

A Model for pH Dependent Equilibrium of Heavy Metal Biosorption

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Abstract—Biosorption of heavy metals can be an effective process for the removal and recovery of heavy metal ions from aqueous solutions. The biomass of marine macro algae has been reported to have high uptake capacities for a number of heavy metal ions and the uptake capacities are strongly influenced by the value of the solution pH. In this paper, a modified Langmuir model was proposed for describing the pH dependent biosorption equilibrium and validated with isotherm data obtained from batch experiments and from the literature. The model assumes that the functional groups for heavy metal interactions are weakly acidic and the uptake capacities of the biomass are affected through the association and dissociation equilibrium between two apparent ionic forms. The model equations fitted the experimental data well, which supports the biosorption mechanism proposed.

Key words: Biosorption of Heavy Metals, Langmuir Equation, *Durvillaea potatorum*, Wastewater Treatment

INTRODUCTION

Environmental pollution from industrial wastewater streams that contain heavy metal ions is an important issue in many parts of the world. Therefore, the removal and recovery of heavy metals from wastewater streams is important in the protection of the environment and human health. A number of technologies have been used to remove heavy metals from waste water streams, such as precipitation, evaporation, solvent extraction and membrane processes [Volesky, 1990]. However, these technologies are most suitable in situations where the concentrations of the heavy metal ions are high. They may be either ineffective or expensive when heavy metals are present in the wastewater at low concentrations, or when very low concentrations of heavy metals in the treated water are required [Kucuyak and Volesky, 1988].

Alternative technologies of treating diluted wastewater streams have been studied in recent decades [Cowan et al., 1991; Fourest and Volesky, 1996; Groffman et al., 1992; Higgins and Satter, 1984; Kaewsarn et al., 1998; Mattuschka and Straube, 1993; Wilms et al., 1988]. Biosorption is one such technology in which an increased amount of study is being focused. Biosorption uses the ability of biological materials to accumulate heavy metals from wastewater streams by either metabolically mediated or purely physico-chemical pathways of uptake [Fourest and Roux, 1992]. Many types of biomass have been reported to have high uptake capacities for heavy metals. For example, the uptake capacities of marine macro algae for divalent heavy metal ions are typically in the range of 1-1.5 mmol/g (dry weight) [Matheickal et al., 1991; Schiewer and Volesky, 1995]. *Durvillaea potatorum* has been previously investigated and showed a high removal capacity for a number of heavy metals [Kaewsarn et al., 1998; Matheickal, 1998; Matheickal and Yu, 1996; Matheickal and

Yu, 1997; Matheickal et al., 1997].

The uptake of heavy metals in biosorption can be influenced by a number of parameters, such as the type of the biomass, the methods of pretreatment, ionic strength, and solution pH. Most biosorption studies have observed large variations in the biosorption capacities with different solution pH values [Chong and Volesky, 1995; Fourest and Roux, 1992; Fourest et al., 1994; Matheickal and Yu, 1996; Matheickal and Yu, 1997; Matheickal et al., 1991; Matheickal et al., 1997; Sag and Kustal, 1995]. It has also been observed that the solution pH may vary during the process of heavy metal biosorption [Schiewer and Volesky, 1995], indicating the involvement of hydrogen ion in the process of heavy metal biosorption. In this aspect, the effects of solution pH on biosorption are similar to those of weakly acidic cation exchange resins.

The effects of solution pH can be related to a number of mechanisms such as metal speciation in solution, changes of ionic forms of the functional groups involved in biosorption, and the competition effects of hydrogen ions. At very low solution pH, the concentration of the hydrogen ion is high, and it can directly compete with the heavy metal ions. The protonation of the binding sites or the ionized functional groups on the cell wall make the binding site inaccessible to heavy metal cations [Chong and Volesky, 1995; Crist et al., 1994; Harris and Ramelow, 1990; Matheickal et al., 1991; Zhou and Kiff, 1991]. At high solution pH values, the metal speciations in solution may become an important factor. The increase in heavy metal uptake has been attributed to reduced solubility and metal precipitation [Harris and Ramelow, 1990; Zhou and Kiff, 1991].

