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Short communication

Sorption isotherm for safranin onto rice husk: Comparison of linear and non-linear methods

K. Vasanth Kumar*, S. Sivanesan*

Department of Chemical Engineering, AC Tech, Anna University, Chennai, Tamilnadu, TN 600 025, India

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Abstract

Comparison analysis of linear least-square method and non-linear method for estimating the isotherm parameters was made. Comparison analysis was made using the experimental equilibrium data of safranin onto rice husk at a solution temperature of 305 K. Sorption data were fitted to Freundlich, Langmuir and Redlich–Peterson isotherm equations. All the three isotherm equations showed a better fit to the experimental data. The results show 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.

Keywords: Sorption; Safranin; Rice husk; Equilibrium isotherm; Linear method; Non-linear method

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1. Introduction

Currently sorption process is proved to be an effective process for the removal of pollutants from wastewaters [1–5]. Sorption process includes the selective transfer of solute components in the fluid phase onto the surface or onto the bulk of solid adsorbent materials. The most commonly used method to design the adsorption system is by having the information on sorption isotherm. The analysis and design of adsorption separation process require the relevant adsorption equilibrium, which is the most important piece of information in understanding the adsorption process. The adsorption isotherms are equilibrium equations and apply 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 both the sorption mechanism and the surface properties and affinity of the sorbent.

The Langmuir, Freundlich and Redlich–Peterson isotherms are the most commonly used isotherms to describe the adsorption equilibrium for wastewater treatment applications. Linear regression was the most commonly used technique to determine the most fitted isotherm. The linear least-square method to the linearly transformed isotherm equations was widely applied to confirm the consistency of the predicted and experimental equilibrium data using coefficient of determination. Some other methods recently reported to predict the optimum isotherm are correlation coefficient, the sum of errors squared, a hybrid error function, Marquardt's percent standard deviation, the average relative error and the sum of absolute errors.

In the present study, a comparison of linear least-square method and non-linear method of three widely

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* Corresponding authors. Tel.: +91 44 222 03525 (work), +91 9444469876 (mobile).

E-mail addresses: vasanth_vit@yahoo.com (K. Vasanth Kumar), sivanesh@yahoo.com (S. Sivanesan).

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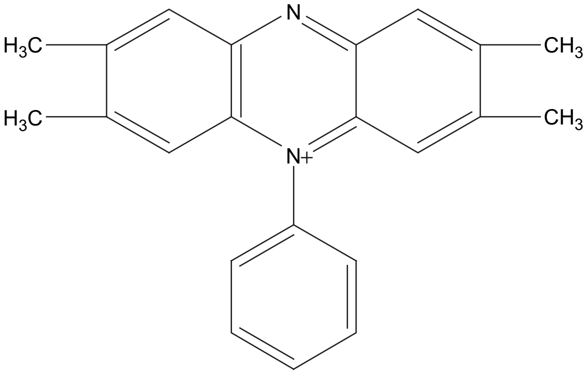
used isotherms, Langmuir [10], Freundlich [11], and Redlich–Peterson [12], was examined to experiment malachite green adsorption onto rice husk. A trial and error procedure was used for non-linear method by using the *solver* add-in with Microsoft's spreadsheet, Microsoft Excel.

2. Materials and methods

The solute used in all the experiments was safranin, a basic (cationic) dye. Synthetic dye solutions were prepared by dissolving weighed amount of safranin in 1 L of double distilled water. The structure of safranin (C.I.: Basic Red 2) is given by:



The stock solution of safranin was prepared by dissolving 1 g of safranin in 1 L of distilled water. All working solutions were prepared by diluting the stock solution with distilled water.

The rice husk used in the present investigation was obtained from local rice mills. The collected materials were then washed with distilled water for several times to remove all the dirt particles. The washing process was continued till the wash water contains no color. The washed materials were then dried in a hot air oven at 60 °C for 24 h. The dried materials were then grinded using a domestic mixer. The grinded materials were then sieved to constant particle size of +60 mesh to −85 mesh. Then the materials were stored in plastic bottles for further use.

