

Isotherm parameters for basic dyes onto activated carbon: Comparison of linear and non-linear method

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Abstract

Equilibrium sorption experiments were carried out at 305 K with four different basic dyes basic red 9 (BR9), basic violet 3 (BV3), basic brown 1 (BB1) and basic violet 10 (BV10) onto activated carbon. The isotherm parameters were estimated linear and non-linear regression analysis. Non-linear method was found to be more appropriate method for estimating the isotherm parameters. The sorption capacity of activated carbon to uptake cationic dye ions in the increasing order was given by: BR9 (131 mg/g) < BV3 (247 mg/g) < BV10 (259 mg/g) < BB1 (404 mg/g).

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1. Introduction

Activated carbon adsorption is the most commonly used technique for the treatment of wastewaters. Activated carbon has widely been used for removing various pollutants from their aqueous solutions. The adsorption capacity of the carbon and also the performance of the activated carbon adsorption system are usually predicted from equilibrium sorption isotherms. The widely used isotherms by several researchers for different sorbate/sorbent systems are Freundlich [1], Langmuir [2] and Redlich and Peterson [3] isotherms. Linear regression was the most commonly used technique to estimate the sorption isotherm parameters. However, previous studies showed that the linearization of a non-linear isotherm expression produce different outcomes [4–7]. In the present study, a non-linear method was used to estimate the Freundlich, Langmuir and Redlich–Peterson isotherm parameters involved during the sorption of four basic dyes: BR9, BV3, BB1 and BV10 onto activated carbon. Basic dye/activated carbon systems were selected as model system in order to study the impact of linearization over the sorption isotherm parameters. A comparison was made between

the linear and non-linear methods of estimating isotherm parameters.

2. Experimental

The dyes BR9, BV3 and BV10 used in the present investigation were obtained from Ranbaxy chemicals, Mumbai and the dye BB1 was obtained Loba chemicals, Mumbai. The structure of dyes used in the present study are shown in Fig. 1a–d. The dye stock solutions were prepared by dissolving 1 g of dye in 1 l of distilled water. All working solutions were prepared by diluting the stock solution with distilled water.

The powdered activated carbon used in the present study was obtained from E-Merck Limited, Mumbai. The commercially obtained activated carbon was directly used as adsorbents without any pretreatment. Some of the specifications of the activated carbon used in the present study as supplied by the manufacturer are given by: substances soluble in water $\leq 1\%$, substances soluble in HCl $\leq 3\%$, Cl $\leq 0.2\%$ and $\text{SO}_4^{2-} \leq 0.2\%$. Heavy metals as lead (Pb) $\leq 0.005\%$, iron (Fe) $\leq 0.1\%$ and incomplete carbonization: passes test, methylene blue adsorption ≤ 180 mg/g, loss on drying $\leq 10\%$ and residue on ignition $\leq 5\%$.

Batch adsorption studies were carried out by contacting 0.01 g of activated carbon with 50 ml of dye solution of known initial dye concentration in 125 ml capped conical flasks. The

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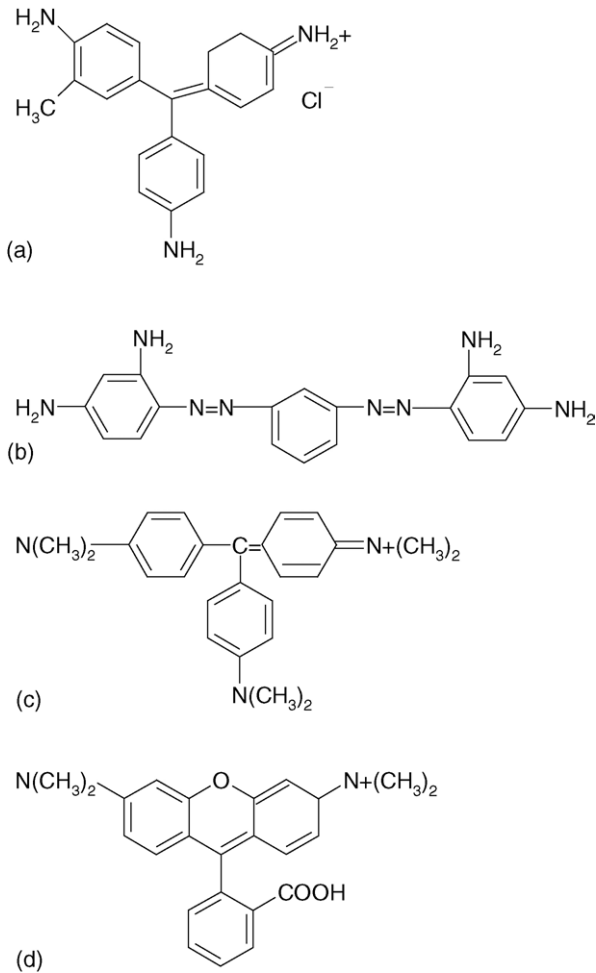