Adsorption models have been used to correlate the equilibrium isotherm data of biosorption. Among them, the standard Langmuir equation has been used extensively [Chong and Volesky, 1995; Matheickal and Yu, 1996; Matheickal and Yu, 1997; Matheickal et al., 1991; Matheickal et al., 1997; Tsezos and Volesky, 1982; Volesky et al., 1993; Volesky and Holan, 1995; Volesky and Prasetyo, 1994]. The Freundlich equation has also

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been used for biosorption system [Asku et al., 1992; Guibal et al., 1992; Ozer et al., 1994; Tsezos and Volesky, 1982; Volesky et al., 1993]. Isotherm data obtained from experiments can usually be well described by the Langmuir or Freundlich equations. In addition, the Langmuir and the Freundlich equations have roughly the same degree of correlation for describing biosorption equilibria over moderate ranges of concentrations, but significant differences occur over wide ranges of concentrations or at low pH values. However, the adsorption models are used empirically to fit the biosorption data, without taking into account the underlying mechanisms of heavy metal biosorption. Recent studies showed the limitations of using the simple Langmuir equation as it fails to include the effects of parameters such as solution pH and ionic strength [Crist et al., 1994; Schiewer and Volesky, 1997]. The adsorption models can only be used to correlate isotherm data under constant solution pH values.

Therefore, the aim of this paper was to study the effects of solution pH on the capacity of heavy metal biosorption and to develop an isotherm model that can be used to correlate biosorption equilibrium data under various solution pH values. A modified Langmuir model that takes into account the association-dissociation equilibrium of the functional groups was proposed and validated with isotherm data of marine macro alga *Durvillaea potatorum* biosorption systems. It was shown that the model equation fitted the experimental data well.

THEORY

The standard Langmuir adsorption model was used to correlate the isotherm data obtained at constant solution pH values,

$$q = \frac{bQ_{\max}c}{1+bc} \quad (1)$$

where q is the amount of heavy metal ions adsorbed at equilibrium (mmol/g), c is the heavy metal ion concentration in solution (mM) at equilibrium, Q_{\max} is the maximum adsorption capacity and b is an affinity constant. For determining the equilibrium parameters, Eq. (1) may be written into a linearised form as follows:

$$\frac{c}{q} = \frac{1}{Q_{\max}b} + \frac{c}{Q_{\max}} \quad (2)$$

The parameters were then obtained by using a least square linear regression analysis.

In Eq. (1), the parameters b and Q_{\max} are solution pH dependent. Thus the application of Eq. (1) is limited to constant solution pH values. However, the biosorption process normally affects solution pH and variations were observed as the heavy metal ions were adsorbed. To take this phenomenon into account, a modified Langmuir model was proposed and used to correlate isotherm data obtained at various solution pH values. In this model, it is assumed that the functional groups responsible for heavy metal interaction are weakly acidic groups. The ionic forms of the functional groups are therefore affected by the association-dissociation equilibrium through the changes in solution pH values. It is further assumed that the weak acid

equilibrium can be represented by the following apparent equilibrium:



where GH and G^- represent the protonated and deprotonated forms of the functional groups. Finally, it is assumed that the maximum adsorption capacities for GH and G^- are $Q_{\max1}$ and $Q_{\max2}$, respectively.

The above equilibrium can be described by the following,

$$K_a = \frac{[\text{G}^-][\text{H}^+]}{[\text{GH}]} \quad (4)$$

where K_a is the apparent equilibrium constant.

