell wall ligands; at lower pH, the concentration of H^+ ions is higher, thus leading to a lower sorption of metal ions. Metal-ion removal is enhanced when the pH is increased.

The weakly acidic carboxyl groups ($R-COOH$) in the algal cell wall are regarded as the main ligands involved in the metal uptake at lower pH by many researchers. Because the pK_a value of $R-COOH$ is in the range of 3.5–5.5,¹³ more carboxyl groups will be deprotonated at pH over this range, and thus resulting in more negative binding sites. As a result, the metal uptake capacity of the biomass is enhanced. There was a good correlation between the degrees of blocking of $-COOH$ groups by esterification in *Sargassum fluitans* and the corresponding decrease in metal uptake.¹⁴ Similar results were also obtained for the carboxyl groups in the biomass of the freshwater algae *Chlorella pyrenoidosa* and *Cyanidium caldarium*.¹⁵ Some other functional groups, e.g., alcoholic, ether, and sulfate ($R-OSO_3^-$)

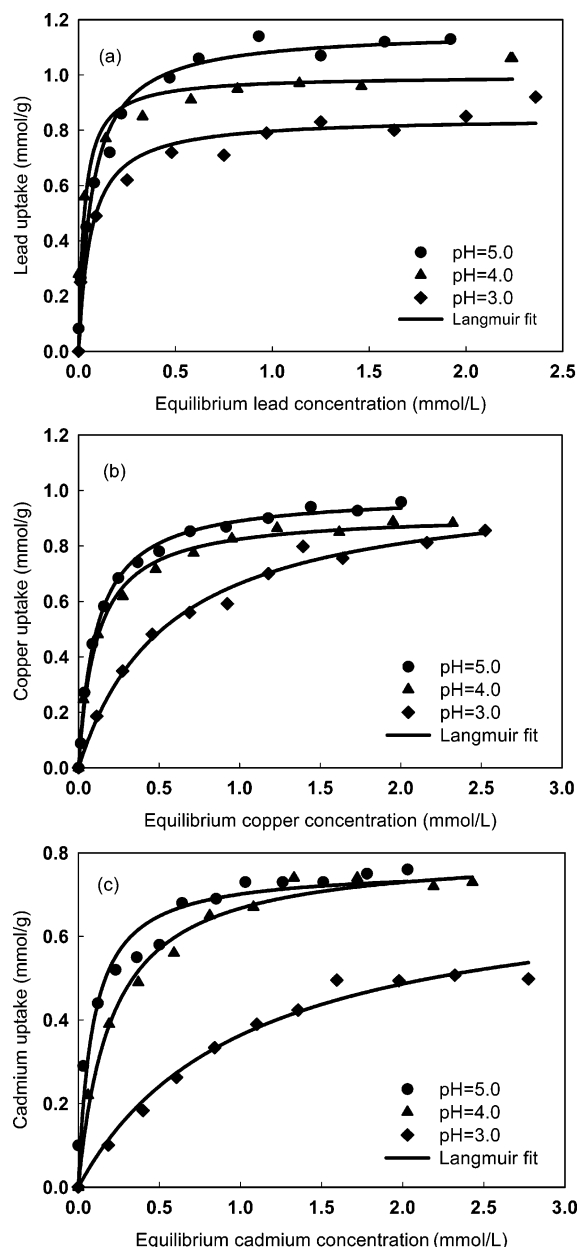


Figure 2. Metal-ion adsorption isotherms for *Sargassum sp.* at different pH values: (a) lead, (b) copper, and (c) cadmium.

groups may contribute to the continued increase in uptake at higher pH.^{1,16}

3.3. Adsorption Equilibrium. Adsorption isotherms were obtained under constant pH values of 5.0, 4.0, and 3.0 (see Figure 2). These isotherms exhibit increased metal adsorption with increasing residual metal concentration, but a decreasing positive slope. These plots indicate a reduction in the number of active sites on the adsorbents at a high residual heavy-metal concentration in the solution phase.

The experimental data were well-modeled by the Langmuir isotherm; the coefficient correlation (r^2), the maximum adsorption capacity (q_{max}), and the affinity constant (b) at different pH values are given in Table 1. The adsorption capacity q_{max} increased as the solution pH increased, which supports the aforementioned discussion on the effect of solution pH on lead, copper, and cadmium uptake.

