

Isotherms and thermodynamics by linear and non-linear regression analysis for the sorption of methylene blue onto activated carbon: Comparison of various error functions

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Abstract

A comparison of linear and non-linear regression method in selecting the optimum isotherm was made to the experimental equilibrium data of methylene blue sorption by activated carbon. The r^2 was used to select the best fit linear theoretical isotherm. In the case of non-linear regression method, six error functions, namely coefficient of determination (r^2), hybrid fractional error function (HYBRID), Marquardt's percent standard deviation (MPSD), average relative error (ARE), sum of the errors squared (ERRSQ) and sum of the absolute errors (EABS) were used to predict the parameters involved in the two and three parameter isotherms and also to predict the optimum isotherm. For two parameter isotherm, MPSD was found to be the best error function in minimizing the error distribution between the experimental equilibrium data and predicted isotherms. In the case of three parameter isotherm, r^2 was found to be the best error function to minimize the error distribution structure between experimental equilibrium data and theoretical isotherms. The present study showed that the size of the error function alone is not a deciding factor to choose the optimum isotherm. In addition to the size of error function, the theory behind the predicted isotherm should be verified with the help of experimental data while selecting the optimum isotherm. A coefficient of non-determination, K^2 was explained and was found to be very useful in identifying the best error function while selecting the optimum isotherm.

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1. Introduction

Activated carbon adsorption is the most commonly used technique for the treatment of wastewaters. At earlier stages activated carbon was used for the removal of basic dyes from their aqueous solutions [1,2]. In later years activated carbon was found to be effective in removing acid dyes and heavy metals from their aqueous solutions [3,4]. Activated carbon has widely been used for removing various pollutants from their aqueous solutions [5–7]. The adsorption capacity of the carbon and also the performance of the activated carbon adsorption system are usually predicted from equilibrium sorption isotherms. Equilibrium studies will give the capacity of the adsorbent for an adsorbate.

Equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms. Freundlich, Langmuir and Redlich Peterson are the widely used isotherms by several researchers to represent the solute uptake process at equilibrium conditions [8,9].

Search for the best fit adsorption isotherm using the method of least squares is the most widely used technique by several researchers [10,11] to predict the optimum isotherm. Currently, non-linear regression method is found to be the best way in selecting the optimum isotherm [8–14]. The method of non-linear regression involves the step of minimizing the error distribution between the experimental data and the predicted isotherm. Normally error functions are used to minimize the error distribution between the experimental equilibrium data and the predicted isotherms. The error distribution between the experimental equilibrium data and the predicted isotherms will be minimized either by minimizing the error function

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Nomenclature

<i>A</i>	Redlich Peterson isotherm constant (L/g)
ARE	average relative error
<i>B</i>	Redlich Peterson isotherm constant (L/mg ^{1-1/A})
<i>C_e</i>	equilibrium concentration (mg/L)
EABS	sum of the absolute errors
ERRSQ	sum of the squares of the error
<i>g</i>	Redlich Peterson constant
ΔG	Gibbs free energy change (kJ/mol)
HYBRID	hybrid fractional error function
ΔH	energy of adsorption (kJ/mol)
<i>K_L</i>	Langmuir isotherm constant (L/mg)
<i>K_F</i>	Freundlich constant (mg/g)(L/g) ^{1/n}
MPSD	Marquardt's percent standard deviation
<i>n</i>	number of experimental measurements (in Table 2)
1/ <i>n</i>	Freundlich exponent
<i>p</i>	number of parameters in isotherm
<i>q_e</i>	amount of dye adsorbed at equilibrium (mg/g)
<i>q_m</i>	monolayer sorption capacity (mg/g)
<i>r</i> ²	coefficient of determination
<i>T</i>	temperature (K)
ΔS	change in entropy (J/mol K)

or by maximizing the error functions based on the definition of the error function. The coefficient of determination, *r*² is the most widely used error function to minimize the error distribution between the experimental equilibrium data and isotherms [8–14]. Recently, some of the researchers have used other error functions such as hybrid fractional error function (HYBRID), Marquardt's percent standard deviation (MPSD), average relative error (ARE), sum of the absolute errors (EABS), and sum of the errors squared (ERRSQ) to predict the optimum isotherm [15–20], no detailed studies were available so far comparing the accuracy of this error functions in predicting the isotherm parameters and also the optimum isotherm.

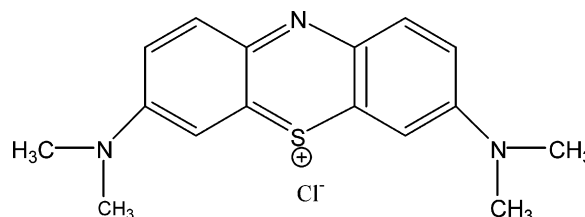
In the present study, a comparison of six different error functions in minimizing the error distribution between the experimental and predicted isotherms is discussed using the experimental data of methylene blue onto powdered activated carbon at four different solution temperatures. The three widely used Freundlich [21], Langmuir [22] and Redlich Peterson [23] isotherms were used to discuss this issue. The method

of least squares was used to predict the isotherm by linear regression method. A trial and error method was used for non-linear regression to minimize or maximize the objective function using the *solver* add-in function, Microsoft Excel, Microsoft Corporation.

2. Experimental**2.1. Adsorbate**

The dye used in all the experiments was methylene blue, a basic (cationic) dye.

Synthetic dye solutions were prepared by dissolving weighed amount of methylene blue in 1 L of double distilled water. The structure of methylene blue (C.I: Basic Blue 9) is given by:



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.

2.2. Adsorbent

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 adsorbent 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 ≤ 1%, substances soluble in HCl ≤ 3%, Cl ≤ 0.2% and SO₄²⁻ ≤ 0.2%, Heavy metals as lead (Pb) ≤ 0.005%, iron (Fe) ≤ 0.1% and incomplete carbonization: passes test, loss on drying ≤ 10% and residue on ignition ≤ 5%.

2.3. Process

Equilibrium studies were carried out for four different solution temperatures at 305, 313, 323 and 333 K. 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 contact was made using water bath shakers at a constant agitation speed of 95 strokes

Table 1
Isotherms and their linearized expressions

Isotherms	Non-linear expression	Linear expression	Plot	Parameters	Reference
Freundlich	$q_e = K_F(C_e)^{1/n}$	$\log(q_e) = \frac{\log(K_F)+1}{n} \log(C_e)$	$\log(q_e)$ vs. $\log(C_e)$	$K_F = \exp(\text{intercept})$, $1/n = \text{slope}$	[21]
Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}$	$\frac{C_e}{q_e}$ vs. C_e	$q_m = 1/\text{slope}$, $K_L = 1/(\text{intercept} \times q_m)$	[22]
Redlich Peterson	$q_e = \frac{AC_e}{1 + BC_e^g}$	$\ln\left(\frac{AC_e}{q_e} - 1\right) = g \ln(C_e) + \ln(B)$	$\ln\left(\frac{AC_e}{q_e} - 1\right)$ vs. $\ln(C_e)$	$g = \text{slope}$, $B = \exp(\text{intercept})$	[23]