From the Eq. (4), the fractions of the two ionic forms of the functional groups can be expressed:

$$f_{\text{GH}} = \frac{[\text{GH}]}{[\text{GH}] + [\text{G}^-]} = \frac{1}{1 + \frac{K_a}{[\text{H}^+]}} = \frac{1}{1 + [10^{pH-pK_a}]} \quad (5)$$

$$f_{\text{G}^-} = \frac{[\text{G}^-]}{[\text{GH}] + [\text{G}^-]} = \frac{\frac{K_a}{[\text{H}^+]}}{1 + \frac{K_a}{[\text{H}^+]}} = \frac{10^{pH-pK_a}}{[1] + [10^{pH-pK_a}]} \quad (6)$$

where $pK_a = -\log K_a$ and $pH = -\log[\text{H}^+]$. The overall maximum adsorption capacity for the biomass is the weighted average of the two ionic forms of the functional groups,

$$Q_{\max} = f_{\text{GH}}Q_{\max1} + f_{\text{G}^-}Q_{\max2} \quad (7)$$

Substituting Eqs. (5) and (6) into Eq. (7);

$$Q_{\max} = \frac{Q_{\max1} + Q_{\max2}10^{pH-pK_a}}{1 + 10^{pH-pK_a}} \quad (8)$$

where $pK_a = -\log K_a$ and K_a is the equilibrium constant for Eq. (3). Eq. (8) gives the pH dependent Q_{\max} values that can be substituted into Eq. (1) for the correlation of pH dependent isotherm data.

By combining Eq. (8) and (1) and re-arrangement, the following linearised form can be obtained:

$$C = \frac{-1}{b} + \left(\frac{C}{q}\right)\left(\frac{1}{1 + 10^{pH-pK_a}}\right)Q_{\max1} + \left(\frac{C}{q}\right)\left(\frac{10^{pH-pK_a}}{1 + 10^{pH-pK_a}}\right)Q_{\max2} \quad (9)$$

In this study, the values of parameter b , $Q_{\max1}$ and $Q_{\max2}$ were obtained from a multilinear regression analysis by using Eq. (9) at a fixed value of pK_a , and the value of pK_a was determined from trial and error. For the multilinear regression analysis, the statistical analysis package SPSS was used.

Eq. (1) and (8) were tested by using the isotherm data of Cu^{2+} , Cd^{2+} and Ni^{2+} biosorption onto the pre-treated biomass of *Durvillaea potatorum*. Isotherm data of Ni^{2+} biosorption were obtained from batch equilibrium experiments and those for Cu^{2+} and Cd^{2+} from the literature [Matheickal, 1998], which were obtained by using similar experimental procedures.

MATERIALS AND METHODS

Kelp Industries Pty Ltd, Tasmania, Australia supplied sun-

dried samples of *Durvillaea potatorum* in ground form. Biomass was pre-treated since the earlier studies proved that it could improve the removal capacity [Kaewsarn et al., 1998; Matheickal, 1998, 1996; Matheickal and Yu, 1997]. Pre-treatment of the biomass was carried out as follows: A sample of 20 grams of 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 pH 5.0 by using 0.1 M HNO_3 or 0.1 M NaOH solution if deviations were observed. The calcium treated biomass was washed several times with deionized water to remove excess calcium from the biomass. The biomass was then heated in an oven at 60 °C for 24 hours and then sieved for particle size of 300-600 μm . This pre-treatment improved the chemical and mechanical stability of biosorbents by reducing the amount of total soluble organic carbon in water extraction, the swelling volumes and the attrition loss [Matheickal, 1998].

All experiments were conducted at room temperature (20 ± 1 °C). For isotherm determination, a series of 125 mL plastic vials (polystyrene) were prepared containing nickel nitrate solutions (100 mL) of known concentrations, which varied from 0.5 to 4.5 mM. Weighed amounts [200 mg (dry)] of biomass were added to each vial and the mixtures were agitated on the 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 hourly in the first 4 hours. The pH of the solution was measured and adjusted if necessary again after 24 hours (no further changes in pH were observed). The biomass was removed by filtration through a 0.45 μm membrane filter and the filtrates were analyzed for Ni^{2+} by atomic absorption spectrometry.