The uptake capacity at pH 5.0 and pH 4.0 followed the order

$$Pb > Cu > Cd$$

and may be correlated with the electronegativities and stability

Table 1. Langmuir Constants for the Biosorption of Lead, Copper, and Cadmium

	Lead			Copper			Cadmium		
	pH 5.0	pH 4.0	pH 3.0	pH 5.0	pH 4.0	pH 3.0	pH 5.0	pH 4.0	pH 3.0
q_{Max} (mmol/g)	1.16	1.00	0.85	0.99	0.92	1.03	0.76	0.80	0.73
b (L/mmol)	14.23	34.30	15.90	8.78	8.92	1.80	11.34	4.87	0.98
correlation coefficient, r^2	0.98	0.81	0.95	0.99	0.99	0.99	0.94	0.98	0.98

Table 2. Correlation between Metal Uptake Capacity and Electronegativity, as Well as the First Stability Constant ($\log K_1$) of Metal-Ion Hydroxides

metal ion	electronegativity, X_p^a	$\log K_1^b$	q_{Max} (mmol/g)	
			pH 5.0	pH 4.0
Pb	2.33	7.50	1.16	1.00
Cu	1.90	6.50	0.99	0.92
Cd	1.69	3.90	0.76	0.80

^a Data taken from ref 17. ^b First stability constant of metal-ion hydroxides at 25 °C and zero ionic strength; data taken from ref 18.

constants of the metal-ion hydroxides (see Table 2). The results suggest that higher electronegativity and first stability constant values correspond to a higher adsorption capacity. Because of the fact that higher electronegativity of a metal ion represents higher attraction of metal ion for electrons, this correlation is not unexpected. A higher first stability constant means that the ligand (on the sorbent) and ionic metal in the aqueous phase readily associate to form a metal–ligand complex, yielding fewer free-metal ions in the solution. Consequently, the uptake capacity of the corresponding metal ions on the sorbent is higher.

The affinity constant b of the isotherms corresponds to the initial gradient, which indicates the sorbent affinity at low metal concentrations; a greater initial gradient corresponds to a higher affinity constant. Figure 2 shows that the lead isotherms are steeper at lower equilibrium concentrations than those for copper and cadmium, indicating the suitability of *Sargassum sp.* to treat dilute lead solutions.

A comparison of the heavy-metal uptake capacities of *Sargassum sp.* with other adsorbents is given in Table 3. Although a direct comparison is difficult, because of the different experimental conditions used in these studies, it is evident that, generally, the heavy-metal uptake capacities of *Sargassum sp.* exceed or are comparable to those of activated carbon, zeolite, activated sludge, and other marine algae.

The cell walls of brown algae contain algin, fucoidan, and cellulose. A mixture of polysaccharides, mainly alginate, has been reported to be responsible for the superior metal-sequestering ability of brown algae.^{1,16,21} Algal cell walls are often porous and allow molecules and ions to pass freely through them.²⁹ In

addition to its porosity, the algal cell constituents provide an array of chemical ligands, which provide binding functional groups for the uptake of metal ions.¹ Many metal-binding mechanisms have been postulated to be active in biosorption process, such as ion exchange, complexation, coordination, and microprecipitation. Because of the complexity of the composition of the biomaterial, it is quite possible that at least some of these mechanisms are acting simultaneously, to varying degrees, depending on the biosorbent and the solution chemistry.

3.4. Competitive Adsorption Isotherms. Adsorption in multicomponent systems is complicated, because of the possible interactions among the solutes. Studies were conducted to determine the sorption of lead, cadmium, and copper in binary and ternary systems (see Table 4). The sorption isotherms at pH 5.0 and at room temperature (22 ± 1 °C) are shown in Figures 3–8. The equilibrium biosorption data from binary and ternary mixtures were analyzed using the modified competitive Langmuir model and the modified Jain–Snoeyink model. The model parameters obtained are given in Table 5. The predicted results from modified competitive Langmuir model are also presented in Figures 3–8 as solid lines.

3.4.1. Effect of the Presence of Copper and/or Cadmium on Lead Binding. The effect of the presence of copper or cadmium on the removal of lead is quantitatively demonstrated in Figure 3, which shows the decrease in the biosorption of lead in the presence of an increasing concentration of copper or cadmium. Copper exerted a greater inhibitory effect on lead removal than cadmium. For example, at $C_{0,\text{Pb}} = 1.0$ mmol/L and when 1.0 or 2.0 mmol/L cadmium was added into the system, the lead removal was decreased to 92% and 89%, respectively. When 1.0 and 2.0 mmol/L copper were added, the lead removal decreased to 88% and 78%, respectively. Lead removal in the single-metal system was 95%.