Equilibrium experiments were carried out by contacting 0.06 g of rice husk particles with 50 mL of dye solution of different initial dye concentrations 125, 100, 70, 50, 30, 10 mg/L. The contact was made in 150 mL capped conical flasks using water bath shakers at a constant agitation speed of 95 strokes/min. The agitation was made for 48 h, which is more than sufficient time to reach equilibrium.

3. Results and discussions

In the present study the coefficient of determination was used to determine the best fit isotherm model. The non-linear and their linearized forms of Freundlich, Langmuir and Redlich–Peterson isotherms are shown in Table 1. From Table 1, it was observed that the Langmuir isotherm can be linearized into at least four different types and simple linear regression will result in different parameter estimates [17]. The details of these different forms of linearized Langmuir equations and the method to estimate the Langmuir constants q_m, and K_L from these plots are explained in Table 1. Out of the four different types of linearized Langmuir isotherm equations, Langmuir-1 and Langmuir-2 are 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_L can be calculated from the slope and intercept of plot between C_e/q_e and C_e. The calculated q_m, and K_L values and the coefficient of determination values are shown in Table 2. Similarly the q_m, and K_L values were predicted for the other linearized forms of Langmuir equations. Langmuir-2, Langmuir-3, and Langmuir-4 can be predicted from the plot between $1/q_e$ and $1/C_e$, q_e and q_e/C_e, and q_e/C_e and 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 the isotherm is

Table 1
Isotherms and their linear forms

Isotherm		Linear form	Plot	Reference
Freundlich	$q_e = K_F C_e^{1/n}$	$\log(q_e) = \log(K_F) + 1/n \log(C_e)$	$\log(q_e)$ vs. $\log(C_e)$	Freundlich [15]
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 [16]
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 [18]

Table 2
Isotherm parameters obtained by using linear method

Freundlich	K_F (mg/g)(L/g)^n	2.488727554
	$1/n$	0.593706603
	r^2	0.759572703
Langmuir-1	q_m (mg/g)	35.6508884
	K_L (L/mg)	0.04528544
	r^2	0.906796606
Langmuir 2	q_m (mg/g)	178.0858883
	K_L (L/mg)	0.00483681
	r^2	0.910909607
Langmuir-3	q_m (mg/g)	28.4409271
	K_L (L/mg)	0.0954953
	r^2	0.215990103
Langmuir-4	q_m (mg/g)	56.97283199
	K_L (L/mg)	0.02062604
	r^2	0.215990103
Redlich Peterson	A (L/g)	107374184.4
	B (L/mg$^{1-1/A}$)	43144209.42
	g	0.596696414
	r^2	0.596696414

linearized, the error distribution changes wither the worse or the better [17]. Further out of the correlation coefficients for Langmuir-1, Langmuir-2, Langmuir-3 and Langmuir-4, r^2 value for Langmuir-2 was found to be relatively higher when compared to the other. As given in Table 2, Langmuir-3 and Langmuir-4 showed a similar r^2 value confirming that both these types are in same error distribution structure.

The experimental equilibrium data representing Freundlich isotherm can be predicted from the plot between $\log(q_e)$ and $\log(C_e)$. The method to determine the Freundlich constants is explained in Table 1. The predicted Freundlich constant K_F, Freundlich exponent $1/n$ and the corresponding linear regression correlation coefficient are shown in Table 2. In Table 2, the very lower r^2 value of 0.7596 confirms that it is not appropriate to use Freundlich isotherm to represent the safranin sorption by rice husk particles.

