Derivation and application of a new model for heavy metal biosorption by algae

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Abstract

An equilibrium model for describing the relationships between important parameters for heavy metal sorption by algae was derived through a thermodynamics approach. In this model, both the removal efficiency of heavy metal and metal adsorption per unit algal biomass are considered to be simple functions of the ratio of algal biomass concentration to the initial metal concentration for selected conditions, i.e. as at constant pH and temperature. The model was found to fit the experimental results well (judged by the correlation–regression coefficient, $R^2$), for the adsorption of cadmium, copper, lead and zinc by two algal species, \textit{Oocystis} sp. (both living and non-living) and \textit{Chlorococcum} sp. The applicability of the model was also supported by the reprocessed results of experimental data given in the literature, i.e. for the metal species, Cd, Pb, Cu and Ag, the algal species, \textit{Chlorella vulgaris}, \textit{Scenedesmus quadricauda} and \textit{Cladophora crispata}, and both batch and continuous fixed-bed reactors. It was also demonstrated that the model could be applied over a broad range of pH for cadmium and copper adsorption by \textit{Oocystis} sp. However, the model was not applicable at very low and high pH levels, due to negligible adsorption and precipitation, respectively.

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1. Introduction

With increasing generation of heavy metals for technological activities, many aquatic environments face metal concentrations that exceed water quality criteria designed to protect the environment, animals and humans. In response to increasing metal toxicity concerns, new technologies involving the use of microalgae [1–5] potentially offer a more economical treatment alternative [6] because many features of algae make them potentially good candidates for heavy metal removal [3,1,7].

From the viewpoint of application, it is important to develop an appropriate mathematical model for describing the equilibrium behavior of an algae–metal system (either batch or continuous system) in order to guide the process design and screening of algal strains. The most widely used models to describe the equilibrium behavior of metal uptake are the well-known Langmuir and Freundlich sorption isotherms [8–23]. The two equations can be expressed as follows:

Freundlich sorption isotherm:

$$\frac{x}{m} = K_f C_e^{1/n}.$$  \hspace{1cm} (1)

Langmuir sorption isotherm:

$$\frac{x}{m} = \frac{b C_e (x/m)_{\text{max}}}{1 + b C_e},$$ \hspace{1cm} (2)

where $x/m$ is the solute (metal) concentration in the sorbent (algae), $C_e$ the equilibrium concentration of solute in the solution, $K_f$ a constant, $(x/m)_{\text{max}}$ the maximum solute concentration in the sorbent, and $b$ and...
Recently, it has also been shown that the Freundlich model has a wider range of application in terms of metal concentration [16,17,19,10,14,24]. One of these models, called the ion-exchange isotherm, was developed from a general ion-exchange reaction between metal species, M1 and M2 (originally bound to the algal biomass) [28]. The model can be summarized as follows:

\[
nM1^{+m} + mM2^{+n} \leftrightarrow nM1^{+m} + mM2^{+n},
\]

ion-exchange reaction

\[
K_{M1M2} = \frac{q_{M1}^n C_{M2}^m}{q_{M2}^m C_{M1}^n}.
\]

(3)

ion-exchange isotherm

\[
q_{M1} = \frac{Q}{1 + C_{M2}/K_{M1M2} C_{M1}},
\]

(4a)

\[
q_{M2} = \frac{Q}{1 + C_{M1}/K_{M1M2} C_{M2}},
\]

(4b)

where M1 and M2 are the targeted heavy metal and the ion originally bound to the algal biomass (e.g., Ca\(^{2+}\), K\(^{+}\), H\(^{+}\), etc.); \(m\) and \(n\) the valence of M1 and M2, respectively; \(Q\) represents the total concentration of binding sites in the algal biomass; \(C_{M1}\) and \(C_{M2}\) are the equilibrium concentrations of M1 and M2 in solution, respectively; \(q_{M1}\) and \(q_{M2}\) the contents of M1 and M2 in the algal biomass. A significant development of the model is that the proton concentration (pH) can be incorporated into the equation as an independent variable if the algal biomass is pre-protonated, i.e. M2 is replaced by H\(^{+}\). However, this model still did not account for how the changes in initial heavy metal and algal biomass concentrations affect the equilibrium metal concentration in the solution and the metal content adsorbed on the algal biomass. Instead, as already seen in the Langmuir isotherm, the equilibrium concentrations of both the displaced and targeted metals.
in solution are treated as independent parameters, which are determined by the initial concentrations of algal biomass and the targeted heavy metal. Furthermore, it will be difficult to apply the model when considering more than one species of ion bound to the sites on the algal biomass, as the number of constants in this models will increase accordingly.