A comparison of the effect of copper and cadmium on the biosorption isotherms of lead (in single-metal and multiple-metal systems) is shown in Figures 4a and 4b, respectively. It is evident that the uptake capacity of the sorbent for lead was reduced in the presence of other metal ions. The inhibitory effect of the competing copper and cadmium increased as the concentration of each of these metal ions increased.

The maximum uptake of lead, at 1.16 mmol/g in the single ion system, was reduced to 1.06 and 0.96 mmol/g in the presence of 1.0 and 1.5 mmol/L copper, respectively, in the system. The difference in the effect of 1.0 and 1.5 mmol/L cadmium on the lead isotherm was not as pronounced; the maximum uptake of lead was reduced to ~ 1.08 mmol/g in both cases. The maximum uptake of lead in the ternary system was 0.87 mmol/g, which was almost same as that in the lead–copper system, but was much less than that in the lead–cadmium system (where the two metal ions were at the same initial concentration). This implies that copper contributed mainly to the reduction in the uptake of lead in the ternary metal system.

3.4.2. Effect of the Presence of Lead and/or Cadmium on Copper Binding. The effect of the presence of lead and cadmium on copper removal is shown in Figure 5; lead exerted a greater impact on copper than cadmium did. For example, copper removal was reduced from 74% to 63% and 51%,

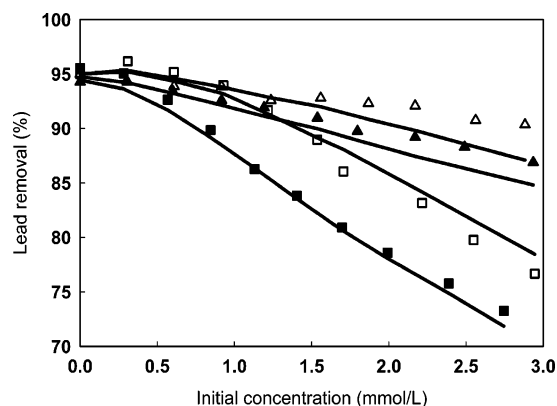


Figure 3. Lead removal as a function of the initial concentration of copper or cadmium in a multiple-metal system ($m = 2.0$ g/L, pH 5.0): (Δ) Pb–Cd-3, (\blacktriangle) Pb–Cd-4, (\square) Pb–Cu-3, and (\blacksquare) Pb–Cu-4. Solid lines show the modified competitive Langmuir model.

Table 3. Comparison of the Uptake Capacities for Different Adsorbents

adsorbent	q_{Max} (mmol/g) ^a			Operating Conditions			reference(s)
	Pb	Cu	Cd	pH	temperature (°C)	m (g/L)	
<i>Sargassum sp.</i>	1.16	0.99	0.76	5	21	1	present work
<i>Cladophora sp.</i>	0.35			4.5	30	2	19
<i>Cyclotella sp.</i>	0.18	0.41	0.20	6			20
<i>Gracilaria sp.</i>	0.20–0.26			4.5	30	2	19
<i>Padina spp.</i>	1.05	0.80		4.5–5	25–30	2	2, 19
<i>Phaeodactylum sp.</i>	1.49 mg/g	1.67 mg/g	1.24 mg/g	6			20
<i>Polysiphonia sp.</i>	0.49			4.5	30	2	19
<i>Porphyridium sp.</i>	0.32 mg/g	0.27 mg/g	0.42 mg/g	6			20
<i>Sargassum spp.</i>	1.13–1.38	0.8–0.93	0.66–0.79	4.5–5	22–30	2	19, 21
<i>Scenedesmus sp.</i>		0.21	0.06	6			20
<i>Schizomeris sp.</i>	0.31		0.44	4.5–5	30	0.5	22
crab shell	0.99	0.82	0.99	5	30	1	23
activated sludge		0.52	0.16	7			24
activated carbon		0.1	0.10	6	22	20	25
GAC	0.78	0.89	0.99	5	30	1	23
PAC (bagasse)			0.34	5	25	6	26
PAC (coconut shell)	0.93	0.90	0.96	5	30	1	23
natural zeolite	0.08						27
zeolite	0.75		0.75				28

^a Expressed in units of mmol/g, unless noted otherwise.**Table 4. Concentration Ranges of the Metals in the Multiple-Metal Systems**

