Application of Two- and Three-Parameter Isotherm Models: Biosorption of Acid Red 88 onto Azolla microphylla

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ABSTRACT  Biosorption potential of *Azolla microphylla* for acid red 88 from aqueous solution was investigated under laboratory conditions as a function of initial pH and temperature. The algal biomass exhibited the highest dye sorption capacity at optimum conditions of pH 3 and temperature 30°C. The experimental isotherms were analyzed using five two-parameter models (Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, and Flory-Huggins) and five three-parameter models (Redlich-Peterson, Sips, Khan, Radke-Prausnitz, and Toth). Three error analysis methods were used to evaluate the experimental data: correlation coefficient, residual root mean square error (RMSE), and chi-square test to find the best fitting isotherm. In particular, Langmuir (two-parameter) and Khan (three-parameter) models described the dye biosorption isotherm data well at all pH and temperature conditions examined.

KEYWORDS  acid red 88, *Azolla microphylla*, biosorption, error analysis, sorption isotherm

INTRODUCTION

Environmental protection using natural products in place of synthetic chemical compounds to eliminate pollution can have distinct advantages. Biological approaches, especially application of biosorption, have been suggested over the last decade for the treatment of dye-bearing wastewaters. During the past two decades, there has been interest in the use of algae for treating polluted wastewater. Seaweeds (marine algae), micro freshwater algae, and macro freshwater algae were used as biosorbents for wastewater biosorption treatment (Veglio and Beolchini, 1997; Aksu and Tezer, 2005). Algae have been found to be suitable biosorbents because they grow quickly and easily in simple medium, are inexpensive, and they have a relatively high surface area and high binding affinity (Roy et al., 1993; Fehrmann and Pohl, 1993; Bakkaloglu et al., 1998). Most biosorption studies have focused on metals sorption onto micro and macro algae. In contrast, there are only a limited number of studies available that examined biological treatment of dyes by algal species, in spite of algae’s ubiquitous distribution and their central role in the fixation and turnover
of carbon and other nutrient elements (Semple et al., 1999).

Biosorption isotherm data modeling is a valuable tool for predicting and comparing biosorption performance of various biomass sorbents. There are two-, three-, and even four-parameter empirical isotherm models available for this purpose (Khan et al., 1997). The simpler two-parameter models are usually preferred for modeling biosorption data, and there is no critical reason to use more complex models if two-parameter models can fit the data well. However, researchers have used three-parameter models such as the Redlich-Peterson and Sips models to describe the biosorption isotherm (Ho et al., 2002). Linear regression analysis has also been used to evaluate the isotherm model parameters. However, transformation of nonlinear isotherm equations to linear forms usually results in parameter estimation errors and distorts the model’s fit (Tsai and Juang, 2000).

In this work, the influences of pH and temperature on acid red 88 (AR88) sorption were investigated using protonated *Azolla microphylla* biomass. A method is presented for direct comparison of the fit of several isotherm models, which was used to select the best-fit and best isotherm parameters for modeling biosorption with *A. microphylla*.

**MATERIALS AND METHODS**

**Biosorbent**

*Azolla microphylla* was obtained from Department of Microbiology, Tamilnadu Agricultural University, Coimbatore, India. The alga was sun dried, crushed (mortar), and then finally sieved (Bureau of Indian Standard test sieves) to particle sizes in the range of 1 to 2 mm. The prepared biomass was then treated with 0.1 M HCl for 5 h, washed with distilled water, and then dried in the shade. This dried biomass was used in the biosorption experiments.

**Experimental Procedure**

Batch biosorption experiments were performed in 250-ml Erlenmeyer flasks on a rotary shaker set at 150 rpm (Orbitek, India). Each flask contained 0.2 g *Azolla* biomass in 50 ml of different acid dye concentrations at desired pH conditions (pH 2 to 4) established using 0.1 M HCl and 0.1 M NaOH (pH Analyser, Elico LI 614). For the desired temperature conditions (25°C to 35°C), each flask containing 0.2 g of biomass in 50 ml of desired different dye concentrations were kept in a temperature-controlled shaker (Orbitek, India). After contacting the biomass with the acid dye for 12 h, the reaction mixture was removed, and centrifuged at 3000 rpm for 10 min. The dye concentration in the supernatant was measured using an ultraviolet-visible-spectrophotometer (Hitachi, Japan) at respective λ_{max} value of 503 nm. All experiments were conducted in duplicate.