In retrospect, all the above equilibrium models may be viewed as “descriptive” rather than “predictive” models, i.e. they describe the relationships between the equilibrium parameters, rather than predict the equilibrium state according to the initial conditions for a particular algal–metal system. In the present study, we derive a new equilibrium model which describes the relationships between the equilibrium concentrations of metal, metal sorption per unit algal biomass and the most important factors affecting these two parameters—the concentration of algal biomass and initial metal concentration. The model was applied to experiments on Cd, Cu, Pb and Zn uptake by two tropical, unicellular algal species, *Oocystis* sp. and *Chlorococcum* sp. In addition, the effects of pH on the application of the model were also explored.

2. Theoretical derivation of model

The model derived in this study was obtained using thermodynamics as an overall approach to the system. The basic equation of the model is:

\[
\frac{C_e}{C_0} = \alpha \exp \left( \frac{\beta M}{C_0} \right).
\]

(5)

In deriving the above equation, first consider the sorption reaction as a simple change in the state of the heavy metal solution:

\[
C_0 \xrightarrow{M} C_e; \ \Delta G^0 ',
\]

where \(C_0\) is the initial concentration of heavy metal in solution, \(C_e\) the equilibrium concentration of metal in solution after sorption, \(M\) the concentration of algal biomass and \(\Delta G^0 '\) is the effective free energy change, which changes with the proceeding of the adsorption reaction.

The total free energy change of the sorption reaction, \(\Delta G\), can thus be expressed as a function of \(C_0\) and \(C_e\):

\[
\Delta G = \Delta G^0 ' - RT \ln \left( \frac{C_e}{C_0} \right).
\]

(6)

which is analogous to the expression for the free energy change of an ideal gas at constant temperature, \(\Delta G = nRT \ln(p_2/p_1)\), where \(p_2\) and \(p_1\) are the final and initial pressures, respectively, [29]. In fact, as pointed out by Morel and Hering [24], Eq. (6) can be rationally extended from the above expression of the free energy change of ideal gas by application of Raoult’s and Henry’s laws for the equilibrium between the concentrations of solvent and solutes and their vapor pressures. From the viewpoint of statistical mechanics, Eq. (6) can be considered similar to the Maxwell–Boltzmann distribution law [24]. It should be noted that the symbol “minus” is used in the above equation because sorption is not a spontaneous reaction, i.e. the metal solution will not shift automatically from state \(C_0\) to state \(C_e\) without the addition of energy.

Consider the empirical facts that if the ratio, \(C_e/C_0\), decreases for increasing \(M\) at constant \(C_0\) and increases for increasing \(C_0\) at constant \(M\), the sorption reaction must become more favorable under conditions of higher \(M\) and lower \(C_0\), i.e. \(\Delta G^0 '\) must decrease (or increase negatively) for increasing \(M\) and decreasing \(C_0\). There are obviously many alternative formulations to account for a negative increase in \(\Delta G^0 '\) for the sorption reaction, as seen in the Langmuir and Freundlich sorption isotherms. We assume that the free energy change of sorption decreases linearly with the concentration of algal biomass (\(M\)) and with the reciprocal of the initial heavy metal concentration (\(C_0\)), then

\[
\Delta G^0 = \Delta G^0 ' + \beta RT \left( \frac{M}{C_0} \right) \ (\beta < 0),
\]

(7)

where \(\beta\) is a negative constant and \(\Delta G^0 '\) the standard free energy change. Note that \(\beta\) should be less than zero, otherwise the reaction cannot proceed.

At equilibrium, Eqs. (6) and (7) can be combined. Assuming \(\Delta G = 0\),

\[
\Delta G = 0 = \Delta G^0 ' + \beta RT \left( \frac{M}{C_0} \right) - RT \ln \left( \frac{C_e}{C_0} \right),
\]

(8)

\[
\ln \left( \frac{C_e}{C_0} \right) = \frac{\Delta G^0 '}{RT} + \beta \frac{M}{C_0}.
\]

(9)

By defining \(z = \exp(\Delta G^0 '/RT)\), the expression (5) can be obtained.

