

Mathematical Isothermal Modeling of Remazol Black B Biosorption by *Aspergillus flavus*

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ABSTRACT

Azo dyes, like Remazol Black B, form covalent bonds with textile fibers like cotton, setting them apart from traditional dyes. Due to their advantageous qualities of vivid color, water resistance, straightforward application processes, and low energy consumption, they are widely used in the textile industry. Major environmental effects of their discharge into receiving streams include reduced photosynthesis in aquatic life as a result of decreased light penetration. Seven isotherm models—Henry, Langmuir, Freundlich, BET, Toth, Fritz-Schlunder IV, and Fritz-Schlunder V—were used to analyze the biosorption isotherm data of Remazol Black B dye biosorption by *Aspergillus flavus* and were fitted using non-linear regression. Based on statistical analysis, the Fritz-Schlunder IV was determined to be the best model using root-mean-square error (RMSE), adjusted coefficient of determination ($\text{adj}R^2$), bias factor (BF), accuracy factor (AF), corrected AICc (Akaike Information Criterion), Bayesian Information Criterion (BIC), and Hannan-Quinn information criterion (HQC). The calculated Fritz-Schlunder IV parameter, b_{FS} value was found to be 3.812 mg/g (95% confidence interval of 0.312 to 7.311) and qm_{FS} value of 0.0224 (95% confidence interval of -21725.002 to 21725.047).

INTRODUCTION

Dyes are complex organic compounds that are used to color various products in various industries. Natural and synthetic dyes are compounds of great interest because they play an important role in our daily lives. A wide range of technical and industrial applications for dyeing or printing textiles, paper, leather, and other materials. Some of these dyes are toxic, carcinogenic, and can cause skin and eye irritation [1]. Azo dyes, like Remazol Black B, form covalent bonds with textile fibers like cotton, setting them apart from traditional dyes. Due to their advantageous qualities of vivid color, water resistance, straightforward application processes, and low energy consumption, they are widely used in the textile industry [2]. Understanding the mechanism of biosorption of Remazol Black B dye requires the study of isotherms. The application of linearization to a nonlinear curve disrupts the error structure of the data. This complicates estimating the uncertainty of isotherm parameters, which are commonly displayed as a 95 percent

confidence interval range [3]. Additionally, it is possible to alter the weights given to each data point, which typically yields different fitted parameter values for the linear and nonlinear isotherm models [4]. This study remodeled the published data from biosorption of Remazol Black B dye (azo dye) by growing *Aspergillus flavus* [5] using various isotherm models, then regressed using a nonlinear regression approach, and the best model was selected using various error function analyses. The reason for this modeling analysis is that the isotherms were not modeled in the original paper.

MATERIALS AND METHODS

Data Acquisition and Fitting

The software Webplotdigitizer, version 2.5 [6] was used to digitize data from **Figure 6** from a published work [5]. Many researchers have used and recognized the accuracy of digitization using this software [6-9]. The data was then nonlinearly

regressed using multiple models in the curve-fitting software CurveExpert Professional, Version 2.6.5. (Table 1).

Table 1. Isotherm models employed in this study

Model	Formula	Ref
1 Henry	$q_e = HC_e$	[10]
2 Langmuir	$q_e = \frac{q_{mL}b_L C_e}{1 + b_L C_e}$	[11]
3 Freundlich	$q_e = K_F C_e^{\frac{1}{n_F}}$	[12]
4 BET	$q_e = \frac{q_{mBET}\alpha_{BET}C_e}{(1 - \beta_{BET}C_e)(1 - \beta_{BET}C_e + \alpha_{BET})}$	[13]
5 Toth	$q_e = \frac{q_{mT}C_e}{(K_T + C_e^{n_T})^{1/n_T}}$	[14]
6 Fritz-Schlunder IV	$q_e = \frac{A_{FS}C_e^{b_{FS}}}{1 + B_{FS}C_e^{b_{FS}}}$	[15]
7 Fritz-Schlunder V	$q_e = \frac{q_{mFS}K_1 C_e^{\alpha_{FS}}}{1 + K_2 C_e^{\beta_{FS}}}$	[15]

Statistical Analysis

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 are examples of commonly used statistical discriminatory methods (R^2). The RMSE was calculated using equation (1) below [16] and it is expected that a smaller number of factors will result in a lower RMSE value. The number of experimental data is n , the experimental and projected data are Ob_i and Pd_i , and the number of parameters is p .

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

Because R^2 or the coefficient of determination ignores the number of parameters in a model, the adjusted R^2 is used to overcome this limitation. The total variance of the y-variable is denoted by S_y^2 in the equation (Eqns. 2 and 3), and RMS is the Residual Mean Square.

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

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

The Akaike Information Criterion (AIC) is based on information theory. It strikes a balance between the goodness of fit of a model and its complexity [17]. To handle data with a large number of parameters or a small number of values, the corrected Akaike information criterion (AICc) is used [18]. The following equation (Eqn. 4) is used to calculate the AICc, where p denotes the number of parameters and n denotes the number of data points. A model is considered more likely to be accurate if its AICc value is lower [17].

