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Binary Adsorption of Copper(II) and Cadmium(II) from Aqueous Solutions by Biomass of Marine Alga *Durvillaea potatorum*

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ABSTRACT

Much work on the biosorption of heavy metals by low-cost, natural biomass has been on the uptake of single metals. In practice, wastewaters often contain multiple heavy metal ions. In this paper the binary adsorption of copper(II) and cadmium(II) by a pretreated biomass of the marine alga *Durvillaea potatorum* from aqueous solutions was studied. The results showed that the uptake capacities for each heavy metal of the binary system were lower when compared with the single metal biosorption for copper and cadmium, respectively, but the total capacities for the binary system were similar to those obtained for single metal biosorption. The uptake capacities for copper and cadmium increased as the equilibrium pH increased and reached a plateau at a pH around 5.0. The uptake process was relatively fast, with 90% of the adsorption completed within 10 minutes for copper and 30 minutes for cadmium, and equilibrium reached after about 60 minutes of stirring. The biosorption isotherms of binary systems were not significantly affected by equilibrium temperature. The presence of light metal ions in solution also did not affect adsorption significantly. The binary adsorption was successfully predicted by the extended Langmuir model, using parameters and capacities obtained from single component systems.

Key Words. Biosorption of heavy metals; Binary adsorption; Copper; Cadmium; *Durvillaea potatorum*; Marine algae

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INTRODUCTION

The release of large quantities of heavy metals into the environment from industries has resulted in a number of environmental problems. The main anthropogenic pathway by which heavy metals enter the environment is through wastewater streams from industrial processes such as electroplating, plastics manufacturing, mining, and metallurgical processes (1, 2). At present a number of different technologies exist for treating heavy-metals-bearing waste streams (2). These technologies include precipitation, evaporation, solvent extraction, and membrane processes. However, these technologies are most suitable in situations where the concentrations of the heavy metal ions are high. They are either ineffective or expensive when heavy metals are present in the wastewater at low concentrations, or when very low concentrations of heavy metals in treated water are required (3).

Alternative technologies of treating diluted wastewater streams have been studied in recent decades (4–6). Biosorption technology is one such technology, and an increased amount of study is being focused on it. Biosorption utilizes the ability of biological materials to accumulate heavy metals from waste streams by either metabolically mediated uptake or by purely physicochemical pathways of uptake (7). The biological materials investigated for heavy metal uptake include fungi (8, 9), bacteria (10, 11), yeast (12), microalgae (13, 14), and others (15–19). Many of these materials are available in large quantities either as industrial by-products or from natural sources.

Marine macroalga is a biological resource available in large quantities. It can be used as a good basis for the development of biosorbent materials. The use of the biomass of brown marine algae *Durvillaea potatorum* (20–22), *Ecklonia radiata* (21), *Ascophyllum nodosum* (23), and *Sargassam baccularia* (24) for heavy metal removal has been reported. *Durvillaea potatorum* is a common brown marine alga found and harvested in the subtidal or intertidal fringe along the rocky coastlines of southern Australia (25).

There have been many binary adsorption studies for activated carbon (26, 27). However, most studies of heavy metal biosorption have been on single component systems (8–24). This paper studies the biosorption of copper and cadmium ions from aqueous solutions in a binary system by a pretreated biomass of *Durvillaea potatorum*. The biosorbent was pretreated by a two-stage process of thermal and chemical modification of the native biomass (20, 21). The binary isotherm was predicted by the extended Langmuir equation using single component system parameters. This study shows that the biomass can accumulate a high amount of copper and cadmium ions from aqueous solutions and that it is a suitable biosorbent for practical metal recovery applications.

MATERIALS AND METHODS

Dry *Durvillaea potatorum* samples in ground form were supplied by Kelp Industries, Tasmania, Australia. Pretreatment of the biomass was carried out as follows: A sample of 20 g of native biomass was treated with 0.2 M $CaCl_2$ solution (400 mL) for 24 hours under slow stirring. The solution pH was kept constant at 5.0 by using 0.1 M HNO_3. The calcium-treated biomass was washed several times with deionized water to remove excess calcium from the biomass. The biomass was then placed in an oven at 60°C for 24 hours and then sieved for a particle size of 300–600 μm.