Note that \(\Delta G^0 '\) is a function of temperature only [29]. Under normal experimental conditions, the difference in temperature between the beginning and end of an experiment is not significant, therefore \(\Delta G^0 '\) can be taken as zero. Consequently, the constant, \(z\), is equal to 1 (under experimental conditions, \(z\) may take on other values less than or larger than 1, as shown and discussed later).

Now consider the situation when the sorption system is not in equilibrium, i.e. \(\Delta G \neq 0\). In turn, we can obtain another expression from Eqs. (6) and (7)
as follows:
\[
\frac{C_e}{C_0} = \exp\left(\frac{\Delta G^0 - \Delta G}{RT} + \frac{\beta M}{C_0}\right).
\]

\[
= \exp\left(\frac{\Delta G^0 - \Delta G}{RT}\right)\exp\left(\frac{\beta M}{C_0}\right).
\] (9')

Again, after defining \( x = \exp(\Delta G^0 - \Delta G/RT) \), an expression can be obtained, of the same form as Eq. (5). This implies that the application of Eq. (5) to fit experimental data does not depend on whether the system is in equilibrium or not; the difference is simply reflected in the value of the coefficient, \( x \).

Now, consider a closed algae–metal system, where the mass balance equation for heavy metal is as follows:
\[
C_0 = C_e + X,
\] (10)
where \( X \) is the sorbed heavy metal calculated as weight per volume (mg/l).

After substituting Eq. (5) into Eq. (10) and defining \( x/m = X/M \), the expression for the metal content per unit algal biomass, \( x/m \), as a function of \( M/C_0 \) is
\[
\frac{x}{m} = \frac{1 - x \exp(\beta M/C_0)}{M/C_0}.
\] (11)

By combining Eqs. (5) and (11), the relationship between the metal content per unit algal biomass \( (x/m) \) and the ratio, \( C_e/C_0 \), can be derived as follows:
\[
\frac{x}{m} = \beta \frac{1 - C_e/C_0}{\ln(C_e/C_0)}.
\] (12)

Eq. (12) shows clearly an important difference from the widely used Freundlich and Langmuir sorption isotherms. In this equation, the metal content per unit algal biomass is expressed as a function of both the equilibrium and initial metal concentrations rather than a function of the equilibrium metal concentration alone, as expressed in the isotherm equations. The model has the advantage of being simple in form and can be applied to a set of experimental data under both equilibrium and non-equilibrium conditions.

The value of \( \beta \) reflects the metal sorption ability of algae. The higher the absolute value of \( \beta \), the bigger the slope of the curve for Eq. (5), and the higher the sorption ability. As shown from Eq. (5), the constant, \( x \), should take a value of 1 under ideal conditions. However, \( x \) may also take on values either larger or smaller than 1 under actual experimental conditions. In the case where \( x \) is greater than 1, it can be demonstrated mathematically that this is due to a constant mass loss of metal, \( \gamma \) (e.g. during any rinsing procedures where samples are filtered and/or sorption of metal to the flask wall).

Consider Eq. (5) and let \( C_0' = C_0 - \gamma \).

Then, Eq. (5) can be written as
\[
\frac{C_e}{C_0'} = \frac{C_e}{C_0 - \gamma} = x' \exp\left(\frac{\beta M}{C_0'}\right).
\]

Since the absolute value of \( \beta \) is small, the difference between \( \beta M/C_0' \) and \( \beta M/C_0 \) is negligible. Hence,
\[
\frac{C_e}{x'C_0'} = \frac{C_e}{x(C_0 - \gamma)}
\]
and
\[
\frac{C_e}{C_0'} < \frac{C_e}{C_0 - \gamma}.
\]

Thus, it can be deduced that \( x' > x = 1 \).

It is interesting to point out that, when the value of \( x \) is greater than 1, a non-monotone relationship for \( x/m \) vs. \( M/C_0 \) and for \( x/m \) vs. \( C_e/C_0 \) can be predicted by Eqs. (11) and (12). Also if \( x > 1 \), by differentiating Eqs. (11) and (12), an expression of the maximum for \( x/m \) can be obtained:
\[
\frac{(x/m)_{\text{max}}}{(x/m)_{\text{max}}} = \frac{-\beta}{1 - \beta(M/C_0)_c}
\]
\[
= -x \exp\left(\frac{\beta \left(\frac{M}{C_0}\right)_c}{c}\right)
\] (13)
when
\[
x \exp\left(\frac{\beta \left(\frac{M}{C_0}\right)_c}{c}\right) = \frac{1}{1 - \beta(M/C_0)_c},
\] (14)
where \( (M/C_0)_c \) is the critical value of \( M/C_0 \).

