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Isothermal Modelling of the Adsorption of Cadmium onto Activated Carbon from *Tridax procumbens*

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ABSTRACT

There is currently no feasible method of recycling Cd compounds, despite the fact that Cd production, consumption, and environmental release have all skyrocketed in recent decades. This raises serious concerns about the potential dangers of Cd compounds to human health. This highlights the pressing need for cadmium pollution cleanup. Biosorption is one of several viable technologies with several advantages, including low operating costs, very efficient detoxification of toxicants at low concentrations, and a low amount of disposal materials. The biosorption of cadmium 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 (adjR^2), bias factor (BF), accuracy factor (AF), and corrected Akaike Information Criterion (AICc). This is in contrast to the published work using a linearized form where the Langmuir model best represents the biosorption. The calculated Freundlich parameters k_F value using nonlinear regression was 1.501 (1/g) (95% confidence interval from 1.223 to 1.778) and n_F value of 4.943 (95% C.I. from 3.492 to 6.393). Confidence intervals for the uncertainty range can be calculated using nonlinear modeling and then used for model comparison and discriminant analysis.

INTRODUCTION

Cd compounds have seen a dramatic increase in production, consumption, and environmental release over the past few decades, yet no practical method exists for recycling them at present. The results suggest that Cd compounds may be very dangerous to human health. In addition to its use in nickel-cadmium batteries, cadmium has found other applications, including as a plasticizer in PVC and a coloring agent in paint. Additionally, cadmium can be found in many different foods, with levels varying greatly from person to person based on their dietary habits. High cadmium concentrations are largely attributable to human activities like burning fossil fuels, metal ore combustion, and waste burning. Leaking sewage sludge can contaminate agricultural soil with cadmium compounds absorbed by plants, which can then accumulate in various human tissues. Another major contributor to cadmium in the body is secondhand smoke. Researchers discovered that cigarette smokers had 4- to 5-times higher levels of cadmium in their blood than nonsmokers. [1].

Over the past century, numerous pathways of cadmium exposure have been identified. There were reports that workers who were exposed to Cd developed lung damage as early as the 1930s. In the decades that followed, there were also reports of cadmium causing toxicity in the bones and kidneys of some individuals. Pollution levels in postwar Japan fluctuated widely throughout the 1960s and 1970s. Itai-itai was one of these illnesses brought on by the continuous cadmium contamination

of rice fields. An estimated 400 people were infected with the disease between 1910 and 2007 [2,3].

Accurately assigning the kinetics and isotherms of biosorption is crucial for understanding the biosorption process of toxicants. The linearization of a clearly nonlinear curve can lead to issues on the error structure of the data, making it more difficult to estimate the uncertainty of the parameters of the kinetics, which are often displayed as a 95 percent confidence interval range [4]. Linearization of data requires transformation, which can introduce error in the independent variable. Furthermore, the weight assigned to each data point can affect the fitted parameter values for the linear and nonlinear versions of the model [5]. In this study the published data from the biosorption of cadmium onto activated carbon from *Tridax 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	$q_e = HC_e$	[7]
Langmuir isotherm	$q_e = \frac{q_{mL} b_L C_e}{1 + b_L C_e}$	[8]
Freundlich isotherm	$q_e = K_F C_e^{\frac{1}{n_F}}$	[9]
Sips isotherm	$q_e = \frac{K_s q_{mS} C_e^{\frac{1}{n_S}}}{1 + K_s C_e^{\frac{1}{n_S}}}$	[10]
Toth isotherm	$q_e = \frac{q_{mT} C_e}{\left(K_T + C_e^{n_T}\right)^{n_T}}$	[11]
BET isotherm	$q_e = \frac{q_{mBET} \alpha_{BET} C_e}{(1 - \beta_{BET} C_e)(1 - \beta_{BET} C_e + \alpha_{BET} C_e)}$	[12]
Baudu isotherm	$q_e = \frac{q_{mB} b_B C_e^{(1+x+y)}}{1 + b_B C_e^{(1+x)}}$	[13]
Fritz-Schlunder-IV isotherm	$q_e = \frac{A_{FS} C_e^{a_{FS}}}{1 + B_{FS} C_e^{b_{FS}}}$	[14]
Fritz-Schlunder-V isotherm	$q_e = \frac{q_{mFS5} K_1 C_e^{\alpha_{FS}}}{1 + K_2 C_e^{\beta_{FS}}}$	[14]

METHODS

Data acquisition and fitting

Data from **Figure 6a** 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_t 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 (Akaike 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, Ob_i and Pd_i are the experimental and predicted data while p is the number of parameters.

