ORIGINAL ARTICLE

Biosorption of binary mixtures of heavy metals by green macro alga, *Caulerpa lentillifera*

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Abstract

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Dried *Caulerpa lentillifera* was shown to have adsorption potential for Cu, Cd, Pb and Zn. The adsorption equilibrium was found to follow the Freundlich isotherm type. The adsorption of binary mixture of heavy metals solution onto the surface of the algae was found to be of competitive type where the adsorption capacity for any single metal decreased by 10-40% in the presence of the others. The total adsorption capacity of the algae was, in most cases, found to decrease by 30-50% when there was more than one heavy metal in the solution. However, the adsorption of mixtures of Cd and Cu, and of Pb and Cu did not show a reduction in the total adsorption capacity.

Key words : adsorption, competitive sorption, algae, wastewater treatment

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การดูดซับสารละลายโลหะหนักผสมสองชนิดด้วยสาหร่ายช่อพริกไทย

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สาหร่ายช่อพริกไทยซึ่งเป็นสาหร่ายที่เจริญเติบโตตามธรรมชาติเมื่อนำมาอบแห้งแล้วพบว่ามีประสิทธิภาพในการดูดซับโลหะหนักบางชนิด ได้แก่ ทองแดง แคดเมียม ตะกั่ว และสังกะสี การศึกษาเบื้องต้นแสดงให้เห็นที่สภาวะสมดุลของการดูดซับเป็นไปตามแบบจำลองไอโซเทอมของฟรุนดิช ผลการดูดซับโลหะหนักผสมพบว่ามีการแข่งขันในการดูดซับระหว่างโลหะหนัก โดยที่ความสามารถในการดูดซับของโลหะหนักแต่ชนิดมีค่าลดลงประมาณ 10-40% เมื่อมีโลหะชนิดอื่นผสมอยู่ และความสามารถในการดูดซับสูงสุดของสารละลายโลหะผสมสองชนิดจะมีค่าประมาณ 30-50% ของความสามารถในการดูดซับโลหะหนักเพียงชนิดเดียว มีข้อยกเว้นสำหรับคู่โลหะหนักสองคู่ได้แก่ แคดเมียมกับทองแดง และตะกั่วกับทองแดง ที่ค่าความสามารถในการดูดซับของโลหะหนักผสมไม่ได้ลดลงเมื่อเทียบกับความสามารถในการดูดซับโลหะในสารละลายที่มีโลหะเพียงชนิดเดียว

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Heavy metals are among the major concerns in wastewater treatment. Heavy metals are often derived from heavy industry, such as electroplating and battery factories. The treatment of this type of wastewater involves high cost techniques such as ion exchange, evaporation, precipitation, membrane separation etc. However, these common techniques are too expensive to treat low levels of heavy metal in wastewater (Banerjee, 2002). Therefore a low cost biosorption process using algae as an adsorbent has lately been introduced as an alternative (Volesky, 1990).

Although actual wastewater treatment systems often have to deal with a mixture of heavy metals, most research work still only focuses on a single metal sorption. Only a few works on the adsorption of a mixture of heavy metals were found in literature. For instance, Sag and Kutsal (1995) investigated the competitive biosorption of Cr^{6+} and Fe^{3+} by *Rhizopus arrhizus* and reported that instantaneous, equilibrium and maximum uptakes of Cr^{6+} and Fe^{3+} were reduced by increasing concentration of other metals. The combined action of competitive uptake of Cr^{6+} and Fe^{3+} by *Rhizopus arrhizus* was generally found to be antagonistic. The most logical reason for the antagonistic action was claimed to be the competition for sorption site on the cell and/or the screening effect by the second metal. In the examination of the biosorption of Cu^{2+} and Zn^{2+} by *Cymodocea nodosa*, Sanchez *et al.* (1999) stated that there was a competition between the two metal species and Cu^{2+} was preferentially adsorbed by this biomass. Kaewsarn (2000) investigated the effect of other heavy metal ions on Cu^{2+} uptake by *Durvilaea potatorum.* He reported that Cu^{2+} uptake was significantly affected by other heavy metals (Ag^{+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Fe^{2+}, Cd^{2+}, Pb^{2+}) and EDTA because the metal binding sites on the biosorbent were limited, so these ions competed simultaneously for the site. The amount of suppression for Cu^{2+} uptake depended on the affinity of these ions for binding sites and binding strength of the respective heavy metal ions to the biosorbent. Singh *et al.* (2001) studied the multi-metals combination between Ni^{2+} and Cr^{6+} by *Microcystis* sp. They found that Ni^{2+} sorption capacity by this biomass was higher than that of Cr^{6+} as the binding sites in the biomass had a greater affinity for Ni^{2+}.

