

Comparative analysis of linear and non-linear method of estimating the sorption isotherm parameters for malachite green onto activated carbon

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Received 2 April 2005; received in revised form 30 August 2005; accepted 11 September 2005

Available online 30 May 2006

Abstract

The experimental equilibrium data of malachite green onto activated carbon were fitted to the Freundlich, Langmuir and Redlich–Peterson isotherms by linear and non-linear method. A comparison between linear and non-linear of estimating the isotherm parameters was discussed. The four different linearized form of Langmuir isotherm were also discussed. The results confirmed that the non-linear method as a better way to obtain isotherm parameters. The best fitting isotherm was Langmuir and Redlich–Peterson isotherm. Redlich–Peterson is a special case of Langmuir when the Redlich–Peterson isotherm constant g was unity.

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Keywords: Adsorption; Malachite green; Activated carbon; Isotherm; Equilibrium; Linear method; Non-linear method

1. Introduction

Currently, adsorption processes is proved to be an effective process for the removal of pollutants from wastewaters [1–5]. Adsorption onto activated carbons is the most commonly used technique for separating the pollutants from the aqueous solutions. Due to the increased awareness of the occurrence of many synthetic and natural organic substances in natural water has led to the emergence of adsorption process by activated carbon. Activated carbons have been widely used for the removal of various pollutants such as dyes [4], flavor esters [5], phenol [6] and heavy metals [7] from their aqueous solutions.

Generally, adsorption process proceeds through various mechanisms such as external mass transfer of solute, intraparticle diffusion and adsorption at sites. Unless extensive experimental data are available concerning the specific adsorption application, determining the rate-controlling step is impossible. Therefore, empirical design procedures based on adsorption equilibrium conditions are the most common method to predict adsorber size and performance. The different parameters and the underlying thermodynamic assumption of these equilibrium models often provide some insight into both the adsorption

mechanism and the surface properties and affinity of adsorbent. The most appropriate method in designing the adsorption systems and assessing the performance of the adsorption systems is to have an idea on adsorption isotherms. Linear regression was frequently used to determine the most fitted isotherm. The linear least-squares method to the linearly transformed isotherm equations was also widely applied to confirm the experimental data and isotherms using coefficient of determination [8]. However, previously researchers showed that, depending on the way isotherm equation is linearized, the error distribution changes wither the worse or the better [9]. So, it will be an inappropriate technique to use the linearization method for estimating the equilibrium isotherm parameters. In this study, a comparison of linear least-squares method and non-linear method of three widely used isotherms, Langmuir [10], Freundlich [11], and Redlich–Peterson [12], were examined to the experiment of malachite green adsorption on activated carbon. The problems associated with transforming the non-linear equations to linear form are also reported.

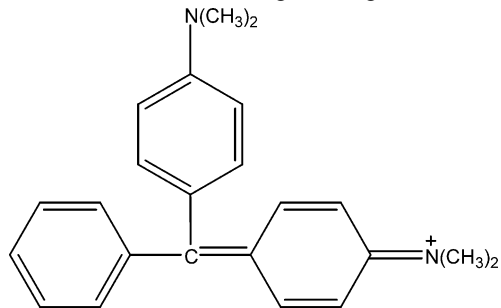
2. Materials and method

2.1. Adsorbate

The dye used in all the experiments was malachite green (C.I.42000). The dye malachite green was obtained from CDH

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chemicals, New Delhi, India. Synthetic dye solutions were prepared by dissolving weighed amount of dye in 1 l of distilled water. The structure of malachite green is given below.



The stock solution of malachite green was prepared by dissolving 1 g of malachite green 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 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 $\leq 180 \text{ mg/g}$, loss on drying $\leq 10\%$, and residue on ignition $\leq 5\%$.