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

In addition to AICc, another statistical approach based on information theory is the Bayesian Information Criterion (BIC) (Eqn. 5). Compared to AICc, this error function penalizes the number of parameters more severely [19].

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

An additional error function approach based on information theory is the Hannan-Quinn Information Criterion (HQC) (Eqn. 6). The HQC is more reliable than the AIC because of the $\ln n$ term in the equation [20].

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

The Accuracy Factor (AF) and Bias Factor (BF) are two additional error function analyses derived from Ross's work [21]. These error functions evaluate models statistically for goodness-of-fit but do not penalize for the number of parameters (Eqns. 7 and 8).

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

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

RESULTS AND DISCUSSION

The biosorption isotherm data from a previously published study [5] on the biosorption of Remazol Black B dye by *Aspergillus flavus* were examined using seven models—Henry, Langmuir, Freundlich, BET, Toth, Fritz-Schlunder IV, and Fritz-Schlunder V and fitted using non-linear regression (Figs. 1-7). Statistical analysis based on root-mean-square error (RMSE), adjusted coefficient of determination ($\text{adj}R^2$), bias factor (BF), accuracy factor (AF), corrected AICc (Akaike Information Criterion), Bayesian Information Criterion (BIC), and Hannan-Quinn information criterion revealed that the Fritz-Schlunder IV model was the best (Table 2). The calculated Fritz-Schlunder IV parameter, b_{FS} value was found to be 3.812 mg/g (95% confidence interval of 0.312 to 7.311) q_{mFS} value of 0.022417 (95% confidence interval of -21725.002 to 21725.047).

In the original published paper, the equilibrium sorption capacity q_e was 4.37 mg/g, which is close to the remodeled value. The results from the published work have been improved in the form of the addition of a 95% confidence interval range which can statistically be used to discriminate model [21]. Some works have proposed sorption mechanisms based on only kinetics results, which should not be done, as numerous recent works have indicated that more results from isotherm, diffusion, and thermodynamics works should be obtained before concluding [22-28].

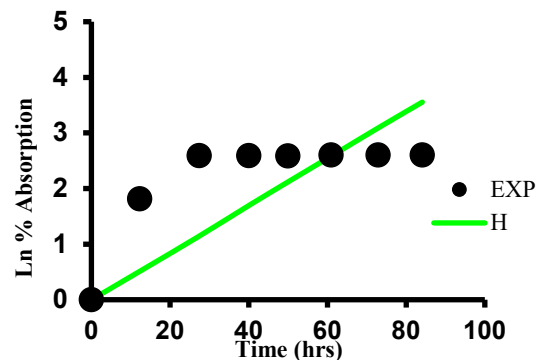


Fig. 1. Biosorption isotherm model of Remazol Black B by *Aspergillus flavus* as modelled using the Henry model.

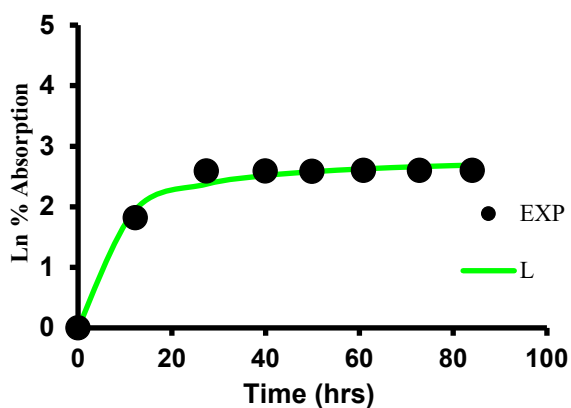


Fig. 2. Biosorption isotherm model of Remazol Black B by *Aspergillus flavus* as modelled using the Langmuir model.

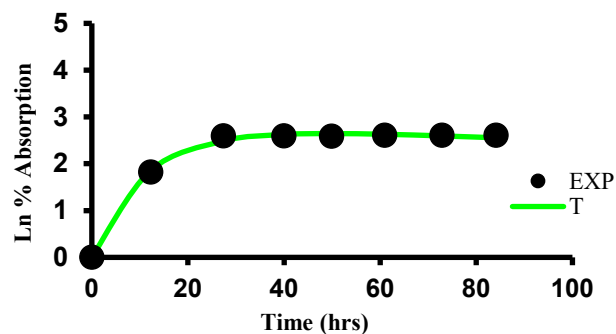


Fig. 5. Biosorption isotherm model of Remazol Black B by *Aspergillus flavus* as modelled using the Toth Model.