However, if \( x > 1 \), the value of \( x/m \) calculated from Eqs. (11) and (12) may take on negative values when \( M/C_0 = -\ln(x)/\beta \). This represents a limit for the application of this model. On the other hand, \( x \) may also take on values much lower than 1. One possible reason is that the actual initial metal concentrations (\( C_0 \)) in the algae–metal system are lower than the pre-designed values due to errors in solution preparation or precipitation of metals. Another possible reason is that a set of relatively high values of \( M/C_0 \) (either very high \( M \) or very low \( C_0 \)) was used in fitting the model.

3. Materials and methods

A series of experiments were designed to test the model for the sorption of Cd, Cu, Pb and Zn using living or heat-treated algal biomass. The algal strains used were tropical fresh-water species, aclimatized by exposure to various concentrations of Cd and Cu. The species were identified as *Oocystis* sp. (about 5μm × 7μm) and *Chlorococcum* sp. (average diameter of 5μm). The algae were cultured at a light intensity of 5000 Lux and room temperature (about 28°C), with the composition of culture media following that of Ting et al. [30]. The heavy metals were used in the form of chloride salts (CdCl₂·1.5H₂O, CuCl₂·2H₂O, PbCl₂·H₂O, ZnCl₂).
The batch experiments were divided into two parts. In the first part, 17 tests were carried out at a selected initial pH, as given in Table 1. In the second part, 10 additional tests were carried out to test the effects of pH on the applicable range of the model (Table 2). Algal cultures were first harvested by centrifugation or filtration (0.45 μm membrane). The biomass was then rinsed with deionized distilled water (DDW) three times and then adjusted to a certain volume. For experiments conducted with heat-treated biomass, the collected fresh algae were treated by heating in an oven (103°C) for 3 h. The dried algae were then re-suspended by ultrasonic treatment (microscope examination showed that the algal cells were still intact). A certain amount of algal biomass was then added to a series of flasks containing a nutrient-free solution of heavy metal. The pH for all these bottles were eventually adjusted to the desired level, except for the two experiments in which the pH were adjusted separately for algal and metal solutions before mixing (Tests 14 and 15, refer to Table 1). The bottles were then placed on a shaker with rotating velocity 60–80rpm for 72h at room temperature (~28°C). After the incubation, the algae were filtered onto 0.45 μm filter membrane, and the algae-free solution (filtrate) was collected for measurement.