Lead–Copper System			Lead–Cadmium System			Copper–Cadmium System		
Initial Concentration (mM)			Initial Concentration (mM)			Initial Concentration (mM)		
experiment	Pb	Cu	experiment	Pb	Cd	experiment	Cu	Cd
Pb–Cu-1	0–3.0	1.0	Pb–Cd-1	0–3.0	1.0	Cu–Cd-1	0–3.0	0.5
Pb–Cu-2	0–3.0	1.5	Pb–Cd-2	0–3.0	1.5	Cu–Cd-2	0–3.0	1.0
Pb–Cu-3	0.5	0–3.0	Pb–Cd-3	0.5	0–3.0	Cu–Cd-3	0.5	0–3.0
Pb–Cu-4	1.0	0–3.0	Pb–Cd-4	1.0	0–3.0	Cu–Cd-4	1.0	0–3.0
Pb–Cu-5	0–3.0 (Pb:Cu = 1:1)		Pb–Cd-5	0–3.0 (Pb:Cd = 1:1)		Cu–Cd-5	0–3.0 (Cu:Cd = 1:1)	
Pb–Cu–Cd	Pb:Cu:Cd = 1:1:1							

Table 5. Model Parameters for the Modified Competitive Langmuir Model and the Modified Jain–Snoeyink Model

model	q_i (mmol/g)			b_i (L/mmol)			η_i		
	Pb	Cu	Cd	Pb	Cu	Cd	Pb	Cu	Cd
Langmuir	1.16	0.99	0.76	14.23	8.78	11.34	0.67	2.50	9.09
Jain–Snoeyink							0.71	1.67	9.09

respectively, when 1.0 mmol/L Cd or Pb ions was added into solutions that contained 1.0 mmol/L Cu ions. The corresponding value was 57% and 32%, respectively, when 2.0 mmol/L cadmium or lead was added.

A comparison of the isotherms in Figures 6a and 6b showed that lead exerted a much great inhibitory effect on the copper isotherms. Furthermore, the inhibitory effect increased as the concentration of competing metal ions (lead or cadmium) increased. For example, in a single-ion system, the observed maximum copper uptake reached a value as high as 1.07 mmol/g. The uptake was reduced to 0.78 and 0.57 mmol/g, respectively, when 0.5 or 1.0 mmol/L lead was present, and was reduced to 0.84 and 0.72 mmol/g, respectively, in the presence of 0.5 or 1.0 mmol/L cadmium.

In the ternary metal system and at equimolar concentrations, the observed maximum copper uptake was reduced to 0.29 mmol/g; the corresponding values were 0.33 and 0.72 mmol/g, respectively, for the binary metal system of the copper–lead and copper–cadmium systems, respectively.

3.4.3. Effect of the Presence of Lead and/or Copper on Cadmium Binding. Although cadmium removal was reduced in the presence of copper and lead (see Figure 7), the inhibitory effect of the two metal ions on the cadmium isotherm was not as significantly different as that noted when lead and copper were the metal ions examined in the presence of competing ions (i.e., see Figures 3 and 5). The peak values experimentally

observed in the systems, at equal initial concentration of the metal ions, were 0.12, 0.22, and 0.23 mmol/g for the ternary metal system, the lead–cadmium system, and the copper–cadmium system, respectively, as shown in Figures 8a and 8b.

The results in the binary and ternary systems clearly showed that the combined action of multiple ions was antagonistic. The most likely reason for the antagonistic effect is the competition for adsorption sites on the cell surfaces and/or the screening effect by the competing metal ions. Results showed that lead exerted the most inhibitory effect on the biosorption of other metals, followed by copper and cadmium. A similar phenomenon had been observed in the binary adsorption of lead, copper, cadmium, and nickel with a natural heterogeneous sorbent, where it was shown that cadmium and nickel strongly competed with each other and were displaced in the presence of lead and copper.³⁰ The values of the interaction coefficient η for both the modified competitive Langmuir model and the modified Jain–Snoeyink model followed the order

$$\text{Pb} < \text{Cu} < \text{Cd}$$

(see Table 5). The lower the value of η , the greater the inhibitory effect of the metal on the biosorption of other competing ions. The modified multicomponent Langmuir model has also been applied in the simultaneous biosorption of chromium(VI) and nickel(II) onto dried activated sludge, where the regressed interaction coefficient was 0.995 and 0.986, respectively, at pH 4.5 for the two metal ions.⁷