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n} (Pd_i - Ob_i)^2}{n - p}} \qquad \text{(Eqn. 1)}$$

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.

$$Adjusted\left(R^2\right) = 1 - \frac{RMS}{s_Y^2} \qquad \text{(Eqn. 2)}$$

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

The Akaike 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 Akaike 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].

$$AICc = 2p + n\ln\left(\frac{RSS}{n}\right) + 2(p+1) + \frac{2(p+1)(p+2)}{n-p-2} \qquad \text{(Eqn. 4)}$$

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].

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

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 ln n term in the equation [19];

$$HQC = n \times ln\frac{RSS}{n} + 2 \times k \times ln(\ln n) \qquad \text{(Eqn. 6)}$$

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**).

$$\text{Bias factor} = 10^{\left\{\sum_{i=1}^{n} \log\frac{(Pd_i / Ob_i)}{n}\right\}} \qquad \text{(Eqn. 7)}$$

$$\text{Accuracy factor} = 10^{\left\{\sum_{i=1}^{n} \log\frac{\left|(Pd_i / Ob_i)\right|}{n}\right\}} \qquad \text{(Eqn. 8)}$$

RESULTS AND DISCUSSION

The equilibrium data for cadmium sorption from a published work [6] was analyzed using nine models—Henry, Langmuir, Freundlich, BET, Toth, Sips, Fritz-Schlunder IV, Baudu 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 (adjR^2), bias factor (BF), accuracy factor (AF), and corrected Akaike Information Criterion (AICc) (**Table 2**). This is in contrast to the published work [6] using a linearized form where the Langmuir model best represents the biosorption. The maximum biosorption capacity for the Freundlich model for cadmium sorption as reported in the original work is k_F (Freundlich isotherm constant) value of 1.3286 1/g and n_F or the Freundlich exponent value of 4.06. In this study, the calculated Freundlich parameters k_F value using nonlinear regression was 1.501 (1/g) (95% confidence interval from 1.223 to 1.778) and n_F value of 4.943 (95% C.I. from 3.492 to 6.393).

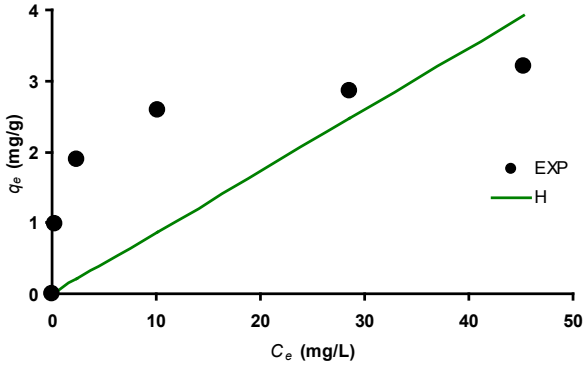

Fig. 1. Isotherm of biosorption of cadmium onto activated carbon from *Tridax procumbens* as modelled using the Henry model.

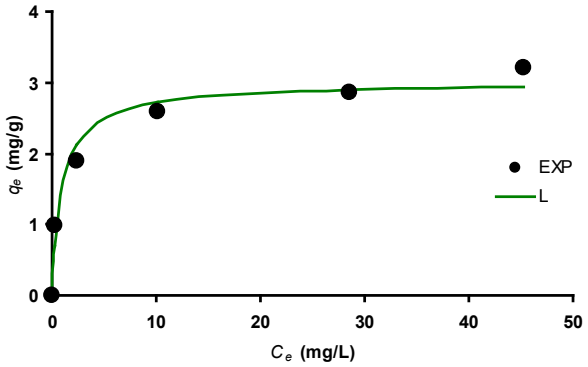

Fig. 2. Isotherm of biosorption of cadmium onto activated carbon from *Tridax procumbens* as modelled using the Langmuir model.

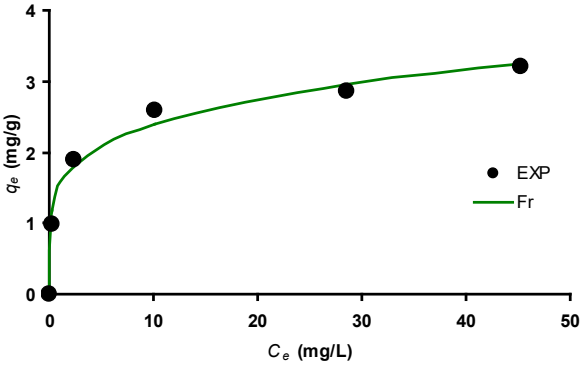

Fig. 3. Isotherm of biosorption of cadmium onto activated carbon from *Tridax procumbens* as modelled using the Freundlich model.

