Short communication

Prediction of optimum sorption isotherm: Comparison of linear and non-linear method

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Abstract

Equilibrium parameters for Bismarck brown onto rice husk were estimated by linear least square and a trial and error non-linear method using Freundlich, Langmuir and Redlich–Peterson isotherms. A comparison between linear and non-linear method of estimating the isotherm parameters was reported. The best fitting isotherm was Langmuir isotherm and Redlich–Peterson isotherm equation. The results show that non-linear method could be a better way to obtain the 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

Sorption processes are proved to be an effective process for the removal of pollutants from wastewaters [1–4]. The most appropriate method in designing the sorption systems and in assessing the performance of the sorption systems is to have an idea on sorption isotherms. Linear regression was frequently used to determine the most fitted isotherm [2,4]. However, previously researchers showed that depending on the way the isotherm equations are linearized, the error distribution changes either the worse or the better [5]. Thus, non-linear method may be a better way to obtain the equilibrium isotherm parameters. In the present study, a comparison of linear least squares method and non-linear method of three widely used isotherms, Freundlich [6], Langmuir [7], and Redlich and Peterson [8] isotherms was made to the experimental equilibrium data of bismarck brown onto rice husk particles.

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2. Experimental

The dye used in all the experiments was Bismarck brown (C.I. Basic brown 1) and the adsorbent used was rice husk. The stock solution of bismarck brown was prepared by dissolving 1 g of bismarck brown in one liter 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 then stored in plastic bottles for use.

Equilibrium experiments were carried out by contacting 50 mL of dye solution of different initial dye concentrations:150, 125, 100, 75, 50 and 25 mg/L with 0.06 g of rice husk particles in six different capped conical flasks. The contact was made using water bath shakers at a constant agitation

speed of 95 strokes/min with a stroke length of 1.5 cm. All the experiments were carried out at room temperature of 305 K. The agitation was made for 48 h, which is more than sufficient time to reach equilibrium. After equilibrium is reached, 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 Freundlich, Langmuir and Redlich–Peterson isotherms and their linearized forms were given in Table 1. The coefficient of determination r^2 values were used to predict the best fit linear equation. From the Table 1, it was observed that the Langmuir isotherm could be linearized to at least four different types [5]. The Langmuir constants q_m, and K_a values can be calculated 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 for type 1, type 2, type 3, and type 4 Langmuir isotherms, respectively. Similarly, the Freundlich isotherm constants K_F and $1/n_F$ can be calculated from the plot of $\log(q_e)$ versus $\log(C_e)$. The Redlich–Peterson isotherm constants can be predicted from the plot between $\ln[(AC_e/q_e) - 1]$ 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. The way to obtaining the isotherm constants were explained in Table 1. The calculated isotherm constants at temperature of 305 K

Table 2
Isotherm parameters obtained by using linear method

Freundlich	K_F (mg/g)(L/g)^{n_F}	9.273
	$1/n$	0.512
	r^2	0.923
Langmuir 1	q_m	84.836
	K_a	0.065
	r^2	0.987
Langmuir 2	q_m	97.716
	K_a	0.048
	r^2	0.995
Langmuir 3	q_m	90.759
	K_a	0.055
	r^2	0.915
Langmuir 4	q_m	94.718
	K_a	0.050
	r^2	0.914
Redlich–Peterson	A	15.673
	B	1.126
	g	0.561
	r^2	0.931

and their corresponding r^2 values for the different linearized forms of isotherm equations are shown in Table 2. In case of Langmuir isotherm, it was observed that coefficient of determination values for all the four linearized form of Langmuir isotherm equations were different (Table 2). From the Table 2, based on r^2 values, type 2 Langmuir isotherms showed a better fit for Bismarck brown onto rice husk particles followed by type 1 Langmuir isotherm. Also types 3 and 4 forms have same r^2 values and showing a very poor fit towards the experimental data of bismarck brown onto rice husk. Further, the lower r^2 value of Freundlich and

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. $\log(C_e)$	[6]
Langmuir-1	$q_e = \dfrac{q_m K_a C_e}{1 + K_a C_e}$	$\dfrac{C_e}{q_e} = \dfrac{1}{q_m}C_e + \dfrac{1}{K_a q_m}$	$\dfrac{C_e}{q_e}$ vs. C_e	[7]
Langmuir-2		$\dfrac{1}{q_e} = \left(\dfrac{1}{K_a q_m}\right)\dfrac{1}{C_e} + \dfrac{1}{q_m}$	$\dfrac{1}{q_e}$ vs. $\dfrac{1}{C_e}$	
Langmuir-3		$q_e = q_m - \left(\dfrac{1}{K_a}\right)\dfrac{q_e}{C_e}$	q_e vs. $\dfrac{q_e}{C_e}$	
Langmuir-4		$\dfrac{q_e}{C_e} = K_a q_m - K_a q_e$	$\dfrac{q_e}{C_e}$ vs. q_e	
Redlich–Peterson	$q_e = \dfrac{AC_e}{1 + BC_e^g}$	$\ln\left(A\dfrac{C_e}{q_e} - 1\right) = g\ln(C_e) + \ln(B)$	$\ln\left(A\dfrac{C_e}{q_e} - 1\right)$ vs. $\ln(C_e)$	[8]

C_e: equilibrium solute concentration, mg/L; q_e: amount of dye sorbed at equilibrium, mg/g; KF: Freundlich isotherm constant $(mg/g)(L/g)^{1/n_F}$; n_F: Freundlich exponent; q_m: maximum sorption capacity, mg/g; K_a: Langmuir constant related to energy of adsorption, L/mg.