2.3. Method

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 at four different solution temperatures 305, 313, 323 and 333 K. The contact was made for 48 h, which is more than sufficient time to attain 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. Linear method

The search for best-fit equation using the linear regression analysis was the most commonly used technique to determine the best-fit isotherm and the method of least squares has been used for finding the parameters of the isotherms. The three isotherms, Freundlich, Langmuir and Redlich–Peterson and their corresponding linearized forms are shown in Table 1. From Table 1, it was observed that the Langmuir isotherm can be linearized to at least four different types [9] and simple linear regres-

sion will result in different parameter estimates. Out of the four different types of linearized Langmuir isotherm equations, Langmuir-1 and Langmuir-2 are the most commonly used by several researchers because of the minimized deviations from the fitted equation resulting in the best error distribution [8]. The q_m , and K_a values for Langmuir-1, Langmuir-2, Langmuir-3, and Langmuir-4 were predicted 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 , respectively. The details of these different forms of linearized Langmuir equations and the method to estimate the Langmuir constants q_m , and K_a from these plots were explained in Table 1. The calculated isotherm parameters were shown in Table 2. From Table 2, it was observed that the Langmuir constants varied for different forms of linear Langmuir equations. This is because depending on the way isotherm is linearized; the error distribution changes with the worse or the better [9]. Further out of the correlation coefficients for Langmuir-1, Langmuir-2, Langmuir-3 and Langmuir-4, r^2 value for Langmuir-1 was found to be relatively higher when compared to the other three except at 305 K. At 305 K, the Langmuir-2 showed a best fit when compared to other three types. Langmuir-3 and Langmuir-4 showed a similar r^2 value (Table 2) confirming that both these types have same error distribution structure. From Table 2, it was also observed that the equilibrium sorption capacity of activated carbon for malachite green was found to be 565 mg/g (calculated based on Langmuir type 1 equation) at 305 K. The very high sorption capacity of activated carbon confirms that the activated carbon can be used as an adsorbent for the removal of malachite green from its aqueous solutions. Further from Table 2, it was observed that the maximum sorption capacity was found to decrease with increase in temperature of the solution. This observation shows that the dye uptake process is endothermic in nature.

Further, the equilibrium data were further analyzed using the linearized form of Freundlich equation using the same set experimental data, by plotting $\log(q_e)$ versus $\log(C_e)$. The calculated Freundlich isotherm parameters and the corresponding r^2 values were shown in Table 2. From Table 2, it was observed that at all solution temperatures, the r^2 values were found to be relatively less than best fit Langmuir isotherm. This suggests that the Freundlich isotherm does not much well represent the experimental adsorption data.

The sorption of malachite green onto activated carbon following the linearized form of Redlich–Peterson isotherm can be predicted from the plot between $\ln(AC_e/q_e)$ versus $\ln(C_e)$ as shown in Fig. 1. 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 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 to obtaining the isotherm constants were explained in Table 1. The calculated Redlich–Peterson constants and their corresponding linear regression coefficient of determination were shown in Table 2. From Table 2, it was observed that the r^2 value for Redlich–Peterson isotherm was found to be more or less nearer to the best-fit Langmuir

Table 1
Isotherms and their linear forms (q_m : mg/g; K_a : L/mg; K_F : (mg/g) (L/g)ⁿ; A: L/g; B: L/mg^{1-1/A})

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. $\log(C_e)$	[10]
Langmuir-1	$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_a q_m}$	$\frac{C_e}{q_e}$ vs. C_e	[11]
Langmuir-2 $q_e = \frac{q_m K_a C_e}{1 + K_a C_e}$	$\frac{1}{q_e} = \left(\frac{1}{K_a q_m}\right) \frac{1}{C_e} + \frac{1}{q_m}$	$\frac{1}{q_e}$ vs. $\frac{1}{C_e}$	
Langmuir-3	$q_e = q_m - \left(\frac{1}{K_a}\right) \frac{q_e}{C_e}$	q_e vs. $\frac{q_e}{C_e}$	
Langmuir-4	$\frac{q_e}{C_e} = K_a q_m - K_a q_e$	$\frac{q_e}{C_e}$ vs. q_e	
Redlich–Peterson $q_e = \frac{AC_e}{1+BC_e^g}$	$\ln\left(A \frac{C_e}{q_e} - 1\right) = g \ln(C_e) + \ln(B)$	$\ln\left(A \frac{C_e}{q_e} - 1\right)$ vs. $\ln(C_e)$	[12]