RESULTS AND DISCUSSION

1. Effect of Solution pH on Heavy Metal Uptake

The effect of solution pH on the uptake of three heavy metal ions by pre-treated biomass of *Durvillaea potatorum* was illustrated first. In Fig. 1, the amount of Ni^{2+} , Cu^{2+} and Cd^{2+} uptake as a function of solution pH is shown. At a pH of less than 2, the amount of Ni^{2+} , Cu^{2+} and Cd^{2+} uptake is small. As pH increases, the amount of uptake increases and the sharpest increases are observed between pH 3 and 4 for Cu^{2+} and Cd^{2+} ,

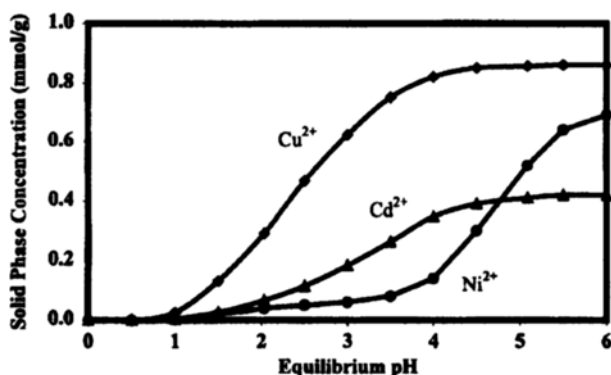


Fig. 1. Amount of Ni^{2+} , Cu^{2+} and Cd^{2+} uptake by pre-treated biomass of *Durvillaea potatorum* at various pH (biomass dose: 2 g/L, initial concentration: 2 mM; data for Cu^{2+} and Cd^{2+} adapted from reference [Matheickal, 1998]).

and 4-5 for Ni^{2+} . For Ni^{2+} , at around pH 6, a plateau is reached, while for Cu^{2+} and Cd^{2+} , at around pH 4 and 5. The trends of pH dependence shown in Fig. 1 have characteristics that are similar to those of titration curves of weak acids, with the inflection points corresponding to the pKa values of the functional groups.

2. Correlation with Standard Langmuir Equation

Equilibrium isotherms for the three heavy metal ions were obtained under controlled solution pH values, and they are shown in Fig. 2. The isotherms are rather steep at lower equilibrium concentrations implying high adsorption affinity and thus the suitability of biosorbents to treat dilute heavy metal solutions. The maximum amounts of adsorption (saturation) for all heavy metal ions decrease with a decreasing value of solution pH.

