

Short communication

# Comparison of linear and non-linear method in estimating the sorption isotherm parameters for safranin onto activated carbon

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## Abstract

Comparison analysis of linear least square method and non-linear method for estimating the isotherm parameters was made using the experimental equilibrium data of safranin onto activated carbon at two different solution temperatures 305 and 313 K. Equilibrium data were fitted to Freundlich, Langmuir and Redlich–Peterson isotherm equations. All the three isotherm equations showed a better fit to the experimental equilibrium data. The results showed that non-linear method could be a better way to obtain the isotherm parameters. Redlich–Peterson isotherm is a special case of Langmuir isotherm when the Redlich–Peterson isotherm constant  $g$  was unity.

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## 1. Introduction

Currently, sorption processes are proved to be an effective process for the removal of pollutants from wastewaters [1–5]. Sorption processes includes the selective transfer of solute components in the fluid phase onto the surface or onto the bulk of solid adsorbent materials. Activated carbon is the most commonly used adsorbent for separating the pollutants from the aqueous solutions. Activated carbon have been widely used for the removal of various pollutants such as phenol [6], dyes [7], heavy metals [8] and flavor esters [5] from their aqueous solutions.

In general, sorption processes were found to proceed through varied mechanisms such as external mass transfer of solute, intraparticle diffusion and adsorption at sites. Unless extensive data are available, it is impossible to predict the rate-determining step involved in the process. However, sorption isotherm equations, which explain the process at equilibrium conditions, provide an easier solution to this complex problem. Also, isotherm equation does not consider the complex mechanism (external mass transfer, pore

diffusion, chelation, ion exchange and chemisorption) involved in the sorption processes; engineers use the equilibrium equation with ease for the design of batch sorption systems. The adsorption isotherms are equilibrium equations and applied to condition resulting after the adsorbate-containing phase have been in contact with the adsorbent for sufficient time to reach equilibrium at a constant temperature. The different parameters and the underlying thermodynamic assumption of these equilibrium models often provide some insight into the sorption mechanism, the surface properties and affinity of sorbent. Some of the isotherm equations that can explain solid–liquid adsorption systems are: Langmuir, Freundlich, Sips, Toth isotherm, Redlich–Peterson, Dubinin–Raduskevich and Harins–Jura isotherm equations [9,10]. Out of these, Freundlich [11], Langmuir [12] and Redlich–Peterson [13] isotherms are the most commonly used isotherms by several researchers for different sorbent/sorbate systems [14–17] and are given by Eqs. (1)–(3), respectively:

$$q_e = K_F C_e^{1/n_F} \quad (1)$$

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \quad (2)$$

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$$q_e = \frac{AC_e}{1 + BC_e^g} \quad (3)$$

where  $C_e$  (mg/L) is the left out solute concentration at equilibrium,  $q_e$  (mg/g) is the amount of dye adsorbed at equilibrium,  $K_F(\text{mg/g})(\text{L/g})^{n_F}$  is the Freundlich constant related to adsorption capacity,  $n_F$  is the Freundlich exponent related to adsorption intensity, respectively,  $q_m$  is the Langmuir monolayer sorption capacity (mg/g),  $K_a$  is related to the energy of adsorption (L/mg),  $A$  is the Redlich–Peterson isotherm constant (L/g),  $B$  is the Redlich–Peterson isotherm constant ( $\text{L/mg}^{1-1/A}$ ) and  $g$  is Redlich–Peterson isotherm exponent, which lies between 0 and 1.

The term  $q_e$  in isotherm equations can be calculated from the simple mass balance equation as follows:

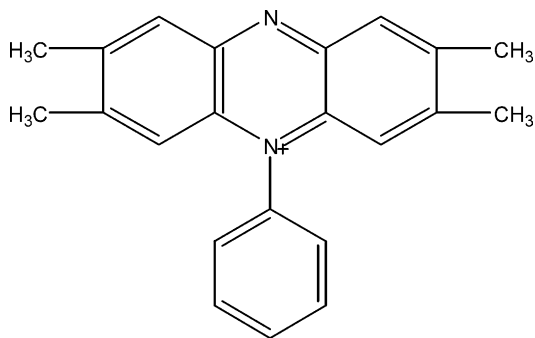
$$q_e = (C_o - C_e)V/M \quad (4)$$

where  $C_o$  is the initial dye concentration (mg/L),  $V$  is the volume of solution (L) and  $M$  is the mass of adsorbent (g).