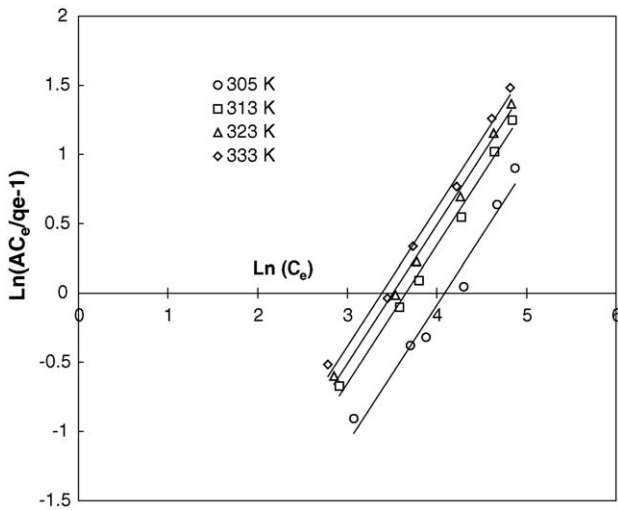


Fig. 1. Redlich–Peterson isotherm for the sorption of malachite green onto activated carbon at different solution temperatures.

Table 2
Isotherm parameters obtained by using linear method (q_m : mg/g; K_a : L/mg; K_F : (mg/g) (L/g)ⁿ; A: L/g; B: L/mg^{1-1/A})

		Temperature (K)			
		305	313	323	333
Langmuir-1	q_m	486	469	465	465
	K_a	0.0218	0.0307	0.0345	0.0404
	r^2	0.974	0.994	0.996	0.995
Langmuir-2	q_m	565	511	498	505
	K_a	0.0158	0.0248	0.0288	0.0320
	r^2	0.984	0.993	0.994	0.988
Langmuir-3	q_m	510	489	482	483
	K_a	0.0195	0.0274	0.0312	0.0359
	r^2	0.852	0.953	0.969	0.944
Langmuir-4	q_m	551	499	488	494
	K_a	0.0166	0.0261	0.0302	0.0339
	r^2	0.852	0.953	0.969	0.944
Freundlich	$1/n$	0.501	0.431	0.408	0.387
	K_F	33.7	49.7	56.3	64.5
	r^2	0.918	0.933	0.935	0.916
Redlich–Peterson	g	1.000	1.000	1.000	1.000
	B	0.1770	0.0259	0.0299	0.0338
	A	9.2	13.0	14.6	16.71
	r^2	0.970	0.993	0.995	0.991

isotherm equation. This shows that both Langmuir isotherm and Redlich–Peterson isotherm model can be used to best represent the experimental data of malachite green onto activated carbon.

3.2. Non-linear method

For non-linear method, a trial and error procedure, which is applicable to computer operation, was developed to determine the isotherm parameters by maximizing the respective the coefficient of determination between experimental data and isotherms using the solver add-in with Microsoft’s spreadsheet, Microsoft Excel.

Figs. 2–5 show experimental data and the predicted equilibrium curve using non linear method for the three-equilibrium isotherm Freundlich, Langmuir and Redlich–Peterson at 305, 313, 323 and 333 K, respectively. The obtained isotherm parameters were listed in Table 3. In the case of Langmuir isotherm, the results from the four Langmuir linear equations are the

Table 3

Isotherm parameters obtained by using non-linear method (q_m : mg/g; K_a : L/mg; K_F : (mg/g)(L/g)ⁿ; A : L/g; B : L/mg^{1-1/A})

		Temperature (K)			
		305	313	323	333
Non-linear Langmuir	q_m	509	481	474	478
	K_a	0.0198	0.0289	0.0328	0.0375
	r^2	0.955	0.983	0.988	0.980
Non-linear Freundlich	$1/n$	0.478	0.407	0.386	0.369
	K_F	37.4	55.0	61.9	69.6
	r^2	0.902	0.929	0.934	0.917
Non-linear Redlich–Peterson	g	1.000	1.000	1.000	1.000
	B	0.0198	0.0289	0.0328	0.0375
	A	10.1	13.9	15.6	17.9
	r^2	0.955	0.983	0.988	0.980

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. In addition, Figs. 2–5 show that the Redlich–Peterson and Langmuir isotherms overlapped each other, and seemed to be the best-fitting models for the experimental 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. Further, the higher r^2 value of Langmuir and Redlich–Peterson isotherm when compared to the r^2 value of Freundlich confirms that both Langmuir and Redlich–Peterson are the best-fit isotherm to represent the experimental data of malachite green onto activated carbon.

