

Short communication

Comparison of various error functions in predicting the optimum isotherm by linear and non-linear regression analysis for the sorption of basic red 9 by activated carbon

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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 basic red 9 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), the 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. Non-linear regression was found to be a better way to obtain the parameters involved in the isotherms and also 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 containing basic dyes, acid dyes [1–3] and heavy metals [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 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

A	Redlich Peterson isotherm constant (L/g)
ARE	the average relative error
B	Redlich Peterson isotherm constant (L/mg ^{1-(1/A)})
C_e	equilibrium concentration (mg/L)
EABS	the sum of the absolute errors
ERRSQ	the sum of the squares of the error
g	Redlich Peterson constant
HYBRID	the hybrid fractional error function
K_L	Langmuir isotherm constant (L/mg)
K_F	Freundlich constant, (mg/g) (L/g) ^{1/n}
MPSD	Marquardt's percent standard deviation
$1/n$	Freundlich exponent
n	number of experimental measurements (in Table 3)
p	number of parameters in isotherm
q_e	amount of dye adsorbed at equilibrium (mg/g)
q_m	monolayer sorption capacity (mg/g)
r^2	coefficient of determination
T	temperature (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 had used other error functions such as the hybrid fractional error function (HYBRID), Marquardt's percent standard deviation (MPSD), the average relative error (ARE), the 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.

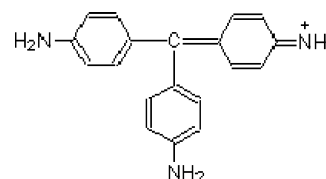
In the present study a comparison of six different error functions in minimizing the error distribution between the experimental and predicted isotherms was discussed using the experimental data of methylene blue onto powdered activated carbon at four different solution temperatures. The three widely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

2. Experimental

2.1. Adsorbate

The dye used in all the experiments was basic red 9, 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 basic red 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 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, loss on drying $\leq 10\%$ and residue on ignition $\leq 5\%$. The physical characteristics of the commercial activated carbon used are given in Table 1. Table 1 confirms the presence of more fractions of meso- and macro-pores. The surface morphology of the carbon particles is characterized by SEM analysis. The SEM images at different magnifications is given in Fig. 1(a) and (b) which further confirms the results by mercury porosimetry.

2.3. Process

Equilibrium studies were carried out at two different solutions temperatures at 313 K 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 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 parameters. Error functions are usually used to select the optimum isotherm. 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 [10]. Sometimes linearization affected the normality assump-

Table 1
Properties of activated carbon used

Pore volume (mercury porosimetry)	7.03×10^{-1} (cm ³ /μm g) at a diameter of 1.496 μm 5.023×10^{-1} (cm ³ /g) at a diameter of 2.834 μm 4.872×10^{-1} (cm ³ /g) at a diameter of 2.183 μm
Surface area (mercury porosimetry)	1.143 m ² /g at a diameter of 1.496 μm 1.036 m ² /g at a diameter of 3.693×10^{-1} μm 1.301 m ² /g at a diameter of 1.306 μm
Pore number fraction (mercury porosimetry)	3.887×10^{-3} at a diameter of 1.498 μm 7.892×10^{-1} at a diameter of 2.928×10^{-1} μm 5.020×10^{-1} at a diameter of 4.511×10^{-1} μm
Bulk particle density (mercury porosimetry)	0.5530 g/cm ³
Apparent density (mercury porosimetry)	0.5530 g/cm ³
Total surface area (mercury porosimetry)	2.6029 m ² /g
Total intruded volume (mercury porosimetry)	0.9741 cm ³ /g
Total interparticle porosity (mercury porosimetry)	2.29%
Total intraparticle porosity (mercury porosimetry)	53.87%
He density (mercury porosimetry)	1.7470 g/cm ³
Theoreticla porosity (mercury porosimetry)	68.35%
BET surface area	1000.1 m ² /g
Microporous volume (BET)	0.38 cm ³ /g
Non-microporous specific surface area (BET)	130 m ² /g

