Chemical Engineering Journal 119 (2006) 135–145

www.elsevier.com/locate/cej

Sorption isotherm model for binary component sorption of copper, cadmium, and lead ions using dried green macroalga, *Caulerpa lentillifera*

Ronbanchob Apiratikul[a], Prasert Pavasant[b,*]

[a] *National Research Center for Environmental and Hazardous Waste Management, Chulalongkorn University, Bangkok 10330, Thailand*
[b] *Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand*

Received 5 December 2005; received in revised form 22 February 2006; accepted 24 February 2006

Abstract

The sorption of Cu^{2+}, Cd^{2+}, and Pb^{2+} by a dried green macroalga *Caulerpa lentillifera* in binary components systems was investigated. The partial competitive binary isotherm model was proven to be effective in describing the experimental data. The model and experimental data of each binary component system demonstrated that the presence of the secondary metal ion always reduced the total sorption capacity of the biomass. This implied that there existed the same pooled binding sites for the sorption of all of these heavy metal ions. Pb^{2+} was demonstrated to be the most uptaken species, followed by Cu^{2+} and Cd^{2+}. The presence of Pb^{2+} more significantly decreased the sorptions of Cu^{2+} and Cd^{2+} than vice versa. Similarly the sorption of Cd^{2+} was more disturbed by the presence of Cu^{2+}, than that of Cu^{2+} by Cd^{2+}. The effect of pH on metal sorption could also be described using similar fundamentals with the sorption of binary metal component, and the partial competitive model could also be applied to predict the effect of pH on the sorption of these metals. It was demonstrated that a decrease in pH resulted in a reduction in the sorption capacity and sorption affinity. Finally, carboxyl, hydroxyl, sulfonate, amine, and amide functional groups in the alga could be responsible for the sorption of all heavy metals in this work.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Binary sorption; Biosorption; Heavy metals; Macroalgae; pH effect

1. Introduction

Recently, biosorption has emerged as an alternative treatment technology for heavy metals. There have been a number of reports stating the success of such technology [1,2]. To ensure the applicability of this technology, more works are still needed for the sorption of a mixture of heavy metals at various operating conditions. Recent reports on the sorption of multi-component systems include that of Al-Asheh et al. [3] who studied the binary sorption of Cu^{2+}, Cd^{2+}, and Ni^{2+} by pine bark using the extended Langmuir (based on competitive sorption), extended Freundlich, extended Sips, and IAST models. They found that these models could be used to describe the sorption of some binary metal systems including Cu^{2+}–Cd^{2+}, Cu^{2+}–Ni^{2+}, and Cd^{2+}–Ni^{2+}. Hammaini et al. [4] employed three Langmuir type models, based on competitive, uncompetitive, and multi-component sorptions, to explain the effect of Pb^{2+} on the sorption of other metals, i.e. Cu^{2+}, Cd^{2+}, and Zn^{2+}, by activated sludge. The results indicated that a competitive uptake was the most appropriate model, and Pb^{2+} was the most preferentially uptaken species. Ma and Tobin [5] reported the applicability of the extended Langmuir models based on competitive sorption for the binary sorptions of Cr^{3+}–Cu^{2+}, Cr^{3+}–Cd^{2+}, and Cu^{2+}–Cd^{2+} on peat biomass. Lee and Suh [6] examined the effect of Al^{3+} on the sorptions of Cr^{3+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, and Zn^{2+} by Ca-loaded *Sargassum fluitans* biomass using a modified multi-component Langmuir isotherm (based on competitive concept). They reported that the presence of Al ion greatly diminished the uptakes of other heavy metals except that of Cr^{3+}. Alimohamadi et al. [7] found that the modified Freundlich model was a better model than the modified Langmuir model in predicting the binary sorption of Pb^{2+} and Cu^{2+} by *Rhizopus arrhizus*. All the above findings suggested that, although the binary sorption could be well described using various types of models, the extended Langmuir using the competitive sorption concept was generally more commonly employed than others.

The influence of pH on sorption characteristics is also an important aspect for actual applications. The effect of pH on the

---

[*] Corresponding author. Tel.: +66 2 218 6870; fax: +66 2 218 6877.
E-mail address: prasert.p@chula.ac.th (P. Pavasant).

1385-8947/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2006.02.010

Nomenclature

b'	affinity constant for the simultaneously bonding of two metals with the same binding site
B	free binding site
b	Langmuir affinity for the single component system
b (pH)	Langmuir affinity for the single component system as a function of pH
b_{HM}	affinity constant of the metal ion on the protonated binding site
b_{M}	affinity constants for metal 'M' (primary component) = $1/K_{\mathrm{M}}$
BM	binding site occupied with metal 'M'
b_{MH}	sorption affinity of proton on the binding site already occupied by metal ion
b_{MN}	affinity constant for the bonding of metal 'N' with the binding site already occupied with metal 'M'
BMN	binding site simultaneously occupied with metals 'M' and 'N'
b_{N}	affinity constants for metal 'N' (secondary component) = $1/K_{\mathrm{N}}$
BN	binding site occupied with metal 'N'
b_{NM}	affinity constant for the bonding of metal 'M' with the binding site already occupied with metal 'N'
$\mathrm{B_t}$	total binding site
C_{e}	equilibrium concentrations
C_{e}[M]	equilibrium concentration of metal 'M' (primary component)
C_{e}[N]	equilibrium concentration of metal 'N' (secondary component)
C_{i}	initial concentrations
E_i	error at point i
$\bar{E}$	average of error from all experimental data
K	equilibrium constant for the simultaneously bonding of two metals with the same binding site
K_{a}	acid dissociation equilibrium constant of binding site
K_{M}	equilibrium constant of the binding site which bonding with metal 'M'
K_{MN}	equilibrium constant for the bonding of metal 'N' with the binding site already occupied with metal 'M'
K_{N}	equilibrium constant of the binding site which bonding with metal 'N'
K_{NM}	equilibrium constant for the bonding of metal 'M' with the binding site already occupied with metal 'N'
M	first sorbate component (metal ion) in the solution
N	number of the experimental data
N	second sorbate component (metal ion) in the solution
q[M]	sorption capacity of metal 'M' (primary component)
q[M + N]	sum of sorption capacity of the two metal components
q[N]	sorption capacity of metal 'N' (secondary component).
$\bar{q}$	average of actual sorption capacity from total experimental data
$q_{\mathrm{c},i}$	calculated sorption capacity datum at point i
q_{e}	amount of metal uptaken per unit mass of the biomass at equilibrium
q_i	actual sorption capacity experimental datum at point i
q_{m}	maximum sorption capacity for the binary components system
q_{max}	maximum sorption capacity for the single component system
q_{max} (pH)	maximum sorption capacity for the single component system as a function of pH
$q_{\mathrm{max,HM}}$	maximum sorption capacity of metal ion on protonated binding site
$q_{\mathrm{max,M}}$	maximum sorption capacity of metal ion on unprotonated binding site
R^2	determination coefficient

sorption could, in fact, be simulated as a binary sorption where hydrogen ion was considered as an additional sorbate, and there existed a competition between hydrogen ion and metal in the sorption mechanism. Xu et al. [8] reported that an increase in pH tended to increase maximum sorption capacity of Ni^{2+} by granular sludge. Similarly, Bektas et al. [9] reported that the sorption capacity of Pb^{2+} by natural sepiolite increased with pH. Pagnanelli et al. [10] investigated the effect of pH on the sorption of Pb^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} onto *Sphaerotilus natans* and suggested that maximum sorption capacity varied significantly with pH where the relationship between these two parameters could be described using either linear, polynomial, or exponential models, depending on the nature of each metal system.

This work was intended to investigate the suitability of various types of multi-component sorption isotherm models in predicting the binary sorption of Cu^{2+}, Cd^{2+}, and Pb^{2+}. Three-dimensional sorption isotherm surfaces of each binary component system were generated where the sorption behavior could be clearly illustrated. It was also shown that such multi-component sorption isotherm could be used with accuracy in predicting the effect of pH on the sorption of single metal component systems.

2. Model development for binary component systems

Three different Langmuirian isotherm models with distinctive assumptions were selected for the investigation of the sorption of each pair of heavy metal species. The three assumptions were: (i) the sorption was competitive, (ii) the sorption was uncompetitive, and (iii) the sorption was partially competitive. This was to be able to identify the type of sorption taken place in each binary system.

