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Isothermal Modelling on the Removal of Copper Using *Durvillaea* antarctica

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ABSTRACT

Heavy metals pollution in the Antarctica is emerging as an important problem due to anthropogenic activities. Bioremediation of metal pollution especially copper in Antarctica in the future using biosorption is the most environmental-friendly method. Biosorption using *Durvillaea antarctica*, an alga that lives in the Antarctic region does not involve the introduction of new potentially foreign species. In this study, the isotherms of copper biosorption by the alga is modelled according to various models ranging from one to five parameters models such as Henry, Langmuir, Dubinin-Radushkevich, Freundlich, BET, Toth, Sips, Fritz-Schlunder IV, Baudu and Fritz-Schlunder V. All gave visually acceptable fitting with the exception of the Henry model. Statistical analysis based on root-mean-square error (RMSE), adjusted coefficient of determination $(adjR^2)$, bias factor (BF), accuracy factor (AF) and corrected AICc (Akaike Information Criterion) showed that the Sips model is the best model. The calculated Sips parameters k_S value of 12.52 (95% confidence interval from 3.593 to 21.439), q_{mS} value of 0.97 (95% confidence interval from 0.531 to 0.806).

INTRODUCTION

Copper (Cu) is abundant in the surroundings and required for the conventional growth and metabolic process of most living creatures. Irregular quantities of copper ingestion may range between quantities so little as to stimulate a dietary insufficiency to quantities excessive they can be extremely harmful. Copper is one of the first metals labored by people some seventy to eighty centuries in the past [1]. The first recognized item of hammered copper was discovered approximately 6000 BCE. The copper alloy brass originated in Roman periods. Copper stems from the Latin cuprum, which is a corruption of cyprium, Cyprus is the source of Egyptian and Roman copper [1]. The metabolic significance of copper in animals and plants had not been thought prior to the 1920's when illnesses as a result of copper insufficiency turned to be acknowledged. Copper insufficiency vertebrates, for instance, is associated to anemia, in gastrointestinal disorder, aortic aneurisms, bone development irregularities, and death [2].

Toxicity to copper in terrestrial higher plants is uncommon but happens on mining areas and instances where copper-rich manures or fungicides are utilized exceedingly [3]. Copper is considered the most dangerous of the heavy metals in marine and freshwater ecology, and frequently builds up and results in irreparable damage to some species at levels merely over the quantities needed for growth and reproduction [4]. On the other hand, in comparison with lower forms, mammalians and birds are relatively not affected to copper [1].

Copper pollution in the recent years has only just began to take centre stage with several reports studying the effect of copper exposure to Antarctic organisms [5,6]. In anticipation of a copper pollution in the future in the Arctic and Antarctica, several remediation approach has been suggested with biosorption being one of the least destructive [7,8].

In order to understand the mechanism of biosorption in these organisms, the correct assignment of the kinetics and isotherms of biosorption is urgently needed. In many instances, a linearized from of an obviously nonlinear curve of these data is popularly reported in the literature. Linearization of nonlinear data disrupts the error structure of the data preventing and it is more difficult to estimate uncertainty, which is commonly shown in the form of a 95% confidence interval range [9]. In this study the published data from a copper biosorption experiment on the seaweed Durvillaea antarctica [7] is remodeled with several more isotherms models (Table 1) and then regressed using nonlinear regression method and assessment of the best mode was carried out using various error function analysis.

Table 1. Isotherm models utilized in this study.