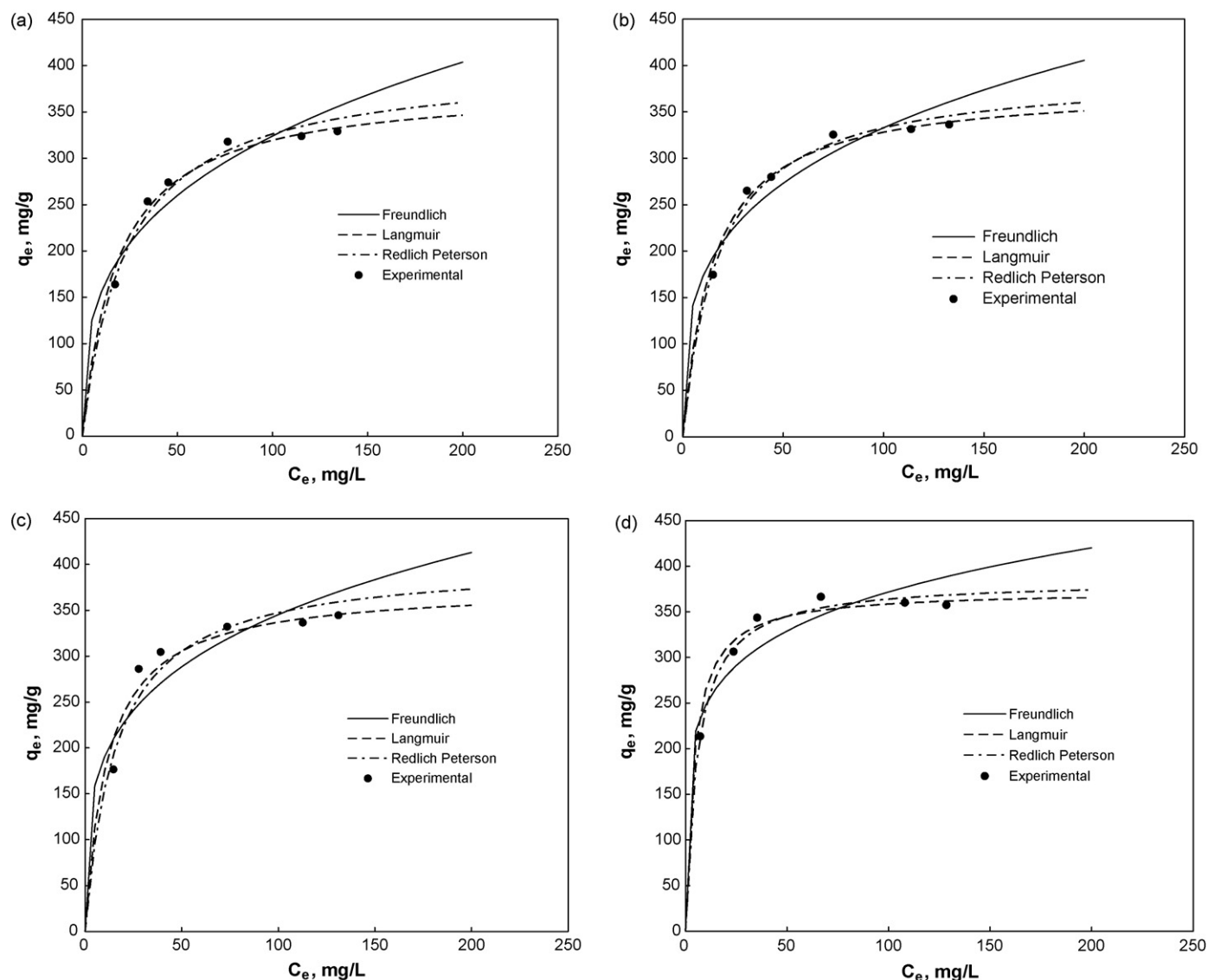


Fig. 1. Experimental equilibrium data and isotherms by linear regression method for the sorption of methylene blue by activated carbon at: (a) 305 K, (b) 313 K, (c) 323 K and (d) 333 K.

with a stroke length of 1.5 cm. The contact was made for 48 h, which is more than sufficient time (predetermined) to reach equilibrium. 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. Adsorption equilibrium

Linear regression using the method of least squares was the most commonly used method in determining the isotherm

Table 2
Isotherms parameters by linear regression method for the sorption of methylene blue by activated carbon

Temperature (K)	Freundlich isotherm			Langmuir isotherm			Redlich Peterson isotherm			
	K_F (mg/g)(L/mg) ⁿ	1/n	r^2	q_m (mg/g)	K_L (L/mg)	r^2	A (L/g)	B (L/mg ^{1-1/A})	g	r^2
305	75.07052	0.317495	0.877073	378.5611	0.054074	0.99645	17.30727	0.043057	1	0.991669
313	89.61008	0.28496	0.888728	377.5898	0.066296	0.998197	21.94494	0.055921	1	0.996111
323	104.6739	0.259081	0.765608	375.866	0.086519	0.996002	25.16061	0.062443	1	0.979032
333	165.0545	0.176332	0.834561	373.3382	0.24352	0.998742	67.2703	0.174834	1	0.999147

Table 3
Explanation of different error functions

Error function	Definition/expression	Reference
The coefficient of determination	$r^2 = \frac{(q_{\text{isotherm}} - \overline{q_{\text{calc}}})^2}{\sum (q_{\text{isotherm}} - \overline{q_{\text{calc}}})^2 + (q_{\text{isotherm}} - q_{\text{calc}})^2}$	[17]
The sum of the squares of the errors (ERRSQ)	$\sum_{i=1}^p (q_{e,\text{calc}} - q_{e,\text{isotherm}})_i^2$	[17]
The hybrid error function (HYBRID)	$\frac{100}{n-p} \sum_{i=1}^n \left[\frac{(q_{e,\text{isotherm}} - q_{e,\text{calc}})^2}{q_{e,\text{isotherm}}} \right]_i$	[17]
Marquardt's percent standard deviation (MPSD)	$100 \sqrt{\frac{1}{n-p} \sum_{i=1}^p \left(\frac{q_{e,\text{isotherm}} - q_{e,\text{calc}}}{q_{e,\text{isotherm}}} \right)_i^2}$	[17]
The average relative error (ARE)	$\frac{100}{n} \sum_{i=1}^p \left \frac{q_{e,\text{calc}} - q_{e,\text{isotherm}}}{q_{e,\text{isotherm}}} \right _i$	[17]
The sum of absolute errors (EABS)	$\sum_{i=1}^p q_{e,\text{calc}} - q_{e,\text{isotherm}} _i$	[17]