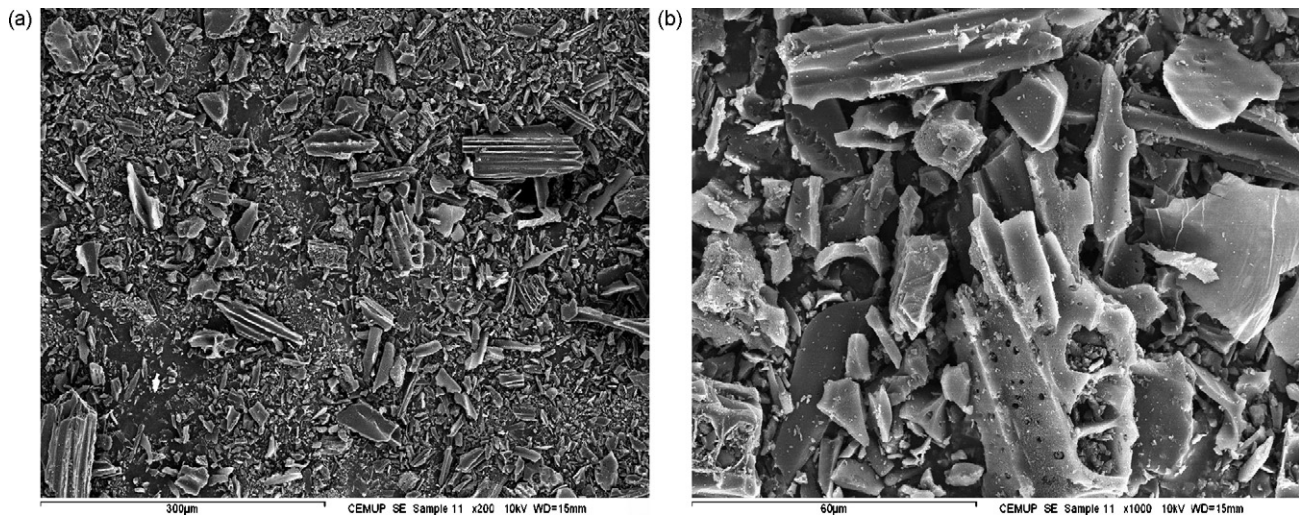


Fig. 1. SEM image of activated carbon: (a) 200× and (b) 1000×.

tions of the least squares and the error distribution was found to be changing to the either the better or worse [10,11]. 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 most widely used linear form of Freundlich, Langmuir and Redlich Peterson isotherms are given in Table 2. The linear expressions of Freundlich,

Langmuir and Redlich Peterson isotherms in Table 2 showed minimum deviations between the experimental equilibrium data and isotherm for most of sorption systems. Table 2 shows a list of linear isotherms reported for various sorption systems. The Freundlich, Langmuir and Redlich Peterson isotherm constants in the linear expressions shown in Table 2 can be calculated from the slope and intercept of the plot between $\log(q_e)$ and $\log(C_e)$, C_e/q_e and C_e and $\ln(AC_e/(q_e - 1))$ and $\ln(C_e)$. In the

Table 2
Isotherms and its linearized expressions

Isotherms	Non-linear expression	Linear expression	Plot	Parameters	References
Freundlich	$q_e = K_F(C_e)^{1/n}$	$\log(q_e) = \log(K_F) + (1/n)\log(C_e)$	$\log(q_e)$ vs. $\log(C_e)$	$K_F = \exp(\text{intercept})$, $1/n = \text{slope}$	[21]
Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}$	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]