Caulerpa lentillifera is a marine macro alga commonly found in culture ponds. It uptakes and keeps a balance of nitrogen compounds in the culture system (Chokwiwattanawanit, 2000). However, its rapid growth necessitates a regular removal of the excess quantity. Hence, there is a need for the management of this overabundance of the algal mass. Previous work (Sungkhum, 2003) illustrated the possibility of using this dried alga for the biosorption of heavy metal ions in an aqueous solution for a single solute system, and it was shown that this alga could be employed for the sorption of Cd, Cu, Pb and Zn. The purpose of this work is therefore to investigate the competitive sorption of *Caulerpa lentillifera* with aqueous binary mixtures of copper (II), cadmium (II), lead (II), and zinc (II).

Materials and Methods

Preparation of biosorbent

A green macro alga, *Caulerpa lentillifera*, was supplied by Bangchong farm in Chacheongsao province, Thailand. The alga was washed with deionized water and oven-dried at 80°C for 12 hours.

Solubility tests

Heavy metals of interest in this study were Cu, Cd, Pb, and Zn. Analytical grade heavy metal reagents (MERCK) in nitrate form were used in all cases. The pH adjustments were done by using 0.1N nitric acid (HNO_3) and 0.1N sodium hydroxide (NaOH) solutions. Firstly, the solubility of heavy metals at different pH levels was determined. The synthetic wastewaters were prepared from 100 mg/l of heavy metal stock solutions (equivalent to 1.57, 0.89, 0.48, and 1.53 mmol/l for Cu, Cd, Pb, and Zn respectively). The pH of the solutions was adjusted and controlled from 4 - 7. The samples were filtered through 0.45 μm cellulose nitrate membrane filter to remove all suspended solids, and the filtrates were measured for heavy metal concentration. This enabled the determination of the solubility of each heavy metal at a different pH level

Biosorption of single component heavy metal solution

The removal efficiency of a single and binary component of heavy metals was investigated. The experiment was performed by adding 0.5 g dried algae to 30 ml of the metal solutions. Initial concentrations of each heavy metal varied from 0 - 100 mg/l. The mixtures were mixed slowly in a rotary shaker at an agitation rate of 150 rpm for 30 minutes. The temperature was controlled at 21 $\pm$ 2 °C. After 30 minutes, solid phase was separated by filtration through No.93 filter paper and GF/C filter. Heavy metals concentrations in the filtrates were measured by Inductively Couple Plasma Atomic Emission Spectroscopy (ICP-AES) from Vista supplier.

Biosorption for binary component heavy metal solution

The adsorption experiment for binary heavy metal mixtures was carried out in a similar fashion to the single metal cases. Two heavy metals were selected from the four heavy metals, i.e. Cu, Cd, Pb and Zn, with the following combinations: Cu-Cd, Cu-Pb, Cu-Zn, Cd-Cu, Cd-Pb, Cd-Zn, Pb-Cu, Pb-Cd, Pb-Zn Zn-Cu, Zn-Cd, and Zn-Pb. The mixture solution was then prepared with a primary heavy metal concentration varied from 10, 25, and 50 mg/l and the secondary heavy metal concentration fixed at 50 mg/l. To convert to molar concentration, the mass concentration was divided by the atomic weight of each metal species and the atomic weights of Cu, Cd, Pb, and Zn were 63.54, 112.4, 207.19, and 65.37 g/mol, respectively.

