Isothermal Modelling of the Adsorption of Lead (II) Onto Activated Carbon from *Tridax procumbens*

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INTRODUCTION

Heavy metals are increasingly being released into the environment as a byproduct of mining, electroplating, alloy preparation, pulp-paper, and fertilizer production, among other industrial processes. The issue of pollution involving heavy metals is of paramount importance due to the accumulation of heavy metals in the food chain and the severe health concerns they cause to living beings. Lead is a naturally occurring toxic element found in the Earth's crust. Polluting large areas, exposing large numbers of people, and negatively impacting public health are all direct results of its widespread use in a variety of countries. More than 75% of all lead is used in the production of lead-acid car batteries. But lead is also used in many other products, such as pigments, paints, solder, stained glass, lead crystal glassware, ammunition, ceramic glazes, jewelry, toys, cosmetics, and traditional medicines. If the water pipes themselves are made of lead or if the pipes are joined together with lead-based solder, then the water you drink may contain lead. The majority of lead in international trade today is derived from recycled materials. Lead's negative effects on children are more severe because their developing brains and nervous systems are more susceptible to its toxicity. Adults who are exposed to high levels of lead are more likely to develop hypertension and kidney damage. Lead exposure is dangerous for everyone, but it can have devastating effects on pregnant women and their babies [1–3]. Anemia, hepatitis, encephalopathy, and nephritic syndrome have all been linked to lead levels in drinking water that are above the legal limit of 0.05 mg/L. Due to its high biosorption capacity and selectivity, low cost, and low environmental risk, biosorption is a promising approach for the removal of heavy metals from wastewater [1–3].

ABSTRACT

Hypertension and kidney damage have been linked to lead exposure in adults. Any person can be harmed by lead, but pregnant women and their unborn children are especially vulnerable. Presently, lead pollution is removed using membrane separation, ion exchange, precipitation, and biosorption. Biosorption's low operating costs, high efficiency at detoxifying low concentrations of toxicants, and small volume of disposal materials make it the least problematic of these technologies. The biosorption of lead (II) onto activated carbon from *Tridax procumbens* is remodeled using nonlinear regression and the optimal mode was determined by a series of error function assessments. The Freundlich model performed best in statistical tests including root-mean-square error (RMSE), adjusted coefficient of determination (adj²), bias factor (BF), accuracy factor (AF), and corrected Akaike Information Criterion (AICc). The calculated Freundlich parameters $k_F$ value using nonlinear regression was 1.334 (1/g) (95% confidence interval from 0.821 to 1.847) and $n_F$ value of 3.872 (95% C.I. from 1.972 to 5.771). Modelling using a nonlinear approach allows for the calculation of uncertainty range in terms of 95% confidence interval that would be useful for model comparison and discriminant in future studies.
It is critical to correctly assign the kinetics and isotherms of biosorption in order to comprehend the biosorption process of toxicants. Estimating uncertainty of the parameters of the kinetics, which are often displayed as a 95 percent confidence interval range, can be made more challenging by the linearization of a clearly nonlinear curve, which can cause problems on the error structure of the data [4]. Error in the independent variable might also be introduced during data transformation for linearization. In addition, the fitted parameter values for the linear and nonlinear variants of the model can differ due to changes in the weight placed on each data point [5]. In this study the published data from the biosorption of lead (II) onto activated carbon from *Tridas procumbens* [6] is remodeled using nonlinear regression of several isothermal models (Table 1) and the optimal mode was determined by a series of error function assessments. Given that the isotherms in the paper were proposed using a linearized modeling version, this modeling analysis was warranted.