3.3. Comparison of linear and non-linear method

When comparing the r^2 values of all the four linearized form of Langmuir equation with Freundlich isotherm alone will result in different outcomes. In Table 2, for all the solution tempera-

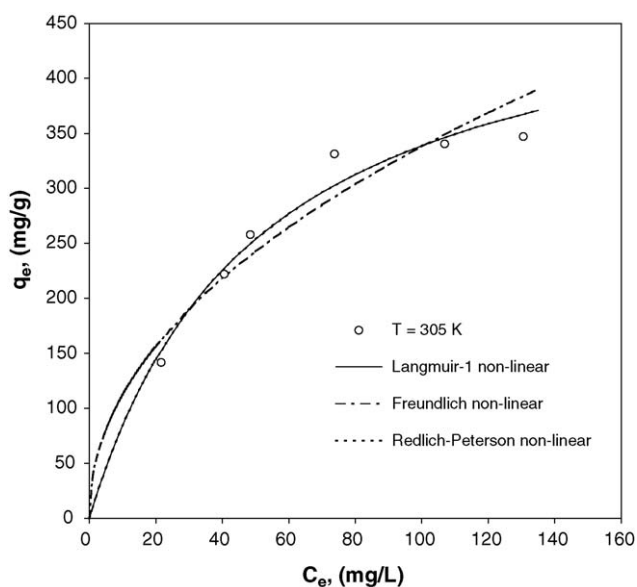


Fig. 2. Isotherms (non-linear method) for malachite green onto activated carbon at 305 K.

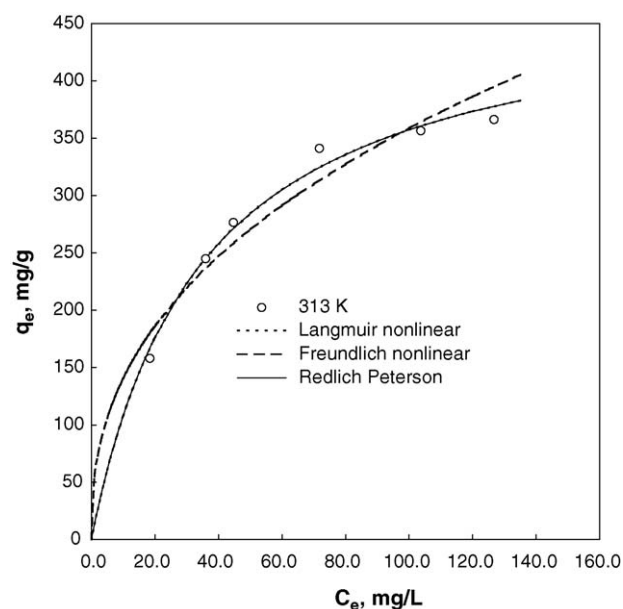


Fig. 3. Isotherms (non-linear method) for malachite green onto activated carbon at 313 K.

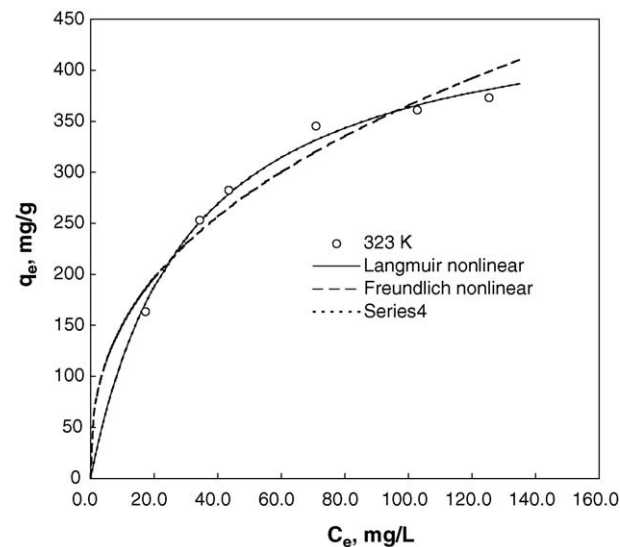


Fig. 4. Isotherms (non-linear method) for malachite green onto activated carbon at 323 K.