Results and Discussion

Solubility tests

It has often been accepted that many biosorbents have high uptake capacities for heavy metals at high pH (Volesky, 1990; Kaewsarn, 2000). However, metal precipitation also takes place at high pH and this would interfere with the adsorption results as it could lead to the misinterpretation of the adsorption capacity. Therefore, it is important to identify a suitable pH for the adsorption. In this work, the suitable pH was defined as the highest pH at which all four heavy metals were still dissolved but not precipitated, and the results are summarized in Table 1. Figure 1 displays the pH at which heavy metals used in this work at 100 mg/l started to precipitate. Thus, all further experiments were performed at pH 5 $\pm$ 0.2 to ensure that metals were presented in dissolved form.

Removal efficiency and isotherm of single component heavy metal solution

To facilitate further discussion in this article, the concentration of the metal species was

Table 1. pH level for the precipitation of the heavy metals

Metal	pH
Cu	> 6
Cd	> 6.3
Pb	> 7
Zn	> 6.5

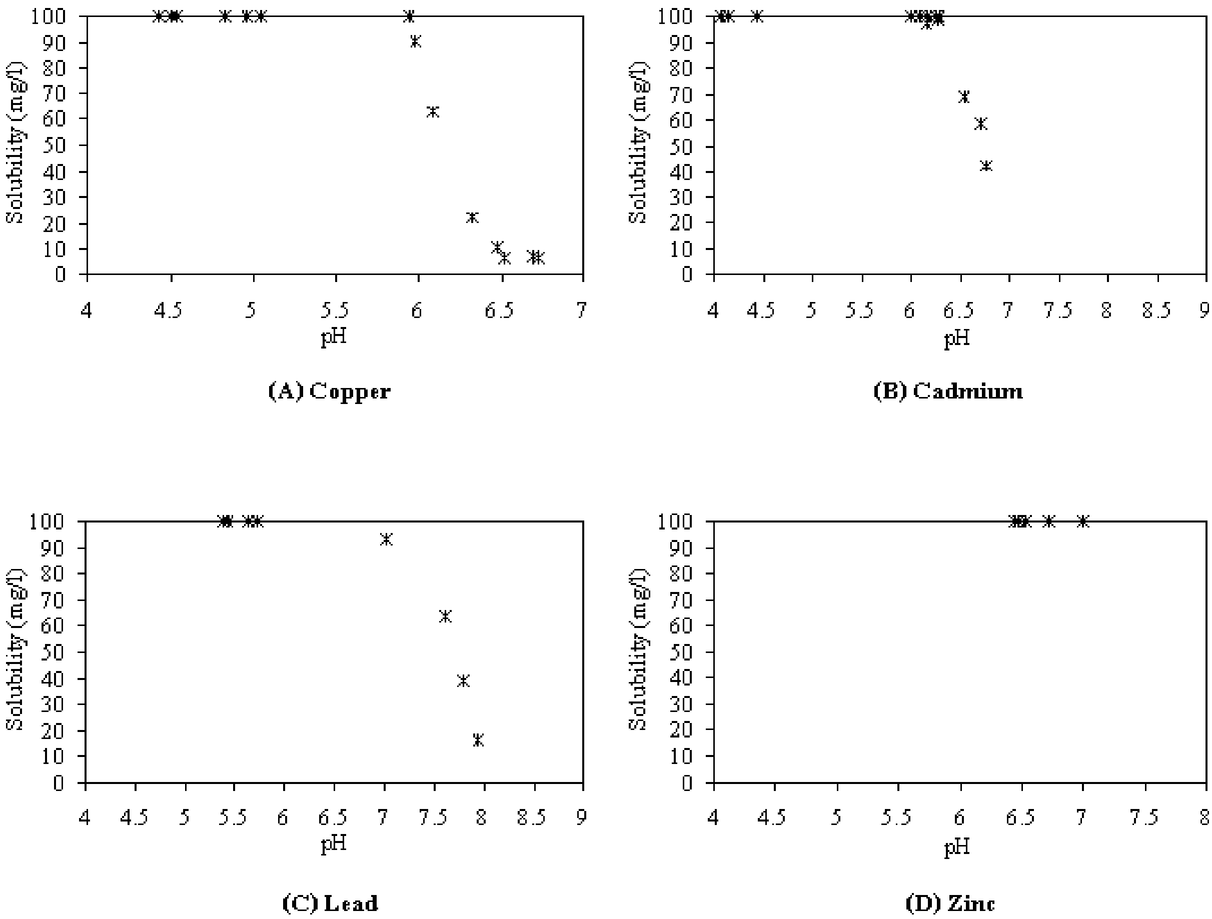


Figure 1. Relationship between pH and the concentration of the dissolved heavy metals examined in this work (with initial heavy metal concentration of 100 mg/l)