**Data Evaluation**

The amount of dye biosorbed was calculated from the difference between the dye quantity added to the biomass and the amount of dye remaining in the supernatant using the following equation:

\[ q = \frac{V(C_0 - C_f)}{M} \]  

where \( q \) is the dye sorption (mg dye/g biomass); \( C_0 \) and \( C_f \) are the initial and equilibrium dye concentrations in the solution (mg/L), respectively; \( V \) is the solution volume (L); and \( M \) is the mass of biosorbent (g).

**Equilibrium Modeling**

Biosorption isotherms, plot of sorption (Q), and the final equilibrium solute concentration (\( C_f \)), obtained at different conditions were fitted to 10 different sorption isotherm models: Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, Flory-Huggins, Redlich-Peterson, Sips, Khan, Radke-Prausnitz, and Toth. Five two-parameter and five three-parameter equilibrium isotherm models were used to fit the experimental data as follows:

**Two-Parameters Isotherms**

\[ q = \frac{q_{\max} b_L C_f}{1 + b_L C_f} \]  
\[ q = K_F C_f^{1/n_F} \]  
\[ q = q_D \exp \left(-B_D \varepsilon_D^2\right) \]  
\[ \varepsilon_D = RT \ln \left(1 + \frac{1}{C_f}\right) \]
where the mean energy of sorption, $E$, is calculated using

$$
E = \frac{1}{\sqrt{2BD}}
$$

(6)

Temkin

$$
q = \frac{RT}{bTe} \ln(aTeC_f)
$$

(7)

Flory-Huggins

$$
\log \frac{\theta}{C_0} = \log K_{FH} + n_{FH} \log(1 - \theta)
$$

(8)

The equilibrium constant, $K_{FH}$, was used to compute the Gibbs free energy ($\Delta G^0$):

$$
\Delta G = -RT \ln K_{FH}
$$

(9)

**Three-Parameters Isotherms**

Redlich-Peterson

$$
q = \frac{K_{RP}C_f}{1 + a_{RP}C_f^{b_{RP}}}
$$

(10)

Radke-Prausnitz

$$
q = \frac{a_{RP}C_f^b}{a_R + r_RC_f^{b-1}}
$$

(11)

Khan

$$
q = \frac{q_{max}b_kC_f}{(1 + b_kC_f)^{a_k}}
$$

(12)

Sips

$$
q = \frac{K_S C_f^{b_S}}{1 + a_SC_f^{b_S}}
$$

(13)

Toth

$$
q = \frac{q_{max}b_TC_f}{[1 + (b_TC_f)^{1/n_T}]^{n_T}}
$$

(14)

where $q_{max}$ is the maximum dye sorption (mg dye/g biomass) and $b_L$ is the Langmuir equilibrium constant (1/mg); $K_F$ is the Freundlich constant (l/g) and $n_F$ is the Freundlich exponent; $q_D$ is the Dubinin-Radushkevich model constant (mg/g); $B_D$ is the Dubinin-Radushkevich model constant (mol²/kJ²) and $\varepsilon_D$ is the Polanyi potential; $b_Te$ is the Temkin constant related to the heat of sorption (J/mol); $a_{Te}$ is the Temkin isotherm constant (l/g), $R$ is the gas constant (8.314 J/mol K) and $T$ is the absolute temperature (K); $\theta = (1 - C_f/C_0)$ is the degree of surface coverage, $K_{FH}$ is the Flory-Huggins model equilibrium constant, and $n_{FH}$ is the Flory-Huggins model exponent; $K_{RP}$ is the Redlich-Peterson model isotherm constant (l/g), $a_{RP}$ is the Redlich-Peterson model constant (1/mg) and $b_{RP}$ is the Redlich-Peterson model exponent; $a_R$ and $r_R$ are Radke-Prausnitz model constants and $\beta_R$ is the Radke-Prausnitz model exponent; $b_K$ is the Khan model constant and $a_K$ is the Khan model exponent; $K_S$ is the Sips model isotherm constant (l/g); $a_S$ is the Sips model constant (l/mg) and $\beta_S$ is the Sips model exponent; $b_T$ is the Toth model constant and $n_T$ is the Toth model exponent.

**Nonlinear Regression Analysis**

All model parameters were evaluated by nonlinear regression using a statistical software program (MATLAB, version 6.5). In addition to the correlation coefficient ($R^2$), the residual root mean square error (RMSE) and the chi-square test also were used to measure the model’s fit to the empirical data. RMSE is defined as:

$$
RMSE = \sqrt{\frac{1}{m - p} \sum_{i=1}^{m} (Q_i - q_i)^2}
$$

(15)

where $Q_i$ is the observation from the batch experiment, $q_i$ is the estimate from the isotherm for the corresponding $Q_i$, $m$ is the number of observations in the experimental design, and $p$ is the number of parameters to be determined. Smaller RMSE values indicate a better model fit (Tsai and Juang, 2000).