It was noted that, in the binary systems, both models gave higher correlation coefficients (r^2) and lower RMSEs for the dominant metal ion than the competing metals. The RMSEs and r^2 values for the dominant metal ions varied over ranges of 0.08–1.14 and 0.92–0.99, respectively; the values for the

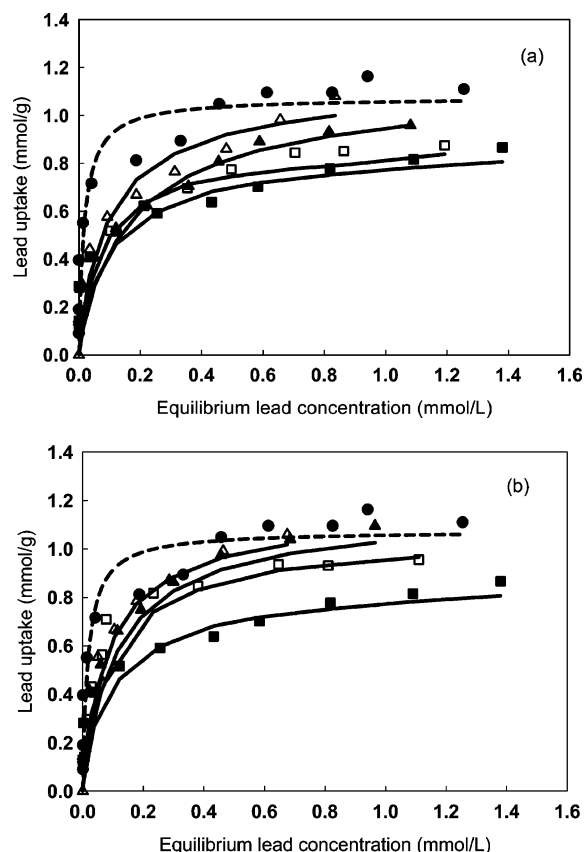


Figure 4. Sorption isotherms of lead in the presence of (a) copper or (b) cadmium in a multiple-metal system ($m = 2.0$ g/L, pH 5.0). Legend for panel a: (●) single Pb, (Δ) Pb-Cu-1, (▲) Pb-Cu-2, (□) Pb-Cu-5, and (■) Pb-Cu-Cd. Legend for panel b: (●) single Pb, (Δ) Pb-Cd-1, (▲) Pb-Cd-2, (□) Pb-Cd-5, and (■) Pb-Cu-Cd. For both panels, the solid lines show the modified competitive Langmuir model.

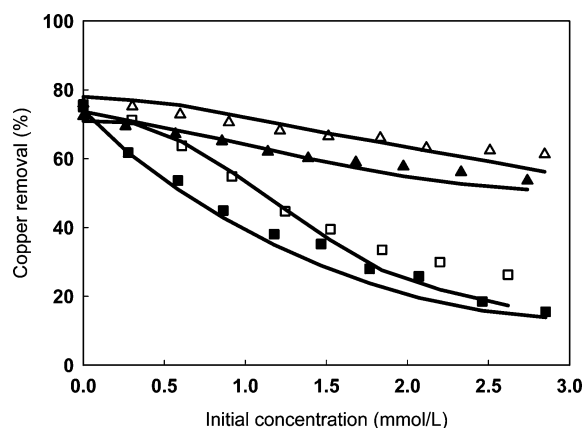


Figure 5. Copper removal as a function of initial concentration of lead or cadmium in a multiple-metal system ($m = 2.0$ g/L, pH 5.0): (Δ) Cu-Cd-3, (▲) Cu-Cd-4, (□) Pb-Cu-1, and (■) Pb-Cu-2. Solid lines show the modified competitive Langmuir model.

competing ions varied over ranges of 0.09–0.78 and 0.38–0.98, respectively (data not shown). In binary systems with equimolar concentration of metals, the models gave a higher correlation coefficient for the metal ion with the higher η value. In the ternary system, the correlation coefficient for lead is highest, followed by copper and cadmium.