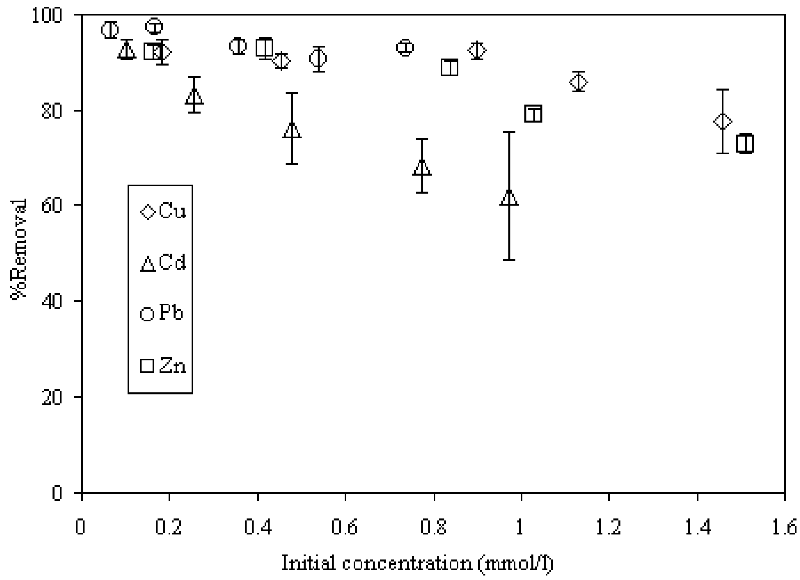


Figure 2. Relationship between removal efficiency and initial concentration

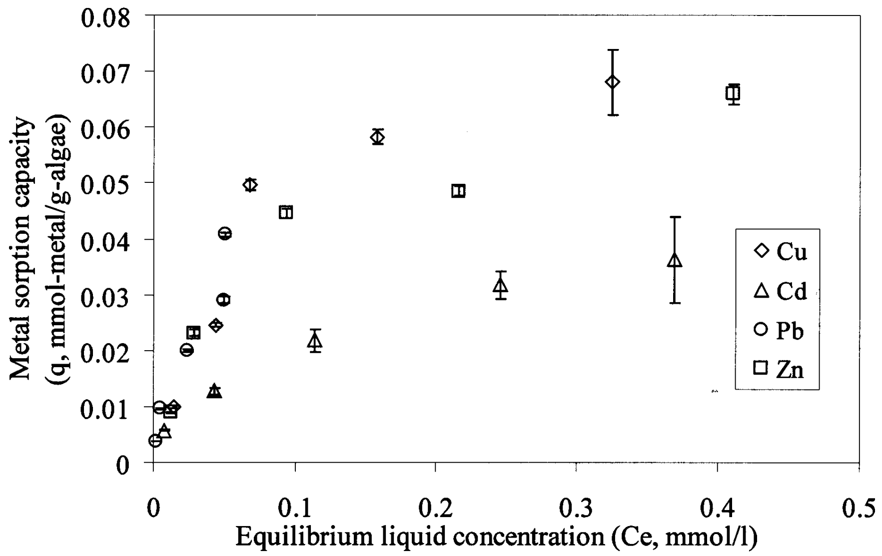


Figure 3. Liquid/solid equilibrium curves (isotherm) for heavy metals examined in this work

converted from the mass concentration into molar units. The removal efficiencies of all heavy metals decreased with increasing of initial concentration (Figure 2). Among the four metals, the biomass exhibited the lowest adsorption efficiency for Cd. The removal efficiencies for the other three metals were in a similar range of about 90-95% at concentration lower than 1 mmol/l and 75-90% at concentration higher than 1 mmol/l. Figure 3 shows liquid/solid equilibrium curves (isotherm) for this adsorption system which emphasized the above findings as biomass was shown to have the lowest adsorption capacity for Cd compared with other heavy metals. Biomass seemed to have lower

Table 2. Parameters of Freundlich isotherm model for each heavy metal

Heavy Metal	Parameters of Freundlich isotherm model			
	K (mmol basis)*	K (mg basis)**	1/n	R^2 (from regression)
Cu	0.1642	0.8848	0.5943	0.8457
Cd	0.0570	0.7469	0.4551	0.9114
Pb	0.1981	1.7135	0.5955	0.9072
Zn	0.1171	0.8762	0.5186	0.8877

* **mmol basis is the unit of K obtained from the isotherm with q as the y-axis in units of mmol/g and C_e as the x-axis in units of mmol/l.**

** **mg basis is the unit of K obtained from the isotherm with q as the y-axis in units of mg/g and C_e as the x-axis in units of mg/l.**