Fig. 1. (a) Basic Red 9; (b) basic brown 1; (c) basic violet 3; (d) basic violet 10.

contact was made using water bath shakers at a constant agitation speed of 95 strokes with a stroke length of 1.5 cm at two different solution temperatures 305 and 313 K. All the experiments were carried out at a constant initial pH of 8. The contact was made for 48 h, which is more than sufficient time to reach equilibrium. Preliminary studies carried out at different dye concentrations

showed that the equilibrium time was found to vary between 38 and 40 h. After 48 h, the dye solutions were separated from the adsorbent by centrifugation. The left out concentration in the supernatant solution was analyzed using a UV Spectrophotometer.

3. Results and discussions

3.1. Error analysis

In the present study, the coefficient of determination r^2 was used to determine the best-fit isotherm model:

$$r^2 = \frac{\sum (q_m - \bar{q}_e)^2}{\sum (q_m - \bar{q}_e)^2 + \sum (q_m - q_e)^2} \quad (1)$$

where q_m is the equilibrium capacity obtained from isotherm model, q_e the equilibrium capacity obtained from experiment and \bar{q}_e is the average of q_e .

3.2. Linear regression analysis

The Freundlich, Langmuir and Redlich–Peterson isotherms and their linearized forms were shown in Table 1. From Table 1, it was observed that the Langmuir isotherms could be linearized to at least four different types. The type 1 Langmuir isotherm was the most commonly used linear expression [7–11] to study the relation between the concentration of solute in liquid phase and in the solid phase at equilibrium conditions. Type 2 Langmuir expressions were also used to explain the equilibria phenomena of dye adsorption process [12–14]. The Langmuir constants q_m and K_a values can be calculated from the plot between C_e/q_e versus C_e , $1/q_e$ versus $1/C_e$, q_e versus q_e/C_e , and q_e/C_e versus q_e for types 1, type 2, type 3 and type 4 Langmuir isotherms, respectively. Similarly the Freundlich isotherm constants K_F and $1/n_F$ can be calculated from the plot of $\log(q_e)$ versus $\log(C_e)$. The Redlich–Peterson isotherm constants can be predicted from the plot between $\ln[(AC_e/q_e) - 1]$ versus $\ln(C_e)$. However, this is not possible as the linearized form of Redlich–Peterson isotherm equation (Table 1) contains three unknown parameters A , B and g . Therefore, a minimization

Table 1
Isotherms and their linear forms

Isotherm	Linear form	Plot	Reference
Freundlich	$q_e = K_F C_e^{1/n}$	$\log(q_e) = \log(K_F) + \frac{1}{n} \log(C_e)$	$\log(q_e)$ vs. $\log(C_e)$ [1]
Type 1 Langmuir	$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_a q_m}$	$\frac{C_e}{q_e}$ vs. C_e	[2]
Type 2 Langmuir	$\frac{1}{q_e} = \left(\frac{1}{K_a q_m} \right) \frac{1}{C_e} + \frac{1}{q_m}$	$\frac{1}{q_e}$ vs. $\frac{1}{C_e}$	
Type 3 Langmuir	$q_e = q_m - \left(\frac{1}{K_a} \right) \frac{q_e}{C_e}$	q_e vs. $\frac{q_e}{C_e}$	[3]
Type 4 Langmuir	$\frac{q_e}{C_e} = K_a q_m - K_a q_e$	$\frac{q_e}{C_e}$ vs. q_e	
Redlich–Peterson	$q_e = \frac{A C_e}{1 + B C_e^g}$	$\ln \left(A \frac{C_e}{q_e} - 1 \right) = g \ln(C_e) + \ln(B)$	$\ln \left(A \frac{C_e}{q_e} - 1 \right)$ vs. $\ln(C_e)$