2.1. Competitive model (Model A)

The competitive model was developed under the concept of the original Langmuir model for single component systems where one binding site was only available for one sorbate. This can be written in a mathematical form as follows [4,5]:

$$\mathrm{B}+\mathrm{M} \xleftrightarrow{K_\mathrm{M}} \mathrm{BM}, \quad K_\mathrm{M}=\frac{k_{-\mathrm{M(desorbed)}}}{k_{+\mathrm{M(uptaken)}}}=\frac{[\mathrm{B}][\mathrm{M}]}{[\mathrm{BM}]} \tag{1}$$

$$\mathrm{B}+\mathrm{N} \xleftrightarrow{K_\mathrm{N}} \mathrm{BN}, \quad K_\mathrm{N}=\frac{k_{-\mathrm{N(desorbed)}}}{k_{+\mathrm{N(uptake)}}}=\frac{[\mathrm{B}][\mathrm{N}]}{[\mathrm{BN}]} \tag{2}$$

where M represents the first sorbate (metal) in the solution, N the second sorbate (metal) in the solution, B the free binding site, K_M and K_N the equilibrium constants of the binding site for metals 'M' and 'N', respectively. BM and BN were the binding sites occupied with metals 'M' and 'N', respectively. The mass balance equation for this case could be written as:

$$[\mathrm{B_t}]=[\mathrm{B}]+[\mathrm{BM}]+[\mathrm{BN}] \tag{3}$$

Assuming that the sorption system rapidly reached the equilibrium resulting in no changes of [BM] and [BN] with respect to time:

$$\frac{\mathrm{d}[\mathrm{BM}]}{\mathrm{d}t}=0 \quad \text{and} \quad \frac{\mathrm{d}[\mathrm{BN}]}{\mathrm{d}t}=0 \tag{4}$$

Combining Eqs. (1)–(4) leads to

$$[\mathrm{BM}]=\frac{([\mathrm{B_t}]/K_\mathrm{M})[\mathrm{M}]}{1+(1/K_\mathrm{M})[\mathrm{M}]+(1/K_\mathrm{N})[\mathrm{N}]} \tag{5}$$

Eq. (5) is well known as an extended Langmuir model for binary component competitive sorption which can be written into Langmuirian type equation as expressed in Eq. (6):

$$q[\mathrm{M}]=\frac{q_\mathrm{m} b_\mathrm{M} C_\mathrm{e}[\mathrm{M}]}{1+b_\mathrm{M} C_\mathrm{e}[\mathrm{M}]+b_\mathrm{N} C_\mathrm{e}[\mathrm{N}]}, \quad b_\mathrm{M}=\frac{1}{K_\mathrm{M}} \text{ and } b_\mathrm{N}=\frac{1}{K_\mathrm{N}} \tag{6}$$

where the total metal uptake (for the two metals) can be expressed as Eq. (7):

$$q[\mathrm{M}+\mathrm{N}]=q[\mathrm{M}]+q[\mathrm{N}]=q_\mathrm{m}\frac{b_\mathrm{M} C_\mathrm{e}[\mathrm{M}]+b_\mathrm{N} C_\mathrm{e}[\mathrm{N}]}{1+b_\mathrm{M} C_\mathrm{e}[\mathrm{M}]+b_\mathrm{N} C_\mathrm{e}[\mathrm{N}]} \tag{7}$$

where $q[\mathrm{M}]$ and $q[\mathrm{N}]$ are the sorption capacities of metals 'M' (primary component) and 'N' (secondary component), respectively, $q[\mathrm{M}+\mathrm{N}]$ the sum of uptakes of the two metal components, $C_\mathrm{e}[\mathrm{M}]$ and $C_\mathrm{e}[\mathrm{N}]$ the equilibrium concentrations of metals 'M' and 'N', respectively, q_m the maximum sorption capacity for the binary components system, b_M and b_N the affinity constants of Langmuir model for the primary and secondary metal components, or 'M' and 'N', respectively.

2.2. Uncompetitive model (Model B)

This model was developed based on the assumption that the two sorbates could be simultaneously uptaken on the same binding site. The equilibrium reaction equations and the mass balance equation based on this assumption can be expressed as:

$$\mathrm{B}+\mathrm{M} \xleftrightarrow{K_\mathrm{M}} \mathrm{BM}, \quad K_\mathrm{M}=\frac{k_{-\mathrm{M(desorbed)}}}{k_{+\mathrm{M(uptaken)}}}=\frac{[\mathrm{B}][\mathrm{M}]}{[\mathrm{BM}]} \tag{8}$$

$$\mathrm{B}+\mathrm{N} \xleftrightarrow{K_\mathrm{N}} \mathrm{BN}, \quad K_\mathrm{N}=\frac{k_{-\mathrm{N(desorbed)}}}{k_{+\mathrm{N(uptake)}}}=\frac{[\mathrm{B}][\mathrm{N}]}{[\mathrm{BN}]} \tag{9}$$

$$\mathrm{B}+\mathrm{M}+\mathrm{N} \xleftrightarrow{K} B_\mathrm{N}^\mathrm{M}, \quad K=\frac{[B][\mathrm{M}][\mathrm{N}]}{[B_\mathrm{N}^\mathrm{M}]} \tag{10}$$

$$[\mathrm{B}]=[\mathrm{B}]+[\mathrm{BM}]+[\mathrm{BN}]+[B_\mathrm{N}^\mathrm{M}] \tag{11}$$

$$\frac{\mathrm{d}[\mathrm{BM}]}{\mathrm{d}t}=\frac{\mathrm{d}[\mathrm{BN}]}{\mathrm{d}t}=\frac{\mathrm{d}[B_\mathrm{N}^\mathrm{M}]}{\mathrm{d}t}=0 \tag{12}$$

Combining these equations results in:

$$[\mathrm{BM}]+[B_\mathrm{N}^\mathrm{M}]=\frac{[\mathrm{M}]\{[\mathrm{B_t}]+[\mathrm{B_t}](K_\mathrm{M}/K)[\mathrm{N}]\}}{K_\mathrm{M}+[\mathrm{M}]+(K_\mathrm{M}/K_\mathrm{N})[\mathrm{N}]+2(K_\mathrm{M}/K)[\mathrm{M}][\mathrm{N}]} \tag{13}$$

Eq. (13) can be rearranged in Langmuirian form as:

$$q[\mathrm{M}]=\frac{q_\mathrm{max}(b_\mathrm{M} C_\mathrm{e}[\mathrm{M}]+b' C_\mathrm{e}[\mathrm{M}] C_\mathrm{e}[\mathrm{N}])}{1+b_M C_\mathrm{e}[\mathrm{M}]+b_\mathrm{N} C_\mathrm{e}[\mathrm{N}]+b'(C_\mathrm{e}[\mathrm{M}])(C_\mathrm{e}[\mathrm{N}])} \tag{14}$$

and the total uptake for the two metals as:

$$q[\mathrm{M}+\mathrm{N}]=q[\mathrm{M}]+q[\mathrm{N}] =\frac{q_\mathrm{max}(b_\mathrm{M} C_\mathrm{e}[\mathrm{M}]+C_\mathrm{e}[\mathrm{N}]+2b'(C_\mathrm{e}[\mathrm{M}])(C_\mathrm{e}[\mathrm{N}]))}{1+b_\mathrm{M} C_\mathrm{e}[\mathrm{M}]+b_\mathrm{N} C_\mathrm{e}[\mathrm{N}]+b'(C_\mathrm{e}[\mathrm{M}])(C_\mathrm{e}[\mathrm{N}])} \tag{15}$$

where $q[\mathrm{M}]$, $q[\mathrm{N}]$, $q[\mathrm{M}+\mathrm{N}]$, $C_\mathrm{e}[\mathrm{M}]$, $C_\mathrm{e}[\mathrm{N}]$, $q_\mathrm{m,}$ b_M, and b_N take the same meanings with the Model A, K and b' are the equilibrium constant and the affinity constant for the simultaneous bonding of two metals with the same binding site, respectively.