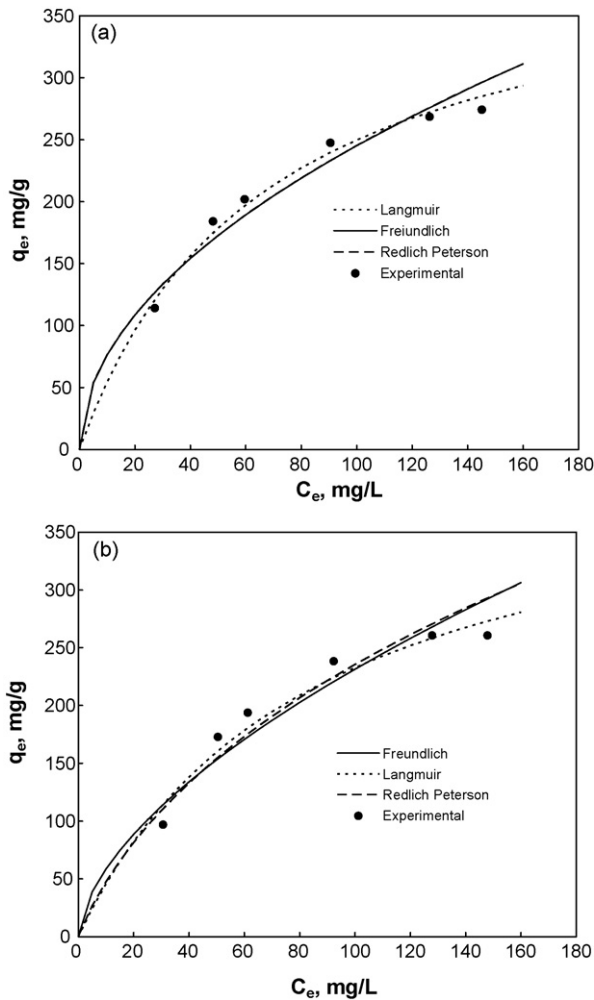


Fig. 2. Experimental equilibrium data and isotherm by linear regression method for the sorption of basic red 9 by activated carbon at (a) 313 K and (b) 333 K.

case of Redlich Peterson isotherm, the constant A was obtained by maximizing the r^2 value using a trial and error method which was optimized for 500 iterations using the solver add-in function, Microsoft Excel, Microsoft Corporation. Fig. 2(a) and (b) shows the experimental and the predicted isotherms by linear regression method at 313 K and 333 K, respectively. The calculated isotherm parameters and the corresponding r^2 values were shown in Table 3. From Table 3, at 303 K the relatively lower r^2 values for Freundlich isotherm when compared to Langmuir and Redlich Peterson isotherm suggests it may not be appropriate to use this model in representing the equilibrium uptake of BR9 by activated carbon particles. The Langmuir and Redlich Peterson were found to be the best fit isotherm for the equilibrium uptake of BR9 by activated carbon. At 333 K, both Redlich Peterson and Freundlich isotherm provides a poor fit to the experimental equi-

ilibrium data. The higher r^2 value at 333 K suggests Langmuir isotherm as the best fit isotherm for the sorption of BR9 at this solution temperature. Though the linear regression was found to be a suitable method for selecting the optimum isotherm, at 313 K, the theory of Redlich Peterson was not explained for the experimental equilibrium data. As per theory, the Redlich Peterson isotherm represents the Langmuir isotherm when the Redlich Peterson isotherm constant g equals unity as follows:

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

Thus the value of g equivalent to unity should predict the Langmuir isotherm with same r^2 value [9,24]. However from Fig. 2(a), it can be observed that Redlich Peterson does not represent the Langmuir isotherm for g value equivalent to unity. A similar observation was previously reported for the dye uptake of copper ions by chitosan at some specified operating conditions [17], sorption of malachite green by activated carbon [14]. Previously several research reports suggested that 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 [8,9,11,14,20]. 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. 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 was found to be varying with the error function used while minimizing the error distribution between the experimental and predicted isotherms [15–17,19,20]. 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. As the degrees of freedom was found to be the one of component in the error functions MPSD and HYBRID, to avoid the consistency with the determined parameters the degrees of freedom was maintained a constant for all the studied solution temperatures. The explanations of various error functions used in the present study are given in Table 4.

Fig. 3(a)–(c) shows the experimental and predicted Freundlich [21], Langmuir [22] and Redlich and Peterson [23]

Table 3
Isotherms by linear regression method for the sorption of methylene blue by activated carbon

Temperature (K)	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
313	23.7	0.50	0.94	393.8	0.016	0.98	6.03	0.014	1	0.97
333	14.86	0.59	0.89	428.4	0.011	0.92	6.66	0.090	0.65	0.80