For isotherm determination, a series of 125 mL vials were prepared containing equimolar copper nitrate and cadmium nitrate solutions (100 mL) of known concentrations (one salt for single isotherms) which varied from 0.5 to 4.5 mM. Weighed amounts (200 mg) of biomass were added to the vials, and the mixtures were agitated on a rotary shaker for 24 hours. The solution pH was adjusted to the required value by using 0.1 M HNO_3 or 0.1 M NaOH before and after the equilibrium period. The pH of the solution was measured again after 1 hour and no changes in pH were observed. The biomass was removed by filtration through a 0.45-μm membrane filter, and the filtrates were analyzed for copper and cadmium by atomic absorption spectrometry. Kinetics experiments were conducted in continuously stirred beakers (200 rpm) containing 500 mL of solution and 1 g of biomass. Samples of 1 mL each were drawn from the mixture at predetermined time intervals for analysis. The pH of the solution was monitored continuously with a pH electrode and adjusted with 0.1 M HNO_3 or 0.1 M NaOH solution if deviations were observed. All experiments were conducted at room temperature (25 ± 2°C), except for those on the influence of temperature, which were conducted in a constant temperature shaker.

RESULTS AND DISCUSSION

Single and Binary Adsorption Isotherms

The equilibrium isotherms for copper and cadmium uptake were obtained at pH 5 for both single and binary systems. These were shown and compared in Fig. 1. The isotherms for the binary system were obtained with an equimolar initial concentration to compare the relative affinity of the two ions. From Fig. 1, the amounts of uptake for both heavy metal ions in the binary system were much lower than those of the respective single component systems, indicating competitive adsorption between the two ions. The binary uptake capacities for copper and cadmium were about 60 and 40% of the single metal uptake capacities, respectively. However, the total uptake capacity in the bi-

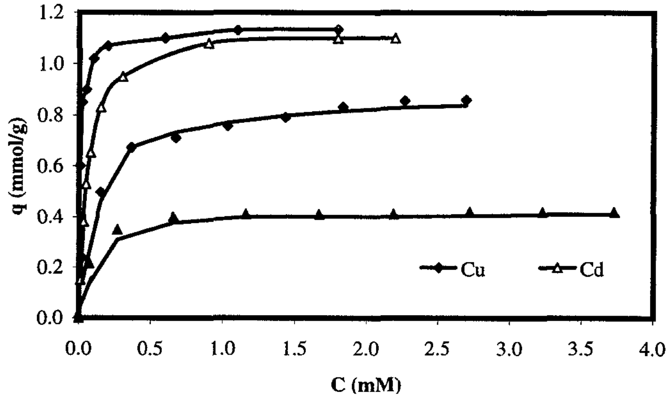

FIG. 1 Isotherms of single and binary adsorption of copper and cadmium onto the biomass of *Durvillaea potatorum* (*c*: solution phase concentration; *q*: biomass phase concentration; temperature: 25°C; pH 5.0). ◆ and ▲ represent experimental data of copper and cadmium, respectively, from single systems. The solid symbols represents experimental data from binary adsorption. Lines show their calculated points using the Langmuir model.

nary system was about the same as those achieved in the single metal uptakes. This indicates that a similar biosorption mechanism might be involved for the two heavy metal ions when they are undergoing competitive adsorption.

The single metal isotherms in Fig. 1 were analyzed with the Langmuir model. The isotherms were well described by the Langmuir equation (solid lines). The Langmuir parameters were obtained through double reciprocal linear regression from single metal isotherms and then used to predict the binary isotherms by using the extended Langmuir model for multicomponent adsorption, as follows:

$$q_{\mathrm{Cu}} = \frac{b_{\mathrm{Cu}} C_{\mathrm{Cu}} q_{\mathrm{Cu,max}}}{1 + b_{\mathrm{Cu}} C_{\mathrm{Cu}} + b_{\mathrm{Cd}} C_{\mathrm{Cd}}} \qquad (1)$$

