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Kinetic Analysis of the Adsorption of Cadmium onto Activated Carbon from Tridax procumbens

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ABSTRACT

While Cd production, consumption, and environmental release have all skyrocketed in recent decades, there is currently no practical way to recycle Cd compounds. This suggests that Cd compounds may be very dangerous to human health. Due to this cadmium remediation from polluted environment is urgently needed. Several viable technologies include biosorption, which has several positive aspects which include low operating expenses, very efficient detoxification of toxicants at low concentrations and low amount of disposal materials. The biosorption of the biosorption of cadmium onto the activated carbon from Tridax procumbens is remodeled using nonlinear regression and the optimal mode was determined by a series of error function assessments. Statistical analysis showed that the best kinetic model for adsorption was pseudo-1st order. All error function analyses supported the pseudo-1st order model. The pseudo-1st order kinetic constants obtained were $q_e (mg/g)$ of 5.808 (95% confidence interval from 5.043 to 6.573) and k₁ (per min) of 0.009 (95% confidence interval from 0.0064 to 0.0117). 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.

INTRODUCTION

There is currently no viable method for recycling Cd compounds, despite their dramatic increase in production, consumption, and environmental release over the past few decades. Accordingly, it appears that Cd compounds may pose a significant health risk to humans. The cadmium in a nickel-cadmium battery can also be used to make polyvinyl chloride plastic and as a pigment in paint. In addition, cadmium can be found in a wide variety of foods, with levels varying greatly from person to person based on their eating habits. Human activities like burning fossil fuels, metal ore combustion, and waste burning contribute significantly to the high cadmium concentrations found in the environment. Cadmium compounds adsorbed by plants may be transferred from leaking sewage sludge to agricultural soil, where they can accumulate in different parts of humans' bodies. Cigarette smoke is another significant source of cadmium exposure. Blood

cadmium levels were found to be 4- to 5-times higher in smokers compared to non-smokers [1]. Several sources of cadmium exposure have been documented over the past one hundred years. As early as the 1930s, reports surfaced indicating that workers exposed to Cd experienced lung damage. Some cases of cadmium-related bone and kidney toxicity were also reported in the succeeding decades. Post-war Japan experienced varying degrees of pollution throughout the 1960s and 1970s. One of these diseases was Itai-itai, which was brought on by the persistent cadmium contamination of rice fields. From 1910 to 2007, a total of about 400 people were thought to have contracted the illness [2,3].

To fully grasp the biosorption process of toxicants, it is crucial to correctly assign the kinetics and isotherms of biosorption. 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]. During the process of data transformation required for linearization, error in the independent variable may also be introduced. Weighting of data points can also 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 the activated carbon from *Tridax procumbens* [6] is remodeled using nonlinear regression of several kinetic models (**Table 1**) and in the end, a series of error function evaluations identified the best possible setting. Because a linearized modeling version was proposed for the kinetics in the aforementioned publication, this modeling analysis was required.

Table 1. Kinetic models and equation utilized in this study.

Model	Equation	Reference
Pseudo-1st order	$q_t = q_e (1 - e^{-K_{1t}})$	[7]
Pseudo-2nd order	$K_2 q_e^2 t$	[8]
	$q_t = \frac{1}{(1 + K_2 q_e t)}$	
h value	$h = K_2 q_e^2$	[8]
Elovich	1 1	[9]
	$q_t = \frac{1}{\beta \ln \alpha \beta} + \frac{1}{\beta \ln t}$	

METHODS

Data acquisition and fitting

Data from Figure 3 from a published work [6] were digitized using the software Webplotdigitizer 2.5 [10]. The accuracy of data digitized with this program has been verified [11,12]. 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.

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n} (Pd_i - Ob_i)^2}{n - p}}$$
(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 $s_y^{y^2}$ while RMS is the Residual Mean Square.

$$Adjusted (R2) = 1 - \frac{RMS}{s_r^2}$$
(Eqn. 2)

$$Adjusted (R2) = 1 - \frac{(1-R^2)(n-1)}{(n-p-1)}$$
(Eqn. 3)

When it comes to evaluating data, the Akaike Information Criterion (AIC) uses principles from the field of information theory. It strikes a balance between a model's complexity and its goodness of fit [13]. To handle data having a high number of parameters or a smaller number of values corrected Akaike information criterion (AICc) is utilized [14]. 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 [14].

$$AICc=2p+n\ln\left(\frac{RSS}{n}\right)+2(p+1)+\frac{2(p+1)(p+2)}{n-p-2}$$
 (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 [15].

$$BIC = n.\ln\frac{RSS}{r} + k.\ln(n)$$
 (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 [14];

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

Further error function analysis that originates from the work of Ross [16] 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**).

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

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

RESULTS AND DISCUSSION

The absorption kinetics data of biosorption isotherm experiment from a published work [6] on the biosorption of cadmium on the activated carbon from *Tridax procumbens* were analyzed using three models—pseudo-1st, pseudo-2nd and Elovich, and fitted using non-linear regression. The Elovich model was the poorest in fitting the curve based on visual observation (**Figs. 1-6**). The optimal model was determined through the application of statistical analysis based on the root-mean-square error (RMSE), adjusted coefficient of determination (adjR2), accuracy factor (AF), bias factor (BF), Bayesian Information Criterion (BIC), corrected Akaike Information Criterion (AICc), and Hannan– Quinn information criterion (HQC).