**Table 1.** Isotherm models utilized in this study.

| Model                  | Formula                                      | Ref  |
|------------------------|----------------------------------------------|------|
| Henry’s law            | $q_e = H C_e$                                 | [7]  |
| Langmuir isotherm      | $q_e = \frac{q_m b C_e}{1 + b C_e}$           | [8]  |
| Freundlich isotherm    | $q_e = K F C_e^{1/n}$                         | [9]  |
| Sips isotherm          | $q_e = \frac{K S C_e^{1/n}}{1 + K S C_e}$     | [10] |
| Toth isotherm          | $q_e = \frac{q_m C_e}{1 + K T C_e}$           | [11] |
| BET isotherm           | $q_e = \frac{q_m}{1 + K B T C_e}$             | [12] |
| Baudou isotherm        | $q_e = \frac{q_m b C_e^{1+\alpha}}{1 + b C_e}$ | [13] |
| Fritz-Schlunder-IV isotherm | $q_e = \frac{A F C_e^{1+\gamma}}{1 + H F C_e}$ | [14] |
| Fritz-Schlunder-V isotherm | $q_e = \frac{A F C_e^{1+\gamma}}{1 + H F C_e}$ | [14] |

**METHODS**

**Data acquisition and fitting**

Data from Figure 5a from a published work [6] were digitized using the software WebPlotDigitizer 2.5 [15]. The accuracy of data digitized with this program has been verified [16,17]. The data were first converted to $q_e$ values and then nonlinearly regressed using the curve-fitting software CurveExpert Professional software (Version 1.6).

**Statistical analysis**

Commonly used statistical discriminatory methods such as corrected AICc (Akaikes Information Criterion), Bayesian Information Criterion (BIC), Hannan and Quinn’s Criterion (HQ), Root-Mean-Square Error (RMSE), bias factor (BF), accuracy factor (AF) and adjusted coefficient of determination ($R^2$).

The RMSE was calculated according to Eq. (1). [4], and smaller number of parameters is expected to give a smaller RMSE values. $n$ is the number of experimental data, $O_{\text{b}}$ and $P_{\text{d}}$ are the experimental and predicted data while $p$ is the number of parameters.

$$\text{RMSE} = \sqrt{\frac{\sum (P_{\text{d}} - O_{\text{b}})^2}{n-p}} \quad (\text{Eqn. 1})$$

As $R^2$ or the coefficient of determination ignores the number of parameters in a model, the adjusted $R^2$ is utilized to overcome this issue. In the equation (Eqns. 2 and 3), the total variance of the y-variable is denoted by $S_y^2$ while RMS is the Residual Mean Square.

$$\text{Adjusted } R^2 = 1 - \frac{\text{RMSE}^2}{S_y^2} \quad (\text{Eqn. 2})$$

$$\text{Adjusted } R^2 = 1 - \frac{1 - R^2}{n-p-1} \quad (\text{Eqn. 3})$$

The Akaikes Information Criterion (AIC) is based on the information theory. It balances between the goodness of fit of a particular model and the complexity of a model [18]. To handle data having a high number of parameters or a smaller number of values corrected Akaikes information criterion (AICc) is utilized [19]. The AICc is calculated as follows (Eqn. 4), where $p$ signifies the quantity of parameters and $n$ signify the quantity of data points. A model with a smaller value of AICc is deemed likely more correct [19].

$$\text{AICc} = 2 p + n \ln \left( \frac{\text{RSS}}{n} \right) + 2 \left( \frac{p+1}{n-p-1} \right)$$

Aside from AICc, Bayesian Information Criterion (BIC) (Eqn. 5) is another statistical method that is based on information theory. This error function penalizes the number of parameters more strongly than AIC [20].

$$\text{BIC} = n \ln \left( \frac{\text{RSS}}{n} \right) + k \ln (n) \quad (\text{Eqn. 5})$$

A further error function method based on the information theory is the Hannan–Quinn information criterion (HQc) (Eqn. 6). The HQc is strongly consistent unlike AIC due to the $\ln n$ term in the equation [19];

$$\text{HQc} = n \times \ln \left( \frac{\text{RSS}}{n} \right) + 2 k \ln (n) \quad (\text{Eqn. 6})$$

Further error function analysis that originates from the work of Ross [21] are the Accuracy Factor (AF) and Bias Factor (BF). These error functions test the statistical evaluation of models for the goodness-of-fit but do not penalize for number of parameter (Eqns. 7 and 8).

$$\text{Bias factor} = 10^{\frac{\sum \sqrt{\text{bias}}}{n}} \quad (\text{Eqn. 7})$$

$$\text{Accuracy factor} = 10^{\frac{\sum \sqrt{\text{bias}}}{n}} \quad (\text{Eqn. 8})$$