2.3. Partial competitive model (Model C)

The partial competitive isotherm model was developed based on the assumption that one sorbate could attach onto only one binding site, and that the sorbate could also attach to the occupied binding sites. This meant that the occupied binding sites (with one metal) could form another linkage with other sorbates. The chemical equilibrium reaction equations and the mass balance equation based on this assumption can be expressed as:

$$\mathrm{B}+\mathrm{M} \xleftrightarrow{K_\mathrm{M}} \mathrm{BM}, \quad K_\mathrm{M}=\frac{k_{-\mathrm{M(desorbed)}}}{k_{+\mathrm{M(uptaken)}}}=\frac{[\mathrm{B}][\mathrm{M}]}{[\mathrm{BM}]} \tag{16}$$

$$\mathrm{B}+\mathrm{N} \xleftrightarrow{K_\mathrm{N}} \mathrm{BN}, \quad K_\mathrm{N}=\frac{k_{-\mathrm{N(desorbed)}}}{k_{+\mathrm{N(uptake)}}}=\frac{[\mathrm{B}][\mathrm{N}]}{[\mathrm{BN}]} \tag{17}$$

$$\mathrm{BM}+\mathrm{N} \xleftrightarrow{K_\mathrm{MN}} (\mathrm{BM})\mathrm{N}, \quad K_\mathrm{MN}=\frac{[\mathrm{BM}][\mathrm{N}]}{[(\mathrm{BM})\mathrm{N}]} \tag{18}$$

$$\mathrm{BN}+\mathrm{M} \xleftrightarrow{K_\mathrm{NM}} (\mathrm{BN})\mathrm{M}, \quad K_\mathrm{NM}=\frac{[\mathrm{BN}][\mathrm{M}]}{[(\mathrm{BN})\mathrm{M}]} \tag{19}$$

$$[\mathrm{B_t}]=[\mathrm{B}]+[\mathrm{BM}]+[\mathrm{BN}]+[(\mathrm{BM})\mathrm{N}]+[(\mathrm{BN})\mathrm{M}] \tag{20}$$

$$\frac{\mathrm{d[BM]}}{\mathrm{d}t}=\frac{\mathrm{d[BN]}}{\mathrm{d}t}=\frac{\mathrm{d[(BM)N]}}{\mathrm{d}t}=\frac{\mathrm{d[(BN)M]}}{\mathrm{d}t}=0 \quad (21)$$

Combining these equations results in:

$$[\mathrm{BM}]+[\mathrm{BNM}]=\frac{([\mathrm{B_t}]/K_\mathrm{M})[\mathrm{M}]+([\mathrm{B_t}]/K_\mathrm{N})(1/K_\mathrm{NM})[\mathrm{M}][\mathrm{N}]}{1+(1/K_\mathrm{M})[\mathrm{M}]+(1/K_\mathrm{N})[\mathrm{N}]+((1/K_\mathrm{M})(1/K_\mathrm{MN})+(1/K_\mathrm{N})(1/K_\mathrm{NM}))\,[\mathrm{M}][\mathrm{N}]} \quad (22)$$

Eq. (22) can be rearranged in Langmuirian form as:

$$q[\mathrm{M}]=\frac{q_\mathrm{max}(b_\mathrm{M}+b_\mathrm{N}b_\mathrm{NM}C_\mathrm{e}[\mathrm{N}])(C_\mathrm{e}[\mathrm{M}])}{1+b_\mathrm{M}C_\mathrm{e}[\mathrm{M}]+b_\mathrm{N}C_\mathrm{e}[\mathrm{N}]+(b_\mathrm{M}b_\mathrm{MN}+b_\mathrm{N}b_\mathrm{NM})(C_\mathrm{e}[\mathrm{M}])(C_\mathrm{e}[\mathrm{N}])} \quad (23)$$

and the total uptake for the two metals as:

$$q[\mathrm{M+N}]=q[\mathrm{M}]+q[\mathrm{N}]=\frac{q_\mathrm{max}(b_\mathrm{M}C_\mathrm{e}[\mathrm{M}]+b_\mathrm{N}C_\mathrm{e}[\mathrm{N}]+(b_\mathrm{M}b_\mathrm{MN}+b_\mathrm{N}b_\mathrm{NM})(C_\mathrm{e}[\mathrm{M}])(C_\mathrm{e}[\mathrm{N}]))}{1+b_\mathrm{M}C_\mathrm{e}[\mathrm{M}]+b_\mathrm{N}C_\mathrm{e}[\mathrm{N}]+(b_\mathrm{M}b_\mathrm{MN}+b_\mathrm{N}b_\mathrm{NM})(C_\mathrm{e}[\mathrm{M}])(C_\mathrm{e}[\mathrm{N}])} \quad (24)$$

where K_MN is the equilibrium constant for metal 'N' with the binding site that is already occupied with metal 'M', K_NM the equilibrium constant for the bonding of metal 'M' with the binding site already occupied with metal 'N', b_MN and b_NM the affinity constants for metal 'N' with the binding site already occupied with metal 'M', and for metal 'M' with the binding site already occupied with metal 'N', respectively. Other parameters have the same meanings as those mentioned in Model B.

2.4. Model verification

Parameters employed to verify the model prediction were: (i) the coefficient of determination (R^2), (ii) average of %Error, and (iii) relative standard distribution (RSD) of %Error. These are calculated from:

$$R^2=1-\frac{\sum_{i=1}^{N}(q_i-q_{\mathrm{c},i})^2}{\sum_{i=1}^{N}(q_i-\bar{q})^2} \quad (25.1)$$

$$E_i=100\times\left|\frac{q_i-q_{\mathrm{c},i}}{q_i}\right| \quad (25.2)$$

$$\text{average of \%Error (\%)}=\frac{100\times\sum_{i=1}^{N}E_i}{N} \quad (25.3)$$

$$\text{RSD of \%Error (\%)}=100\times\sqrt{\frac{\sum_{i=1}^{N}(E_i-\bar{E})^2}{N\bar{E}^2}} \quad (25.4)$$

where q_i is the actual sorption capacity at point i, $q_{\mathrm{c},i}$ the predicted sorption capacity at the same point as q_i, $\bar{q}$ the average of actual sorption capacity from all experimental data, E_i the error at point i, $\bar{E}$ the average of error from all experimental data, and N is the number of experimental data.

3. Experimental

Caulerpa lentillifera is the residue green macro alga from local shrimp farms in Chachoengsao province, Thailand. In this work, this particular algal species was dried and used as the biosorbent for the sorption of $\mathrm{Cu^{2+}}$, $\mathrm{Cd^{2+}}$, and $\mathrm{Pb^{2+}}$ ions from binary component systems ($\mathrm{Pb^{2+}}$–$\mathrm{Cu^{2+}}$, $\mathrm{Pb^{2+}}$–$\mathrm{Cd^{2+}}$, and $\mathrm{Cu^{2+}}$–$\mathrm{Cd^{2+}}$) in batch experiments. The experiment was performed by mixing 0.5 g dried biomass in 30 mL of the synthetic mixture of primary and secondary heavy metal ions solution with initial concentrations in the range of 0–3 mol $\mathrm{m^{-3}}$. Analytical grade heavy metal reagents (UNIVAR) in nitrate form were used in all cases. For most experiments, pH of the synthetic wastewater was controlled at 5 ± 0.2 using 0.1N nitric acid ($\mathrm{HNO_3}$) and 0.1N sodium hydroxide (NaOH) solutions. The mixtures were then mixed in a rotary shaker at a constant rate of 150 rpm for 30 min to ensure the equilibrium state of sorption [11]. The temperature of the solution was controlled at 20 ± 1 °C. Suspended solids were separated out with GF/C paper. Heavy metal ion concentrations in the filtrate were then measured by ICP-AES with argon plasma. Experiments were repeated at least three times to evaluate the accuracy of the results.

The equilibrium sorption capacity can be calculated from Eq. (26):

$$q_\mathrm{e}=\frac{V(C_\mathrm{i}-C_\mathrm{e})}{m} \quad (26)$$

q_e represents the amount of metal uptaken per unit mass of the biomass at equilibrium (mol $\mathrm{kg^{-1}}$), V the volume of the solution ($\mathrm{m^3}$), m the dry mass of the alga (kg), and C_i and C_e are the initial and equilibrium concentrations (mol $\mathrm{m^{-3}}$), respectively.

The pH of the wastewater was controlled at 1.5, 3, 4, and 5 to investigate the effect of pH on the sorption of a single component heavy metal system, i.e. $\mathrm{Cu^{2+}}$, $\mathrm{Cd^{2+}}$, and $\mathrm{Pb^{2+}}$ solutions.

4. Results and discussion

4.1. Model selection and interpretation

The parameter assessment for each binary system was obtained from the non-linear estimation using STATISTICA version 6 and the results are summarized in Table 1. One obvious finding from this parameter estimation was that the parameter b' of Model B always had negative value which potentially indicated that the two heavy metal ions could not simultaneously bonded on the same binding site. Hence, the assumption of uncompetitive sorption became insignificant and was thereafter discarded from further consideration.