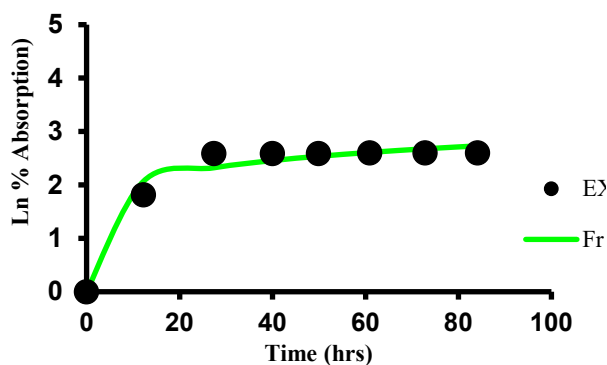


Fig. 3. Biosorption isotherm model of Remazol Black B by *Aspergillus flavus* as modelled using the Freundlich model.

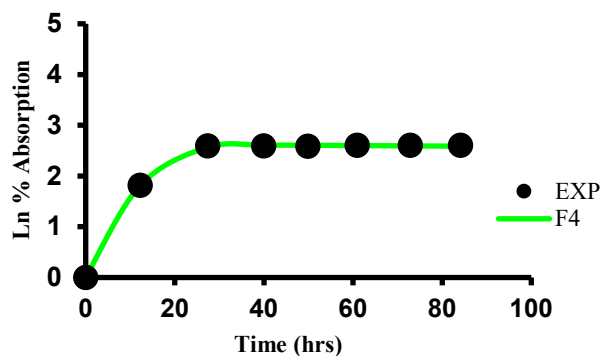


Fig. 6. Biosorption isotherm model of Remazol Black B by *Aspergillus flavus* as modelled using the Fritz-Schlunder IV Model.

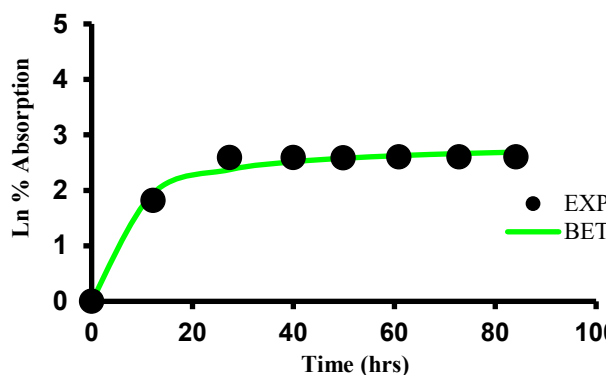


Fig. 4. Biosorption isotherm model of Remazol Black b by *Aspergillus flavus* as modelled using the BET Model

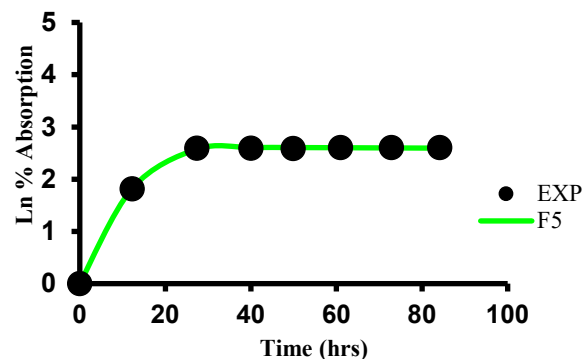


Fig. 7. Biosorption isotherm model of Remazol Black B by *Aspergillus flavus* as modelled using the Fritz-Schlunder V model.

Table 2. Error functions analysis for the regressed isotherm models.

Model	<i>p</i>	RMSE	adR ²	AICc	BIC	HQC	BF	AF
H	1	0.92	0.35	6.07	-0.25	-0.86	0.48	2.06
L	2	0.12	0.98	-20.58	-32.42	-33.65	1.53	2.19
Fr	2	0.17	0.96	-14.46	-26.31	-27.54	2.43	3.26
BET	3	0.13	0.98	-9.24	-30.34	-32.18	9.57	10.46
Toth	3	0.06	0.99	-20.71	-41.80	-43.65	7.26	8.21
F ₄	4	0.02	1.00	-21.75	-61.43	-63.89	15.65	15.88
F ₅	5	0.02	1.00	32.92	-62.69	-65.76	16.47	16.47

Note:
 RMSE Root Mean Square Error
P number 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
 H Henry
 L Langmuir
 Fr Freundlich
 F₄ Fritz-Schlunder IV
 F₅ Fritz-Schlunder V

CONCLUSION

Conclusively, the biosorption of remazol Black B dye by *Aspergillus flavus* was effectively modeled using seven isotherm models: Henry, Langmuir, Freundlich, BET, Toth, Fritz-Schlunder IV, and Fritz-Schlunder V, which were fitted using non-linear regression. Based on statistical analysis using root-mean-square error (RMSE), adjusted coefficient of determination (adjR²), bias factor (BF), accuracy factor (AF), and corrected AICc, (Akaike Information Criterion). The Fritz-Schlunder IV model was determined to be the best. The calculated Fritz-Schlunder IV parameter, *bFS* value was found to be 3.812 mg/g (95% confidence interval of 0.312 to 7.311) qmFS value of 0.022417 (95% confidence interval of -21725.002 to 21725.047).

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