### Table 1
Experimental conditions of the batch tests for metal sorption

<table>
<thead>
<tr>
<th>Test</th>
<th>Algae</th>
<th>Metal</th>
<th>pH</th>
<th>Metal concentration (mg/l)</th>
<th>Biomass concentration (mg/l)</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><em>Oocystis</em></td>
<td>Cd</td>
<td>7.5</td>
<td>5</td>
<td>2–171</td>
<td>12</td>
</tr>
<tr>
<td>2</td>
<td><em>Oocystis</em></td>
<td>Cd</td>
<td>7.5</td>
<td>10</td>
<td>6.5–345</td>
<td>7</td>
</tr>
<tr>
<td>3</td>
<td><em>Oocystis</em></td>
<td>Cu</td>
<td>5.5</td>
<td>0.5–35</td>
<td>28, 51</td>
<td>21</td>
</tr>
<tr>
<td>4</td>
<td><em>Oocystis</em></td>
<td>Cu</td>
<td>5.5</td>
<td>10</td>
<td>2.5–304</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td><em>Oocystis</em></td>
<td>Cu</td>
<td>5.5</td>
<td>0.5–25</td>
<td>6–338.5</td>
<td>7</td>
</tr>
<tr>
<td>6</td>
<td><em>Oocystis</em></td>
<td>Pb</td>
<td>5.5</td>
<td>20</td>
<td>4.5, 60</td>
<td>10</td>
</tr>
<tr>
<td>7</td>
<td><em>Oocystis</em></td>
<td>Pb</td>
<td>6.5</td>
<td>10, 20, 30</td>
<td>2.5–80.5</td>
<td>12</td>
</tr>
<tr>
<td>8</td>
<td><em>Oocystis</em></td>
<td>Zn</td>
<td>5.5</td>
<td>20</td>
<td>0.5–157.5</td>
<td>11</td>
</tr>
<tr>
<td>9</td>
<td><em>Oocystis</em></td>
<td>Zn</td>
<td>7.0</td>
<td>2, 5, 8, 10, 12</td>
<td>6, 30, 140, 100</td>
<td>13</td>
</tr>
<tr>
<td>10</td>
<td><em>Oocystis</em></td>
<td>Cd</td>
<td>7.5</td>
<td>2, 5, 8, 10</td>
<td>10–60</td>
<td>12</td>
</tr>
<tr>
<td>11</td>
<td><em>Chlorococcum</em></td>
<td>Cd</td>
<td>3.5</td>
<td>5.5, 3.5</td>
<td>12, 25, 73, 143</td>
<td>8</td>
</tr>
<tr>
<td>12</td>
<td><em>Chlorococcum</em></td>
<td>Cu</td>
<td>5.5</td>
<td>5, 10, 15</td>
<td>13, 26, 77, 154</td>
<td>12</td>
</tr>
<tr>
<td>13</td>
<td><em>Chlorococcum</em></td>
<td>Pb</td>
<td>3.5</td>
<td>5, 10</td>
<td>14, 48, 79, 105</td>
<td>8</td>
</tr>
<tr>
<td>14</td>
<td><em>Chlorococcum</em></td>
<td>Pb</td>
<td>4.5</td>
<td>5, 10</td>
<td>11–225</td>
<td>12</td>
</tr>
<tr>
<td>15</td>
<td><em>Chlorococcum</em></td>
<td>Zn</td>
<td>4.5</td>
<td>1, 3, 5, 10</td>
<td>33, 100, 170</td>
<td>12</td>
</tr>
<tr>
<td>16</td>
<td><em>Chlorococcum</em></td>
<td>Zn</td>
<td>6.5</td>
<td>5, 10</td>
<td>8.5–130</td>
<td>12</td>
</tr>
<tr>
<td>17</td>
<td><em>Chlorococcum</em></td>
<td>Zn</td>
<td>7.0</td>
<td>2, 5, 8, 10, 12</td>
<td>6, 30, 140, 100</td>
<td>13</td>
</tr>
</tbody>
</table>

*a* Sample number.

*b* Heat-treated algal biomass was used.

*c* The pH were adjusted separately before mixing algal suspension with metal solution.

### Table 2
Experimental conditions of batch tests to determine the effect of pH on the model using the fresh biomass of *Oocys** sp.

<table>
<thead>
<tr>
<th>Test</th>
<th>Metal</th>
<th>pH</th>
<th>Metal concentration (mg/l)</th>
<th>Biomass concentration (mg/l)</th>
<th>Sample number</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>Cd</td>
<td>4.5</td>
<td>2</td>
<td>7–104.5</td>
<td>7</td>
</tr>
<tr>
<td>19</td>
<td>Cd</td>
<td>6.0</td>
<td>2</td>
<td>7.5–99</td>
<td>9</td>
</tr>
<tr>
<td>20</td>
<td>Cd</td>
<td>7.5</td>
<td>2</td>
<td>1.0–179</td>
<td>8</td>
</tr>
<tr>
<td>21</td>
<td>Cd</td>
<td>9.0</td>
<td>2</td>
<td>7–134</td>
<td>7</td>
</tr>
<tr>
<td>22</td>
<td>Cd</td>
<td>10.5</td>
<td>2</td>
<td>8–58</td>
<td>6</td>
</tr>
<tr>
<td>23</td>
<td>Cu</td>
<td>2.5</td>
<td>10</td>
<td>8.0–249</td>
<td>9</td>
</tr>
<tr>
<td>24</td>
<td>Cu</td>
<td>3.5</td>
<td>2, 5, 8, 10</td>
<td>7, 41.5, 200</td>
<td>12</td>
</tr>
<tr>
<td>25</td>
<td>Cu</td>
<td>4.5</td>
<td>2, 5, 8, 10</td>
<td>1.0, 20, 115</td>
<td>11</td>
</tr>
<tr>
<td>26</td>
<td>Cu</td>
<td>5.5</td>
<td>0.5–35</td>
<td>44</td>
<td>10</td>
</tr>
<tr>
<td>27</td>
<td>Cu</td>
<td>7.0</td>
<td>10</td>
<td>23.5–373</td>
<td>9</td>
</tr>
</tbody>
</table>
pH values were measured using a digital Horiba F-22 pH meter. Algal biomass was measured as follows: the samples were filtered onto pre-weighed 0.45 μm membrane, dried at 103°C for 24 h, cooled in a desiccator for 24 h, and weighed to obtain the dry weight of algae. Metal concentration was measured using a AA-6701F SHIMADZU Atomic Absorption Spectrophotometer (flame continuous mode). For measurement of metal concentration in the algae sample, the filter membrane containing algae was digested with concentrated nitric acid on an electrothermal plate till the sample solution became colorless (modified from that in Ref. [30]). The digested samples were then diluted with DDW so as to allow the concentration of metals to be within the measuring range of the instrument. For measurement of metal in solution, the algae-free samples were measured directly with F-AAS or measured after dilution. Correlation–regression analysis was conducted with Microsoft Excel 97.