The original competitive Langmuir model (eq 2) and the Jain–Snoeyink model (eq 3) failed to fit the experimental data adequately, with all the correlation coefficients being <0.70 (data not shown). It is evident that the modified models, with the introduction of the interaction coefficient (η), considerably

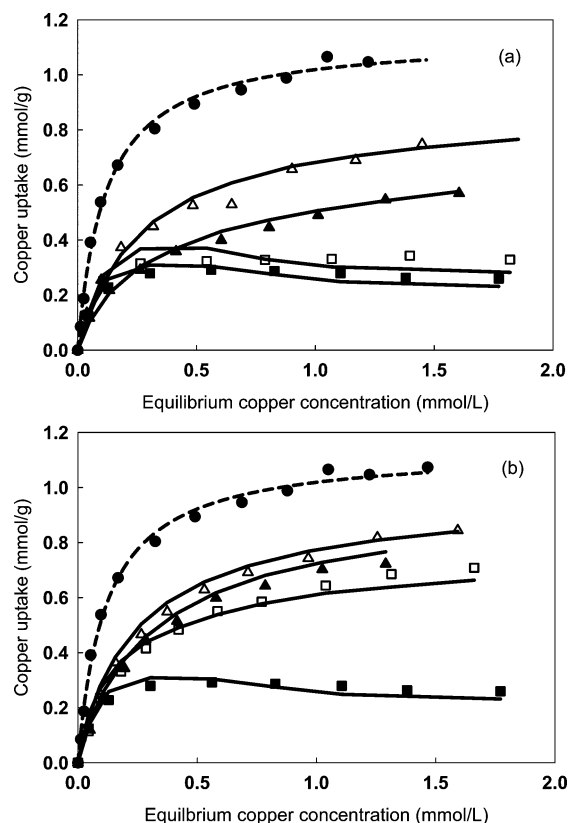


Figure 6. Sorption isotherms of copper in the presence of (a) lead or (b) cadmium in a multiple-metal system ($m = 2.0$ g/L, pH 5.0). Legend for panel a: (●) single Cu, (Δ) Pb-Cu-3, (▲) Pb-Cu-4, (□) Pb-Cu-5, and (■) Pb-Cu-Cd. Legend for panel b: (●) single Cu, (Δ) Cu-Cd-1, (▲) Cu-Cd-2, (□) Cu-Cd-5, and (■) Pb-Cu-Cd. For both panels, the solid lines show the modified competitive Langmuir model.

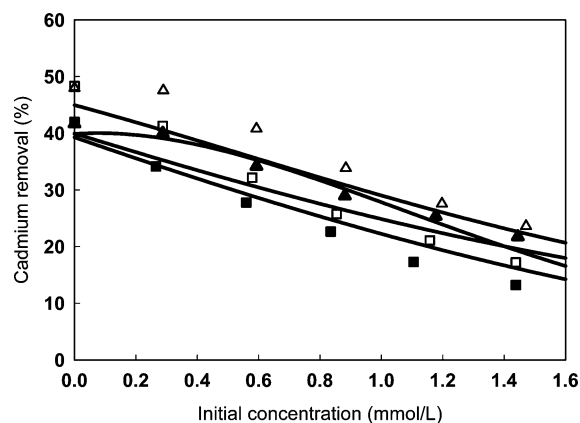


Figure 7. Cadmium removal as a function of initial concentration of lead or copper in a multiple-metal system ($m = 2.0$ g/L, pH 5.0): (Δ) Cu-Cd-1, (▲) Cu-Cd-2, (□) Pb-Cd-1, and (■) Pb-Cd-2. Solid lines show the modified competitive Langmuir model.

improved the accuracy of the modeling. Furthermore, it is also shown that interaction coefficient η derived from the binary metal system could be successfully applied to the ternary metal system, thus indicating the possibility of predicting biosorption performance of such complex systems, based on the modeling parameters obtained from simpler experiments.

4. Conclusion

The biosorption of lead, copper, and cadmium in systems with single and multiple metal ions by *Sargassum sp.* was investigated. In the single-ion system, metal uptake was