Linear regression was frequently used to determine the most fitted isotherm. The linear least-squares method to the linearly transformed isotherm equations was widely applied to confirm the experimental data and isotherms using coefficient of determination [15]. However, previously researchers showed that, depending on the way isotherm equation is linearized, the error distribution changes either the worse or the better [18]. So, it will be an inappropriate technique to use the linearization method for estimating the equilibrium isotherm parameters. Thus, in the present study, non-linear method is used to determine the adsorption isotherm parameters. Also, a comparative analysis was made between the linear and non-linear method in estimating the rate parameters for the sorption of safranin and activated carbon systems. The problems associated with transforming the non-linear equations to linear form are also reported.

## 2. Materials and methods

The solute used in all the experiments was safranin, a basic (cationic) dye. The structure of safranin (C.I: Basic Red 2) is given by:



The stock solution of safranin was prepared by dissolving one gram of safranin in one liter of distilled water. All working

solutions of desired initial dye concentrations 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 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  $\leq 180$  mg/g, loss on drying  $\leq 10\%$  and residue on ignition  $\leq 5\%$ ; particle size:  $>60\%$  passes through 300 mesh.

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 two different solution temperatures 305 and 313 K. 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

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 Langmuir isotherm can be linearized into at least four different types and simple linear regression will result in different parameter estimates [18]. 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. Out of the four different type 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. For Langmuir-1, the isotherm constants, monolayer sorption capacity  $q_m$  and  $K_a$  can be calculated from the slope and intercept of plot between  $C_e/q_e$  versus  $C_e$ . The calculated  $q_m$  and  $K_a$  values and the coefficient of determination values were shown in Table 2. The  $q_m$  and  $K_a$  values predicted from the other linearized forms of Langmuir equations, Langmuir-2, Langmuir-3 and Langmuir-4, were obtained from the plot between  $1/q_e$  versus  $1/C_e$ ,  $q_e$  versus  $q_e/C_e$  and  $q_e/C_e$  versus  $q_e$ , respectively. The calculated isotherm parameters are 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

Table 1  
Isotherms and their linear forms

Isotherm	Linear form	Plot	Reference	
Freundlich	$q_e = K_F C_e^{1/n_F}$	$\log(q_e) = \log(K_F) + 1/n_F \log(C_e)$	$\log(q_e)$ vs. $\log(C_e)$	Freundlich [11]
Langmuir-1	$q_e = \frac{q_m K_a C_e}{1 + K_a C_e}$	$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_a q_m}$	$\frac{C_e}{q_e}$ vs. $C_e$	Langmuir [12]
Langmuir-2		$\frac{1}{q_e} = \left(\frac{1}{K_a q_m}\right) \frac{1}{C_e} + \frac{1}{q_m}$	$\frac{1}{q_e}$ 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	$q_e = \frac{A C_e}{1 + B C_e^g}$	$\ln\left(A \frac{C_e}{q_e} - 1\right) = g \ln(C_e) + \ln(B)$	$\ln\left(A \frac{C_e}{q_e} - 1\right)$ vs. $\ln(C_e)$	Redlich and Peterson [13]

changes either the worse or the better [18]. Further out of the coefficient of determination 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 others. In addition, (Table 2) Langmuir-3 and Langmuir-4 showed a similar  $r^2$  value confirming that both these types are in same error distribution structure. From Table 2, it was also observed that the equilibrium sorption capacity of activated carbon for safranin was found to be 576 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 safranin from its aqueous solutions.

The equilibrium data were further analyzed using the linearized form of Freundlich equation using the same set of experimental data, by plotting  $\log(q_e)$  versus  $\log(C_e)$ . The cal-

culated 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 linearized Langmuir isotherm. This suggests that the Langmuir isotherm as the most appropriate isotherm than the Freundlich isotherm for the present system.

The sorption of safranin onto activated carbon following the linearized form of Redlich–Peterson isotherm can be observed from the plot between  $\ln(A C_e/q_e)$  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 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. Fig. 1 shows the plot between  $\ln(A C_e/q_e)$  versus  $\ln(C_e)$ . The calculated Redlich–Peterson constants from Fig. 1 and their corresponding linear