A high R^2, low average of percentage error (average of %Error), and low relative standard deviation of percentage error (RSD of %Error) as shown in Table 1 for Model C suggested that the predictions from this model conformed well to experimental data. Model A also performed well in this regards but a lower R^2 than that of Model C meant that the accuracy of the predictions

Table 1
Parameters of binary sorption isotherms

Metal system[a]	Model	$q_\mathrm{m} \pm \sigma_{q_\mathrm{m}}$ (mol kg^{-1})	$b_\mathrm{M} \pm \sigma_{b_\mathrm{M}}$ (m^3 mol^{-1})	$b_\mathrm{N} \pm \sigma_{b_\mathrm{N}}$ (m^3 mol^{-1})	$b' \pm \sigma_{b'}$ (m^3 mol^{-1})	$b_\mathrm{MN} \pm \sigma_{b_\mathrm{MN}}$ (m^3 mol^{-1})	$b_\mathrm{NM} \pm \sigma_{b_\mathrm{NM}}$ (m^3 mol^{-1})	Average %Error (%)	RSD of %Error (%)	R^2
Pb^{2+}–Cu^{2+}	A	0.07 ± 0.004	44 ± 8.6	8 ± 1.3	–	–	–	22.8	21.7	0.80
	B	0.09 ± 0.01	25 ± 4	4.8 ± 0.7	−54 ± 6	–	–	–	–	–
	C	0.09 ± 0.01	25 ± 4	4.7 ± 0.5	–	1.3 ± 0.2	5.3 ± 1.3	16.5	21	0.89
Pb^{2+}–Cd^{2+}	A	0.09 ± 0.01	21 ± 6.2	1 ± 0.2	–	–	–	30.9	37.2	0.74
	B	0.10 ± 0.01	24 ± 4.9	1.2 ± 0.1	−51 ± 8	–	–	–	–	–
	C	0.11 ± 0.01	20 ± 4.5	0.9 ± 0.17	–	0.6 ± 0.25	11 ± 1.2	25.1	23.6	0.87
Cu^{2+}–Cd^{2+}	A	0.06 ± 0.01	10 ± 2.4	2.1 ± 0.4	–	–	–	37.4	57.5	0.68
	B	0.09 ± 0.01	5 ± 1.4	1.2 ± 0.3	−7.8 ± 1.4	–	–	–	–	–
	C	0.10 ± 0.01	4 ± 1.5	1 ± 0.3	–	1.4 ± 0.51	5.5 ± 0.49	31.7	46.6	0.78

[a] Primary metal (M)–secondary metal (N).

of Model C was superior. Hence, in the subsequent analysis of the three-dimensional sorption isotherm surfaces, only Model C was employed.

Figs. 1–3 illustrate the three-dimensional sorption isotherm surfaces of the binary mixture. It was noticed that the presence of secondary metal ion in the system, most of the time, resulted in a decrease in the sorption capacity of the primary metal. This antagonistic competitive effect was both observed for the sorption capacity of each single metal ion and for the total sorption capacity, particularly at high concentration range. This indicated that there was a competitive sorption between the two metals on the surface of this algal biomass. For example, the sorption capacity of Pb^{2+} was about 0.081 mol kg^{-1} in a single component system (at the equilibrium concentration of 0.35 mol-Pb^{2+} m^{-3}), but this was reduced to approx. 0.071 mol-Pb^{2+} kg^{-1} (12% decrease) with the presence of Cu^{2+} (at 0.1 mol-Cu^{2+} m^{-3} equilibrium concentration) And vice versa, the sorption capacity of Cu^{2+} was about 0.056 mol-Cu^{2+} kg^{-1} (at 0.35 mol-Cu^{2+} m^{-3} equilibrium concentration), and this was reduced to 0.028 mol-Cu^{2+} kg^{-1} (49% decrease) with the presence of Pb^{2+} at 0.1 mol m^{-3} equilibrium concentration.

Table 2 summarizes the percentage reduction in the sorption capacities of the primary metal ion when there was a secondary metal ion presented in the system. It was interesting to note that Pb^{2+} as secondary ions more effectively decreased the sorption capacity of Cu^{2+} than the effect of Cu^{2+} to Pb^{2+}. Similar effect was also observed for the mixture between Pb^{2+} and Cd^{2+}. This potentially implied that the sorption of Pb^{2+} by *C. lentillifera* biomass was more favorable than the sorptions of the other two metal ions. For the pair of Cu^{2+} and Cd^{2+}, Table 2 illustrates that the uptake of Cd^{2+} decreased more significantly with the presence of Cu^{2+} than the uptake of Cu^{2+} with the presence of Cd^{2+}. This indicated that Cu^{2+} was more preferable to be uptaken than Cd^{2+}.

Table 2
Percentage reduction in sorption capacity of primary metal ion (at C_e = 0.35 mol m^{-3}) with the presence of secondary metal ion (at C_e = 0.1 mol m^{-3})

2nd ion	1st ion		
	Cu^{2+}	Cd^{2+}	Pb^{2+}
Cu^{2+}	–	1.3 ± 1.2	12 ± 1.9
Cd^{2+}	6 ± 5.7	–	5.2 ± 2.3
Pb^{2+}	49 ± 7.6	26 ± 20	–

Equilibrium concentrations (C_e) of primary and secondary metal ions were arbitrarily selected to illustrate the antagonistic effect.

Figs. 1(c), 2(c), and 3(c) reveal that, at a low range of equilibrium concentration for all mixtures, the total sorption increased with the presence of the secondary metal ion. This was due to large availability of binding sites and therefore the competitive effect appeared to be insignificant. As more metals were presented in the system, the availability of binding sites when compared with the metal became limited, and hence, the competition among the metal ions was more obvious.

Table 1 illustrates that the total sorption capacities, q_m, were approx. 0.09, 0.11, 0.10 mol kg^{-1} for Pb^{2+}–Cu^{2+}, Pb^{2+}–Cd^{2+}, and Cu^{2+}–Cd^{2+} binary mixtures, respectively. This indicated that there was a limitation in the maximum sorption capacities at about 0.1 mol kg^{-1}. In addition, it was observed that b_M and b_N were always higher than b_NM and b_MN, For instance, $b_{\mathrm{Pb}^{2+}}$ (24.56 m^3 mol^{-1}) in the Pb^{2+}–Cu^{2+} system was higher than $b_{\mathrm{Cu}^{2+}}$–Pb^{2+} (5.30 m^3 mol^{-1}) and $b_{\mathrm{Cu}^{2+}}$ (4.70 m^3 mol^{-1}) higher than $b_{\mathrm{Pb}^{2+}}$–Cu^{2+} (1.30 m^3 mol^{-1}). Based on the model assumptions, this finding could lead to a potential supposition that metal ions showed higher sorption affinity in bonding with the free binding site than with the binding sites occupied with another metal ion. In other words, the metal may not be easily bonded with the occupied binding sites.

4.2. Partial competitive model in describing the effect of pH on metal sorption

The sorption isotherms of each metal ion in single component system at pH 1.5, 3, 4, 5 could be modeled using Langmuir isotherm as expressed in Eq. (27):

$$q_\mathrm{e} = \frac{q_\mathrm{max} b C_\mathrm{e}}{1 + b C_\mathrm{e}} \tag{27}$$