Table 4
Explanation of different error functions

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

isotherms at 305 K by minimizing the error distribution between the experimental and the theoretical isotherms using various error functions explained in Table 4. From Fig. 3(a)–(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 temperature of 313 K. The variation in the predicted isotherms was found to be more pronounced in case of the three parameter isotherm (Fig. 3(c)). The calculated isotherm parameters and the corresponding error functions for the minimum error distribution between the experimental equilibrium data and predicted isotherm for the studied solution temperatures 313 K and 333 K is given in Tables 5a and 5b, respectively. From Tables 5a and 5b, other than r^2 , all the other error functions studied corresponding to the minimized deviations between the experimental equilibrium data and predicted isotherms suggested that Langmuir as the best fit isotherm followed by the Freundlich isotherm. In the case of r^2 , the Langmuir isotherm was found to be the best fit isotherm followed by Redlich Peterson isotherm. The predicted isotherm parameter, $g = 1$ in the case of r^2 suggested that isotherm is approaching the Langmuir and not the Freundlich. Fig. 4(a) shows the experimental equilibrium data and predicted isotherms for the sorption of BR9 onto activated carbon at 313 K. From Fig. 4(a), it can be observed that the Langmuir isotherm exactly overlaps the Redlich Peterson isotherm with the same r^2 value for a g value equal to unity. This suggests the sorption process follows the Langmuir isotherm as per the theory of Redlich Peterson isotherm. A similar observation was observed at 333 K (not shown). In the case of 313 K and 333 K, the higher A and B values by all the error functions except r^2 suggests isotherm is following Freundlich but not Langmuir isotherm. Fig. 4(b) shows the experimental equilibrium data and predicted isotherms by minimizing the HYBRID error function. From Fig. 4(b), it can be observed that Redlich Peterson isotherm exactly overlaps the Freundlich isotherm. Thus the Redlich Peterson is a special case of Freundlich when the constant A and $B \gg 1$. A similar effect was

observed for the predicted isotherms by minimizing the error functions MPSD, ARE, EABS and ERRSQ (not shown). These two observations suggesting the homogeneous and heterogeneous sorption of BR9 by activated carbon based on the size of r^2 and HYBRID error function reflects the complexity in non-linear regression method. This suggests that the size of the

Table 5a
Predicted isotherm by minimizing the error distribution using five different error functions at 313 K

Freundlich (two parameter isotherm)				
	K_F	$1/n$	OF ^a	
r^2	27.56172	0.473704	0.945537	
ERRSQ	31.02066	0.446813	170.4375	
HYBRID	23.76322	0.506828	1.640162	
MPSD	40.22904	0.392311	3.051139	
ARE	24.71892	0.499472	1.476294	
EABS	31.02066	0.446813	170.4375	
Langmuir (two parameter isotherm)				
	q_m	K_L	OF ^a	
r^2	397.3789	0.016793	0.984615	
ERRSQ	392.3573	0.017304	46.05281	
HYBRID	415.3666	0.015075	0.465141	
MPSD	380.8251	0.018926	1.716673	
ARE	414.4908	0.015214	0.426644	
EABS	392.3572	0.017304	46.05281	
Redlich Peterson (three parameter isotherm)				
	A	B	g	OF ^a
r^2	6.672883	0.016792	1	0.984615
ERRSQ	13914.79	448.201	0.553325	170.3894
HYBRID	13913.86	585.1058	0.493288	1.639809
MPSD	13913	582.9822	0.480798	3.891856
ARE	13911.08	562.3569	0.500649	1.47597
EABS	13896.65	447.6218	0.553322	170.3893

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

Table 5b

Predicted isotherm by minimizing the error distribution using five different error functions at 333 K

Freundlich (two parameter isotherm)			
	K_F	$1/n$	OF ^a
r^2	18.29817	0.550554	0.90936
ERRSQ	23.10751	0.497932	310.6824
HYBRID	14.80056	0.597084	3.69433
MPSD	30.64622	0.441143	4.31941
ARE	16.52082	0.575684	3.22092
EABS	23.10751	0.497932	310.6824

Langmuir (two parameter isotherm)

	q_m	K_L	OF ^a
r^2	431.6687	0.012048	0.951762
ERRSQ	410.597	0.013354	152.8925
HYBRID	474.0225	0.009893	2.014523
MPSD	389.0933	0.015839	3.126749
ARE	464.556	0.010431	1.781433
EABS	410.597	0.013354	152.8925

Redlich Peterson (three parameter isotherm)

	A	B	g	OF ^a
r^2	5.200778	0.012049	1	0.951762
ERRSQ	13915.01	443.3888	0.550798	679.5748
HYBRID	13913.94	583.3008	0.488905	7.831363
MPSD	13913	583	0.48	7.48437
ARE	13911.35	555.7613	0.498191	5.799476
EABS	13896.81	442.7958	0.550804	679.6021

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

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.