Table 2  
Isotherm parameters obtained by using linear method

		Temperature (K)	
		305	313
Langmuir-1	$q_m$ (mg/g)	576	564
	$K_a$ (L/mg)	0.0646	0.0390
	$r^2$	0.999	1.000
Langmuir-2	$q_m$ (mg/g)	560	566
	$K_a$ (L/mg)	0.0743	0.0386
	$r^2$	0.990	0.997
Langmuir-3	$q_m$ (mg/g)	563	564
	$K_a$ (L/mg)	0.0728	0.0389
	$r^2$	0.980	0.994
Langmuir-4	$q_m$ (mg/g)	565	565
	$K_a$ (L/mg)	0.0713	0.0387
	$r^2$	0.980	0.994
Freundlich	$1/n_F$	0.240	0.312
	$K_F$ (mg/g)(L/g) <sup><math>n_F</math></sup>	165.5	106.3
	$r^2$	0.998	0.981
Redlich–Peterson	$g$	0.836	1.000
	$B$ (L/mg <sup><math>1-1/A</math></sup> )	0	0
	$A$ (L/g)	106	22
	$r^2$	1.000	0.999

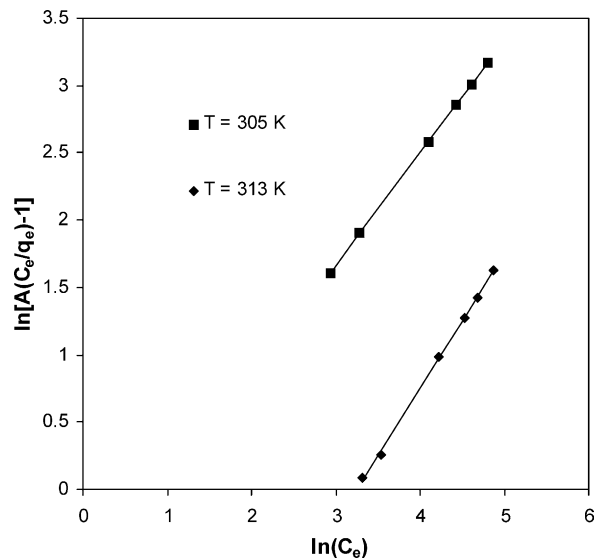


Fig. 1. Redlich–Peterson isotherm for safranin onto activated carbon.

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 1 and 0.999 ( $\sim 1$ ) at 305 and 313 K, respectively. This shows that in addition to Langmuir isotherm, Redlich–Peterson isotherm model can be used to explain the present system at equilibrium conditions.

The present investigation shows that linearization can be successfully applied in predicting the equilibrium parameters. However, comparison analysis of the  $r^2$  values of all the four linearized form of Langmuir equation with Redlich–Peterson isotherm and Freundlich isotherm show different outcomes. At 305 K, when comparing the  $r^2$  value of Langmuir-1 with Freundlich isotherm equation, Langmuir-1 was found to better represent the experimental equilibrium data. But, when comparing the  $r^2$  value of Langmuir-2, Langmuir-3 and Langmuir-4 with Freundlich, it was observed that Freundlich isotherm as an appropriate relation to explain the present system. This makes a confusion to decide whether the sorption process is due to monolayer coverage of solute particle or not. Further, based on the calculated  $q_m$  values by the four type of linear Langmuir equations, the following observations are made: for Langmuir-1 form, the  $q_m$  value gets decreased with increasing temperature. But, the  $q_m$  value calculated by Langmuir-2 shows an increase in  $q_m$  with increasing temperature. Whereas in case of Langmuir-4, the calculated  $q_m$  value was found to be the same, suggesting that the temperature had no effect on adsorption. But, experimental data confirms that there is a definite effect of temperature on the dye uptake process. In addition, the Langmuir constant  $K_a$  calculated by the four different linearized forms of Langmuir isotherm equations also gets varied for the same experimental equilibrium data. These different outcomes show the real complexities and problems in estimating the isotherm parameters by linearization technique. The different outcomes for different linearized form of Langmuir isotherm are because the error structure will get varied upon linearizing the non-linear equation. The error distribution may vary the better or worse depending on the way the equation is linearized. Various outcomes for the four linearized equations are also due to the different axial settings, that would alter the result of linear regression and influence the determination process [15]. Thus, it will be more appropriate to use non-linear method to estimate the parameters involved in the isotherm or any rate equation. Also, non-linear method had an advantage that the error distribution does not get altered as in linear technique, as all the isotherm parameters are fixed in the same axis.