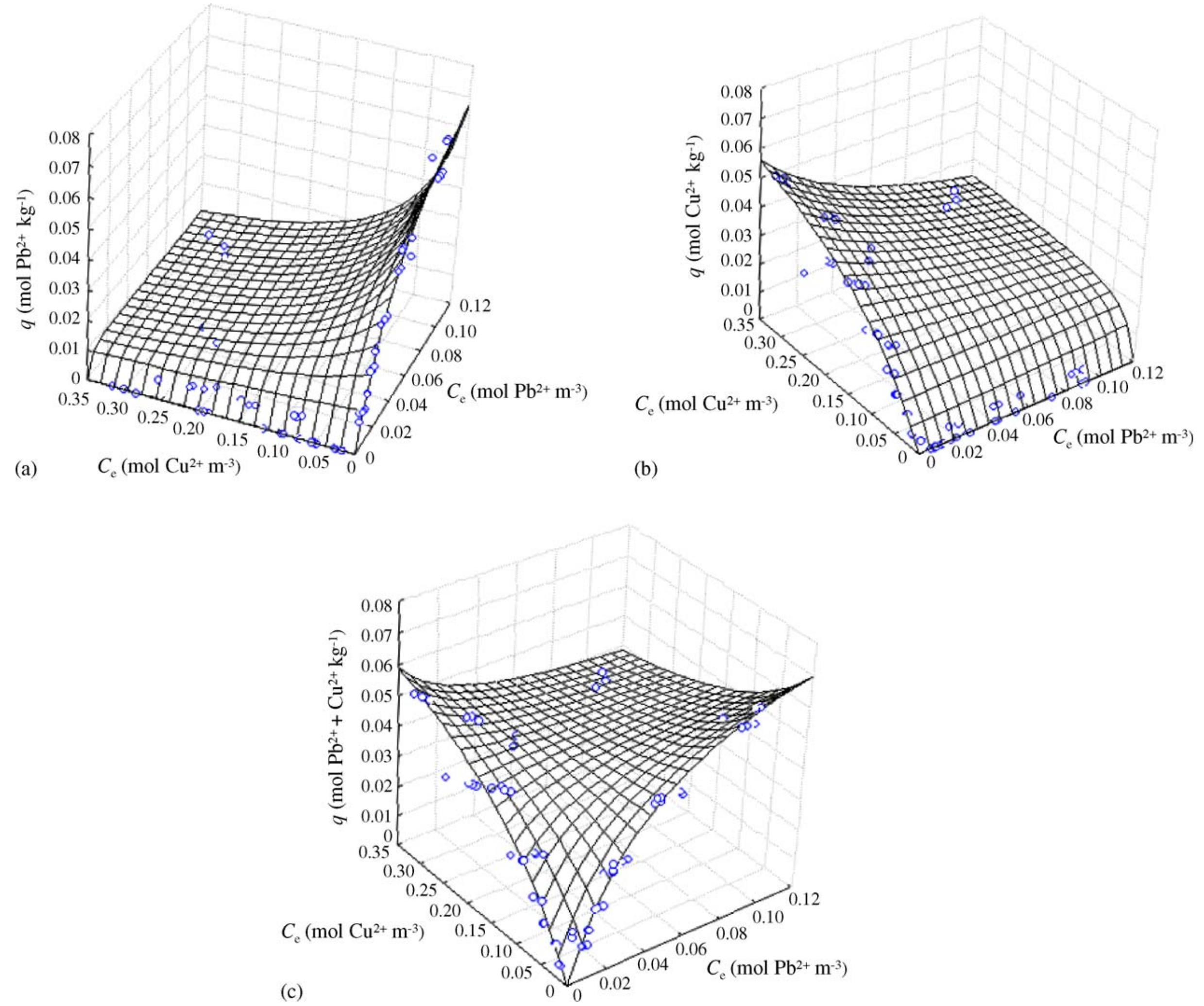

Fig. 1. Three-dimensional sorption isotherm surface for Pb^{2+}–Cu^{2+} system. (a) Sorption capacity of Pb^{2+}; (b) sorption capacity of Cu^{2+}; (c) total sorption capacities ($Pb^{2+} + Cu^{2+}$).

where q_e and C_e have the same meanings as those in Eq. (26), q_{max} the maximum amount of metal ion uptaken per unit mass of the biomass (mol kg^{-1}), and b is the Langmuir affinity constant (m^3 mol^{-1}). A non-linear regression of experimental results for all three heavy metals was applied, and the resulting Langmuir parameters are summarized in Table 3. It could be seen from Table 3 that pH played an important role in the sorption of heavy metal ions. The fundamental explanation was that pH was inversely related to the quantity of positive charged hydrogen ion (proton). Therefore, a solution with lower pH would accommodate a higher concentration of hydrogen ion than that with higher pH. This proton could compete with the heavy metal ion for the sorption on the available binding sites on the surface of the alga, and hence, resulted in a decrease in sorption capacity. This phenomenon could potentially be considered as a partial competitive effect between the metal ion and the proton. It could be that the metal ion could be attached on the free binding more easily than proton, and that the metal ion could be attached on the binding site pre-occupied by proton at a rate higher than proton being attached on the binding site pre-occupied by metal ion, and vice versa.

Table 3
Isotherm parameters for metal ion sorption by dried *C. lentillifera*

Metal ion	pH	Langmuir parameters, q_{max} (mol kg^{-1}), b (m^3 mol^{-1})	Accuracy (R^2)
Pb^{2+}	5	0.14, 13.4	0.98
	4	0.12, 5.8	0.97
	3	0.08, 2.6	0.97
	1.5	0.07, 0.8	0.91
Cu^{2+}	5	0.13, 2.7	0.98
	4	0.1, 1.9	0.96
	3	0.07, 1.1	0.97
	1.5	0.05, 0.5	0.90
Cd^{2+}	5	0.042, 8.0	0.98
	4	0.035, 2.6	0.95
	3	0.022, 1.6	0.99
	1.5	0.016, 1.7	0.96

4.2.1. Modified partial competitive model

Proton could be considered as another cation which interfered the sorption. The reaction of proton on the binding site could

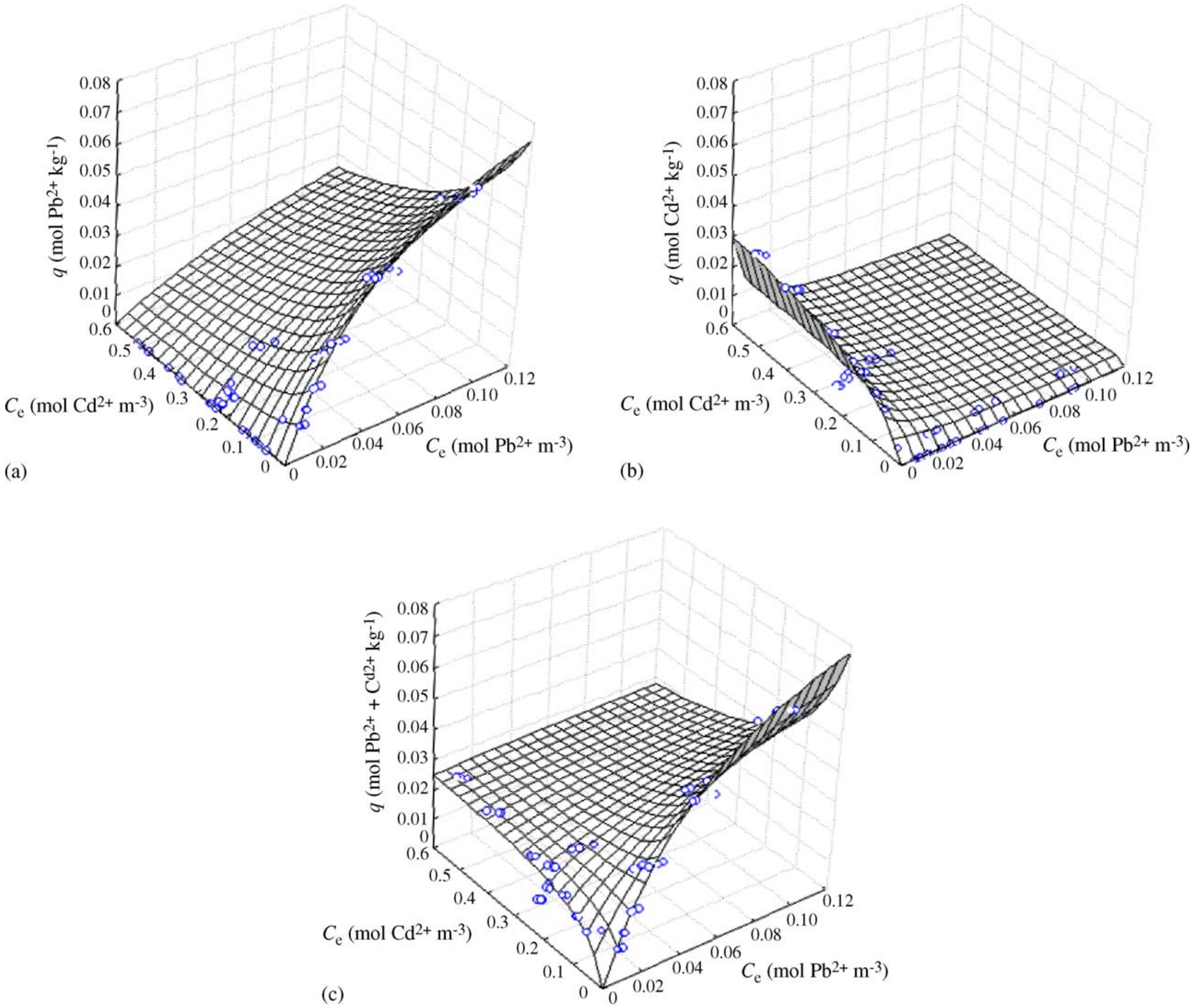

Fig. 2. Three-dimensional sorption isotherm surface for Pb^{2+}–Cd^{2+} system. (a) Sorption capacity of Pb^{2+}; (b) sorption capacity of Cd^{2+}; (c) total sorption capacity ($Pb^{2+} + Cd^{2+}$).