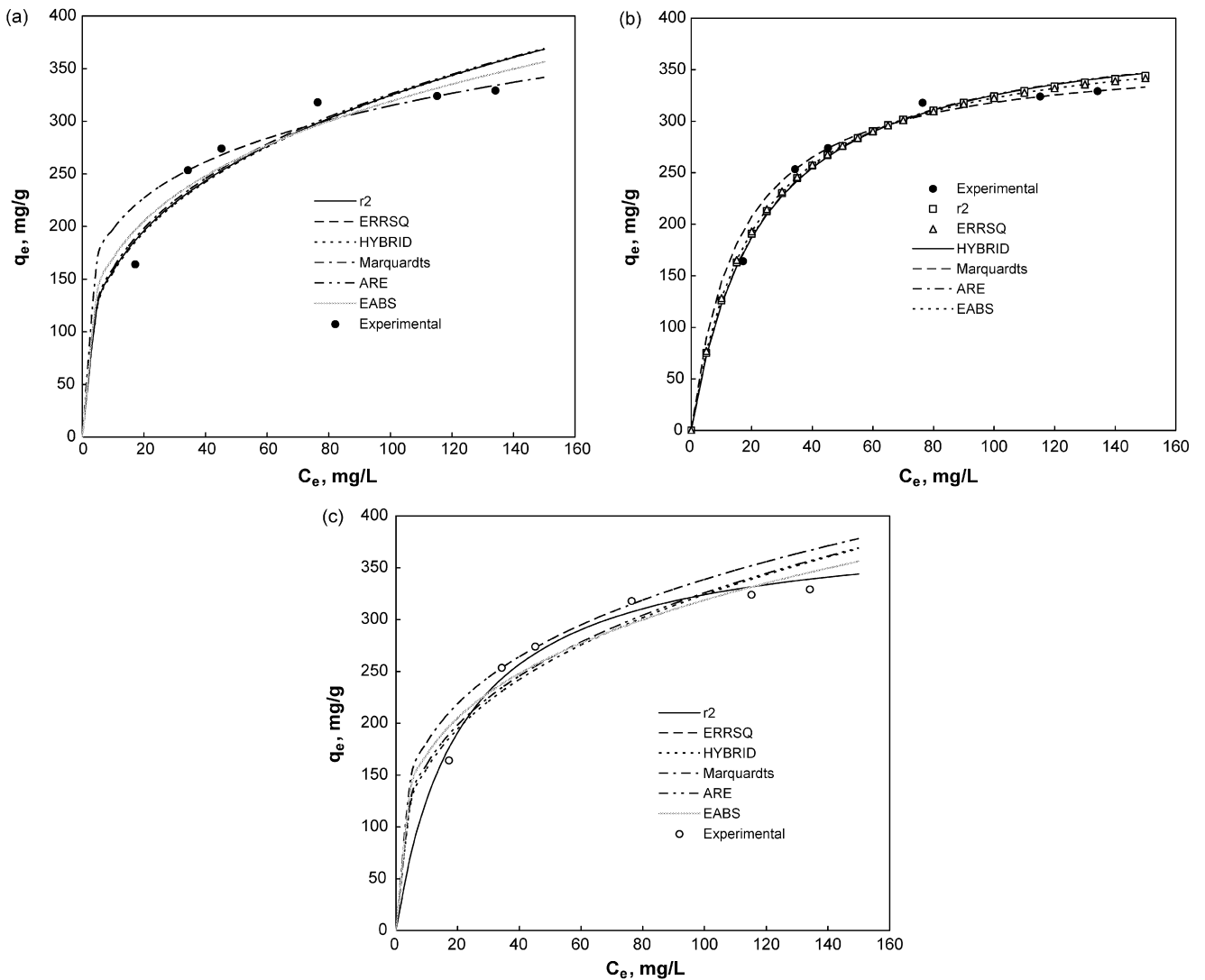


Fig. 2. (a) Experimental data and predicted Freundlich isotherm for methylene blue onto activated carbon at 305 K. (b) Experimental data and predicted Langmuir isotherm for methylene blue onto activated carbon at 305 K. (c) Experimental data and predicted Redlich Peterson isotherm for methylene blue onto activated carbon at 305 K.

parameters. The best fit isotherm was selected based on the error functions that produced minimum error distribution between the predicted and experimental isotherms. Our previous research in this area found that linear regression may not be appropriate technique to predict the optimum isotherm [9,10,13,14]. Sometimes linearization affected the normality assumptions of the least squares and the error distribution was found to be changing to either the better or worse [8,10,13,14]. However, the search for best fit expression is a valid approach provided the normality assumptions behind the method of least squares are not violated due to linearization, i.e. transformation of experimental data. The widely used linearized form of Freundlich [21], Langmuir [22] and Redlich Peterson [23] isotherms which are found to be the best fit expressions in representing most of the experimental equilibrium data are shown in Table 1. The Freundlich, Langmuir, and Redlich Peterson constants can be obtained from the slope and intercept of plot between, $\log(q_e)$ versus $\log(C_e)$, C_e/q_e versus C_e and $\ln(AC_e/q_e - 1)$ versus $\ln(C_e)$. In the case of Redlich Peterson isotherm, the constant A was obtained by maximizing the r^2 value using a trial and error method using solver *add-in* function, Microsoft Excel, Microsoft Corporation. The way to obtain the isotherm parameters are explained in Table 1. Fig. 1a–d shows the experimental equilibrium data and the predicted isotherms by linear regression method at 305, 313, 323 and 333 K, respectively. The calculated isotherm parameters at the studied solution temperatures and the corresponding r^2 values were shown in Table 2. From Table 2, at all the studied

solution temperatures, the r^2 values were lower for Freundlich isotherm and were found to be in the range of 0.76–0.88. The very lower r^2 value suggests that it is not appropriate to use this isotherm to represent the uptake of methylene blue by activated carbon particles. The very higher r^2 values for both Langmuir and Redlich Peterson isotherms (Table 2) suggest that both models can be used to explain the equilibrium dye uptake at four solution temperatures studied. In addition the value of Redlich Peterson isotherm constant g equal to unity (Table 2) at all solution temperature studied confirms that isotherm is approaching the Langmuir and not the Freundlich isotherm. Thus, according to a linear regression method, the dye uptake is due to monolayer coverage of solute particles on to the surface of activated carbon.

According to the theory of Redlich Peterson, when the Redlich Peterson constant, g equal to unity, the isotherm will represent a Langmuir expression and can be represented as [23]:

$$q_e = \frac{AC_e}{1 + BC_e} \quad (1)$$

Thus according to Eq. (1), for a value of g equal to unity, the Redlich Peterson isotherm should overlap Langmuir with same coefficient of determination [11,24]. From Table 2, it can be observed that Redlich Peterson and Langmuir isotherm very well represents the experimental equilibrium data with a higher r^2 value (>0.97) with g value equal to unity. However from Fig. 1a–d, it can be observed that, for all solution tempera-

Table 4a

Predicted isotherms by minimizing the error distribution using five different error functions at 305 K

	K_F	$1/n$	OF ^a	
Freundlich (two parameter isotherm)				
r^2	76.50926	0.313729	0.88547	
ERRSQ	90.08994	0.274425	403.4177	
HYBRID	75.04919	0.317561	2.163121	
MPSD	123.6765	0.202805	3.458008	
ARE	78.62546	0.308643	1.941999	
EABS	90.08984	0.274424	403.4177	
	q_m	K_L	OF ^a	
Langmuir (two parameter isotherm)				
r^2	392.3318	0.047372	0.971407	
ERRSQ	387.7223	0.049544	91.55623	
HYBRID	398.6518	0.044281	0.464278	
MPSD	367.2883	0.064771	1.871759	
ARE	398.8188	0.044557	0.429019	
EABS	387.7198	0.049544	91.55623	
	A	B	g	OF ^a
Redlich Peterson (three parameter isotherm)				
r^2	18.58683	0.047376	1	0.971407
ERRSQ	13926.31	154.3262	0.725884	402.9575
HYBRID	13930.7	185.332	0.682728	2.161025
MPSD	13896.03	143.111	0.728631	3.990424
ARE	13926.69	176.8456	0.691655	1.940089
EABS	13908.16	154.1247	0.725885	402.9569

^a Objective function for the minimum error distribution between experimental and predicted isotherms.