The function r^2 and the other error functions studied suggest the homogeneous and heterogeneous sorption of methylene by activated carbon particles, respectively. Thus in order to check which error function minimize the error distribution between the experimental and theoretical isotherms, the another statistical term coefficient of non-determination, K^2 was used. The coefficient of non-determination, K^2 was defined as [26]:

$$K^2 = \frac{\text{unexplained variance}}{\text{total variance}} = 1 - \frac{\text{explained variance}}{\text{total variance}} = 1 - r^2 \quad (2)$$

The coefficient of non-determination is 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. 5 shows the calculated K^2 values for the isotherms predicted by minimizing or maximizing the various error functions at 313 K.

From Fig. 5, it is observed that MPSD function least unexplained the two parameter isotherm suggesting this function as

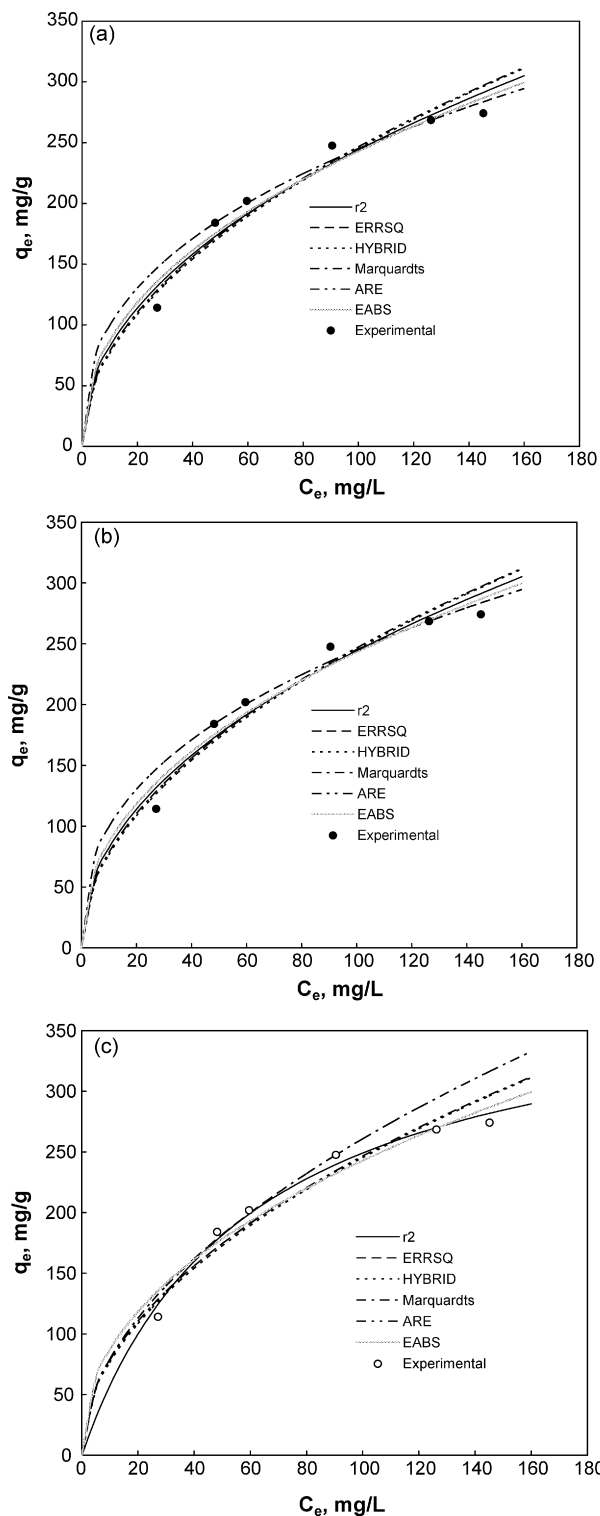


Fig. 3. Experimental data and predicted: (a) Freundlich isotherm, (b) Langmuir isotherm, and (c) Redlich Peterson isotherm for basic red 9 onto activated carbon at 305 K.

the very best function to minimize the error distribution between the experimental and predicted two parameter isotherms namely the Freundlich and Langmuir isotherm. A similar trend was observed for isotherms at 333 K (not shown). Thus for the studied system, MPSD was found to be the best error function to be