be demonstrated in a mathematical form as expressed in Eqs. (16)–(21) where N was replaced with H^+ (proton) and K_N was replaced with K_a (the acid dissociation equilibrium constant of binding site). Thus, Eq. (23) can be rearranged to

$$q_e = \frac{(q_{\max,M} b_M 10^{pH} + q_{\max,HM} b_{HM} 10^{pK_a})C_e}{(1 + b_M C_e)10^{pH} + (1 + b_{HM} C_e)10^{pK_a} + b_M b_{MH} C_e} \qquad (28)$$

where $pK_a = -\log K_a$ and $pH = -\log[H^+]$, b_M takes the same meaning as that in Model C, $q_{\max,M}$ represents the maximum sorption capacity of metal ion on the free binding site, $q_{\max,HM}$ and b_{HM} the maximum sorption capacity and affinity constant of the metal ion on the binding site occupied by proton, respectively, and b_{MH} is the sorption affinity of proton on the binding site already occupied by metal ion.

Eq. (28) demonstrates that the equilibrium sorption capacity was a function of equilibrium concentration and equilibrium pH. This model was used to fit experimental data using the non-linear analysis where the model parameters are displayed in Table 4, and the results are shown in Fig. 4.

The high R^2 of more than 0.95 illustrated that the model prediction agreed reasonably well with experimental data. This indicated that the partial competitive model could be applied for the prediction of pH effect on the sorption using *C. lentillifera*. The results from Table 4 indicate that pK_a of Cd^{2+} was about 6 while that of Cu^{2+} and Pb^{2+} were about 4. This could imply a different main sorption site for Cd^{2+} from those for Cu^{2+} and Pb^{2+}. In addition, the maximum sorption capacity and sorption affinity of each metal on the free binding site ($q_{\max,M}$, b_M) was always higher than those of metal on the same binding site pre-occupied by proton ($q_{\max,HM}$, b_{HM}). This suggested that the sorption of metal mainly occurred on the free binding site rather than on the binding site already occupied by proton. However, the later binding site could also be responsible for the sorption of these metals but at different capacity and affinity. It could be that the sorption of metal to this biomass was by physical means such as electrostatic and van der waal's force, and therefore the sorption could occur on both free and proton-occupied binding sites. In the same way, the sorption affinity of proton attached on the binding site pre-occupied by metal ion (b_{MH}) was always

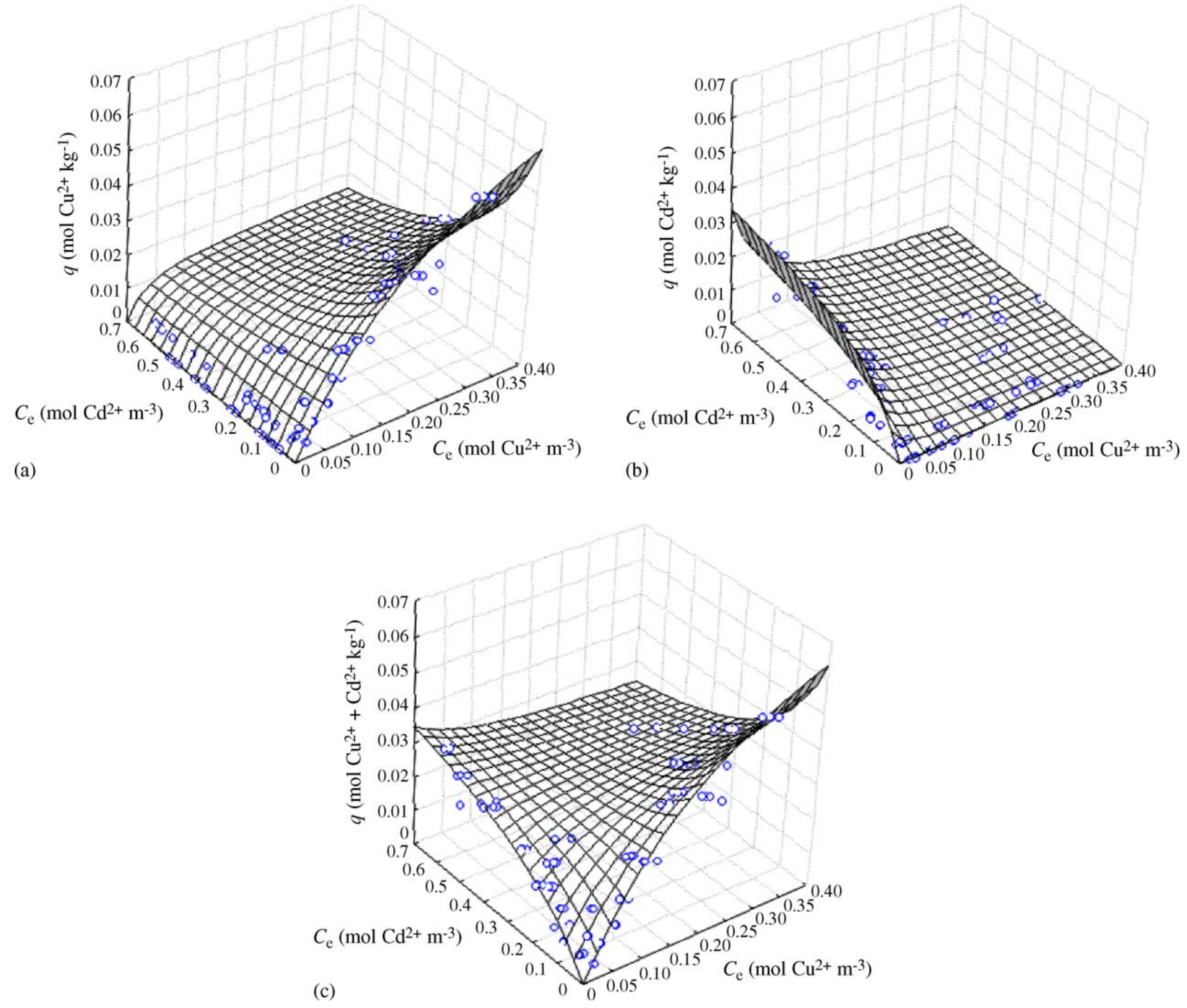

Fig. 3. Three-dimensional sorption isotherm surface for Cu^{2+}–Cd^{2+} system. (a) Sorption capacity of Cu^{2+}; (b) sorption capacity of Cd^{2+}; (c) total sorption capacity ($Cu^{2+} + Cd^{2+}$).

lower than that of metal on both free and proton-occupied binding sites (b_{M}, b_{HM}). This suggested that proton might not be a favorably positive charged species for the binding site in the alga when compared with the metal ion species.

4.2.2. Prediction of q_{max} and b

It can be observed from Table 3 that the maximum sorption capacity (q_{max}) and sorption affinity (b) changed with pH. Hence, the relationship between q_{max} and b, and pH must be determined. This could be achieved using the following technique.