The chi-square test is defined as:

$$
\chi^2 = \sum_{i=1}^{m} \frac{(Q_i - q_i)^2}{q_i}
$$

(16)

If data from model are similar to the experimental data, $\chi^2$ will be a small number (Ho et al., 2005).

**RESULTS AND DISCUSSION**

**Effect of pH and Temperature**

In order to study the influence of pH on the biosorption capacity of *A. microphylla*, experiments were performed at initial solution pH values ranging from 2 to 7. Maximum AR88 sorption was obtained at pH 3 with further pH increase resulting in decreased sorption (Figure 1). This trend was attributed to the solution pH influencing both the cell-surface dye-binding sites and the dye chemistry in water. Hence the biosorption isotherm experiments were carried out in the pH range of 2 to 4. The temperature was varied in the range of 25°C to 35°C. The optimum adsorption temperature
FIGURE 1  Effect of pH on AR88 onto A. microphylla.

FIGURE 2  Biosorption isotherms of AR88 for A. microphylla at different conditions (biomass dosage = 4 g/L and agitation rate = 150 rpm). (Top) pH ($\bullet$) 2; ($\square$) 3; ($\triangle$) 4, and (bottom) temperature (○) 25°C; (■) 30°C; (□) 35°C.

Two-Parameter Models

Langmuir Isotherm

The assumption made on the Langmuir adsorption isotherm model (Langmuir, 1918) is that all adsorption sites have equal affinities for adsorbate molecules and that the presences of adsorbed molecules at one site do not affect the adsorption of molecules at an adjacent site. The Langmuir model has produced good fit with wide variety of experimental data. The Langmuir model served to estimate the maximum dye sorption values where they could not be reached in the experiments. The linearized form of Langmuir isotherm is given below:

$$\frac{1}{q} = \frac{1}{q_{\text{max}}} + \frac{1}{b q_{\text{max}} C_f}$$  \hspace{1cm} (17)

In order to obtain the constants, straight-line was plotted between $1/q$ against $1/C_f$. The constant $b_L$ represents the affinity between the sorbent and sorbate. The maximum sorption, $q_{\text{max}}$, increased with increasing pH from 2 to 3 and temperature from 25 to 30°C, whereas further, pH and temperature increase in decreased sorption (Table 1). High values of $b_L$ were reflected by the steep initial slope of the sorption isotherm, which was indicative of a high affinity of the biomass of the dye. In general, a high $q_{\text{max}}$ and steep initial isotherm slope (i.e., high $b_L$) are desirable characteristics of good biosorbents (Davis et al., 2003). A. microphylla performed well in dye biosorption at pH 3 and 30°C, when compared to other conditions. High correlation coefficients and low values of RMSE and chi-square were obtained in the case of Langmuir model, among the two-parameter models (Table 1).

Freundlich Isotherm

The Freundlich equation (Freundlich, 1907) is an empirical relationship that describes the sorption of solute from liquid to solid surface and assumes that the stronger binding sites are occupied first and that the binding strength decreases with the increasing degree of site occupation. To obtain the Freundlich constants, Equation 3 was linearized as:

$$\ln q = \ln K + \frac{1}{n} \ln C_f$$  \hspace{1cm} (18)

By plotting $\ln q$ against $\ln C_f$ we obtain the Freundlich constants $K$ and $n$ as intercept and slope. Both $K_F$ and
\[ \ln q = \ln q_D - B_D \times \varepsilon_D^2 \]  

(19)

The values of isotherm constants were obtained from the straight-line plot \( \ln q \) versus \( \varepsilon_D^2 \). The values of Dubinin-Radushkevich constants and mean free energy are given in Table 1. The constant \( q_D \) agreed well with experimental data and the maximum value of 55 mg/g observed at pH 3 and 30\(^\circ\)C.