$$q_{\mathrm{Cd}} = \frac{b_{\mathrm{Cd}} C_{\mathrm{Cd}} q_{\mathrm{Cd,max}}}{1 + b_{\mathrm{Cd}} C_{\mathrm{Cd}} + b_{\mathrm{Cu}} C_{\mathrm{Cu}}} \qquad (2)$$

where q_{Cu} = predicted Langmuir capacity of copper (mmol/g)
q_{Cd} = predicted Langmuir capacity of cadmium (mmol/g)
C_{Cu} = equilibrium concentration of copper in binary adsorption (mM)
C_{Cd} = equilibrium concentration of cadmium in binary adsorption (mM)
b_{Cu} = Langmuir parameter of copper from single heavy metal ad-

sorption (16.68, 1/mM, obtained from single component isotherm)

b_{Cd} = Langmuir parameter of cadmium from single heavy metal adsorption (6.15, 1/mM)

$q_{Cu,\,max}$ = Langmuir capacity of copper from single heavy metal adsorption (1.30 mmol/g)

$q_{Cd,\,max}$ = Langmuir capacity of cadmium from single heavy metal adsorption (1.12 mmol/g)

The predicted isotherms for the binary systems are shown as solid lines in Fig. 1. It was found that the difference between the experimental data and the predicted lines was small, with a correlation coefficient of 0.98 for the two binary data sets. This also indicated that the competitive adsorption of the two heavy metal ions may involve similar biosorption mechanisms. From the Langmuir parameters, copper has a higher relative affinity than cadmium, and the separation factor ($\alpha_{Cu/Cd}$) was calculated from Eqs. (1) and (2) as follows:

$$\alpha_{Cu/Cd} = \frac{q_{Cu}/C_{Cu}}{q_{Cd}/C_{Cd}} = \frac{b_{Cu}q_{Cu,Max}}{b_{Cd}q_{Cd,Max}} = 3.05 \qquad (3)$$

It is noted that the q_{max} for the two metals are different. The extended Langmuir model is not thermodynamically consistent in this case (28). Therefore, Eqs. (1) and (2) are used here as empirical correlations of experimental data.

Effects of Solution pH, Temperature, and Light Metal Ions on Binary Adsorption

Figure 2 shows the initial and equilibrium pH values for a range of binary solutions of copper and cadmium equimolar concentrations varying from 0.5

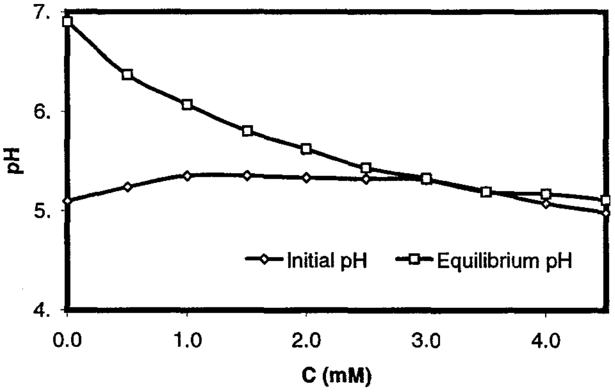

FIG. 2 Initial and equilibrium pH values for *Durvillaea potatorum*–copper–cadmium systems at different initial equimolar concentrations of copper and cadmium (biomass dosage: 2 g/L).

to 4.5 mM. It was observed that during equilibrium studies of the copper–cadmium–*Durvillaea potatorum* system, the pH of the solution increased during the bisorption process. The initial pH varied from 5.1 to 5.3, and the equilibrium pH was in the 5.3 to 6.9 range. The biomass has an equilibrium pH of around 6.9 in water. The uptake of heavy metals decreased this equilibrium pH in the solution. This could be the results of competitive binding between the cations involved. The biomass mainly contained H^+, Ca^{2+}, and Mg^{2+}, and there was equilibria among them (29). The uptake of Cu^{2+} and Cd^{2+} displaced some H^+ into the solution, resulting in a decrease of solution pH.