For single metal systems, Langmuir equation can be expressed as in Eq. (27) where the maximum sorption capacity q_{max} could be estimated from the limit theorem:

$$q_{\mathrm{max}} = \lim_{C_{\mathrm{e}} \to \infty} q_{\mathrm{e}} \tag{29}$$

Similarly, the sorption affinity (b) could be determined by

$$\lim_{C_{\mathrm{e}} \to 0} \left(\frac{q_{\mathrm{e}}}{C_{\mathrm{e}}} \right) = b q_{\mathrm{max}} \tag{30}$$

Table 4
Parameters of the pH prediction model

Metal	$q_{\mathrm{max,M}} \pm \sigma_{q_{\mathrm{max,M}}}$ (mol kg^{-1})	$q_{\mathrm{max,HM}} \pm \sigma_{q_{\mathrm{max,HM}}}$ (mol kg^{-1})	$b_{\mathrm{M}} \pm \sigma_{b_{\mathrm{M}}}$ (m^3 mol^{-1})	$b_{\mathrm{HM}} \pm \sigma_{b_{\mathrm{HM}}}$ (m^3 mol^{-1})	$b_{\mathrm{MH}} \pm \sigma_{b_{\mathrm{MH}}}$ (m^3 mol^{-1})	p$K_{\mathrm{a}} \pm \sigma_{\mathrm{p}K_{\mathrm{a}}}$ (−)	Average %Error (%)	RSD of %Error (%)	R^2
Pb^{2+}	0.13 ± 0.01	0.05 ± 0.00	19 ± 1.2	1.2 ± 0.20	0.09 ± 0.00	4.4 ± 0.5	15.5	22.5	0.98
Cu^{2+}	0.13 ± 0.02	0.04 ± 0.00	2.9 ± 0.5	0.7 ± 0.3	0.10 ± 0.01	4.1 ± 0.7	18.0	18.1	0.96
Cd^{2+}	0.044 ± 0.004	0.016 ± 0.003	80 ± 9.7	1.3 ± 0.4	0.10 ± 0.02	6 ± 0.8	17.7	15.5	0.96

M: metal ion, H: hydrogen ion.

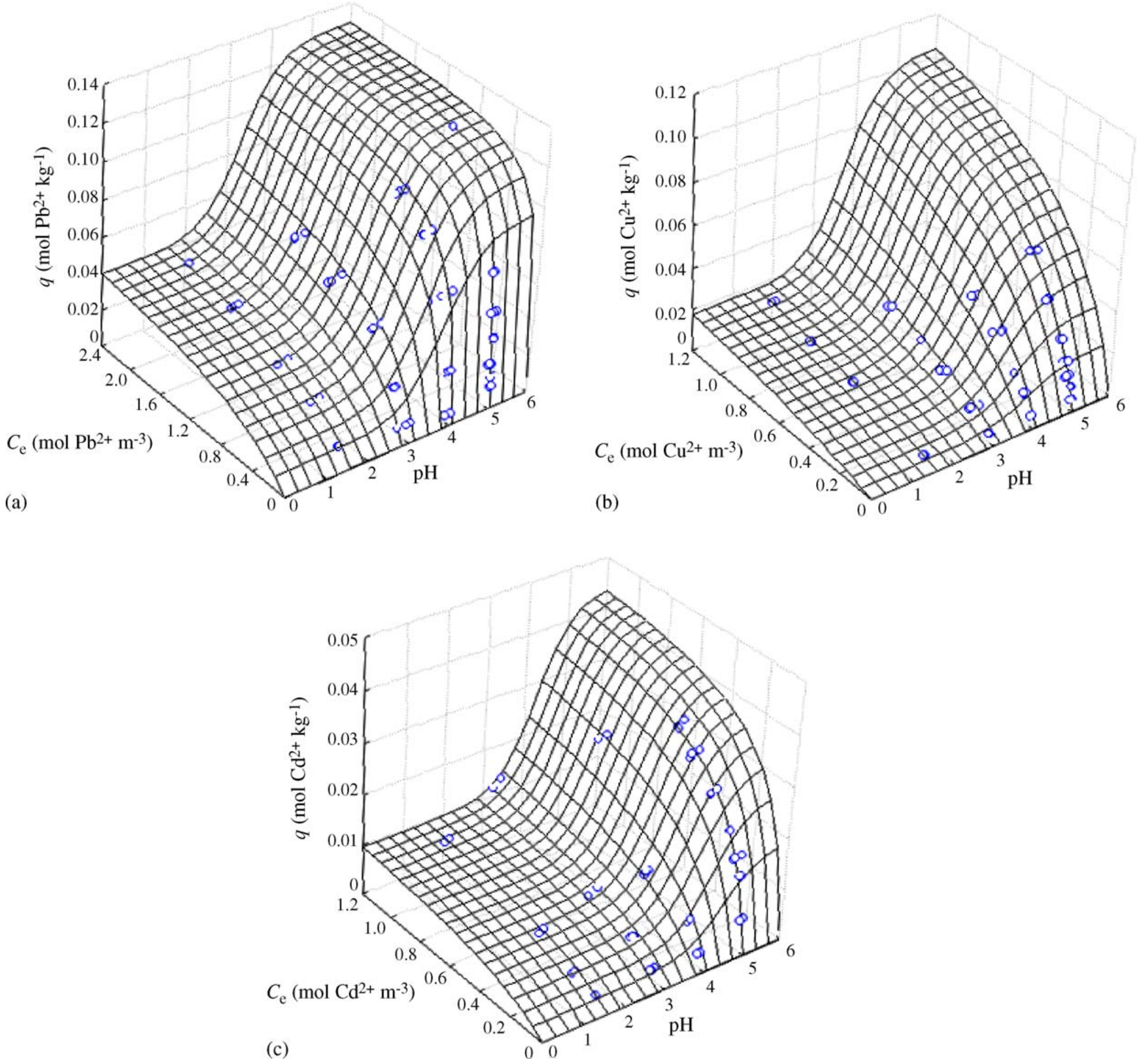

Fig. 4. Effect of pH on sorption capacity on *C. lentillifera*. (a) Pb^{2+}; (b) Cu^{2+}; (c) Cd^{2+}.

Thus,

$$b = \frac{\lim\limits_{C_e \to 0}(q_e/C_e)}{q_{max}} = \frac{\lim\limits_{C_e \to 0}(q_e/C_e)}{\lim\limits_{C_e \to \infty} q_e} \tag{31}$$

This concept could be applied to the partial competitive model to predict the effect of pH on the sorption (Eq. (28)) and the resulting expressions were obtained:

$$q_{max}\,(\mathrm{pH}) = \lim_{C_e \to \infty} q = \frac{(q_{max,M} b_M 10^{\mathrm{pH}} + q_{max,HM} b_{HM} 10^{\mathrm{p}K_a})}{b_M 10^{\mathrm{pH}} + b_{HM} 10^{\mathrm{p}K_a} + b_M b_{MH}} \tag{32}$$

$$b\,(\mathrm{pH}) = \frac{\lim\limits_{C_e \to 0}[q/C_e]}{q_{max}(\mathrm{pH})} = \frac{b_M 10^{\mathrm{pH}} + b_{HM} 10^{\mathrm{p}K_a} + b_M b_{MH}}{10^{\mathrm{pH}} + 10^{\mathrm{p}K_a}} \tag{33}$$

The results from applying Eqs. (32) and (33) in estimating the effect of pH are demonstrated in Fig. 5 where agreement between experimental data and model prediction was clearly observed. The maximum sorption capacity and sorption affinity increased with increasing pH following the S-shape curve. This meant that, at low pH, the amount of protonated binding site was higher than the unprotonated, and therefore resulting in low metal sorption character. Increasing pH resulted in an increase in the quantity of unprotonated binding sites, and hence, a higher metal sorption was observed. As the sorption reached its equilibrium, a further increase in pH no longer influenced the sorption characteristics and the sorption capacity was leveled off.

4.3. Potential sorption characteristics for metal sorption

Our previous work on the examination of the alga with FTIR revealed that possible functional groups involved in metal biosorption using *C. lentillifera* biomass were carboxyl,