### Temkin Isotherm

Temkin and Pyzhev (1940) considered the effects that certain indirect adsorbate/adsorbent interactions have on adsorption isotherms. They suggested that because of these interactions, the heat of adsorption of all the molecules in the layer would decrease linearly with coverage. The linear form of Temkin isotherm was given

### Dubinin-Radushkevich Isotherm

Dubinin and Radushkevich (Dubinin, 1960) proposed an equation for the analysis of isotherms of a high degree of rectangularity. The model was chosen to estimate the apparent free energy of adsorption. The linearized form of Dubinin-Radushkevich isotherm was given as:

\[ \ln q = \ln q_D - B_D \times \varepsilon_D^2 \]  

(19)

The values of isotherm constants were obtained from the straight-line plot \( \ln q \) versus \( \varepsilon_D^2 \). The values of Dubinin-Radushkevich constants and mean free energy are given in Table 1. The constant \( q_D \) agreed well with experimental data and the maximum value of 55 mg/g observed at pH 3 and 30\(^\circ\)C.
below:

\[ q = \frac{RT}{b_{Te}} \ln a_{Te} + \frac{RT}{b_{Te}} \ln C_f \]  

(20)

The linear plot \((q \text{ versus } \ln C_f)\) gives the values of Temkin isotherm constants \((b_{Te} \text{ and } a_{Te})\). The Temkin sorption potential, \(a_{Te}\), increased with increasing pH and reached a maximum value of 37.95 l/g at pH 3 and 30°C. The Temkin constant, \(b_{Te}\), related to the heat of sorption, decreased as the pH increased and reached its lowest value at pH 3 and 30°C (Table 1). However, the model did not fit the data as well as to other two-parameter models based on the low correlation coefficients and higher RMSE and chi-square values (Table 1).

**Flory-Huggins Isotherm**

Equation (8) represents the linear form of Flory-Huggins model (Horsfall and Spiff, 2005). The isotherm constants were extrapolated from plots of \(\log \theta/C_0 \text{ versus } \log(1 - \theta)\). The model was examined to account for the degree of surface coverage characteristics of the sorbate on the sorbent. Both Flory-Huggins constants increase with increasing pH and reached its maximum at pH 3 (Table 1). The negative values of \(\Delta G^0\) (Table 1) confirmed the feasibility of the process and the spontaneous nature of AR88 biosorption onto *A. microphylla*.

**Three-parameter Models**

**Redlich-Peterson Isotherm**

Redlich and Peterson (1959) incorporated the features of the Langmuir and Freundlich isotherms into a single equation. The exponent, \(\beta_{RP}\), lies between 0 and 1. There are two limiting behaviors: the Langmuir form for \(\beta = 1\), and the Henry’s law form for \(\beta = 0\). The linearized form of isotherm was represented as follows:

\[ \ln \left( \frac{K_{RP} C_f}{q} - 1 \right) = \beta_{RP} \ln C_f + \ln a_{RP} \]  

(21)

The linear plot \((\ln(K_{RP}(C_f/q) - 1) \text{ against } \ln C_f)\) gave the values of the isotherm constants. Table 2 shows the Redlich-Peterson isotherm constants for biosorption of AR88 onto *A. microphylla*. The isotherm constant \(K_{RP}\) and exponent \(\beta_{RP}\) increased with pH and reached maximum at pH 3 and 30°C. On the contrary, a reverse trend was observed with \(a_{RP}\), which was the lowest at pH 3 and 30°C. It is worth noting that \(\beta_{RP}\) values were close to unity (i.e., the data could preferably be fitted with Langmuir model).

**Radke-Prausnitz Isotherm**

The linearized form of Radke-Prausnitz isotherm was represented as follows:

\[ \frac{1}{q} = \frac{1}{a_{RP} C_f} + \frac{1}{r_{RP} C_f^{\beta_{RP}}} \]  

(22)

By plotting the straight-line plot of \(1/q \text{ versus } 1/C_f\) gives the isotherm constants. The AR88 biosorption data did not correlate well with Radke-Prausnitz model and as confirmed by the low correlation coefficients and high RMSE and chi-square values (Table 2).

**Khan Isotherm**

The simplified form of the Khan model (Equation 12) (Khan et al., 1997) predicted the maximum sorption values \((q_{max})\) with relatively high correlation coefficients and minimum RMSE and chi-square values. On the basis of correlation coefficient, RMSE, and chi-square test, the Khan model fit the sorption isotherm data better than the other three-parameter models (Table 2).

**Sips Isotherm**

At low sorbate concentrations, the Sips or Langmuir-Freundlich isotherm (Equation 13) effectively reduces to the Freundlich isotherm and thus does not obey Henry’s law. At high sorbate concentrations, this isotherm predicts a monolayer sorption capacity characteristic of the Langmuir isotherm (Ho et al., 2002). Both Sips model constants \((K_S \text{ and } a_S)\) reached their maximums at optimum conditions of pH 3 and 30°C. The exponent \(\beta_S\) values were close to unity (Table 2). This suggested that the AR88 sorption data obtained in this study better fit the Langmuir form rather than the Freundlich form, which was also confirmed by the data in Table 1.