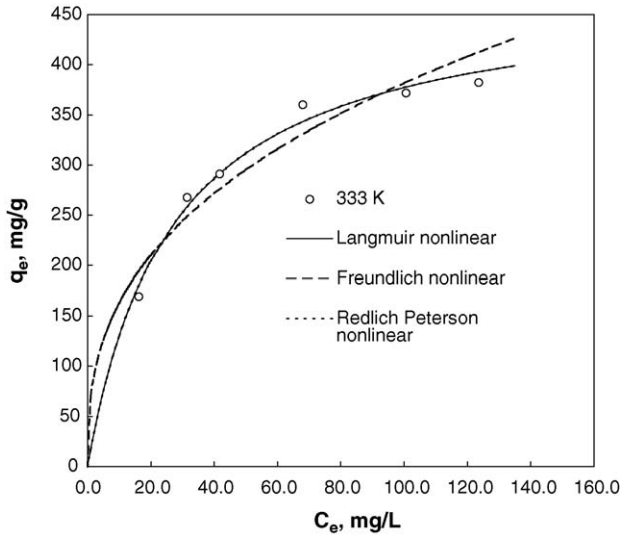


Fig. 5. Isotherms (non-linear method) for malachite green onto activated carbon at 333 K.

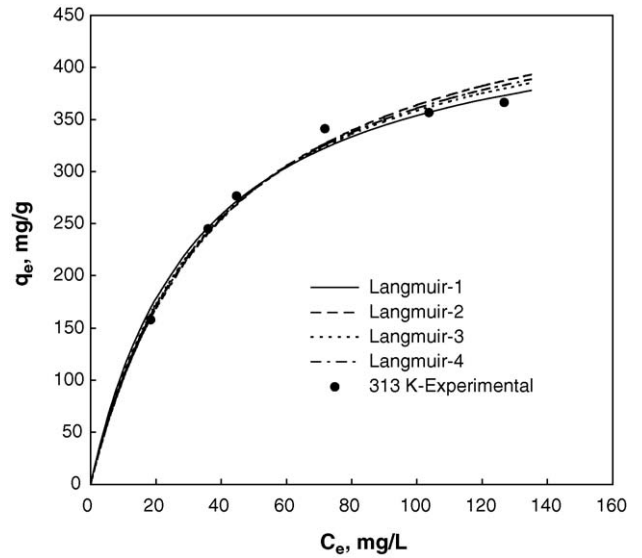


Fig. 7. Langmuir isotherm (linear method) for the sorption of malachite green onto activated carbon at 313 K.

ture range studied, the r^2 value for Langmuir-1 and Langmuir-2 isotherm was found to be greater than the r^2 value of Freundlich isotherm, thus confirming the monolayer coverage of malachite green onto activated carbon. But, when comparing the r^2 value of Langmuir-3 and Langmuir-4 isotherm with Freundlich isotherm, Freundlich was seemed to well represent the experimental data than the other two. Thus, the theoretical assumption of Langmuir, monolayer coverage of malachite green onto activated carbon was getting valid in case of Langmuir-1 and Langmuir-2 isotherms but not getting valid for Langmuir-3 and Langmuir-4 isotherms. Further different predicted values were obtained for different linearized forms of Langmuir isotherm equations for the same experimental equilibrium data. The experimental and the predicted values obtained from the four linearized forms of Langmuir isotherm equations are shown in Figs. 6–9

for 305, 313, 323 and 333 K, respectively. From these figures, it was observed that the predicted values by four different linearized forms of Langmuir isotherm equation are different for the same experimental equilibrium data. The different outcomes shown by the four linearized forms of a non-linear Langmuir isotherm shows the mathematical complexities associated with using linear method in estimating the rate parameters. The different r^2 values (Table 2) for different linearized form of Langmuir isotherm equation are due to the variation in distribution of error structure for different linear equations. The variation in error distribution is due to the different axial settings; as a result the dependent variables are transformed to different axial positions. Thus, the different axial settings in linear method would effect r^2 significantly and impact the final determination of parameters.

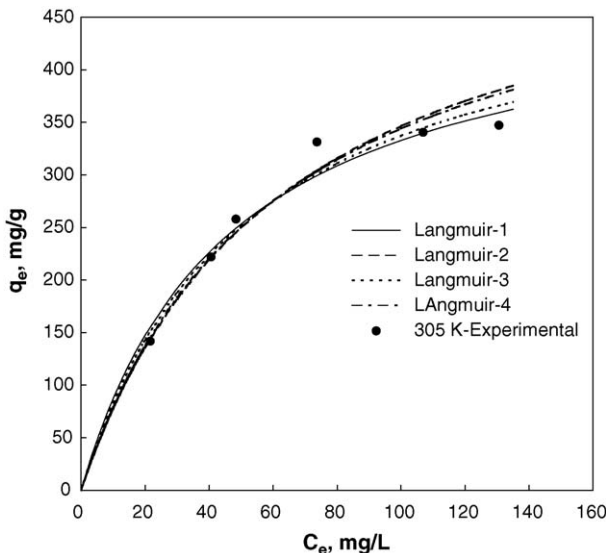


Fig. 6. Langmuir isotherm (linear method) for the sorption of malachite green onto activated carbon at 305 K.