Each individual isotherm in Fig. 2 was fitted with the stand-

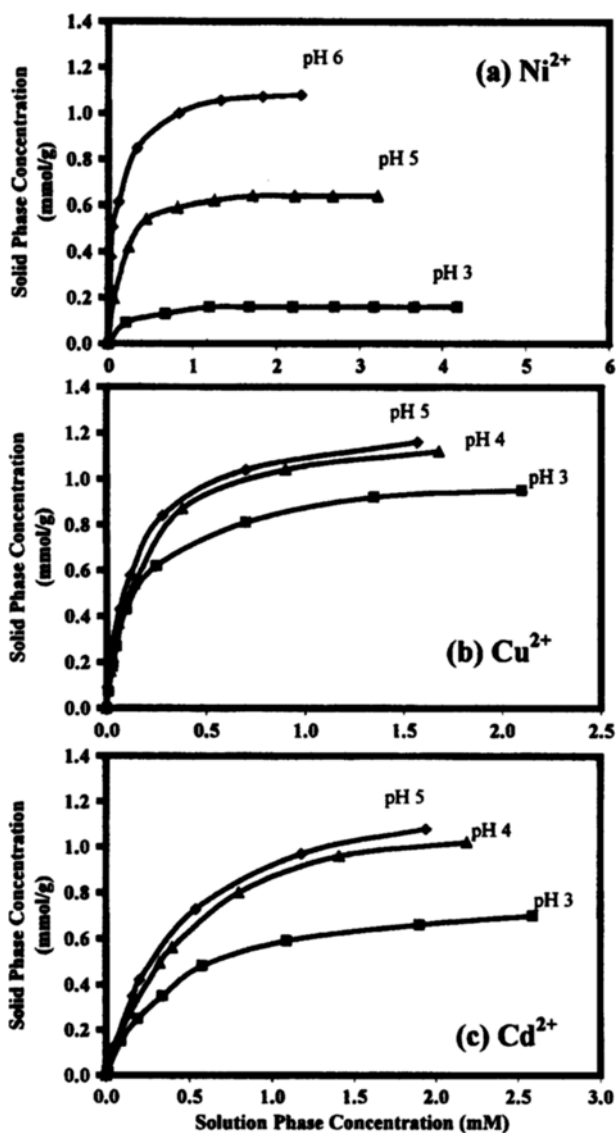


Fig. 2. Adsorption isotherms of Ni^{2+} , Cu^{2+} and Cd^{2+} onto pre-treated biomass of *Durvillaea potatorum* at various pH with the standard Langmuir model (solid line), data for Cu^{2+} and Cd^{2+} adapted from reference [Matheickal, 1998].

Table 1. Langmuir equation constants for Ni^{2+} , Cu^{2+} and Cd^{2+} biosorption

Heavy metals	Equation	pH	Q_{\max} (mmol/g)	b	r^2
Ni^{2+}	1	3	0.17	6.23	0.995
	1	5	0.68	7.98	0.994
	1	6	1.13	8.05	0.997
	1 and 8	all pH	$Q_{\max 1} = 0.15$, $Q_{\max 2} = 1.23$	8.96	0.992
Cu^{2+}	1	3	0.99	7.28	0.986
	1	4	1.21	11.1	0.995
	1	5	1.40	16.7	0.994
	1 and 8	all pH	$Q_{\max 1} = 0.13$, $Q_{\max 2} = 1.31$	6.14	0.984
Cd^{2+}	1	3	1.02	1.11	0.987
	1	4	1.15	2.69	0.968
	1	5	1.18	5.56	0.985
	1 and 8	all pH	$Q_{\max 1} = 0.06$, $Q_{\max 2} = 1.29$	2.90	0.941

ard Langmuir equation (solid line) and the Langmuir parameters for each isotherm under fixed pH values shown in Table 1. From Fig. 2 and Table 1, it can be seen that the correlation of the data is good ($r^2=0.968-0.997$), indicating the suitability of the standard Langmuir equation in describing the isotherm data under constant pH values. It is also noted that the value of parameter Q_{\max} varied considerably with solution pH. The variation in parameter b with solution pH was less than those in Q_{\max} for Ni^{2+} . However, for Cu^{2+} and Cd^{2+} the variation in parameter b with solution pH was greater than those in Q_{\max} .

3. Correlation with Modified Langmuir Equation

The isotherm data of the three heavy metal ions under all pH values were fitted with the modified Langmuir equation [Eqs. (1) and (8)]. The resulting equations were plotted in Fig. 3 (solid lines) and the corresponding values of the parameters $Q_{\max 1}$, $Q_{\max 2}$ and b are also shown in Table 1. The coefficients of correlation ($r^2=0.992$ for Ni^{2+} , $r^2=0.984$ for Cu^{2+} and $r^2=0.941$ for Cd^{2+}) were reasonably good, but they are slightly lower than those are for standard Langmuir equation fits. Overall, it can be said that modified Langmuir equation described the isotherm data well.

From Table 1, the values of $Q_{\max 1}$ are quite low. This is consistent with the low uptake of heavy metal ions at low solution pH values. On the other hand, the values of $Q_{\max 2}$ are much higher. They are about the same as the Q_{\max} values obtained at pH 5 for Cu^{2+} and Cd^{2+} and at pH 6 for Ni^{2+} . This is consistent with the assumption that the deprotonated forms of the functional groups are mainly responsible for heavy metal binding and electrostatic interaction may be the main mechanism of biosorption of heavy metals. This is further supported by the fact that Ca^{2+} and Mg^{2+} were eluted from the biosorbent in the process of heavy metal uptakes [Matheickal, 1998].