Redlich–Peterson isotherm when compared to the best fit Langmuir (type 2) isotherm confirms that it is inappropriate to use these isotherm relations for bismarck brown onto rice husk particles. Further, when comparing the r^2 values for types 3 and 4 isotherms with Freundlich isotherm, it was observed that Freundlich is a more appropriate isotherm to obtain the equilibrium parameters. But when comparing r^2 value of types 1 and 3 Langmuir isotherm, it was observed that Langmuir as best fit isotherm for the experimental equilibrium data of bismarck brown onto rice husk. These observations, especially from the Langmuir isotherm equation shows the mathematical complexities associated with using linear method in estimating the rate parameters. The different r^2 values for different linearized form of Langmuir isotherm equation is 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, 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.

For non-linear method, a trial and error procedure, which is applicable to computer operation, was used to determine the isotherm parameters by minimizing the respective the coefficient of determination between experimental data and isotherms using the *solver* add-in with Microsoft's spreadsheet, Microsoft Excel. Fig. 1. shows the experimental data and the predicted equilibrium curve using non-linear method for the three-equilibrium isotherm Freundlich, Langmuir and Redlich–Peterson at 305 K. The obtained isotherm parameters at temperature of 305 K are listed in Table 3. In the case of Langmuir isotherm, the results from the four Lang-
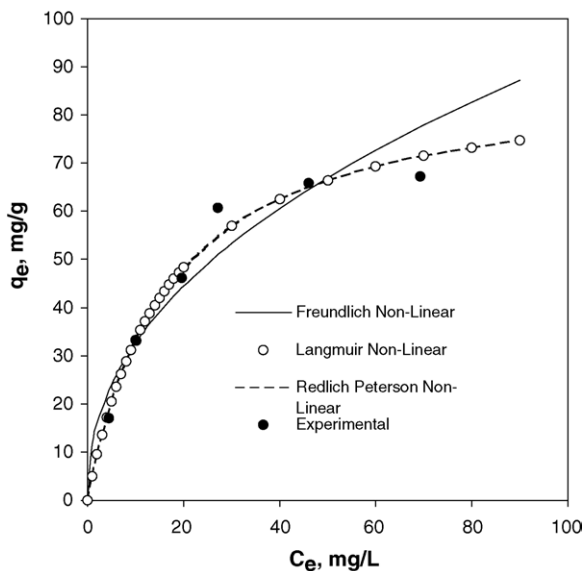
Table 3
Isotherm parameters obtained by using non-linear method

Freundlich	K_F (mg/g)(L/g)^{n_F}	11.666
	$1/n$	0.447
	r^2	0.895
Redlich–Peterson	A	5.341
	B	0.060
	g	1
	r^2	0.971
Langmuir	q_m	88.440
	K_a	0.060
	r^2	0.971

muir 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, the isotherm parameters and the r^2 values calculated by non-linear method completely differ from the values obtained by linear method (Table 2). Further, the r^2 values for Redlich–Peterson and Langmuir were found to be the same. Fig. 1 show that the Redlich–Peterson and Langmuir isotherms overlapped each other, and seemed to be the best-fitting models for the experiment 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. Also the higher r^2 values for Redlich–Peterson and Langmuir isotherm when compared to Freundlich isotherm shows that it is inappropriate to use Freundlich isotherm for bismarck brown onto rice husk particles.

The difference in predicted and experimental equilibrium data by linear and non-linear methods can be due to the problems with the transformation of non-linear to linear expression 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 isotherm models (as most of the isotherm models are non-linear) as the error distribution gets altered after transforming the data to a linear. Unlike the linear analysis, due to different axial settings, different isotherm would effect r^2 significantly, and impact the final determination of isotherm parameters where non-linear method would be avoiding such errors. Thus non-linear method will be a more appropriate technique to obtain the isotherm parameters.

4. Conclusions

Experimental equilibrium data of bismarck brown onto rice husk particles were fitted to theoretical isotherms by both linear and non-linear method. Both the linear and non-linear method suggests that the experimental equilibrium data was found to follow both Langmuir and Redlich–Peterson isotherm equation. Non-linear method is a better way to obtain equilibrium isotherm parameters. Langmuir is a

Fig. 1. Equilibrium curve for Bismarck brown onto rice husk at 305 K.

special case of Redlich–Peterson isotherm when constant g is unity.

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