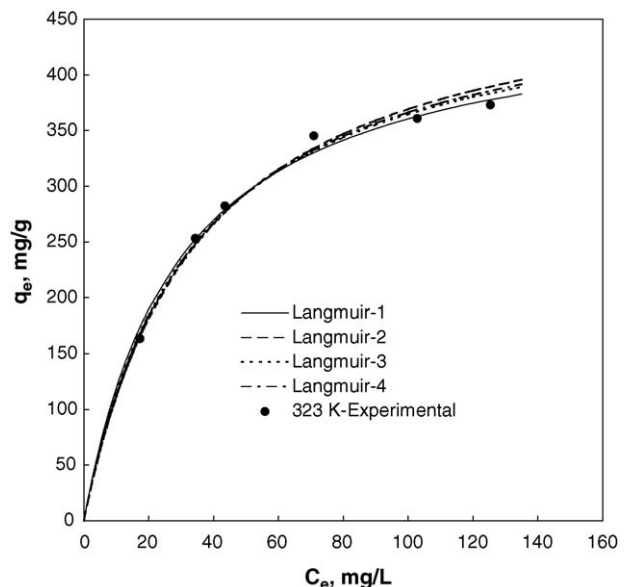


Fig. 8. Langmuir isotherm (linear method) for the sorption of malachite green onto activated carbon at 323 K.

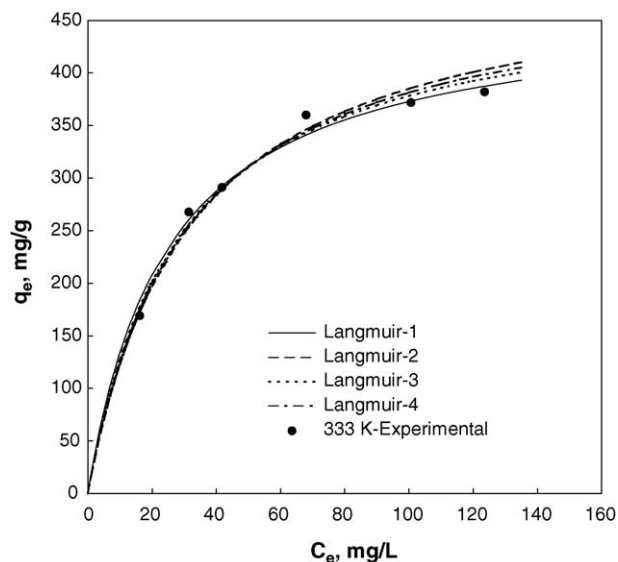


Fig. 9. Langmuir isotherm (linear method) for the sorption of malachite green onto activated carbon at 333 K.

The problems with these transformations distort the experimental error. The linear method assumes 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 relationships (as most of the equilibrium relationships are non-linear) as the error distribution gets altered after transforming the data to a linear. Thus, it may be inappropriate to minimize the r^2 of the vertical distances of points from the line unless the error distribution is same at every value at X . Thus, the different outcomes for different linearized forms is because: for different axial settings the predicted Y values were fixed to a line that assumes a trend line which assumes a uniform distribution of error for all values of X . Thus, it will be an inappropriate method to get isotherm parameters by fitting the experimental data by linear method, instead it is better to go for non linear method which have a uniform error distribution

(irrespective of the linear form) for the whole range of experimental data. Further, in non-linear method there is no such linear trend line fit that assumes the equal error distribution for all the values of X . Thus, non-linear method will be a more appropriate technique to obtain the isotherm parameters.

4. Conclusions

Present study shows that the non-linear method is the better way to obtain the adsorption parameters than the linear regression method. Redlich–Peterson and Langmuir isotherm well represent the sorption of malachite green onto activated carbon. Langmuir is a special case of Redlich–Peterson isotherm when constant g was unity.

Acknowledgement

The author like to thank CSIR, India for the SRF award.

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