4. Results and discussion

4.1. Application of the model

The experiments conducted were initially focused on Cd and Cu sorption. From the results, it can be seen that the exponential equation (Eq. (5)), \( \frac{C_x}{C_0} = ax \exp(bM/C_0) \), is able to fit the experimental data reasonably well for the sorption of Cd and Cu by the algal biomass of both Oocystis sp. and Chlorococcum sp. (either in living or dead form) at different pH (Figs. 1a, 2a, 3a and 4a). The experiments conducted with both different initial metal concentrations and biomass concentrations (Tests 3, 6, 11–13, refer to Table 1) test the applicability of the model (Figs. 3a and 4a). The results of metal content per unit algal biomass, \( x/m \) (calculated with Eqs. (11) or (12) according to the values of \( a \) and \( b \) obtained from fitting Eq. (5)) are also consistent with the experimental data, particularly for higher values of \( M/C_0 \), where the effect of mass loss is less significant (Figs. 1b and c, 2b and c, 3b and c, 4b and c). (Note that because of the more significant effects of mass loss and experimental errors at lower values of \( M \), the calculated values of \( x/m \) deviated from the experimental data more significantly for lower values of \( M/C_0 \), compared to higher values.) Furthermore, non-monotone curves for the relationships of \( x/m \) vs. \( M/C_0 \) and \( x/m \) vs. \( C_x/C_0 \) were also observed for the experiments conducted with the same initial cadmium concentrations, as shown in Figs. 1b and c. However, these non-monotone characteristics were not observed for other experiments (Tests 3, 4, 6 and 7). Some possible explanations for this are as follows: (1) for the experiments conducted with different initial metal and biomass concentrations (i.e. Tests 3, 6, 10–17), the value of \( M/C_0 \) were often higher than the critical value, \( (M/C_0)_c \), and (2) the non-monotone characteristics may be shaded or blurred by the variation in metal mass loss, as different \( C_0 \) and \( M \) were used. From the viewpoint of application of the model, this problem can be lessened by limiting the mass loss as much as possible, or by using only the experimental data corresponding to the right side of the maximum value of \( x/m \) in the curves for \( x/m \) vs. \( M/C_0 \).

From Eq. (12), it can be seen that \( x/m \) is expressed as a function of both \( C_e \) and \( C_0 \) in the model, and is basically determined by the ratio of algal biomass to initial metal concentration, as shown in Eq. (11). We also attempted to fit the experimental data to the Freundlich and Langmuir isotherms. However, except for some experiments (i.e. those with the same \( C_0 \) or same \( M \)), these two isotherms were unable to fit the data well for the experiments conducted with both different \( C_0 \) and \( M \). From Fig. 5, it can be seen that the plots for \( x/m \) vs. \( C_e \) do not show a monotone functional relationship whereas plots for \( x/m \) vs. \( C_e/C_0 \) do show a functional
relationship. In fact, Hashim et al. [25] also found that a unique isotherm equation could not be obtained if different initial metal concentrations and algal biomass dosage were used for the same set of experiments. These results show that there is a limit to the application of the Freundlich and Langmuir isotherms. Mathematically, the expressions for the ratio of $C_e = C_0$ can be obtained, respectively, as follows:

$$\frac{C_e}{C_0} = 1 - K_f \left( \frac{M}{C_0} \right)^{1/n}, \quad (15)$$

$$\frac{C_e}{C_0} = 1 - \left( \frac{x/m}{(x/m)_{\text{max}}} \right) \left( \frac{C_e}{C_0} \right) \frac{M}{1 + bC_e}, \quad (16)$$

Note that Eqs. (15) and (16) are expressed in terms of both $C_e$ and $M/C_0$, whereas Eq. (5) is a function of $M/C_0$ only.