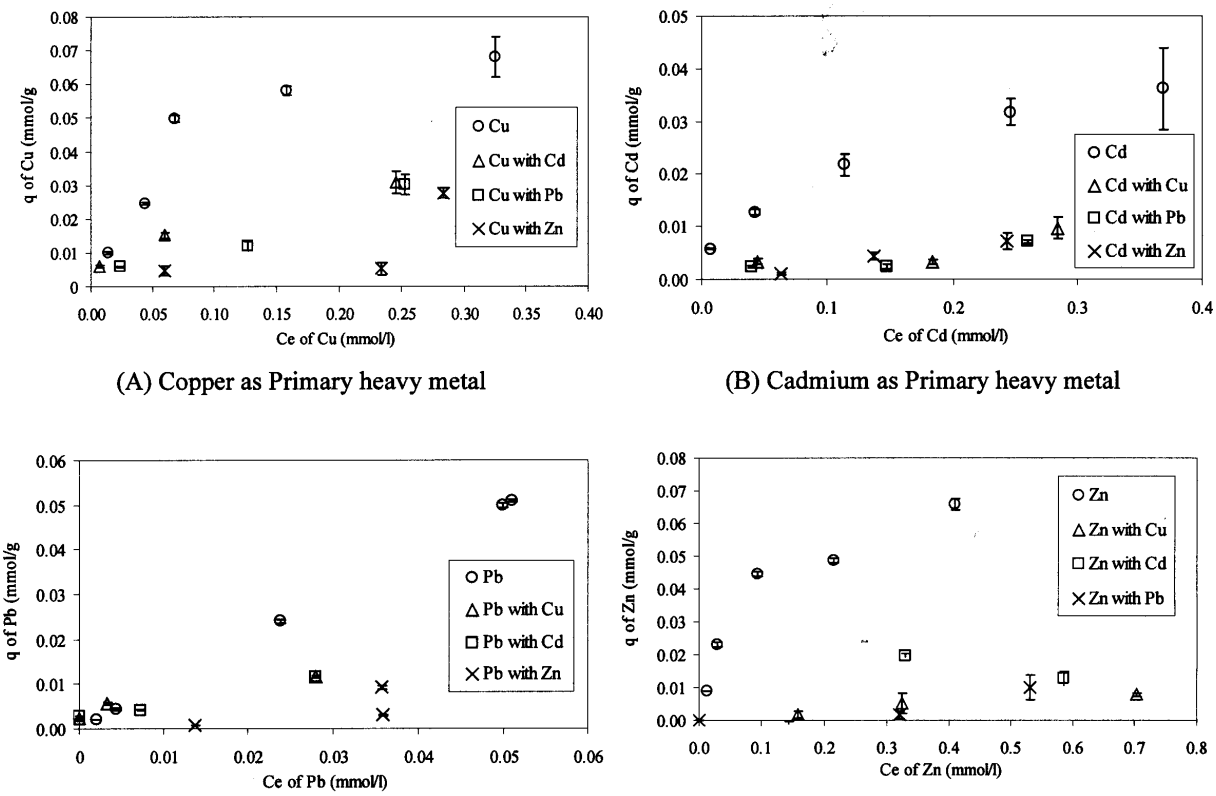
maximum adsorption capacity for Zn than Cu. Within the experimental range of concentration, the adsorption of Pb had not yet reached its maximum capacity. This indicated that the alga still had capability to adsorb Pb. In all cases, the adsorption was found to follow Freundlich adsorption isotherm. The corresponding parameters for the adsorption of each heavy metal are summarized in Table 2. The last column in Table 2 indicates the R^2 obtained from the fitting of experimental data to the isotherm, and a relatively high R^2 demonstrates that the isotherm could be used with high confidence (in the range of concentration reported in this article).

It should be noted that the concentrations of the four metals as reported in Figures 2 and 3 were not in the same range. This was because the concentration of heavy metal under investigation was controlled within the range of 0-100 mg/l. Thus, the four metal species showed an unequal range when converted to molar concentration. The molar unit was used for this report to facilitate the comparison between the adsorption of the four metal species. The adsorption at higher range of concentration was not the focus of this work as the biosorption would not be cost-effective.

Isotherm of binary component heavy metal

Figure 4 illustrates the adsorption isotherm for the binary mixture sorption. Table 3 summarizes the total adsorption capacities of single component heavy metals compared with binary component heavy metals. It can be observed from this table that the adsorption capacity of the alga for the binary mixture was always lower than that for the single component system. For instance, in the case where Cu was set as a primary component and Cd, Pb or Zn as secondary components, the adsorption capacity for Cu of the alga was only about 45.5, 44.5, and 40.7%, respectively, of the capacity obtained when the solution only contained Cu ion. This indicated strongly that there was a competitive adsorption of these four metals on the surface of the alga.

The total adsorption capacity for the heavy metals seemed to be lower in the binary mixture cases than the single component system. This comparison can be achieved by adding the number of moles of all metals adsorbed on the surface of the alga. The second column in Table 3 illustrates the adsorption capacity for the single component system whereas the last column represents the total combined adsorption capacity for the binary systems. It can be seen that, most of the time, the total adsorption capacity was lower for the binary system than the single component. This led to a conclusion that there was also an inhibitory effect exerted from one heavy metal to the other. There were only exceptions for the adsorptions of Cd with Cu and Pb with Cu where the total adsorp-