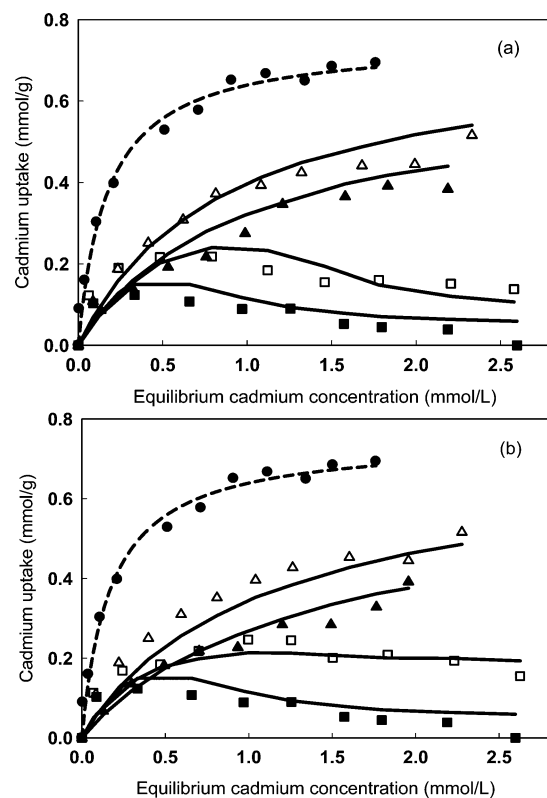


Figure 8. Sorption isotherms of cadmium in the presence of (a) lead or (b) copper in a multiple-metal system ($m = 2.0$ g/L, pH 5.0). Legend for panel a: (●) single Cd, (△) Pb–Cd-3, (▲) Pb–Cd-4, (□) Pb–Cd-5, and (■) Pb–Cu–Cd. Legend for panel b: (●) single Cd, (△) Cu–Cd-3, (▲) Cu–Cd-4, (□) Cu–Cd-5, and (■) Pb–Cu–Cd. For both panels, the solid lines show the modified competitive Langmuir model.

dependent on pH and increased significantly from pH 2 to pH 4.5. The sorption data at different pH values were well-modeled by the Langmuir isotherm. The maximum uptake capacity of lead was the highest, followed by copper and cadmium. The order of sorption by the algal biomass correlates well with the electronegativity and stability constants of the metal-ion hydroxides.

The sorption of metal ions in binary and ternary systems was investigated in terms of metal-ion removal and equilibrium isotherms. Experimental data fitted both the modified competitive Langmuir model and modified Jain–Snoeyink model well. The sorption of metal ions was reduced by the presence of co-ion(s), with the inhibitory effect increasing as the concentration of the co-ion(s) increased. Lead manifested the highest inhibitory effect on the biosorption of other metal ions, followed by copper and cadmium.

Literature Cited

- (1) Volesky, B. *Sorption and Biosorption*; BV Sorbex, Inc.: Montreal–St. Lambert, Quebec, Canada, 2003.
- (2) Kaewsarn, P. Biosorption of copper(II) from aqueous solutions by pre-treated biomass of marine algae *Padina* sp. *Chemosphere* **2002**, *47*, 1081.
- (3) Ting, Y. P.; Lawson, F.; Prince, I. G. Uptake of cadmium and zinc by the alga *Chlorella vulgaris*: II. Multi-ion situation. *Biotechnol. Bioeng.* **1991**, *37*, 445.
- (4) Hammami, A.; Ballester, A.; Blazquez, M. L.; Gonzalez, F.; Munoz, J. Effect of the presence of lead on the biosorption of copper, cadmium and zinc by activated sludge. *Hydrometallurgy* **2002**, *67*, 109.
- (5) Nurba, M.; Nourbakhsh, S.; Kiliçarslan, S.; İlhan, S.; Ozdag, H. Biosorption of Cr^{6+} , Pb^{2+} and Cu^{2+} ions in industrial waste water on *Bacillus* sp. *Chem. Eng. J.* **2002**, *85*, 351.
- (6) Jain, J. S.; Snoeyink, V. L. Adsorption from bisolute systems on active carbon. *J. Water Pollut. Control Fed.* **1973**, *45*, 2463.