The equilibrium metal uptake of *Durvillaea potatorum* from a 4.5-mM equimolar solution of copper and cadmium at various equilibrium pH values is presented in Fig. 3. It is seen from this figure that adsorption of copper and cadmium increased with increasing solution pH. The uptakes increased from 0.005 mmol/g at pH 1.0 to 0.86 mmol/g for copper and to 0.42 mmol/g for cadmium at pH 5.5. The sharpest increase was obtained between pH 1.5 and 2.5; a plateau was reached at around pH 5.0. It is most likely that the dominant mechanism involves ion exchange between the heavy metal ions and the Ca^{2+} and Mg^{2+} ions in the biomass (30). The functional groups in the biomass are weakly acidic groups that are affected by the acid–base equilibrium (31). The number of available binding sites are much lower when the pH is lower than the pK_a values of the functional groups. At lower pH values the H^+ concentration is also higher, which can compete with the heavy metal ions. From Fig. 3, the inflection points in curves occur at a pH value around

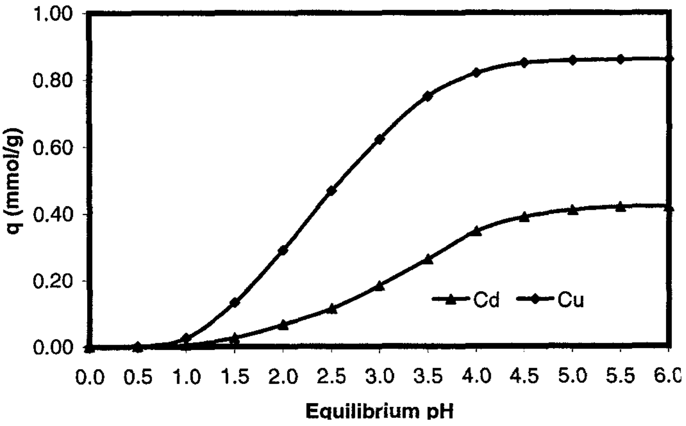

FIG. 3 Copper and cadmium uptake by *Durvillaea potatorum* as a function of equilibrium solution pH (biomass dosage: 2 g/L; temperature: 25°C, initial concentration: 4.5 mM).

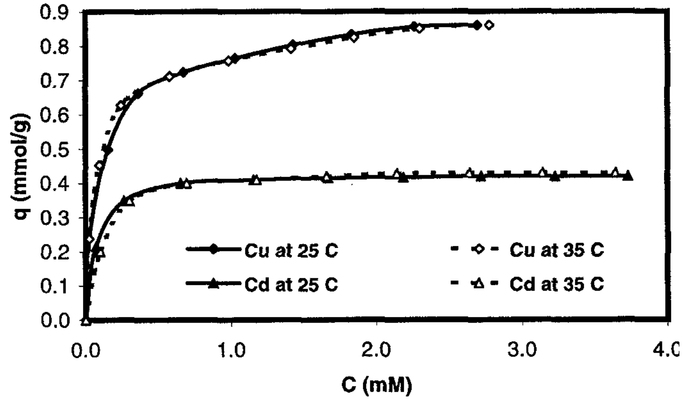

FIG. 4 Isotherms of binary adsorption of copper and cadmium at different temperatures (pH 5.0).

2.5, which is consistent with the pK_a values of carboxylic groups in the biomass (31).

The effects of equilibrium temperature were studied with isotherms obtained at 25 and 35°C (Fig. 4). Copper and cadmium isotherms at 25 and 35°C showed similar values, which indicates that biosorption was not significantly affected by the variation in temperature. This is consistent with the ion-exchange mechanism involved in the biosorption process. Ion-exchange processes normally have a small heat effect and therefore the equilibrium is not highly temperature-dependent.