Table 4b

Predicted isotherms by minimizing the error distribution using five different error functions at 313 K

	K_F	$1/n$	OF ^a	
Freundlich (two parameter isotherm)				
R^2	90.86228	0.282235	0.895456	
ERRSQ	103.7364	0.250029	351.0466	
HYBRID	89.59612	0.284996	1.734167	
MPSD	101.8045	0.249405	3.935497	
ARE	92.86289	0.278157	1.57209	
EABS	103.7351	0.250032	351.0466	
	q_m	K_L	OF ^a	
Langmuir (two parameter isotherm)				
r^2	387.5393	0.059282	0.980309	
ERRSQ	384.7859	0.061111	61.06126	
HYBRID	391.2008	0.056666	0.273321	
MPSD	375.8728	0.066376	1.481644	
ARE	391.3729	0.056863	0.256425	
EABS	384.7704	0.061118	61.06121	
	A	B	g	OF ^a
Redlich Peterson (three parameter isotherm)				
r^2	22.9761	0.059288	1	0.980309
ERRSQ	13927.79	134.0143	0.750319	350.4633
HYBRID	13931.97	155.2177	0.715346	1.731623
MPSD	13922.17	155	0.701618	4.062685
ARE	13927.79	149.7112	0.722189	1.569766
EABS	13909.64	133.8393	0.750319	350.4625

^a Objective function for the minimum error distribution between experimental and predicted isotherms.

tures studied, the predicted Redlich Peterson isotherm does not overlap the Langmuir isotherm. A similar observation was previously reported for the dye uptake of copper ions by chitosan for $g = 1$ [17] and for sorption of malachite green by activated carbon [10]. Previously, several research reports suggested non-linear method as a better way to obtain the isotherm parameters as sometime linearization of non-linear experimental data may distort the error distribution structure of isotherm [8–14]. This sometimes may lead to violation of the theories behind the isotherm [25]. The problems due to linearization can be avoided if the isotherms were fitted to the experimental data by non-linear regression method. In addition, in the case of non-linear method, the experimental equilibrium data and the isotherms are in a fixed x and y axis, thus making the comparison study of isotherms more reliable than in the linear regression method (Kumar, 2006a). Thus in the present study, non-linear regression method was used to determine the optimum isotherm out of the three widely used isotherms (Freundlich, Langmuir and Redlich Peterson) studied.

In the case of non-linear method previous research studies reported that the predicted isotherms were found to be varying with the error function used while minimizing the error distribution between the experimental and predicted isotherms [15–20]. Thus, in order to analyze the impact of various error functions on the predicted isotherms, six different error functions namely r^2 , HYBRID, MPSD, ERRSQ, ARE and EABS were optimized by non-linear regression method to minimize the error distribution

between the experimental equilibrium data and the isotherms studied. The explanations of various error functions used in the present study are given in Table 3.

Fig. 2a–c show the experimental and predicted Freundlich [21], Langmuir [22] and Redlich Peterson [23] isotherms at 305 K by minimizing the error distribution between the experimental and the theoretical isotherms using various error functions explained in Table 3. From Fig. 2a–c, it is observed that for a solution temperature of 305 K, the predicted theoretical isotherm was found to be varying with respect to the error functions used. A similar observation was found for the solution temperatures of 313, 323 and 333 K. The variation in the predicted isotherms was found to be more pronounced in case of the three parameter isotherm (Fig. 2c). The calculated isotherm parameters and the corresponding error functions for the minimum error distribution between the experimental equilibrium data and predicted isotherm for solution temperature of 305, 313, 323 and 333 K are given in Tables 4a–4d, respectively. From Table 4a to Table 4d, the error functions corresponding to the minimized deviations between the experimental equilibrium data and predicted isotherms suggested Langmuir as the best fit isotherm followed by the Redlich Peterson isotherm suggesting the monolayer coverage of methylene blue onto activated carbon. The important point to be identified from Table 4a to Table 4d, is that, in the case of Redlich Peterson isotherm, except r^2 , for all the four studied solution temperatures, all the error functions showed a very higher A and B values are

Table 4c
Predicted isotherms by minimizing the error distribution using five different error functions at 323 K

	K_F	$1/n$	OF ^a	
Freundlich (two parameter isotherm)				
R^2	95.98649	0.281703	0.806245	
ERRSQ	124.861	0.216891	738.8382	
HYBRID	104.599	0.259256	3.747556	
MPSD	191.9021	0.12	3.79132	
ARE	116.4576	0.236562	3.294138	
EABS	124.8611	0.216891	738.8382	
	q_m	K_L	OF ^a	
Langmuir (two parameter isotherm)				
r^2	399.0229	0.066215	0.912913	
ERRSQ	387.2368	0.075751	283.5819	
HYBRID	400.6645	0.063854	1.416549	
MPSD	365.0284	0.12856	2.73173	
ARE	399.3519	0.066489	1.321466	
EABS	387.2368	0.075751	283.5819	
	A	B	g	OF ^a
Redlich Peterson (three parameter isotherm)				
r^2	26.42034	0.066213	1	0.912913
ERRSQ	13930.15	111.3303	0.783512	737.7983
HYBRID	13932.91	132.9314	0.741139	3.743286
MPSD	13934	83.99996	0.811171	4.134678
ARE	13929.02	119.3597	0.763838	3.290243
EABS	13912	111.1857	0.783511	737.797

^a Objective function for the minimum error distribution between experimental and predicted isotherms.