The experimental data were further fitted to the three parameter Redlich–Peterson isotherm equation. The Redlich–Peterson isotherm constants can be obtained from the plot between $\ln(AC_e/q_e - 1)$ and $\ln(C_e)$. As the Redlich–Peterson isotherm contains three unknown parameters A, B and g, it is not possible to obtain simply by linearization technique. So a minimization procedure is adopted to maximize the coefficient of determination r^2, between the theoretical Redlich–Peterson isotherm data for q_e and the experimental data. The calculated Redlich–Peterson isotherm constants A, B, g and their corresponding coefficients of determination are shown in Table 2. In Table 2, the very lower r^2 value of 0.5967 shows that it is inappropriate to use Redlich–Peterson isotherm for the sorption of safranin onto rice husk particles.

The present study showed that the linearization technique is helpful in determining the optimum sorption isotherm. However, the different outcome for different linearized Langmuir isotherm (Table 2) suggests that it may not be a good approach to predict the optimum isotherm by linear method. For eg, from Table 2, it was observed that the equilibrium sorption capacity of rice husk for safranin was found to be highly varying from 28.44 mg/g to 178.08 mg/g for different types of linearized Langmuir isotherm equations but for the same experimental data.

In addition, when comparing the r^2 values of all the four linearized forms of Langmuir equations with Redlich–Peterson isotherm and Freundlich isotherm several outcomes for the same experimental equilibrium data are produced. For eg, the r^2 value for Langmuir-1 and Langmuir-2 isotherms was found to be greater than the r^2 value of Freundlich and Redlich–Peterson isotherms, thus confirming the monolayer coverage of safranin onto rice husk particles. Thus the optimum isotherm for the present safranin/rice husk system was determined to be Langmuir isotherm. But when comparing the r^2 values of Langmuir-3 and Langmui-4 isotherms with Freundlich and Redlich–Peterson isotherms, Freundlich isotherm was found to be the optimum isotherm. The different outcomes show the real complexities and problems in estimating the isotherm parameters by linearization technique. The different outcomes for different linearized forms of equations are because the error structure will get varied upon linearizing the non-linear equation. The error distribution may vary either to better or to worse depending on the way the equation is linearized. The different outcomes for different linearized forms of a single non-linear equation for the same set of experimental data are due to the variation in the error structure upon linearizing a non-linear equation. Various outcomes for the four linearized equations are also due to the different axial settings, so that it would alter the result of linear regression and influence the determination process [11].

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, because all the equilibrium parameters are fixed on the same axis. Thus in the present study in addition to linear method, non-linear method is also used to determine the adsorption isotherm parameters. A trial and error procedure was used for non-linear method by using the *solver* add-in with Microsoft's spreadsheet, Microsoft Excel.

Fig. 1 shows experimental data and the predicted equilibrium curve using non-linear method for the three-equilibrium isotherms Freundlich, Langmuir and Redlich–Peterson at 305 K. The obtained isotherm parameters are listed in Table 3. In the case of Langmuir

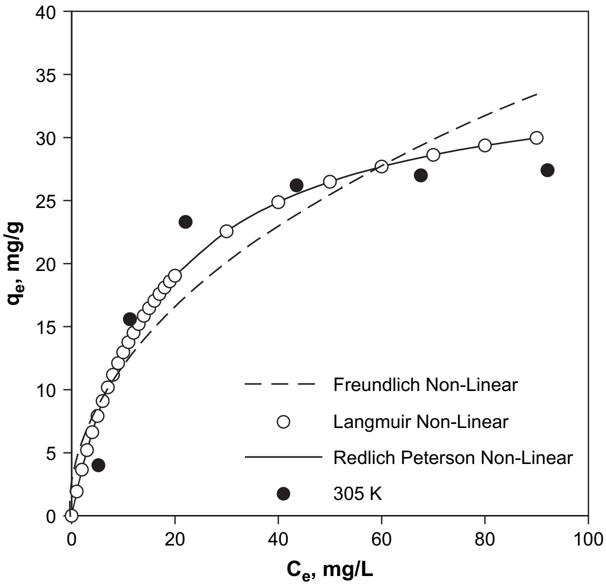


Fig. 1. Adsorption isotherm for safranin onto rice husk particles at 305 K.