	Model	Formula	References							
Single-parameter model										
1	Henry's law	$q_e = HC_e$	[10]							
2	Langmuir isotherm	Two-parameter models $q_e = \frac{q_{mL}b_LC_e}{1+b_LC_e}$	[11]							
3	Freundlich isotherm	$q_e = K_F C_e^{\frac{1}{n_F}}$	[12]							
4	Dubinin- Radushkevich	$q_e = q_{mDR} exp \left\{ -K_{DR} \left[RTln \left(1 \right) \right] \right\}$	[13,14]							
5	Sips isotherm	$+\frac{1}{C_e}\Big]\Big]^2\Big\}$ Three-parameter models $q_e = \frac{K_s q_{mS} C_e^{\frac{1}{n_s}}}{\frac{1}{m_s}}$	[15]							
6	Toth isotherm	$q_{e} = \frac{\frac{1 + K_{s}C_{e}^{n_{s}}}{q_{mT}C_{e}}}{(K_{r} + C_{e}^{n_{T}})^{n_{T}}}$	[16]							
7	Bet isotherm	$\begin{aligned} q_e & \\ = \frac{q_{mBET} \alpha_{BET} C_e}{(1 - \beta_{BET} C_e)(1 - \beta_{BET} C_e + \alpha_{BET} C_e)} \end{aligned}$	[17]							
Four-parameter models										
8	Baudu isotherm	$q_{e} = \frac{q_{mB}b_{B}C_{e}^{(1+x+y)}}{1+b_{D}C_{e}^{(1+x)}}$	[18]							
9	Fritz-	$A_{FC}C_{e}^{a_{FS}}$	[19]							

Schlunder-IV
isotherm
$$\begin{array}{c}
q_e = \frac{1}{1 + B_{FS}C_e^{B_{FS}}} \\
Five-parameter models \\
\text{Five-parameter models} \\
10 \ \text{Fritz-} \\
\text{Schlunder-V} \\
\text{isotherm} \\
q_e = \frac{q_{mFSS}K_1C_e^{\alpha_{FS}}}{1 + K_2C_e^{\beta_{FS}}} \\
\end{array}$$
[19]

MATERIALS AND METHODS

Data acquisition and fitting

Schlunder-IV

Data from Figure 3 from a published work [7] were downloaded and processed using the software Webplotdigitizer 2.5 [20] which digitizes the scanned figure into a comma separated data. This method has been utilized by many researchers and acknowledged for its reliability [21,22]. The generated comma separated data were then inputted into the curve-fitting software CurveExpert Professional software (Version 1.6) utilizing the Marquardt algorithm.

Statistical analysis

In several instances, the F-test has been used as a discriminatory method to choose the best model. However, F-test only works for nested models [9]. Due to this, other statistical discriminatory methods that take into account penalty to number of parameters used were utilized and include corrected AICc (Akaike Information Criterion), 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. (i), [9], 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.

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

The coefficient of determination or R^2 does not take into account the number of parameters in models, hence, in order to solve this issue, the adjusted R^2 is utilized. the total variance of the y-variable is denoted by S_y^2 is and RMS is the Residual Mean Square (Eqns. ii and iii).

$$Adjusted\left(R^{2}\right) = 1 - \frac{RMS}{s_{Y}^{2}}$$
(ii)

Adjusted
$$(R^2) = 1 - \frac{(1 - R^2)(n - 1)}{(n - p - 1)}$$
 (iii)

The Akaike Information Criterion (AIC) handles the tradeoff between the goodness of fit and the complexity of a model and is based on the information theory [23]. The Akaike information criterion (AIC) with correction or AICc is a corrected version of the AIC, and is utilized to handle data with a smaller number of values or a high number of parameters [24]. The AICc is calculated as follows (Eqn. iv);

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

Where p signifies the quantity of parameters and n signify the quantity of data points. The model having the smallest AICc value is more likely correct [24].

Accuracy Factor (AF) and Bias Factor (BF) are statistical evaluation of models originating from the work of Ross [25] to test for the goodness-of-fit of the models and were calculated (Eqns. v and vi) as follows;

Bias factor =
$$10^{\left(\sum_{i=1}^{n} \log \frac{(Pd_i/Ob_i)}{n}\right)}$$
 (v)
Accuracy factor = $10^{\left(\sum_{i=1}^{n} \log \frac{(Pd_i/Ob_i)}{n}\right)}$ (vi)