Fig. 2. Experimental data of copper sorption by fresh or heat-treated biomass of *Oocystis* sp. with the same initial metal concentration at an initial pH of 5.5 (Tests 4 and 5, refer to Table 1): (a) relationship between $C_e = C_0$ vs. $M/C_0$; (b) relationship between $x/m$ vs. $M/C_0$; (c) relationship between $x/m$ vs. $C_e/C_0$.

Fig. 3. Experimental data of cadmium and copper sorption by fresh biomass of *Oocystis* sp. with different initial metal and algal concentrations at a constant initial pH (Tests 3 and 6, refer to Table 1): (a) relationship between $C_e/C_0$ vs. $M/C_0$; (b) relationship between $x/m$ vs. $M/C_0$; (c) relationship between $x/m$ vs. $C_e/C_0$.

The fact that the model could also be used to fit the data of both Cd and Cu sorption by heat-treated *Oocystis* sp. (refer to Figs. 1 and 2) demonstrates that the model does not depend on whether the algae are living or dead. This implies that the metal sorption by *Oocystis* sp. is based on some physical-chemical mechanisms, such as ion exchange [31]. In addition, the model was able to fit the data for Pb and Zn sorption by both the biomass of *Oocystis* sp. and *Chlorococcum* sp. (the exception is for Pb sorption conducted at pH 6.5 due to precipitation) (Table 3), showing that the model is not metal-species specific nor algal-species specific. However, whether it can be applied to the sorption/uptake of metals existing in the form of negative ions (e.g. UO$_2^{2-}$) is still open to question. From Table 3, it can be seen that the absolute values of $\beta$ at higher pH were larger than those at lower pH for both Pb and Zn adsorption by *Oocystis* sp. and *Chlorococcum* sp. This reflects the higher metal adsorption ability of algal
biomass at higher pH levels, as pointed out previously in the derivation of the model. The model is also supported by the re-processed results of experimental data given by other researchers [32,10,33] (Table 4). In these studies, different metals (Pb, Ag, Cu and Cd) and different algae (Chlorella vulgaris, Scenedesmus quadricauda, and Cladophora crispata) were used, together with much higher ranges of initial metal concentrations (3.75–200mg/l) and algal biomass (3.0–6000mg/l). Furthermore, according to the model fit to data obtained from experiments on a continuous fixed-bed reactor with different detention time of metals (Table 4), it can be seen that the application of the model does not depend on whether sorption is at equilibrium, as already shown theoretically in the derivation of the model.

Fig. 4. Experimental data of cadmium and copper sorption by fresh biomass of Chlorococcum sp. with different initial metal and algal concentrations at a constant initial pH (Tests 11–13, refer to Table 1): (a) relationship between \( C_e/C_0 \) vs. \( M/C_0 \); (b) relationship between \( x/m \) vs. \( M/C_0 \); (c) relationship between \( x/m \) vs. \( C_e/C_0 \).

Fig. 5. The different scatter lines for the relationships for \( x/m \) vs. \( C_e \) and \( x/m \) vs. \( C_e/C_0 \) when both different initial metal and algal biomass concentrations were applied. The experiment was conducted with 5, 10, and 15mg/l for the initial Cu concentrations and 13, 25, 75, and 155mg/l of Chlorococcum sp. at pH 5.5.

### Table 3

Correlation–regression analysis using Eq. (5) for the experimental data of Pb and Zn sorption by fresh algal biomass of Oocysis sp. and Chlorococcum sp.

<table>
<thead>
<tr>
<th>Test</th>
<th>Metal</th>
<th>pH</th>
<th>( \alpha )</th>
<th>( -\beta )</th>
<th>( R^2 )</th>
<th>( n^b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>7c</td>
<td>Pb</td>
<td>5.5</td>
<td>0.9827</td>
<td>0.0688</td>
<td>0.9615</td>
<td>12</td>
</tr>
<tr>
<td>8c</td>
<td>Pb</td>
<td>6.5</td>
<td></td>
<td></td>
<td>0.1378</td>
<td>9</td>
</tr>
<tr>
<td>9c</td>
<td>Zn</td>
<td>5.5</td>
<td>0.9973</td>
<td>0.0086</td>
<td>0.9988</td>
<td>11</td>
</tr>
<tr>
<td>10d</td>
<td>Zn</td>
<td>7.0</td>
<td>0.9169</td>
<td>0.0173</td>
<td>0.9641</td>
<td>11</td>
</tr>
<tr>
<td>14d</td>
<td>Pb</td>
<td>3.5</td>
<td>0.9949</td>
<td>0.0026</td>
<td>0.9208</td>
<td>8</td>
</tr>
<tr>
<td>15d</td>
<td>Pb</td>
<td>4.5</td>
<td>0.9684</td>
<td>0.0138</td>
<td>0.9522</td>
<td>12</td>
</tr>
<tr>
<td>16d</td>
<td>Zn</td>
<td>4.5</td>
<td>0.9821</td>
<td>0.0020</td>
<td>0.8928</td>
<td>12</td>
</tr>
<tr>
<td>17d</td>
<td>Zn</td>
<td>6.5</td>
<td>0.9361</td>
<td>0.0195</td>
<td>0.9188</td>
<td>12</td>
</tr>
</tbody>
</table>