- (7) Aksu, Z.; Açıkel, Ü.; Kabasakal, E.; Tezer, S. Equilibrium modelling of individual and simultaneous biosorption of chromium(VI) and nickel(II) onto dried activated sludge. *Water Res.* **2002**, *36*, 3063.
- (8) Çeribasi, I. H.; Yetis, Ü. Biosorption of Ni(II) and Pb(II) by *Phanerochaete chrysosporium* from a binary metal system—Kinetics. *Water SA* **2001**, *27*, 15.
- (9) Matheickal, J. T.; Yu, Q.; Woodburn, G. M. Biosorption of cadmium(II) from aqueous solutions by pre-treated biomass of marine alga *Durvillaea potatorum*. *Water Res.* **1999**, *33*, 335.
- (10) Beolchini, F.; Pagnanelli, F.; Toro, L.; Vegliò, F. Biosorption of copper by *Sphaerotilus natans* immobilised in polysulfone matrix: equilibrium and kinetic analysis. *Hydrometallurgy* **2002**, *70*, 101.
- (11) Seki, H.; Suzuki, A. Kinetic Study of Metal Biosorption to a Brown Alga, *Kjellmaniella Crassifolia*. *J. Colloid Interface Sci.* **2002**, *246*, 259.
- (12) Sheng, P. X. Biosorption of heavy metals by locally-derived macroalgae: equilibrium, kinetics and mechanisms, Ph.D. Thesis, National University of Singapore, 2005.
- (13) Buffle, J. *Complexation reactions in aqueous systems: An analytical approach*; Ellis Horwood, Ltd.: Chichester, U.K., 1988.
- (14) Fourest, E.; Serre, A.; Roux, J. C. Contribution of carboxyl groups to heavy metal binding sites in fungal wall. *Toxicol. Environ. Chem.* **1996**, *54*, 1.
- (15) Gardea-Torresdey, J. L.; Becker-Hapak, M. K.; Hosea, J. M.; Darnall, D. W. Effect of chemical modification of algal carboxyl groups on metal ion binding. *Environ. Sci. Technol.* **1990**, *24*, 1372.
- (16) Figueira, M. M.; Volesky, B.; Mathieu, H. J. Instrumental analysis study of iron species biosorption by *Sargassum* biomass. *Environ. Sci. Technol.* **1999**, *33*, 1840.
- (17) Dean, J. A. *Lange's Handbook of Chemistry*; McGraw–Hill: New York, 1999. (ISBN 0070163847.)
- (18) Smith, R. M.; Martell, A. E.; Gaithersburg, M. D. NIST critically selected stability constants of metal complexes database, Version 5.0. National Institute of Standards and Technology (NIST), Gaithersburg, MD, 1998.
- (19) Jalali, R.; Ghafourian, H.; Asef, Y.; Davarpanah, S. J.; Sepehr, S. Removal and recovery of lead using nonliving biomass of marine algae. *J. Hazard. Mater.* **2002**, *92*, 253.
- (20) Schmitt, D.; Müller, A.; Csögör, Z.; Frimmel, F. H.; Posten, C. The adsorption kinetics of metal ions onto different microalgae and siliceous earth. *Water Res.* **2001**, *35*, 779.
- (21) Davis, T. A.; Volesky, B.; Vieira, R. H. S. F. *Sargassum* seaweed as biosorbent for heavy metals. *Water Res.* **2001**, *34*, 4270.
- (22) Özer, A.; Özer, D.; Ekiz, H. I. Application of Freundlich and Langmuir models to multistage purification process to remove heavy metal ions by using *Schizomeris leibleinii*. *Proc. Biochem.* **1999**, *34*, 919.
- (23) An, H. K.; Park, B. Y.; Kim, D. S. Crab shell for the removal of heavy metals from aqueous solution. *Water Res.* **2001**, *35*, 3551.
- (24) Kim, D. W.; Cha, D. K.; Wang, J.; Huang, C. P. Heavy metal removal by activated sludge: influence of *Nocardia amarae*. *Chemosphere* **2002**, *46*, 137.
- (25) Ulmanu, M.; Marañón, E.; Fernández, Y.; Castrillón, L.; Anger, L.; Dumitriu, D. Removal of copper and cadmium ions from diluted aqueous solutions by low cost and waste material adsorbents. *Water Air Soil Pollut.* **2003**, *142*, 357.
- (26) Mohan, D.; Singh, K. P. Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse—an agricultural waste. *Water Res.* **2002**, *36*, 2304.
- (27) Matheickal, J. T.; Yu, Q. Biosorption of lead from aqueous solutions by marine algae *Ecklonia radiata*. *Water Sci. Technol.* **1996**, *34*, 1.
- (28) Leppert, D. Heavy metal sorption with clinoptilolite zeolite: alternatives for treating contaminated soil and water. *Min. Eng.* **1990**, *42*, 604.
- (29) Hope, A. B.; Walker, N. A. *The Physiology of Giant Algal Cells*; Cambridge University Press: Oxford, U.K., 1975. (ISBN 0521205131.)
- (30) Papini, M. P.; Saurini, T.; Bianchi, A.; Majone, M.; Beccari, M. Modeling the Competitive Adsorption of Pb, Cu, Cd, and Ni onto a Natural Heterogeneous Sorbent Material (Italian “Red Soil”). *Ind. Eng. Chem. Res.* **2004**, *43*, 5032.

Received for review December 8, 2006
 Revised manuscript received February 7, 2007
 Accepted February 9, 2007