Table 4d
Predicted isotherms by minimizing the error distribution using five different error functions at 333 K

	K_F	$1/n$	OF ^a	
Freundlich (two parameter isotherm)				
R^2	156.6846	0.190489	0.829491	
ERRSQ	181.5712	0.152499	548.2328	
HYBRID	165.0468	0.176345	1.78112	
MPSD	195.9908	0.129863	3.95918	
ARE	168.091	0.173833	1.635314	
EABS	181.5653	0.152505	548.2328	
	q_m	K_L	OF ^a	
Langmuir (two parameter isotherm)				
r^2	386.6813	0.170636	0.973118	
ERRSQ	384.5356	0.177735	76.94606	
HYBRID	385.8882	0.172363	0.19045	
MPSD	380.239	0.175385	1.125188	
ARE	386.4452	0.171822	0.177888	
EABS	384.5356	0.177735	76.94606	
	A	B	g	OF ^a
Redlich Peterson (three parameter isotherm)				
R^2	65.98846	0.170655	1	0.973118
ERRSQ	13934.26	76.46851	0.848235	544.9167
HYBRID	13934.99	84.12764	0.824404	1.770701
MPSD	13890.2	80.88709	0.841854	4.279322
ARE	13930.53	82.58032	0.82692	1.625736
EABS	13916.16	76.36892	0.848235	544.9124

^a Objective function for the minimum error distribution between experimental and predicted isotherms.

found to much greater than 1 (A and $B \gg 1$) for the constant $g \ll 1$. This suggests that the isotherm is approaching Freundlich and not Langmuir isotherm [8,9]. However, the size of error functions suggested that isotherm is following the Langmuir isotherm and not the Freundlich (Tables 4a–4d). In addition to check how well the optimized error functions other than r^2 support the theory behind the isotherms studied, the Freundlich and Redlich Peterson isotherms were generated over the experimental data. Fig. 3a–d shows the experimental data and the predicted isotherms by minimizing the error distribution between the experimental equilibrium data and predicted isotherms by minimizing HYBRID error function, at 305, 313, 323 and 333 K. From Fig. 3a–d, it can be observed that for A and $B \gg 1$, the Freundlich exactly overlapped the Redlich Peterson isotherm. This depicts that the sorption process follows the Freundlich isotherm and suggests the heterogeneous sorption of methylene blue by activated carbon particles [9]. A similar effect was observed for the predicted isotherms by minimizing the error functions MPSD, ARE, EABS and ERRSQ (not shown).

However, when comparing the size of MPSD, HYBRID, ARE, EABS and ERRSQ for Langmuir isotherm with Freundlich and Redlich Peterson isotherm, Langmuir isotherm was found to be the optimum isotherm. This suggests that the size of the error function alone should not be considered while selecting the optimum isotherm. Instead, while selecting the optimum isotherm both the size of error function and also the determined isotherm parameters should be verified to the theory behind the isotherm. Fig. 4a–d show the plot of predicted isotherms by maximizing the r^2 values at 305, 313, 323 and 333 K, respectively. From Fig. 4a–d, it can be observed that Langmuir isotherm exactly overlaps the Redlich Peterson isotherm with same r^2 value (Tables 4a–4d) suggesting that isotherm is approaching the Langmuir isotherm and not Freundlich. This suggests the monolayer coverage of methylene blue onto activated carbon as per the theory. This observation is also in good agreement with the higher r^2 value for Langmuir isotherm when compared to the r^2 value of Freundlich and Redlich Peterson isotherms. These different and exactly opposite observations based on r^2

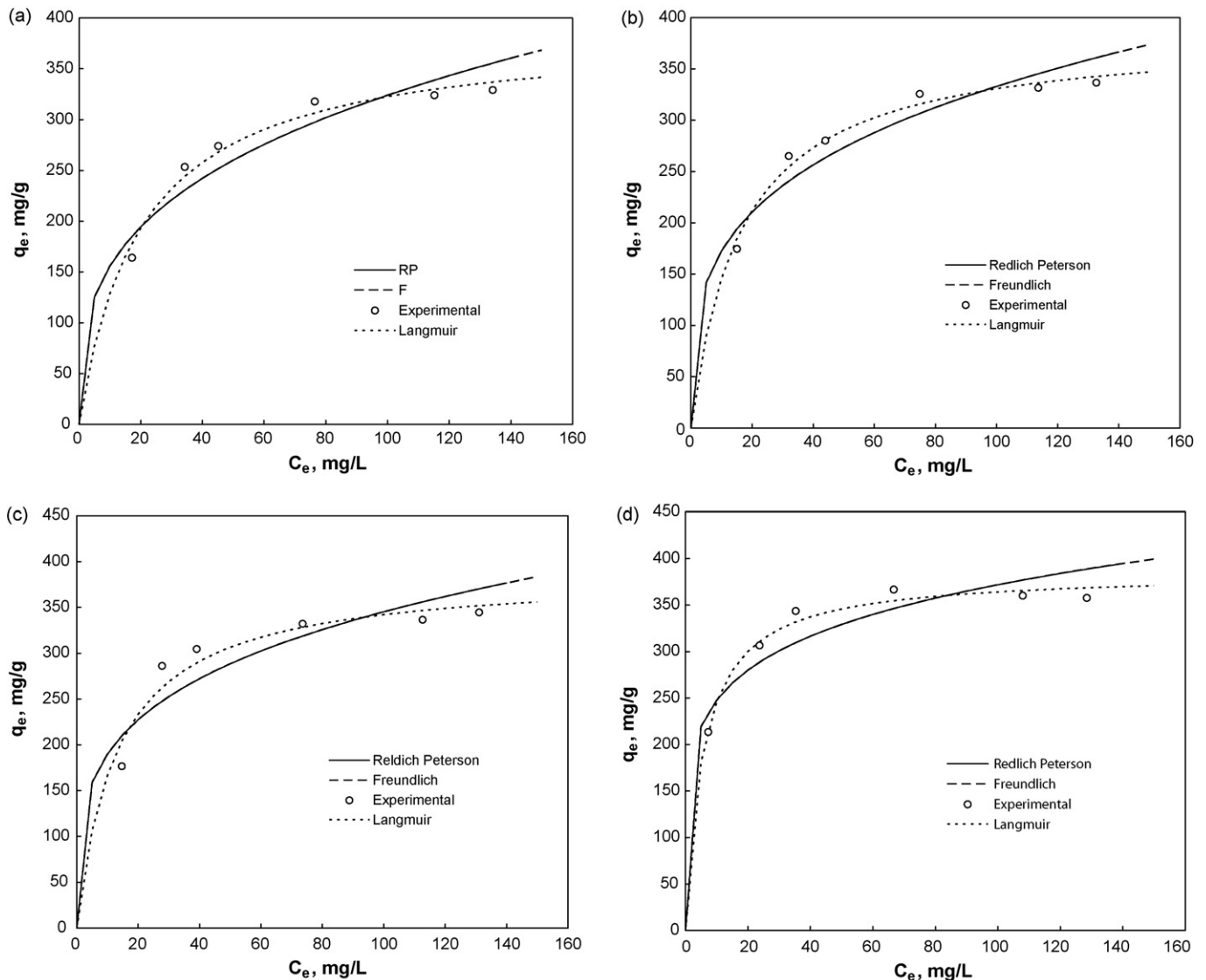


Fig. 3. Isotherms by minimizing HYBRID function for methylene blue onto activated carbon at: (a) 305 K, (b) 313 K, (c) 323 K and (d) 333 K.