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 equations to linear forms, and also they are in the same error structures. From Table 3, it was observed that, the isotherm parameters estimated for different isotherms by linear and non-linear methods were entirely different. The values of Redlich–Peterson constant g equal to unity suggest that the isotherm is approaching the Langmuir instead of Freundlich. Further r^2 values suggest that the Redlich–Peterson and Langmuir isotherms fit the experimental data equally well with the same values of coefficient of determination (Table 3). Thus both Langmuir and Redlich–Peterson isotherms can be used to explain the sorption of safranin onto rice husk particles. From Fig. 1, it was also observed that the Langmuir isotherm exactly overlapped the Redlich–Peterson isotherm. Thus Langmuir isotherm is a special case of Redlich–Peterson isotherm when constant g was unity.

4. Conclusion

Present study shows that the non-linear method is a more appropriate technique to predict the optimum sorption isotherm than the linear method. The experimental equilibrium data of safranin onto rice husk follow Langmuir and Redlich–Peterson isotherms equally well. Langmuir is a special case of Redlich–Peterson isotherm when constant g was unity.

Table 3
Isotherm parameters obtained by using non-linear method

Non-linear isotherms	T, K	
Non-linear Langmuir	q_m, mg/g	35.83062708
	K_a, dm^3/mg	0.056686345
	r^2	0.901187957
Non-linear Freundlich	$1/n$	0.460668715
	K_F, (mg/g)(L/g)^n	4.197444614
	r^2	0.79851614
Non-linear Redlich–Peterson	g	1
	B, L/mg$^{1-1/A}$	0.056685497
	A, L/g	2.031089845
	r^2	0.901187957

References

[1] Ho YS, McKay G. The kinetics of sorption of basic dyes from aqueous solutions by sphagnum moss peat. Canadian Journal of Chemical Engineering 1998;76:822–6.
[2] Walker G, Hansen L, Hanna JA, Allen SJ. Kinetics of a reactive dye adsorption onto dolomite sorbents. Water Research 2003; 37:2081–9.
[3] McKay G, Allen SJ, McConvey IF, Otterburn MS. Transport process in the sorption of colored ions by peat particles. Journal of Colloid and Interface Science 1981;80(2):323–39.
[4] McKay G, Allen SJ. Surface mass transfer process using peat as an adsorbent for dyestuffs. Canadian Journal of Chemical Engineering 1980;58:521–6.
[5] Suryadi I, Bhatia SK. Adsorption of flavor esters on granular activated carbon. Canadian Journal of Chemical Engineering 2000;78:892–901.
[10] Gürses A, Karaca S, Do YX, Bayrak R, Acikyildiz A, Yalcin M. Determination of adsorptive properties of clay/water system: methylene blue sorption. Journal of Colloid and Interface Science 2004;269:310–4.
[11] Ho YS, Chiu WT, Hsu CS, Huang CT. Sorption of lead ions from aqueous solution using tree fern as a sorbent. Hydrometallurgy 2004;73:55–61.
[12] Ho YS. Selection of optimum sorption isotherm. Carbon 2004; 42(10):2115–7.
[15] Freundlich HMF. Over the adsorption in solution. Zeitschrift fur Physikalische Chemie 1906;57A:385–470.
[16] Langmuir I. The constitution and fundamental properties of solids and liquids. Journal of the American Chemical Society 1916;38:2221–95.
[17] Longhinotti EPF, Furlan L, Sanchez MDND, Klug M, Laranjeira MCM, Favere VT. Adsorption of anionic dyes on the biopolymer chitin. Journal of Brazilian Chemical Society 1998;9:435–40.
[18] Redlich O, Peterson DL. A useful adsorption isotherm. Journal of Physical Chemistry 1959;63:1024.