Fig. 1. Kinetics of on the biosorption of cadmium onto activated carbon from *Tridax procumbens* modelled using the Elovich model.



Fig. 2. Kinetics of on the biosorption of cadmium onto activated carbon from *Tridax procumbens* modelled using the pseudo-1st order model.



Fig. 3. Kinetics of on the biosorption of cadmium onto activated carbon from *Tridax procumbens* modelled using the pseudo-2nd order model.

The best kinetic model for adsorption of cadmium was Pseudo-1st with a reasonable difference in terms of corrected Akaike Information Criterion to the next best model, which was pseudo-2nd order, and the worst model was Elovich (**Table 2**). The error function analyses supported the pseudo-1st order model. The kinetic constants for all of the models are shown in **Table 3**. The *h* value, (mg/g.min) utilized to calculate the initial adsorption rate constant indicates the driving force to accelerate the diffusion of adsorbate from solution onto the adsorbent [17].

Table 2. Error function analysis for the kinetic models.

Model	р	RMSE	R^2	adR^2	AICc	BIC	HQC	AF	BF
Pseudo-1st order	2	0.196	0.989	0.985	-16.80	-27.21	-28.45	1.036	1.005
Pseudo-2nd order	2	0.226	0.985	0.980	-14.21	-24.62	-25.86	1.046	1.009
Elovich	2	0.244	0.983	0.978	-12.88	-23.29	-24.54	1.060	0.997

Note:

RMSE Root mean Square Error

p no of parameters adR² Adjusted Coefficient of determination

BF Bias factor

AF Accuracy factor

AICc Adjusted Akaike Information Criterion

BIC Bayesian Information Criterion

HQC Hannan-Quinn information criterion

Table 3. Calculated constants for the kinetics models fitting the biosorption of cadmium onto activated carbon from *Tridax procumbens*.

Model		(95%, C.I.)	
Pseudo-1st			
k1 (per min)	0.009	0.0064 to 0.0117	
$q_e (\mathrm{mg/g})$	5.808	5.043 to 6.573	
Pseudo-2nd			
k2 (g/mg/min)	0.001	0.00025 to 0.0014	
$q_e (mg/g)$	8.347	6.429 to 10.265	
h (mg/g.min)	0.106	0.063 to 0.160	
Elovich			
Alpha (mg/g.min)	0.121	0.095 to 0.147	
Beta (g/mg)	0.528	0.431 to 0.624	

Through the use of kinetic models, researchers have been able to analyze experimental data and gain insight into the sorption mechanism and potential rate controlling steps, such as chemical reaction and mass transport processes. These kinetic models incorporated not only the Elovich equation but also the pseudo-1st order and pseudo-2nd order equations. The initial adsorption rate (in mg/g min) and the surface coverage (in g/mg) are given by and respectively in the Elovich model. In the pseudo-1st order reaction, the adsorbate concentration is maintained at a constant saturation value.

The adsorbate is adsorbed at a constant rate because its level is independent of the adsorbate concentration. Under the control of film diffusion, the rate is inversely proportional to the particle size, the distribution coefficient, and the film thickness. The ratelimiting step here is diffusion, which is not concentration or reactant-dependent, so we call it physisorption (physical exchange) [18-22]. If the reaction is governed by a pseudo-2nd order reaction, then chemisorption occurs because a chemical reaction is in charge of the rate-controlling step. When the sorbate to sorbent ratio is small, the sorption kinetics is similar to a reversible second order reaction, while when it is larger, two competitive reversible second order reactions take place [23]. However, additional proofs, such as evaluation results of the activation energies via experiment repetition at different temperatures and checking the process rates dependences to the sizes of the adsorbent particle, should be provided to confirm the mechanism is a chemisorption [24].

The pseudo-1st order model has also been reported to be the best model for cadmium sorption onto nano-clay/TiO2 composite [25], coco-peat biomass [26], alginate-calcium carbonate composite beads [27], poly(acrylamide-co-sodium methacrylate) hydrogels [28], the bacterium, Salmonella enterica 43C [29], water hyacinth (Eichhornia crassipes) biochar alginate beads [30], zerovalent iron nanoparticles [31] and Mactra aequisulcata shells [32]. On the other hand, the pseudo-2nd order kinetics model has been reported to be the best model in several other cadmium sorption studies such as sorption of cadmium onto C-4-phenacyloxy-phenylcalix[4], resorcinarene [33], modified palm shell powder [34], chemically modified biomass from Triticum aestivum [35] and several other heavy metals such as the biosorption of Cr(VI) to magnetic iron oxide nanoparticlemulti-walled carbon nanotube [36], Cu(II) adsorption onto functionalized cellulose beads from Tunisian almond (Prunus dulcis) shell [37], the sorption of Zn(II) by Streptomyces ciscaucasicus [38] and other heavy metals [23,39-43].

CONCLUSION

In conclusion, the biosorption of the biosorption of cadmium onto activated carbon from *Tridax procumbens* was successfully modelled using three models—pseudo-1st, pseudo-2nd and Elovich, and fitted using non-linear regression. Statistical analysis showed that the best kinetic model for adsorption was pseudo-1st order. The pseudo-1st order kinetic constants obtained were q_e (mg/g) of 5.808 (95% confidence interval from 5.043 to 6.573) and k_1 (per min) of 0.009 (95% confidence interval from 0.0064 to 0.0117). 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.

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