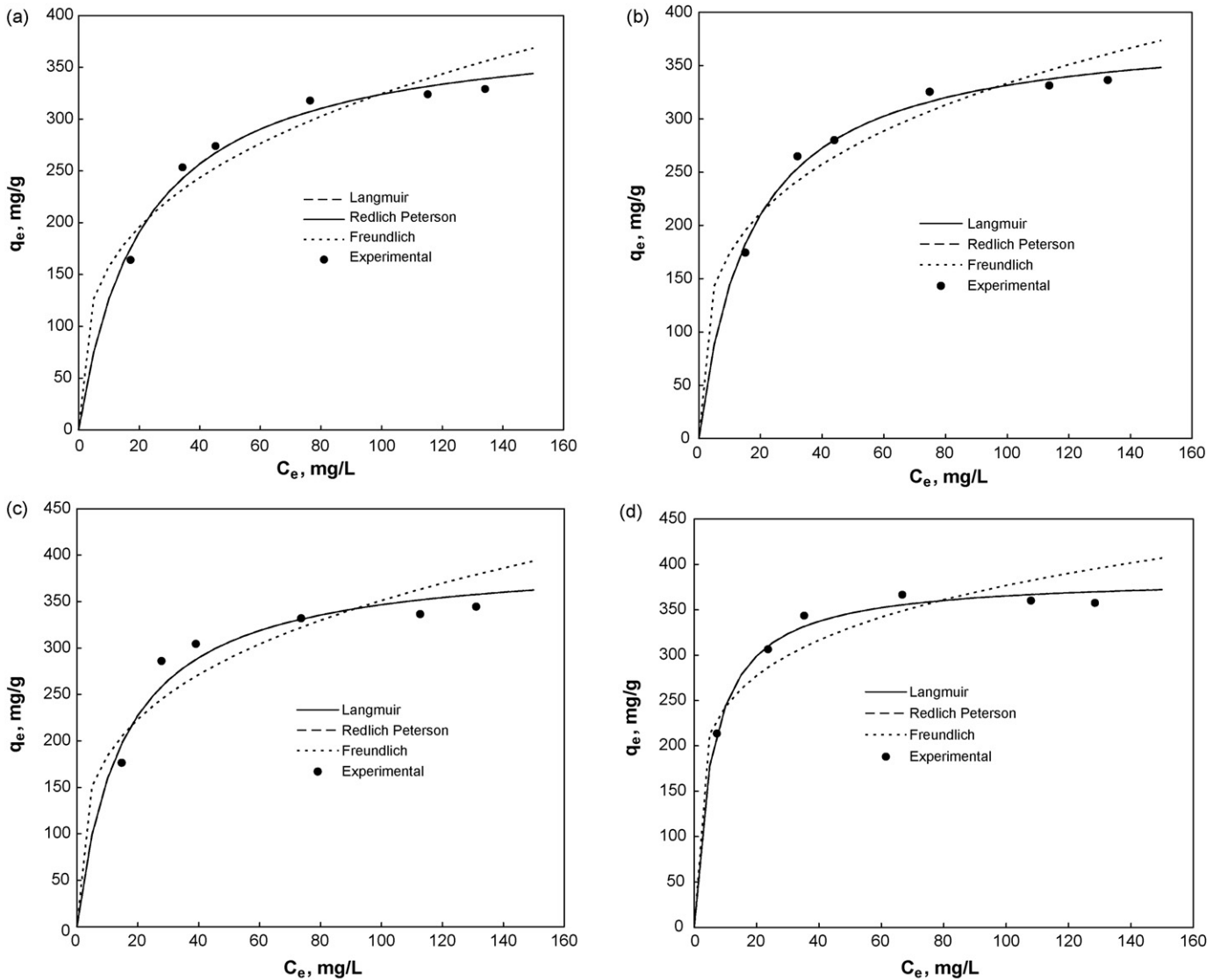


Fig. 4. Isotherms by maximizing r^2 function for methylene blue onto activated carbon at: (a) 305 K, (b) 313 K, (c) 323 K and (d) 333 K.

and other error functions show the complexity in the process of selecting the optimum isotherm using the non-linear regression method.

The error function r^2 and the other error functions suggested the homogeneous and heterogeneous sorption of methylene by activated carbon particles, respectively. Thus, in order to check which error function minimizes the error distribution between the experimental and theoretical isotherms, another statistical term coefficient of non-determination, K^2 was used. The coefficient of non-determination, K^2 was defined as:

$$\begin{aligned}
 K^2 &= \frac{\text{Unexplained variance}}{\text{Total variance}} \\
 &= 1 - \frac{\text{Explained variance}}{\text{Total variance}} = 1 - r^2 \quad (2)
 \end{aligned}$$

The coefficient of non-determination is a much more useful measure of the linear or non-linear co-variation of two variables. The K^2 will be very much useful to come any conclusion

about the extent of the relationship between the transformed experimental data and the predicted isotherms. Fig. 5a–d show the calculated K^2 values for the isotherms predicted by minimizing or maximizing the various error functions at 305, 313, 323 and 333 K, respectively. From Fig. 5a–d, it is observed that MPD function least unexplain the two parameter isotherm suggesting this function as the best function to minimize the error distribution between the experimental and predicted two parameter isotherms, namely the Freundlich and Langmuir isotherms. Thus, for the studied system, MPD was found to be the best error function to be used in predicting the optimum isotherm if the objective is to select the best fit isotherm out of two parameter isotherms. In the case of three parameter Redlich Peterson isotherm, it can be observed that r^2 was found to be the best error function in minimizing the error distribution between the experimental equilibrium data and the predicted isotherms (Fig. 5a–d). Thus, the results of r^2 can be useful in predicting the optimum isotherm based on the three parameter Redlich Peterson isotherm. As the Redlich Peterson isotherm incorpo-