Table 2
Isotherm constants for basic dyes onto activated carbon by linear method at 305 K

Adsorbate/adsorbent system	BB1/AC	BR9/AC	BV3/AC	BV10/AC
Type 1 Langmuir				
q_m (mg/g)	404	127	244	254
K_a (L/mg)	0.0168	0.0115	0.0167	0.0417
r^2	0.987	0.974	0.990	0.999
Type 2 Langmuir				
q_m (mg/g)	465	145	273	261
K_a (L/mg)	0.0126	0.0088	0.0129	0.0367
r^2	0.982	0.985	0.982	0.992
Type 3 Langmuir				
q_m (mg/g)	415	132	251	260
K_a (L/mg)	0.0159	0.0107	0.0156	0.0376
r^2	0.906	0.882	0.915	0.980
Type 4 Langmuir				
q_m (mg/g)	435	140	261	261
K_a (L/mg)	0.0144	0.0094	0.0142	0.0368
r^2	0.906	0.882	0.915	0.980
Freundlich				
$1/n$	0.511	0.524	0.469	0.225
K_F (mg/g) (L/g) ⁿ	23.8	5.9	17.1	71.3
r^2	0.937	0.939	0.932	0.927
Redlich–Peterson				
g	1.000	1.000	1.000	1.000
B	0.0138	0.0094	0.0139	0.0376
A	6.1	1.3	3.7	9.76
r^2	0.966	0.972	0.977	0.999

procedure is adopted to maximize the coefficient of determination r^2 between the theoretical data for q_e predicted from the linearized form of Redlich–Peterson isotherm equation and the experimental data. The way of obtaining the isotherm constants were explained in Table 1. The predicted isotherm constants for the four different basic dyes and their corresponding r^2 values by the linear method were shown in Table 2. From Table 2, it was observed that the calculated isotherm parameters and their corresponding r^2 values varied for the four linearized types (types 1–4) of Langmuir isotherm. Type 1 Langmuir isotherm showed a better fit for BV10, BV3 and BB1 activated carbon followed by type 2 Langmuir isotherms. In case of BR9/activated carbon system, type 2 Langmuir isotherm was found to be the best-fitting isotherm followed by type 1 Langmuir isotherm. Types 3 and 4 forms have same r^2 values and showed a very poor fit towards the experimental equilibrium data of all the four basic dyes studied onto activated carbon. Except for BR9/activated carbon system the type 1 Langmuir isotherm was found to be the best-fitting isotherm followed by Redlich–Peterson and Freundlich isotherm, whereas the type 1 Langmuir was found to be best-fitting isotherm for the remaining systems followed by Redlich–Peterson and Freundlich isotherm.

The present investigation suggests that the linear least squares method as a reasonable approach to determine the optimum isotherm and also for estimating the isotherm parameters. However, while comparing the r^2 values of the four types of linearized

Langmuir isotherms with Freundlich and Redlich–Peterson isotherm alone will produce different outcomes. In the case of BB1/activated carbon system, the higher r^2 value of type 1 or 2 Langmuir isotherm suggest that Langmuir isotherm was found to be the best-fitting isotherm followed by Redlich–Peterson and Freundlich isotherm. The lower r^2 value of types 3 and 4 Langmuir isotherm suggest that the Redlich–Peterson isotherm is the best-fit isotherm followed by Freundlich and Langmuir isotherm for BB1/activated carbon systems. For BR9 onto activated carbon system, the r^2 values for types 1 and 2 isotherm suggest the Langmuir is the best-fitting isotherm followed by Redlich–Peterson and Freundlich isotherm. The lower r^2 value of types 3 and 4 Langmuir isotherm suggest that the Redlich–Peterson is the best-fit isotherm for BR9 onto activated carbon followed by Freundlich and Langmuir isotherms. Similarly, different outcomes were observed for the sorption of BV3 and BV10 onto activated carbon. These different outcomes show the real complexities in estimating the isotherm parameters using the linearization technique. The different outcomes further suggest that the better fit of a set of experimental data in a particular isotherm model over another model alone is not sufficient to predict the sorption mechanism. The difference between the predicted and experimental equilibrium data by different linear expressions can be due to the problems with the transformation of non-linear to linear expression which will distort the experimental error and also the normality assumptions of the least squares method. Further linear method does not test whether the experimental data are linear. It assumes the experimental data were linear and predicts the slope and intercept that makes a straight line that predicts the best-fit of experimental equilibrium data. The linear method assumes that the scatter of points around the line follows a Gaussian distribution and the error distribution is the same at every value of X . But this is rarely true or practically impossible with equilibrium isotherm models (as most of the isotherm models are non-linear) as the error distribution gets altered after transforming the data to a linear form. The linear method just predicts the Y for the corresponding X . It considers only the error distribution along the Y -axis irrespective of the corresponding X -axis resulting in the different determined parameters (Table 2) for the four different types of linearized Langmuir isotherms for the same experimental data. Thus, the experimental data were further fitted to the experimental equilibrium data of BR9, BV3, BB1 and BV10 onto activated carbon by non-linear method.