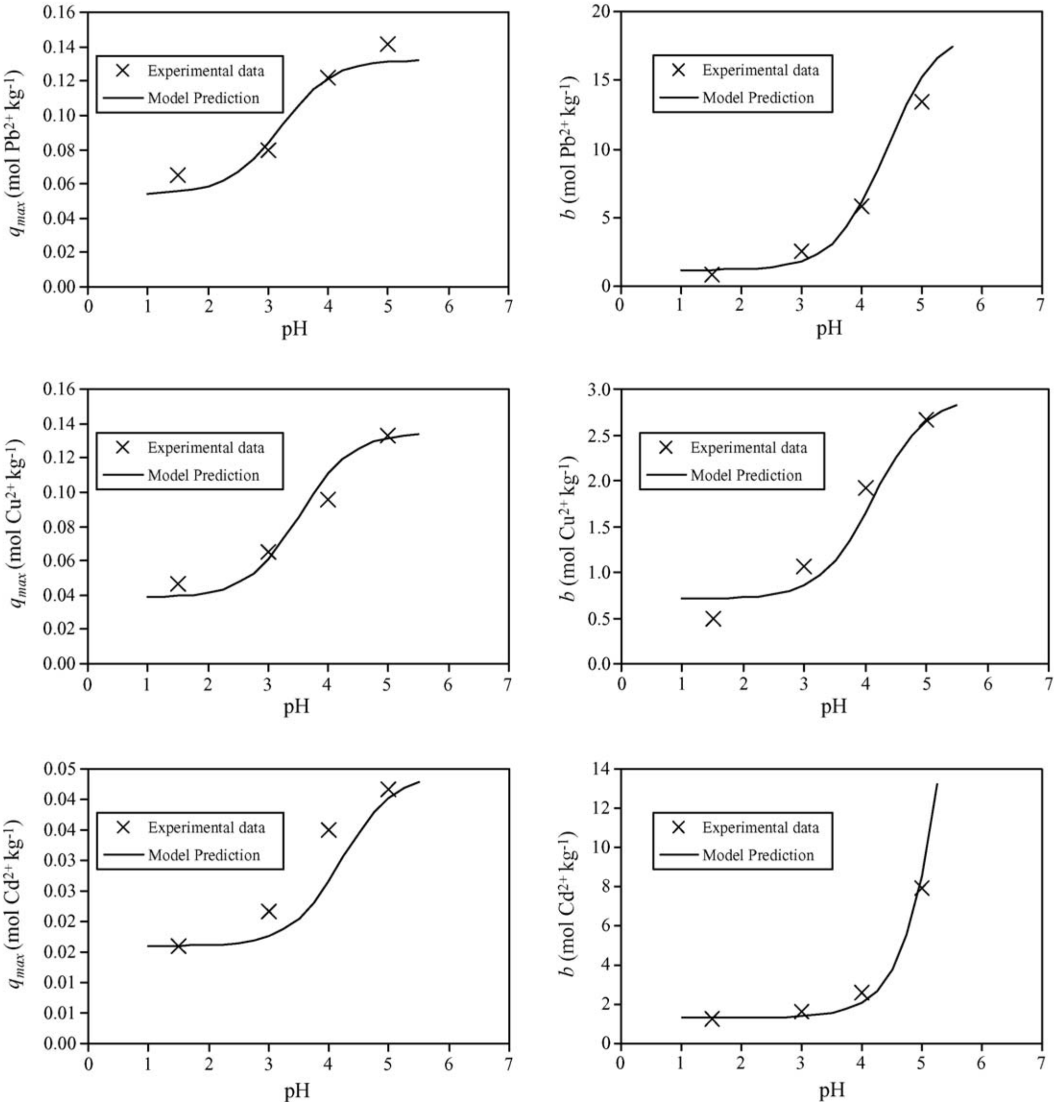

Fig. 5. Relationships between Langmuir parameters ($q_{\max}$ and b) and pH.

hydroxyl, sulfonate, amine, and amide [12]. Details of these functional groups are displayed in Table 5. This finding suggested that the sulfonate group in the algal biomass with pK_a of about 1.3 could be responsible for the sorption of Cu^{2+}, Cd^{2+}, and Pb^{2+} (as some experiments were carried out at pH as low as 1.5). In addition, the hard and soft acid base (HSAB) theory of Pearson stated that hard functional groups formed strong bonds with hard cations, soft functional groups formed strong bond with soft cations, whereas intermediate types could form bonds with any type of metals. As Cu^{2+} and Pb^{2+} were classified as intermediate type, whilst Cd^{2+} was soft [13], Table 5 suggests that Cu^{2+} and Pb^{2+} could form bond with all functional groups listed in this table while Cd^{2+} could mainly form bond with amine and amide groups and had difficulty in forming bonds with carboxyl, hydroxyl, and sulfonate groups. Due to the limitation on the availability of binding sites for Cd^{2+}, this theoretical interpretation might explain the finding that the sorption capacity of Cd^{2+} was always lower than those of Cu^{2+}

Table 5
Detail of functional groups[a] involved with metal biosorption by *Caulerpa* sp.

Functional group	Structural formula	pK_a	HSAB[b] classification
Carboxyl	$-\overset{\overset{O}{\|}}{C}-OH$	1.7–4.7	Hard
Hydroxyl	–OH	9.5–13	Hard
Sulfonate	$-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}=OH$	1.3	Hard
Amine	$-NH_2$	8–11	Intermediate
Amide	$-\overset{\overset{O}{\|}}{C}-NH_2$	–	Intermediate

[a] Volesky [1].
[b] Hard and soft acid base theory of Pearson.

and Pb^{2+} under the same operating conditions. In fact, Table 4 suggests that the actual binding site for Cd^{2+} might be amine as, among all the functional groups presented in the alga, pK_a of amine ($pK_a = 8–11$) was nearest to the pK_a of the functional group of Cd^{2+} ($pK_a = 6$).

5. Conclusions

The studying of binary component biosorption model using three concepts consist of competitive, uncompetitive, and partial competitive sorption isotherm models suggested that the partial competitive isotherm model could accurately predict the sorption performance. Antagonistic competitive effect was found to occur for the sorption in binary component systems where the sorption capacity of primary metal ion decreased with the presence of the secondary metal ions. The maximum sorption capacity of the pooled binding site of the two metal ions was about $0.1\,\mathrm{mol\,kg^{-1}}$ for the binary component system. It was also illustrated that the effect of pH on metal sorption on this biomass could well be explained using a similar type of isotherm model as that for the sorption of binary metal component systems. The experimental results matched with the HSAB theory of Pearson where the maximum sorption capacity of Cd was always found to be lower than those of Cu and Pb. The success in developing a mathematical model for such sorption systems will be beneficial for a further design and scale up of the system.

Acknowledgements

The authors wish to acknowledge the Thailand Research Fund (Royal Golden Jubilee Ph.D. Scholarship) for their financial support and Banchong farm, Chachoengsao Province, Thailand, for the supply of fresh algal biomass.

References

[1] B. Volesky, Sorption and Biosorption, BV-Sorbex Inc., St. Lambert, Quebec, 2004.

[2] F. Pagnanelli, M. Trifonia, F. Beolchini, A. Espositoc, L. Toroa, F. Vegliò, Equilibrium biosorption studies in single and multi-metal systems, Process Biochem. 37 (2001) 115–124.

[3] S. Al-Asheh, F. Banat, R. Al-Omari, Z. Duvnjak, Predictions of binary sorption isotherms for the sorption of heavy metals by pine bark using single isotherm data, Chemosphere 41 (2000) 659–665.

[4] A. Hammaini, A. Ballester, M.L. Blázquez, F. González, J. Muñoz, Effect of the presence of lead on the biosorption of copper, cadmium and zinc by activated sludge, Hydrometallurgy 67 (2002) 109–116.

[5] W. Ma, J.M. Tobin, Development of multimetal binding model and application to binary metal biosorption onto peat biomass, Water Res. 37 (2003) 3967–3977.

[6] H.S. Lee, J.H. Suh, Interference of aluminum in heavy metal biosorption by a seaweed biosorbent, Korean J. Chem. Eng. 18 (5) (2001) 692–697.

[7] M. Alimohamadi, G. Abolhamd, A. Keshtkar, Pb(II) and Cu(II) biosorption on *Rhizopus arrhizus* modeling mono- and multicomponent systems modeling mono- and multicomponent systems, Miner. Eng. 18 (2005) 1325–1330.

[8] H. Xu, Y. Liu, J.H. Tay, Effect of pH on nickel biosorption by aerobic granular sludge, Bioresource Technol. 97 (3) (2006) 359–363.

[9] N. Bektas, B.A. Agim, S. Kara, Kinetic and equilibrium studies in removing lead ions from aqueous solutions by natural sepiolite, J. Hazard. Mater. B112 (2004) 115–122.

[10] F. Pagnanelli, A. Esposito, L. Toro, F. Veglio, Metal speciation and pH effect on Pb^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} biosorption onto *Sphaerotilus natans*: Langmuir-type empirical model, Water Res. 37 (2003) 627–633.

[11] R. Apiratikul, T.F. Marhaba, S. Wattanachira, P. Pavasant, Biosorption of binary mixtures of heavy metals mixture solution by green macro alga, *Caulerpa lentillifera*, Songklanakarin J. Sci. Technol. 26 (Suppl. 1) (2004) 199–207.

[12] P. Pavasant, R. Apiratikul, V. Sungkhum, P. Suthiparinyanont, S. Wattanachira, T.F. Marhaba, Biosorption of Cu^{2+}, Cd^{2+}, Pb^{2+}, and Zn^{2+} using dried marine green macroalga *Caulerpa lentillifera*, Bioresource Technol., in press.

[13] R.G. Pearson, Hard and soft acids and bases, J. Am. Chem. Soc. 85 (1963) 3533–3539.