**Toth Isotherm**

The Toth isotherm (Equation 14) is derived from the potential theory, and is applicable for heterogeneous adsorption (Toth, 1971). This model assumes a quasi-Gaussian energy distribution, where most sites
have adsorption energies lower than the peak or maximum adsorption energy. The maximum biosorption capacity agreed very well with the experimental data (Table 2). The other two constants, $b_T$ and $n_T$, were at their maximum at pH 3 and 30°C.

Figure 3 shows the applications of all two and three parameters onto the nonlinear isotherm models. From the figure, it can be observed that the predicted Freundlich isotherm curve fits better at low dye concentrations than at high dye concentration. On the other hand, the predicted Dubinin-Raduskevich model curve fits well at high dye concentrations. Upon comparing all the isotherm models, the isotherm curve predicted by the Langmuir model coincides with the experimental curve with a high correlation coefficient.

As far as three-parameter isotherm models were concerned, it was observed that the isotherm curve predicted by Redlich-Peterson model coincides with experimental curves only at low dye concentration. In contrast, the Radke-Prausnitz model curve fits only at high dye concentrations. The isotherm curve predicted by the Khan model coincides better with the experimental curve than the other three-parameter models and with higher correlation coefficients.

### Table 2: Isotherm Constants of Three-Parameter Models for AR88 Biosorption Onto A. microphylla

<table>
<thead>
<tr>
<th>Two-parameter model</th>
<th>pH (Temperature = 30°C)</th>
<th>Temperature (pH = 3)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH 2</td>
<td>pH 3</td>
</tr>
<tr>
<td>Redlich-Peterson</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_{RP}$</td>
<td>3.54</td>
<td>4.97</td>
</tr>
<tr>
<td>$a_{RP}$</td>
<td>0.070</td>
<td>0.049</td>
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<tr>
<td>$\beta_{RP}$</td>
<td>0.999</td>
<td>0.988</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.979</td>
<td>0.991</td>
</tr>
<tr>
<td>RMSE</td>
<td>4.13</td>
<td>2.41</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>13.17</td>
<td>5.27</td>
</tr>
<tr>
<td>Radke-Prausnitz</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_R$</td>
<td>59.96</td>
<td>59.97</td>
</tr>
<tr>
<td>$r_R$</td>
<td>16.60</td>
<td>16.72</td>
</tr>
<tr>
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</tr>
<tr>
<td>$R^2$</td>
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<td>0.872</td>
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<tr>
<td>RMSE</td>
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<td>7.62</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>36.26</td>
<td>26.76</td>
</tr>
<tr>
<td>Khan</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q_{max}$</td>
<td>50.49</td>
<td>55.96</td>
</tr>
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<td>$b_K$</td>
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<td>$a_K$</td>
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<tr>
<td>$R^2$</td>
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<td>0.991</td>
</tr>
<tr>
<td>RMSE</td>
<td>4.49</td>
<td>2.54</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>4.72</td>
<td>5.27</td>
</tr>
<tr>
<td>Sips</td>
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<td>3.51</td>
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<td>$\chi^2$</td>
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<tr>
<td>Toth</td>
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<tr>
<td>$q_{max}$</td>
<td>49.85</td>
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<tr>
<td>$\chi^2$</td>
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<td>4.95</td>
</tr>
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</table>
FIGURE 3 Application of Langmuir, Freundlich, Dubinin-Radushkevich, Temkin, Flory-Huggins, Redlich-Peterson, Radke-Prausnitz, Khan, Sips, and Toth isotherm models to experimental isotherm data obtained during AR88 biosorption by *A. microphylla* (pH = 3, temperature = 30°C, agitation rate = 150 rpm, biosorbent dosage = 4 g/L).

CONCLUSIONS

A detailed analysis of the fits of several isotherm models to experimental biosorption of AR88 onto *A. microphylla* data was carried out. Five two-parameter sorption isotherm models (Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, and Flory-Huggins) and five three-parameter models (Redlich-Peterson, Khan, Radke-Prausnitz, and Toth) were investigated from this analysis. The following conclusions are made based on the results obtained. Among two-parameter models, the Langmuir model better described the experimental data, having a high $R^2$ and low values of RMSE and $\chi^2$. In the case of three-parameter models, the Khan model was found to provide the best fit to the equilibrium experimental data.

REFERENCES