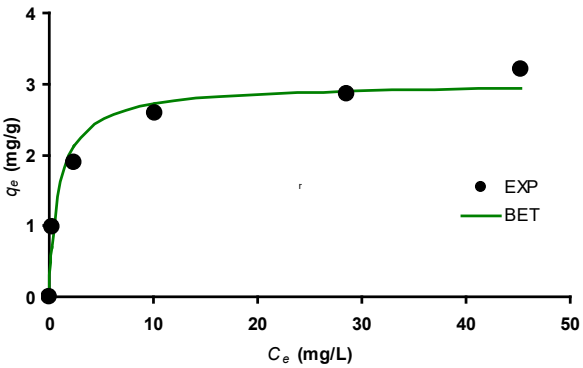

Fig. 4. Isotherm of biosorption of cadmium onto activated carbon from *Tridax procumbens* as modelled using the BET model.

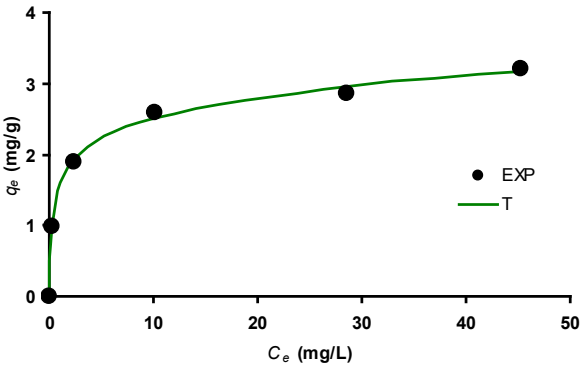

Fig. 5. Isotherm of biosorption of cadmium onto activated carbon from *Tridax procumbens* as modelled using the Toth model.

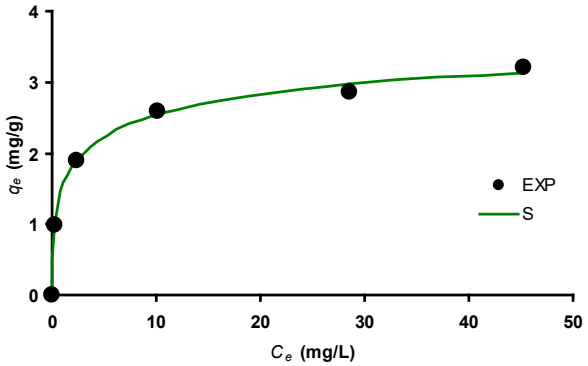

Fig. 6. Isotherm of biosorption of cadmium onto activated carbon from *Tridax procumbens* as modelled using the Sips model.

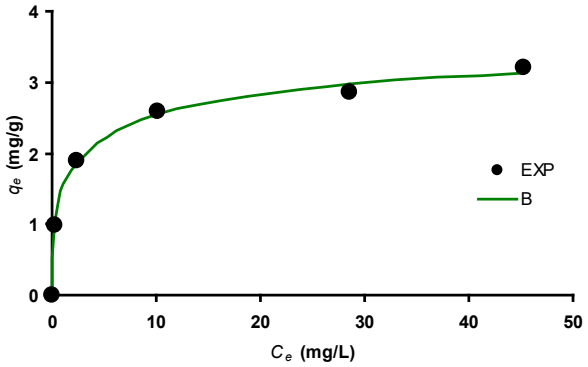

Fig. 7. Isotherm of biosorption of cadmium onto activated carbon from *Tridax procumbens* as modelled using the Baudu model.

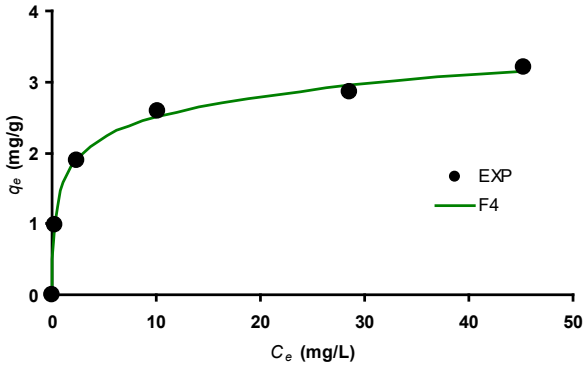

Fig. 8. Isotherm of biosorption of cadmium onto activated carbon from *Tridax procumbens* as modelled using the Fritz-Schlunder-IV model.