**RESULTS AND DISCUSSION**

The equilibrium data from [6] was analyzed using nine models—Henry, Langmuir, Freundlich, BET, Toth, Sips, Fritz-Schlunder IV, Baudou and Fritz-Schlunder V, and fitted using non-linear
regression (Figs. 1-9). The Freundlich model performed best in statistical tests including root-mean-square error (RMSE), adjusted coefficient of determination (adjR²), bias factor (BF), accuracy factor (AF), and corrected Akaike Information Criterion (AICc) (Table 2). This is the same to the published work [6] using a linearized form where the Freundlich models best represent the biosorption and the maximum biosorption capacity for the model k_F (Freundlich isotherm constant) is 1.2511 1/g and n_F or the Freundlich exponent value of 3.53. The calculated Freundlich parameters k_F value using nonlinear regression was 1.334 (1/g) (95% confidence interval from 0.821 to 1.847) and n_F value of 3.872 (95% C.I. from 1.972 to 5.771).

Fig. 1. Isotherm of biosorption of lead (II) onto activated carbon from Tridax procumbens as modelled using the Henry model.

Fig. 2. Isotherm of biosorption of lead (II) onto activated carbon from Tridax procumbens as modelled using the Langmuir model.

Fig. 3. Isotherm of biosorption of lead (II) onto activated carbon from Tridax procumbens as modelled using the Freundlich model.

Fig. 4. Isotherm of biosorption of lead (II) onto activated carbon from Tridax procumbens as modelled using the BET model.

Fig. 5. Isotherm of biosorption of lead (II) onto activated carbon from Tridax procumbens as modelled using the Toth model.

Fig. 6. Isotherm of biosorption of lead (II) onto activated carbon from Tridax procumbens as modelled using the Sips model.

Fig. 7. Isotherm of biosorption of lead (II) onto activated carbon from Tridax procumbens as modelled using the Baudu model.
In a Freundlich adsorption isotherm, the adsorbate forms a monomolecular layer on the adsorbent's surface. The Freundlich equation, originally developed to describe adsorption and desorption in the gas phase, is a popular empirical adsorption model. The Freundlich equation is valid up to a certain concentration after which it becomes nonlinear, and while it does provide important information about sorption of particles, it is purely empirical [9,22,23]. The reversible and non-ideal adsorption process is described by the Freundlich adsorption isotherm model. The Freundlich model, in contrast to the Langmuir isotherm model, can be applied to multilayer adsorption. Because of this isotherm model, the adsorption heat and affinities can be unevenly distributed across a heterogeneous surface. The exponential distribution of active sites and their energies, as well as the heterogeneity of the surface, are all defined by the expression of the Freundlich isotherm model. The Freundlich isotherm adsorption model was first created for the adsorption of animal charcoal. This experiment proved that the mass ratio of the adsorbate onto a fixed adsorbent changed depending on the solution concentration. What this means is that the adsorbed amount is the total amount of adsorption at all of the sites. After the more stable binding sites are taken up first, the adsorption energy drops off exponentially [24–26]. The Freundlich model was also the best model for lead(II) sorption by a modified Jordanian zeolite [27], by a Guargum/bentonite biocomposite [28], Chlorococcum aquaticum biomass [29] and nanoparticle adsorbents of cellulose origin [30] and the sorption of other metal and radionuclides [31–36].

**CONCLUSION**

Finally, the biosorption isotherm data for lead (II) onto activated carbon from Tridax procumbens was successfully analyzed using a variety of models with one to five parameters, including the Henry, BET, Langmuir, Freundlich, Toth, Baudu, Sips, Fritz-Schlunder IV, and Fritz-Schlunder V models. The Freundlich model performed best in statistical tests including root-mean-square error (RMSE), adjusted coefficient of determination (adjR²), bias factor (BF), accuracy factor (AF), and corrected Akaike Information Criterion (AICc). The calculated Freundlich parameters k_F value using nonlinear regression was 1.334 (1/g) (95% confidence interval from 0.821 to 1.847) and n value of 3.872 (95% C.I. from 1.972 to 5.771). Nonlinear modeling enables the determination of a 95 percent confidence interval for the uncertainty range, which can be used in model comparison and discriminant analysis.

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