3.3. Non-linear method

For non-linear method, a trial and error procedure, which is applicable to computer operation, was used to determine the isotherm parameters by minimizing the respective the coefficient of determination between experimental data and isotherms using the solver add-in with Microsoft's spreadsheet, Microsoft excel. Fig. 2 shows the experimental equilibrium data and the predicted theoretical isotherms for the sorption of BR9, BV3, BB1 and BV10 onto activated carbon. The calculated isotherm constants by non-linear method were shown

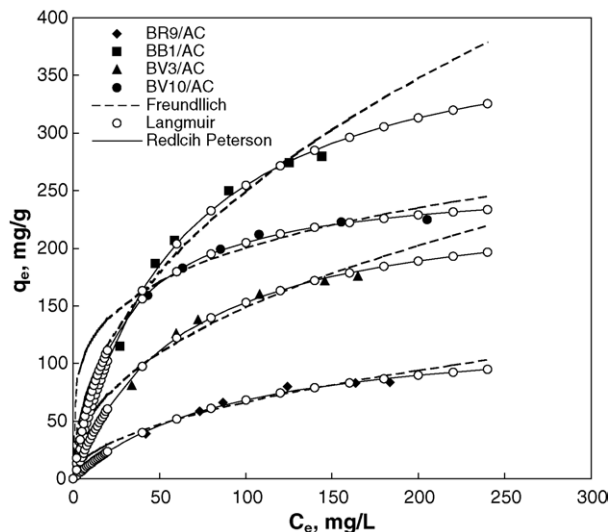


Fig. 2. Adsorption isotherms for basic red 9, basic brown 1, basic violet 3 and basic violet 10 onto activated carbon at 305 K.

Table 3
Isotherm constants for basic dyes onto activated carbon by non-linear method at 305 K

Adsorbate/adsorbent system	BB1/AC	BR9/AC	BV3/AC	BV10/AC
Langmuir				
q_m (mg/g)	406	131	247	259
K_d (L/mg)	0.0168	0.0110	0.0163	0.0378
r^2	0.984	0.969	0.982	0.987
Freundlich				
$1/n$	0.476	0.502	0.444	0.230
K_F (mg/g) (L/g) ⁿ	27.9	6.6	19.2	69.6
r^2	0.946	0.930	0.939	0.926
Redlich–Peterson				
g	1.000	1.000	1.000	1.000
B	0.0168	0.0110	0.0163	0.0377
A	6.8	1.4	4.0	9.8
r^2	0.984	0.969	0.982	0.987

in Table 3. From Table 3, it was observed that the results from the four Langmuir linear equations are the same. By using non-linear method there are no problems with transformations of non-linear Langmuir isotherm equation to linear

forms, and also they are in the same error structures. Fig. 2 shows that the Redlich–Peterson and Langmuir isotherms overlapped each other, and seemed to be the best-fitting models for the experiment results with the same values of coefficient of determination (Table 3). Thus, Langmuir isotherm is a special case of Redlich–Peterson isotherm when constant g was unity. The sorption capacity of activated carbon to uptake cationic dye ions in the increasing order (Table 3) was given by: BR9 (131 mg/g) < BV3 (247 mg/g) < BV10 (259 mg/g) < BB1 (404 mg/g).

4. Conclusions

The present investigation showed that the non-linear method is a better way to obtain the isotherm parameters. The experimental equilibrium data of BR9, BV3, BB1 and BV10 onto activated carbon were well represented by both Langmuir and Redlich–Peterson isotherms. Langmuir is a special case of Redlich–Peterson isotherm when the constant g equals unity.

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