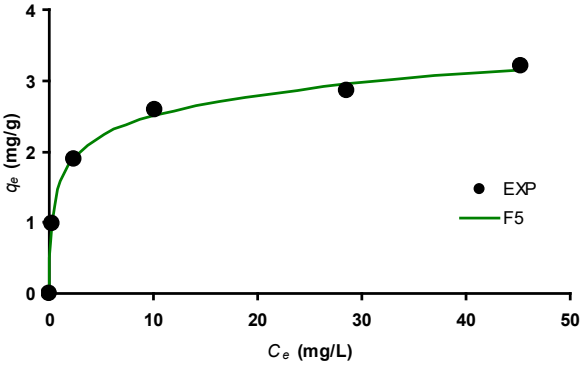

Fig. 9. Isotherm of biosorption of cadmium onto activated carbon from *Tridax procumbens* as modelled using the Fritz-Schlunder-V model.

Table 2. Error function analysis for the fitting of the isotherms of cadmium onto activated carbon from *Tridax procumbens* .

Model	*p*	RMSE	adR2	AICc	BIC	HQC	BF	AF
Henry	1	1.21	0.29	11.22	3.01	2.39	0.32	3.36
Langmuir	2	0.25	0.95	2.72	-15.70	-16.95	0.96	1.11
Freundlich	2	0.15	0.98	-3.25	-21.66	-22.92	1.01	1.06
BET	3	0.28	0.92	34.72	-13.91	-15.78	0.96	1.11
Toth	3	0.08	0.99	18.89	-29.74	-31.61	1.00	1.02
Sips	3	0.08	0.99	19.87	-28.75	-30.63	1.00	1.02
Baudu	4	0.11	0.98	n.a.	-25.49	-27.99	1.00	1.02
F4	4	0.09	0.99	n.a.	-28.12	-30.62	1.00	1.01
F5	5	0.13	n.a.	-97.28	-26.32	-29.45	1.00	1.01

Note:
RMSE Root mean Square Error
p no of parameters
adR^2 Adjusted Coefficient of determination
BF Bias factor
AF Accuracy factor
AICc Adjusted Akaike Information Criterion
BIC Bayesian Information Criterion
HQC Hannan–Quinn information criterion
n.a. Not available

The adsorbate forms a monomolecular layer on the adsorbent's surface in a Freundlich adsorption isotherm. An example of an empirical adsorption model is the Freundlich equation, which was initially developed to describe gas-phase adsorption and desorption. Although the Freundlich equation is useful for calculating the sorption of particles, its use is limited by the fact that it is only valid up to a certain concentration and then becomes nonlinear [9,22,23]. The Freundlich adsorption isotherm model describes the reversible and non-ideal adsorption process. Although the Langmuir isotherm cannot be extended to multilayer adsorption, the Freundlich model can. It is possible for the adsorption heat and affinities to be unevenly distributed across a heterogeneous surface using this isotherm model. The expression of the Freundlich isotherm model defines the exponential distribution of active sites and their energies, as well as the heterogeneity of the surface.

The adsorption of animal charcoal was the original application of the Freundlich isotherm model. The results of this experiment demonstrated that the mass ratio of the adsorbate onto a constant adsorbent varied with the concentration of the solution. In other words, the sum of the amounts adsorbed at all of the sites is the amount that has been adsorbed. Adsorption energy decreases exponentially after the strongest bonds are formed [24–26]. The Freundlich model was also the best model for lead(II) sorption by a modified Jordanian zeolite [27], by a Guar gum/bentonite bionanocomposite [28], *Chlorococcum aquaticum* biomass [29] and nanoparticle adsorbents of cellulose origin [30] and the sorption of other metal and radionuclides [31–36].

CONCLUSION

Conclusively, a variety of one-to-five-parameter models, including the Henry, Langmuir, Freundlich, BET, Sips, Toth, Baudu, Fritz-Schlunder IV, and Fritz-Schlunder V models, were successfully applied to the biosorption isotherm data for cadmium onto activated carbon from *Tridax procumbens*. The Freundlich model performed best in statistical tests including root-mean-square error (RMSE), adjusted coefficient of determination (adjR^2), bias factor (BF), accuracy factor (AF), and corrected Akaike Information Criterion (AICc). This is in contrast to the published work using a linearized form where the Langmuir model best represents the biosorption. The calculated Freundlich parameters k_F value using nonlinear regression was 1.501 (1/g) (95% confidence interval from 1.223 to 1.778) and n_F value of 4.943 (95% C.I. from 3.492 to 6.393). Confidence intervals for the uncertainty range can be calculated using nonlinear modeling and then used for model comparison and discriminant analysis.

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