a The initial metal concentrations and the concentrations of algal biomass are given in Table 1.
b Sample number.
c Conducted with the alga, Oocysis sp.
d Conducted with the alga, Chlorococcum sp.
4.2. Effect of pH on the model

In order to test whether the model can be applied to other pH conditions, a series of experiments (experiments 18–27, Table 2) were conducted with the live algal biomass of *Oocystis* sp. for Cd and Cu sorption at different initial pH levels. In general, the model could be applied to a broad range of pH levels (Table 5), as reflected by the values of $R^2$. However, the applicable ranges of pH were different for Cd and Cu, with Cd having a wider range than Cu. For Cd, the values of $R^2$ were still satisfactory at pH values where precipitation might occur (e.g. pH 10.5). However, for low values of pH, the value of $R^2$ decreased significantly, e.g. at pH 4.5, $R^2 = 0.8666$. For Cu, the model could be applied satisfactorily within the pH range from 3.5 to 5.5, but...
the values of $R^2$ decreased drastically when the initial pH was as low as 2.5 ($R^2 = 0.5431$) or as high as 7.0 ($R^2 = 0.0006$) (Table 5). Note that the model failed for Pb sorption by Oocystis sp. at pH 6.5 (Table 3) and for Zn sorption by Chlorococcum sp. at pH 7.0 (data not shown).

From the above results, the applicable range of pH for the model depends on the specific combination of metal and algal species. In general, the pH range has two limits: a “lower point” and a “higher point”. The “lower point” may be reasonably assumed to be the “inflection point” of zeta potential where the algal cell surface carries an approximate zero net charge [25]. When the pH is lower than the “inflection point”, the sorption of metal can be negligible (or is very low if it still occurs due to “entrapment” or some other physical mechanism). The low sorption of metals at low pH is also reflected by the small absolute value of the coefficient $\beta$, as observed in Table 3 and Fig. 4 (for Cu). This is consistent with other researchers’ results [32,12,25,34]. The “higher point” depends mostly on the solubility of the specific metal in water. However, it may also depend on the affinity of a specific algal species to a specific metal, and the experimental conditions (e.g. ion intensity, temperature, chelatins). When precipitation could be incorporated, for example, by quantifying the effect of pH (or concentration of protons). (This could be incorporated, for example, by quantifying the relationship between the coefficients of the model and pH.) Nevertheless, as the model stands, it can be used to predict the heavy metal concentration in solution and the metal sorption capacity of algae for both batch and continuous algae–metal systems within the range of pH most possibly used in practice.

5. Conclusions

- The developed model has the following advantages:
  (a) simplicity of form, (b) theoretical derivation and (c) it can be applied to a set of experimental data under both equilibrium and non-equilibrium conditions.
- From this study, it was found that the model gave a good fit to the data for sorption of Cd, Cu, Pb and Zn by both living and heat-treated biomass of Oocystis sp. and Chlorococcum sp. at fixed pH levels. The robustness of the model was also demonstrated by the re-processed results of experimental data given in the literature. It was also shown that the model could be applied to a broad range of pH for Cd and Cu sorption by algae, although the range depended on the species of metal and algae present.
- As this model was derived through a thermodynamics approach, it does not provide any information on the actual sorption mechanism. Further studies to derive this model based on assumptions of mechanisms, such as ion exchange and Coulombic attraction, would be useful. In addition, the model is limited because it does not specifically consider the effect of pH (or concentration of protons). (This could be incorporated, for example, by quantifying the relationship between the coefficients of the model and pH.). Nevertheless, as the model stands, it can be used to predict the heavy metal concentration in solution and the metal sorption capacity of algae for both batch and continuous algae–metal systems within the range of pH most possibly used in practice.

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References