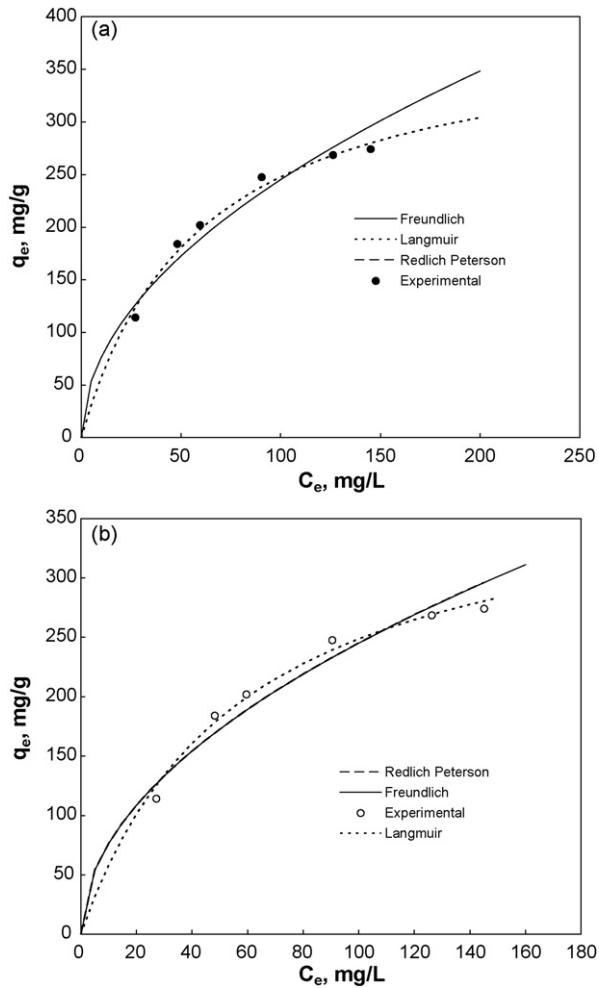


Fig. 4. (a) Isotherms by maximizing r^2 function for methylene blue onto activated carbon at 313 K. (b) Isotherms by minimizing HYBRID function for basic red 9 onto activated carbon at 313 K.

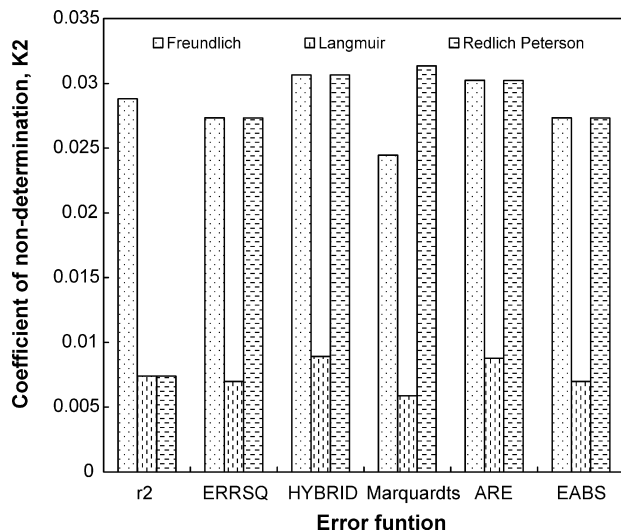


Fig. 5. Coefficient of non-determination for isotherms of basic red 9 onto activated carbon at 313 K.

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. 5). 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 incorporates the features of Freundlich and Langmuir isotherm, the trend of the isotherm can be predicted based on the parameters obtained by maximizing r^2 . Thus the mechanism of BR9 sorption by activated carbon is due to the monolayer coverage of solute particle. This is also validated by the best fit in Langmuir isotherm obtained by minimizing the MPSD error function at the two studied solution temperatures studied. The another important observation from Fig. 5 is that, the MPSD 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 MPSD function (Fig. 3(c)). From Fig. 3(c), it can be observed that MPSD 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 agrees with theory of isotherms and vice versa.

4. Conclusions

The equilibrium sorption of basic red by activated carbon was explained using the Freundlich, Langmuir and Redlich Peterson isotherm. The present study shows that non-linear regression method as a best way to obtain the isotherm parameters and also to select the optimum isotherm. Langmuir isotherm was found to be the best fit isotherm suggesting the monolayer coverage of BR9 by activated carbon. 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. 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 more useful statistical term in identifying the best error function while selecting the optimum isotherm.

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