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

Figs. 2 and 3 shows experimental data and the predicted equilibrium curve using non-linear method for the three-equilibrium isotherm Freundlich, Langmuir and Redlich–Peterson at 305 and 313 K, respectively. The ob-

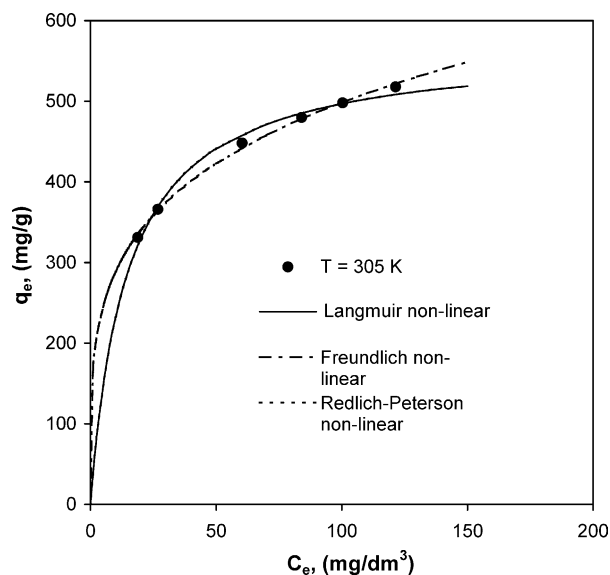


Fig. 2. Adsorption isotherm for safranin onto activated carbon at 305 K.

tained isotherm parameters were listed in Table 3. In the case of Langmuir isotherm, 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. From Table 3, it was observed that at both the solution temperature of 305 and 313 K, the isotherm parameters estimated for different isotherms were found to be more or less same except the value of Redlich–Peterson isotherm constant  $A$  at 305 K. The Redlich–Peterson constant  $g$  was found to be unity at all the solution temperatures. The Redlich–Peterson constant  $g$  approaching unity suggests that the isotherm is approaching Langmuir instead of Freundlich. Further,  $r^2$  values suggest that the Redlich–Peterson

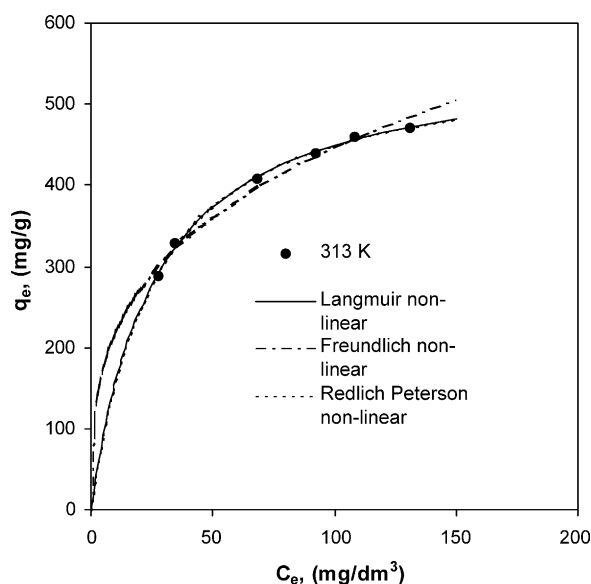


Fig. 3. Adsorption isotherm for safranin onto activated carbon at 313 K.

Table 3  
Isotherm parameters obtained by using non-linear method

		Temperature (K)	
		305	313
Non-linear Langmuir	$q_m$ (mg/g)	569	565
	$K_a$ (L/mg)	0.0690	0.0389
	$r^2$	0.988	0.998
Non-linear Freundlich	$1/n_F$	0.238	0.308
	$K_F(\text{mg/g})(\text{L/g})^{n_F}$	166.8	108.0
	$r^2$	0.997	0.980
Non-linear Redlich–Peterson	$g$	1.000	1.000
	$B$ ( $\text{L/mg}^{1-1/A}$ )	0.0690	0.0389
	$A$ (L/g)	39.3	21.9
	$r^2$	0.988	0.998

and Langmuir isotherms fit the experimental data equally well with the same values of coefficient of determination (Table 3). From Figs. 2 and 3, it was also observed that the Langmuir isotherm overlapped the Redlich–Peterson isotherm. Thus, Langmuir isotherm is a special case of Redlich–Peterson isotherm when constant  $g$  was unity.

#### 4. Conclusions

Present study shows that all the three isotherm equations Freundlich, Langmuir and Redlich–Peterson models well represent the sorption of safranin onto activated carbon. Non-linear method is a better way to obtain the adsorption parameters. Langmuir is a special case of Redlich–Peterson isotherm when constant  $g$  was unity. The relatively better fit

of experimental equilibrium data in Langmuir isotherm suggests the monolayer coverage and chemisorption of safranin onto activated carbon.

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