The values of pKa for Cu^{2+} (2.56) and Cd^{2+} (2.90) are close, while that for Ni^{2+} (5.05) is about two pH unit higher. These values correspond to the variations of Q_{\max} with solution pH

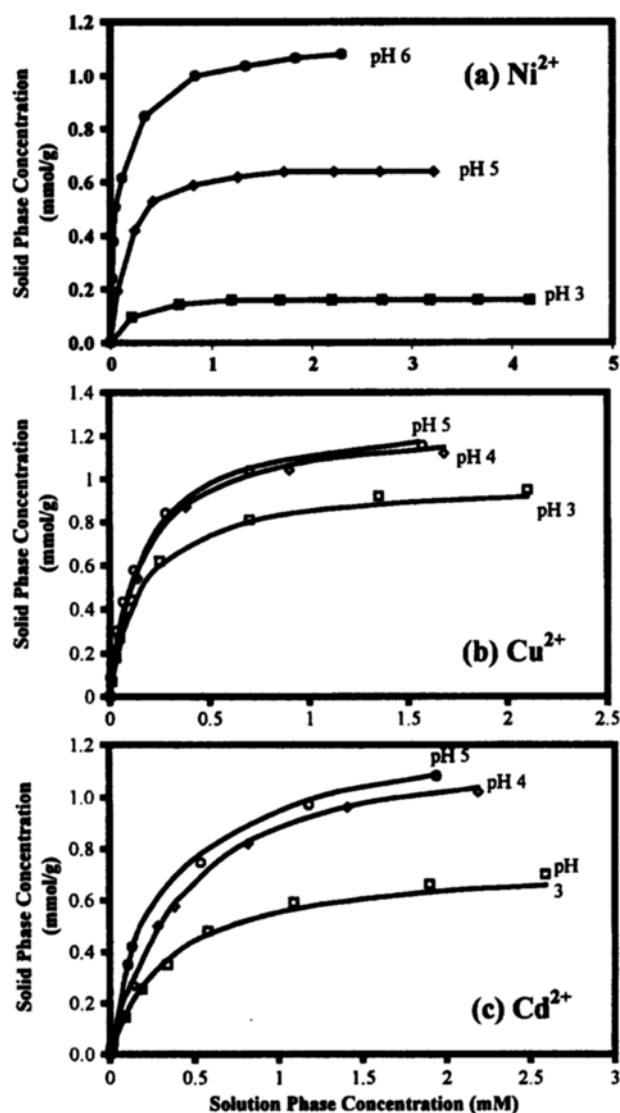


Fig. 3. Adsorption isotherms of Ni^{2+} , Cu^{2+} and Cd^{2+} onto pre-treated biomass of *Durvillaea potatorum* at various pH with the modified Langmuir (solid line).

observed in experiments and they are generally consistent with weakly acidic functional groups such as the carboxyl ($-\text{COOH}$) and the sulfhydryl ($-\text{SH}$) groups. Since the pKa values are the association-dissociation equilibrium constants, it is suggested that the functional groups for Ni^{2+} binding may be different, or in different parts of the cellular structure of the biomass, from those involved with Cu^{2+} and Cd^{2+} binding.

CONCLUSIONS

Equilibrium isotherms of Ni^{2+} , Cu^{2+} and Cd^{2+} biosorption are strongly solution pH dependent. The amount of heavy metal ion uptake is low at a low pH value, increases with solution pH and reaches a plateau at high pH values. Under constant pH values, the isotherm data can be well described by the standard Langmuir equation. For isotherm data under different pH values, a modified Langmuir equation can be used to describe the data, with a correlation coefficient of about 0.95 or higher. The

correlation supports the association-dissociation mechanism of the functional groups involved in heavy metal biosorption. It was also indicated that different functional groups might be involved for different heavy metal ions.

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