Industrial wastewater effluents often contain large amounts of light metal ions such as calcium, magnesium, sodium, and potassium along with heavy metal ions (3, 32). These light metal ions often reduce the binding capacity of commercial ion-exchange resins (12). This effect can be smaller in biosorption systems (30). The effects of light metal ions on the binary adsorption capacities of copper and cadmium of *Durvillaea potatorum* were studied. The removal efficiencies for 100 mL of 2.5 mM equimolar copper and cadmium by 0.2 g of biomass in the presence of light metal ions are compared in Table 1. From Table 1, the effects of sodium and potassium ions on copper and cadmium uptake are marginal, even at a 10-mM concentration of these ions. Calcium ions at a 10-mM concentration reduced the removal efficiency by 8%, while magnesium ions reduced the efficiency by 5%. These phenomena were similar to those observed in a number of single component biosorption system, indicating that the relative affinity of light metal ions is much lower than those of copper and cadmium (20, 21, 30).

TABLE 1
Copper and Cadmium Removal Efficiencies of *Durvillaea potatorum* in the Presence of Various Light Metal Ions (initial concentration: 2.5 mM; biomass dosage: 2 g/L)

	% Removal	
Light metal	Cu	Cd
None	92	90
Na^+ (10 mM)	92	90
K^+ (10 mM)	92	90
Ca^{2+} (10 mM)	84	82
Mg^{2+} (10 mM)	87	85

Kinetics of Copper and Cadmium Uptake by *Durvillaea potatorum*

The kinetic profiles of copper and cadmium biosorption by *Durvillaea potatorum* at various initial concentrations are shown in Fig. 5. The copper uptake was relatively fast for all the concentrations studied. At an initial concentration of 1.0 mM, the system reached equilibrium, corresponding to 100% of the total copper uptake by *Durvillaea potatorum*, within 15 minutes. In general, the system reached over 90% of the total copper uptake within 10 minutes of contact. The cadmium uptake showed a similar trend, but the final

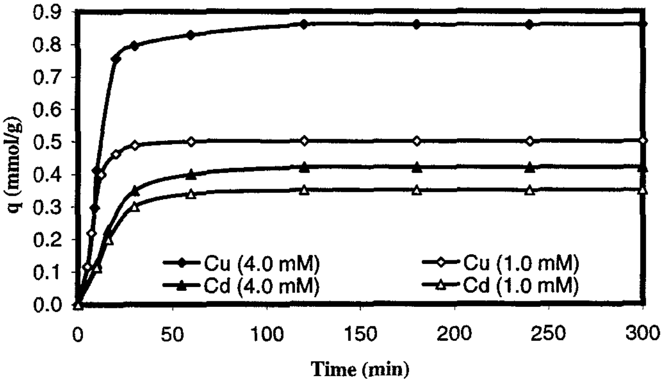

FIG. 5 Kinetic profiles of copper and cadmium biosorption by *Durvillaea potatorum* at different heavy metal concentrations (biomass dosage: 2 g/L; temperature: 25°C; pH 5.0).

equilibrium was reached within 30 minutes. These kinetic profile were similar to those observed in single component systems (20, 30). The rapid kinetics have significant practical importance as they will facilitate the use of smaller adsorber volumes to ensure efficiency and economy.

CONCLUSIONS

The study indicated that a pretreated biomass of the Australian marine alga *Durvillaea potatorum* may be used as an efficient biosorbent material for the treatment of copper- and cadmium-bearing aqueous waste streams. The total copper and cadmium adsorption capacity of *Durvillaea potatorum* in the binary system was found to be similar to those of single systems. The equilibrium isotherm was predicted by the extended Langmuir model using Langmuir parameters and capacities obtained from single component systems. Copper ion has a higher adsorption affinity, and the separation factor $\alpha_{Cu/Cd}$ is 3.05.

An optimal pH range of 4.1 to 5.4 was established experimentally for the maximum adsorption of copper and cadmium. A decrease in the solution pH resulted in a decrease in the adsorption capacity of the biomass. Variations of temperature did not show significant effects on the uptake capacity of *Durvillaea potatorum* for copper and cadmium. Light metal ions, in particular calcium and magnesium ions, were found to interfere with the binding of copper and cadmium to the biomass, but the effects were small. The binary adsorption kinetics was found to be fast. The biomass appears to be reasonably well suited for the treatment of the copper- and cadmium-bearing aqueous waste streams.

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