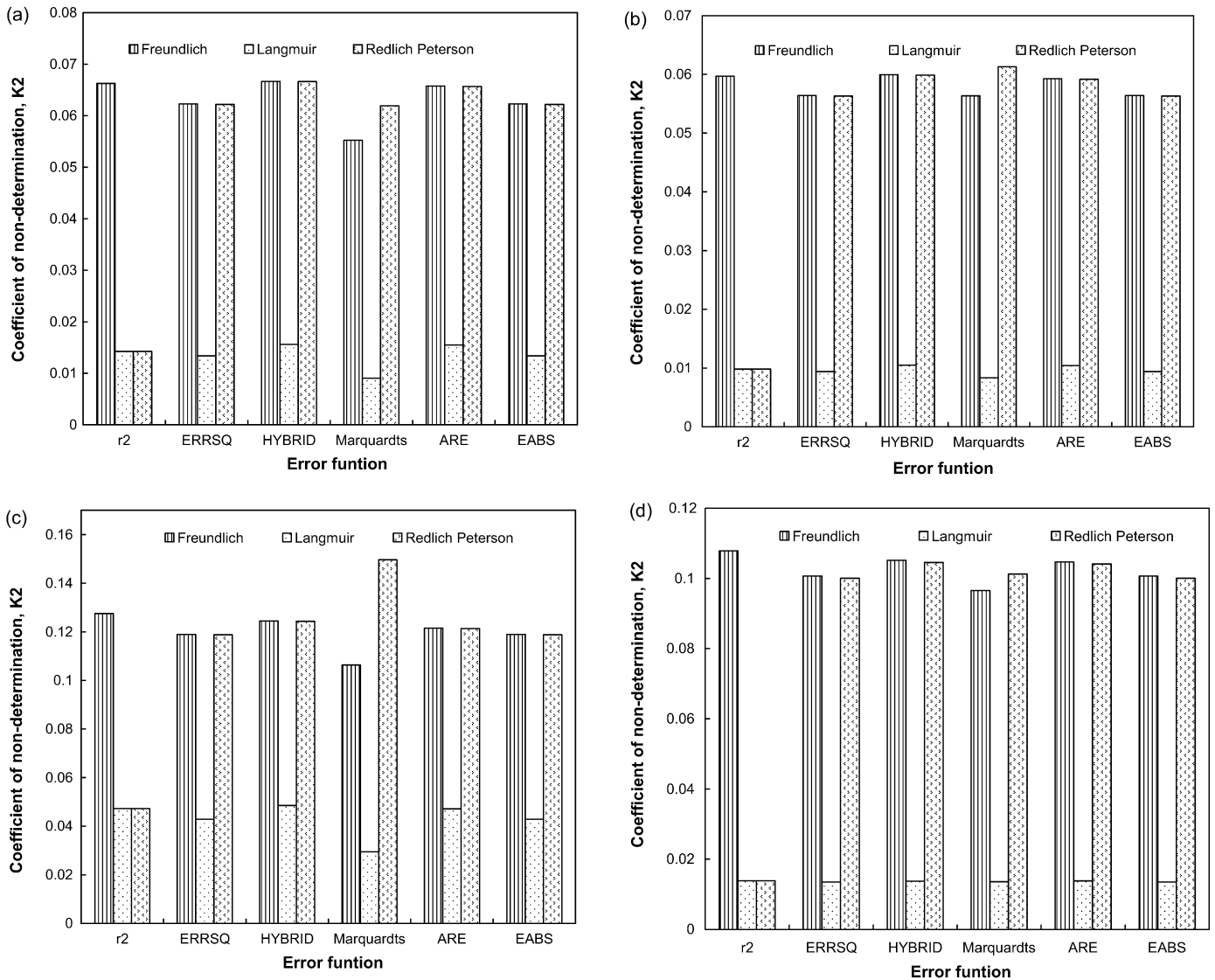


Fig. 5. Coefficient of non-determination for isotherms of methylene blue onto activated carbon at: (a) 305 K, (b) 313 K, (c) 323 K and (d) 333 K.

rates the features of Freundlich and Langmuir isotherm, the trend of the isotherm can be predicted based on the parameters obtained by maximizing r^2 . From Fig. 4a–d, it can be observed that for all the studied solution temperatures, Redlich Peterson isotherm exactly overlaps the Langmuir isotherm with the same r^2 (Tables 4a–4d) value suggesting the monolayer coverage of methylene blue onto activated carbon. This is also validated by the best fit in Langmuir isotherm obtained by minimizing the MPSPD error function at all the four solution temperatures studied. The another important observation from Fig. 5a–d is that, the MPSPD function which had lower K^2 value for two parameter isotherm showed a very higher K^2 value in the case of two parameter isotherm. This suggests it is better to avoid using this error function to minimize the error distribution between the predicted and experimental isotherms. This can also be visualized from the poor representation of Redlich Peterson isotherm predicted by minimizing MPSPD function (Fig. 3a–c). From Fig. 3a–c, it can be observed that MPSPD showed an exponential type curve for Redlich Peterson isotherm and thereby failing to explain the

saturation limitation of the sorption process. The important finding of the present study is that to select the optimum isotherm, it is necessary to consider both the size of the error function and also the determined theoretical isotherm parameters. In addition before selecting the optimum isotherm it is a necessary step to analyze how well the experimental data agree with theory of isotherms and vice versa.

3.2. Adsorption thermodynamics

In the design of sorption systems, two types of thermodynamic properties, namely the directly measurable properties like temperature, equilibrium constant and properties which cannot be measured directly such as entropy, S , and free energy, G , are required. Thus, to establish the thermodynamic properties which cannot be directly measured, the famous thermodynamical relation known as Gibbs free energy, G , was used. The Gibbs free energy and entropy is used to decide the nature of sorption chemical reactions or the nature of sorption process. The evaluation

Table 5
Thermodynamic parameters for the sorption of methylene blue onto activated carbon

Temperature	ΔG (L/mol)	$T\Delta S$	ΔH	ΔS
305	-7.28853	43.28408		
313	-8.06333	44.4194	36.33103	0.141915
323	-8.61798	45.83855		
333	-11.5056	47.2577		

of thermodynamic parameters will be useful to check will the process occur spontaneously. The change in Gibbs free energy, which is a function of temperature is given by:

$$\Delta G = \Delta H - T \Delta S \quad (3)$$

The change in free energy can be calculated using the Langmuir constant, K_L , that is related to the energy of adsorption:

$$\Delta G = -RTK \ln(K_L) \quad (4)$$

The thermodynamic parameters ΔH and ΔS can be calculated from the plot of change in free energy, ΔG versus temperature, T (not shown). The calculated thermodynamic parameters for the sorption of methylene blue by activated carbon are given in Table 5. The negative value of ΔG indicates the feasibility of the process and indicates the spontaneous nature of the sorption. The decrease in the negative ΔG value with an increasing temperature indicates the spontaneous sorption process is inversely proportional to the temperature. The positive value of entropy shows the increased randomness at the solid liquid interface during the sorption process and also suggests the process is entropy driven and not enthalpy driven. This is also suggested by the higher $T\Delta S$ values when compared to the ΔH value [26]. The positive value of ΔH suggests the endothermic nature of the sorption process. Previously a positive value of ΔH for a positive change in entropy was reported for the sorption of basic red 9 onto activated carbon [27], malachite green onto waste slurry [28], methylene blue onto fullers earth [29] and congo red onto coir pith [30]. The positive change in enthalpy and entropy was also reported for the sorption of several heavy metals onto various low cost adsorbents [31–34].

4. Conclusions

The equilibrium sorption of methylene blue by activated carbon was explained using the Freundlich, Langmuir and Redlich Peterson isotherms. The present study shows non-linear regression method as a best way to obtain the isotherm parameters and also to select the optimum isotherm. The present investigation suggests that the size of error function alone is not a deciding factor to select the optimum isotherm. In addition to the size of coefficient of determination, the validation of the theory behind the isotherm should be verified with the help of experimental data while selecting the optimum isotherm. Comparison studies with several error functions showed that there are no problems with the error functions used while minimizing the error distribution between the experimental equilibrium data and the predicted two parameter isotherms. In the case of

three parameter isotherms, r^2 was found to be the best objective function in minimizing the error distribution between the experimental equilibrium data and isotherms without violating the theory behind the isotherm models. For two parameter isotherms, a MPSD function was found to be a better option to minimize the error distribution between the experimental and predicted isotherms. The coefficient of non-determination was found to be a useful statistical term in identifying the best error function while selecting the optimum isotherm. The sorption of methylene blue by activated carbon was found to be well represented by both Langmuir and Redlich Peterson isotherm. Redlich Peterson is a special case of Langmuir when the constant g equals unity. The dye uptake process was found to be endothermic and spontaneous.