(A) Copper as Primary heavy metal

(B) Cadmium as Primary heavy metal

(C) Lead as Primary heavy metal

(D) Zinc as Primary heavy metal

Figure 4. Comparative sorption isotherms for competitive sorption system of each heavy metal

tion capacities for the binary mixture were not less than the single component case. Overall adsorption capacity for the mixture of Cd and Cu was found to be higher than the adsorption for Cd alone (but was lower than the adsorption of Cu in a single component system). This indicated that the binding sites for Cd might not be the same as those for Cu and the adsorption of Cu was more favorable than Cd for this alga. For the case of Pb and Cu, the total adsorption capacities for the mixture was approximately the same as the capacity of Pb (for the single component case). Interestingly, the capacity for this mixture was lower than that for the single component - Cu system. It was anticipated that these two metals competed for the same binding site. However, the isotherm of the single component - Pb system illustrated that, for the range of Pb concentration employed in this work, the adsorption of Pb had not reached its maximum level. Therefore the adsorption of binary mixture might not be at the saturation point for Pb resulting in a lower adsorption capacity for the binary mixture than the single component - Cu case.

Conclusion

This work demonstrated the biosorption of a mixture of heavy metals solution with *Caulerpa lentillifera*. The results suggested that there should exist a competitive adsorption for the binary mixture solution as the adsorption capacity for the primary heavy metal often dropped with the introduction of the secondary heavy metal. The total adsorption capacity was also found to decrease for the cases of binary adsorption. The

Table 3. Total sorption capacity for binary mixture of heavy metal solution

A: Cu as primary heavy metal

Mixture	q_{Cu} for single system (mmol/g algae)	Binary System (q in mmol/g algae)		
		q_{Cu} (q_1)	$q_{secondary\ metal}$ (q_2)	Total q ($q_1 + q_2$)
Cu with Cd	0.0680	0.0310	0.0099	0.0409
Cu with Pb	0.0680	0.0303	0.0116	0.0419
Cu with Zn	0.0680	0.0277	0.0078	0.0355

B: Cd as primary heavy metal

Mixture	q_{Cd} for single system (mmol/g algae)	Binary System (q in mmol/g algae)		
		q_{Cd} (q_1)	$q_{secondary\ metal}$ (q_2)	Total q ($q_1 + q_2$)
Cd with Cu	0.0318	0.0099	0.0310	0.0409
Cd with Pb	0.0318	0.0072	0.0116	0.0188
Cd with Zn	0.0318	0.0079	0.0128	0.0207

C: Pb as primary heavy metal

Mixture	q_{Pb} for single system (mmol/g algae)	Binary System (q in mmol/g algae)		
		q_{Pb} (q_1)	$q_{secondary\ metal}$ (q_2)	Total q ($q_1 + q_2$)
Pb with Cu	0.0407	0.0116	0.0303	0.0419
Pb with Cd	0.0407	0.0116	0.0072	0.0188
Pb with Zn	0.0407	0.0092	0.0099	0.0191

D: Zn as primary heavy metal

Mixture	q_{Pb} for single system (mmol/g algae)	Binary System (q in mmol/g algae)		
		q_{Pb} (q_1)	$q_{secondary\ metal}$ (q_2)	Total q ($q_1 + q_2$)
Zn with Cu	0.0659	0.0078	0.0277	0.0355
Zn with Cd	0.0659	0.0128	0.0079	0.0207
Zn with Pb	0.0659	0.0099	0.0092	0.0191

Caulerpa lentillifera biomass was found to have the lowest adsorption capacity for Cd whereas Cu and Pb were the highest adsorbed species among the four. It was expected that Cu and Cd were adsorbed at different binding sites whereas Cu and Pb competed for the same binding site. The results also demonstrated that the alga still had spare capacity of the adsorption of Pb as Pb did not seem to reach its maximum adsorption capacity during the range of initial concentration employed in this work.

The results from this work indicated that there was a complex interaction between each metal species in the biosorption. This finding is highly important for the design of the adsorption system for the actual wastewater containing a mixture of heavy metals as it provided the adsorption characteristics of the binary component mixture.

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