RESULTS AND DISCUSSION

The equilibrium data of a biosorption isotherm experiment from a published work [7] on the biosorption of copper by D. *antarctica* were analyzed using ten models—Henry, Langmuir, Dubinin-Radushkevich, Freundlich, BET, Toth, Sips, Fritz-Schlunder IV, Baudu and Fritz-Schlunder V, and fitted using non-linear regression. The results of the fitting were visually acceptable (Figs. 2-10) with the exception of the one-parameter Henry model (Fig. 1). Statistical analysis based on root-meansquare error (RMSE), adjusted coefficient of determination $(adjR^2)$, bias factor (BF), accuracy factor (AF) and corrected AICc (Akaike Information Criterion) showed that the Sips model

is the best model (**Table 2**). This is contrast with the published work using linearized form that shows that the best model was the Dubinin–Radushkevish model. The results from the published work will definitely be improved if a nonlinearized data is used instead of a linearized form as the latter tends to exhibit problem in data structure and it is more difficult to estimate uncertainty, which is commonly shown in the form of a 95% confidence interval range [9]. The calculated Sips parameters were k_S value of 12.52 (95% confidence interval from 3.593 to 21.439), q_{mS} value of 0.97 (95% confidence interval from 0.905 to 1.026) and n_S value of 0.67 (95% confidence interval from 0.531 to 0.806).



Fig. 1. Biosorption isotherm of Cu (II) on *D. antarctica* dead biomass at pH 5.0 as modelled using the Henry model.



Fig. 2. Biosorption isotherm of Cu (II) on *D. antarctica* dead biomass at pH 5.0 as modelled using the Langmuir model.



Fig. 3. Biosorption isotherm of Cu (II) on *D. antarctica* dead biomass at pH 5.0 as modelled using the Dubinin-Radushkevich model.



Fig. 4. Biosorption isotherm of Cu (II) on *D. antarctica* dead biomass at pH 5.0 as modelled using the Freundlich model.



Fig. 5. Biosorption isotherm of Cu (II) on *D. antarctica* dead biomass at pH 5.0 as modelled using the BET model.



Fig. 6. Biosorption isotherm of Cu (II) on *D. antarctica* dead biomass at pH 5.0 as modelled using the Toth model.



Fig. 7. Biosorption isotherm of Cu (II) on *D. antarctica* dead biomass at pH 5.0 as modelled using the Sips model.



Fig. 8. Biosorption isotherm of Cu (II) on *D. antarctica* dead biomass at pH 5.0 as modelled using the Fritz-Schlunder IV model.



Fig. 9. Biosorption isotherm of Cu (II) on *D. antarctica* dead biomass at pH 5.0 as modelled using the Baudu model.



Fig. 10. Biosorption isotherm of Cu (II) on *D. antarctica* dead biomass at pH 5.0 as modelled using the Fritz-Schlunder V model.

Table 2. Error function analysis of all isotherms.

Model	р	RMSE	adR^2	AICc	BF	AF
Henry	1	0.33	0.36	-13.09	0.36	2.92
Langmuir	2	0.06	0.97	-38.36	1.30	1.37
Dubinin-Radushkevich		0.06	0.97	-38.82	1.36	1.36
Freundlich	2	0.15	0.79	-21.91	1.42	1.64
Bet	3	0.05	0.98	-32.79	1.26	1.33
Toth	3	0.05	0.98	-34.59	1.25	1.31
Sips	3	0.03	0.99	-43.35	1.15	1.19
Fritz-Schlunder IV	4	0.03	0.99	-30.88	1.11	1.15
Baudu	4	0.03	0.99	-30.88	1.11	1.15
Fritz-Schlunder V		0.03	0.99	-4.88	1.11	1.15

The Sips model is a combination of the Langmuir and Freundlich isotherms useful for predicting the heterogeneous adsorption systems. This model triumphs over the drawback to problem in modelling increasing solute concentration associated with the Freundlich isotherm. The model efficiently reduces to the Freundlich isotherm at low solute concentrations, while at excessive solute concentrations, the equation reduces to the Langmuir model of monolayer sorption capacity [26]. The Sips model has been successfully used to model numerous isothermal data of biosorption [27–32].

CONCLUSION

In conclusion, extensive modelling of a nonlinearized data shows a different best model compared to the original linearized data regression. The Sips model was found to be the best model based on extensive error function analysis as opposed to the original Dubinin–Radushkevish model. This difference can lead to a different interpretation of the mechanism of adsorption.

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