References

- [1] T.G. Lamond, C.R. Price, Size of carbon black micropores deduced from nitrogen and dye adsorption, *J. Colloid Interface Sci.* 31 (1) (1969) 104–110.
- [2] J.O. Peterson, G.F. Lee, Sorption capacity estimation for activated carbon packed columns, *Water Res.* 5 (9) (1971) 717–721.
- [3] G. McKay, M.S. Otterburn, P. Poosunthornsri, A.G. Sweeney, Factors affecting the rate acid dye removal from effluent using activated carbon, *Colourage* 27 (3) (1980) 3–5.
- [4] G. Bressa, L. Lima, F. Giunta, C. Maccà, Adsorptive power of different activated charcoal samples of some metals at various pH, *Inorg. Chim. Acta* 79 (1983) 304–305.
- [5] C.Y. Yin, M.K. Aroua, W.M.A.W. Daud, Review of modifications of activated carbon for enhancing contaminant uptakes from aqueous solutions, *Sep. Purif. Technol.* 52 (2007) 403–415.
- [6] A. Dąbrowski, P. Podkościelny, Z. Hubicki, M. Barczak, Adsorption of phenolic compounds by activated carbon—a critical review, *Chemosphere* 58 (2005) 1049–1070.
- [7] D. Mohan, C.U. Pittman Jr., Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water, *J. Hazard. Mater.* B137 (2006) 762–811.
- [8] Y.S. Ho, Selection of optimum isotherm, *Carbon* 10 (2004) 2115–2116.
- [9] K.V. Kumarm, Selection of optimum isotherm and kinetics, Ph.D. Thesis (submitted), Anna University, India.
- [10] K.V. Kumar, Optimum sorption isotherm by linear and non-linear methods for malachite green onto lemon peel, *Dyes and Pigments* 74 (2007) 595–597.
- [11] K.V. Kumar, K. Porkodi, Relation between some two- and three-parameter isotherm models for the sorption of methylene blue onto lemon peel, *J. Hazard. Mater.* 138 (2006) 633–635.
- [12] Y.S. Ho, W.T. Chiu, C.C. Wang, Regression analysis for the sorption isotherms of basic dyes on sugarcane dust, *Bioresour. Technol.* 96 (2005) 1285–1291.
- [13] Y.S. Ho, Isotherms for the sorption of lead onto peat: comparison of linear and non-linear methods, *Polish J. Environ. Stud.* 15 (1) (2006) 81–86.
- [14] K.V. Kumar, Comparative analysis of linear and non-linear method of estimating the sorption isotherm parameters for malachite green onto activated carbon, *J. Hazard. Mater.* 136 (21) (2006) 197–202.
- [15] Y.C. Wong, Y.S. Szeto, W.H. Cheung, G. McKay, Adsorption of acid dyes on chitosan—equilibrium isotherm analyses, *Process Biochem.* 39 (2004) 695–704.
- [16] J.F. Porter, G. McKay, H.K. Choy, The prediction of sorption from a binary mixture of acidic dyes using single- and mixed-isotherm variants of the ideal adsorbed solute theory, *Chem. Eng. Sci.* 54 (1999) 5863–5885.
- [17] J.C.Y. Ng, W.H. Cheung, G. McKay, Equilibrium studies of the sorption of Cu(II) ions onto chitosan, *J. Colloid Interface Sci.* 255 (2002) 64–74.
- [18] S.J. Allen, Q. Gan, R. Matthews, P.A. Johnson, Comparison of optimised isotherm models for basic dye adsorption by kudzu, *Bioresour. Technol.* 88 (2003) 143–152.

- [19] Y.S. Ho, J.F. Porter, G. McKay, Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: copper, nickel and lead single component systems, *Water Air Soil Pollut.* 141 (2002) 1–31.
- [20] K.V. Kumar, K. Porkodi, Mass transfer, kinetics and equilibrium studies for the biosorption of methylene blue using *Paspalum notatum*, *J. Hazard. Mater.* 146 (2007) 214–226.
- [21] H.M.F. Freundlich, Over the adsorption in solution, *Zeitschrift für Physikalische Chemie* 57A (1906) 385.
- [22] I. Langmuir, The constitution and fundamental properties of solids and liquids, *J. Am. Chem. Soc.* 38 (1916) 2221.
- [23] O. Redlich, D.L. Peterson, A useful adsorption isotherm, *J. Phys. Chem.* 63 (1959) 1024.
- [24] K. Porkodi, K.V. Kumar, Equilibrium, kinetics and mechanism modeling and simulation of basic and acid dyes sorption onto jute fiber carbon: Eosin yellow, malachite green and crystal violet single component systems, *J. Hazard. Mater.* 143 (2007) 311–327.
- [25] D.G. Kinniburgh, General purpose adsorption isotherms, *Environ. Sci. Technol.* 20 (1986) 895–904.
- [26] R. Pendleton, S.H.W. Schumann, Microcystin-LR adsorption by activated carbon, *J. Colloid Interface Sci.* 240 (2001) 1–8.
- [27] V.K. Gupta, I. Ali, Suhas, D. Mohan, Equilibrium uptake and sorption dynamics for the removal of a basic dye (basic red) using low-cost adsorbents, *J. Colloid Interface Sci.* 265 (2003) 257–264.
- [28] V.K. Gupta, S.K. Srivastava, D. Mohan, Equilibrium uptake, sorption dynamics, process optimization and column operations for the removal and recovery of malachite green from wastewater using activated carbon and activated slag, *Ind. Eng. Chem. Res.* 36 (1997) 2207–2218.
- [29] A. Kumar, N.N. Rao, S.N. Kaul, Alkali-treated straw and insoluble straw xanthate as low cost adsorbents for heavy metal removal—preparation, characterization and application, *Bioresour. Technol.* 71 (2000) 133–142.
- [30] C. Namasivayam, D. Kavitha, Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste, *Dyes Pigments* 54 (2002) 47–58.
- [31] Ö. Yavuz, Y. Altunkaynak, F. Güzel, Removal of copper, nickel, cobalt and manganese from aqueous solution by kaolinite, *Water Res.* 37 (2003) 948–952.
- [32] M. Ajmal, R.A.K. Rao, R. Ahmad, J. Ahmad, Adsorption studies on *Citrus reticulata* (fruit peel of orange): removal and recovery of Ni(II) from electroplating wastewater, *J. Hazard. Mater.* 79 (2000) 117–131.
- [33] L. Čurković, Š.C. Stefanović, A. Rastovčan-Mioè, Batch Pb^{2+} and Cu^{2+} removal by electric furnace slag, *Water Res.* 35 (2001) 3436–3440.
- [34] D. Mohan, K.P. Singh, Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse—an agricultural waste, *Water Res.* 36 (2002) 2304–2318.