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Original Research

Optimum Isotherm Parameters for Reactive Azo Dye onto Pistachio Nut Shells: Comparison of Linear and Non-Linear Methods

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Abstract

Comparison analysis of linear least-square method and non-linear method of three widely used isotherms (Langmuir, Freundlich, and Redlich-Peterson) were examined to experiment with Remazol Red (C.I. 18221) onto pistachio nut shells at a solution temperature of 293 K. All three isotherm equations showed a better fit to the experimental equilibrium data. The results show that the Langmuir model shows the best fit compared to Freundlich and Redlich-Peterson models using the linear method. However, when using the non-linear method the Freundlich and Langmuir models show the best fit compared to others. Redlich-Peterson isotherm is a special case of Langmuir isotherm when the Redlich-Peterson isotherm constant g was unity.

Keywords: adsorption, pistachio nut shell, Remazol Red, equilibrium isotherm, linear method, non-linear method

Introduction

Adsorption is rapidly becoming a prominent method for treating aqueous effluents and has been extensively used in industrial processes for a variety of separation and purification purposes [1]. The removal of colored and colorless organic pollutants from industrial wastewater is considered an important application of the adsorption process using suitable adsorbents [2]. Activated carbon and polymer resins appear to be the best adsorbents for removing chemicals from relatively concentrated wastewater, but these are expensive and necessitate regeneration [3, 4]. If the adsorbent material is inexpensive and does not require any expensive additional pretreatment step, the adsorption process will become economically viable [5]. For this reason, many studies have revealed that other alternative adsorbents, such as agaricus campestris [6], synthetic calcium phosphates [7], peanut hull [8], hazelnut shells [9], rice husk [10], eggshell [11], cellulose [12], cotton seed shell [13], tree leaves [14], and chitosan [15] are viable.

Adsorption isotherms are the basic requirements for the analysis and design of the adsorption separation process [16]. In order to optimize the design of a specific adsorbate/adsorbent system to remove dyes from effluents, it is important to establish the most appropriate correlation for the experimental equilibrium curves [17]. The widely used isotherms by several researchers for different adsorbate/adsorbent systems are Langmuir [18], Freundlich [19], and Redlich and Peterson [20]. Linear regression was the most commonly used technique to estimate the adsorption isotherm parameters. However, researchers previously showed that, depending on the way isotherm equation is linearized, the error distribution changes either for the worse or the better [21]. So it will be an inappropriate technique to use the linearization method for estimating the

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equilibrium isotherm parameters [16]. Thus, in the present study, a comparison of linear least-square method and non-linear method of three widely used isotherms (Langmuir, Redlich-Peterson, and Freundlich) were examined to experiment with Remazol Red onto pistachio shells. A trial and error procedure was used for the non-linear method by using the solver add-in with Microsoft Excel.

Experimental Procedures

A commercial textile reactive azo dye, Remazol Red (C.I. 18221), was provided from Bursa, Turkey, and used in all adsorption experiments without further purification. The chemical structure of Remazol Red is illustrated in Fig. 1. It contains anionic sulfonate groups to various degrees. The pistachio shells, low-cost agricultural waste as well as a profoundly accessible potential dye adsorbent, were obtained commercially from Sanliurfa, Turkey. It consists of internal and external shells. In this study, internal pistachio nut shell samples were used, and washed several times with distilled water to remove surface impurities and then dried at 110ºC in an oven for 12 h to reduce the moisture content. The pistachio nut shell was crushed, ground, and sieved to obtain a particle size in the range of 250-2,000 µm with a coffee grinder (waring commercial) to increase the surface area.

Batch adsorption studies were carried out by contacting 0.003 g/mL (0.3%) of the pistachio shell particles with 40 mL of dye solution of known initial dye concentration. After such solution preparation, the bottles were placed on an orbital shaker at 150 rpm at room temperature for 4 h followed by centrifugation at 4,000 rpm for 10 min. All the absorbance measurements of Remazol Red were made with a UV-vis spectrophotometer (Shimadsu T70) at the $\lambda_{max.}$=520 nm. The reproducibility of the data varied in the range of ±1.5%. Distilled and deionized water with a conductivity value of 2.10^{-6} mhos·cm^{-1} was used in all experiments.

Results and Discussions

Linear Regression Analysis

By plotting solid-phase concentration against residual liquid-phase concentration graphically it is possible to depict the equilibrium adsorption isotherm. In order to optimize the design of a sorption system to remove dyes from aqueous solution, it is important to establish the most appropriate correlation for the equilibrium curve [17]. 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 [15]. 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 qe/C_e, and q_e/C_e and q_e, respectively. The calculated isotherm parameters also are shown in Table 2. As seen in 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 linearized, the error distribution changes with the worse or the better [18]. 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-1 and Langmuir-4 showed a similar R^2 value, confirming that both these types are in the same error distribution structure.

Similarly, the Freundlich isotherm constants K_F and $1/n_F$ can be calculated from the plot of $\log(q_e)$ versus $\log(C_e)$ [19]. 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 0.84 confirms that it is not appropriate to use the Freundlich isotherm to represent the Remazol Red dye adsorption by pistachio shell.

The Redlich-Peterson isotherm constants can be predicted from the polt between ln [(AC_e/q_e)-1] versus ln(C_e).

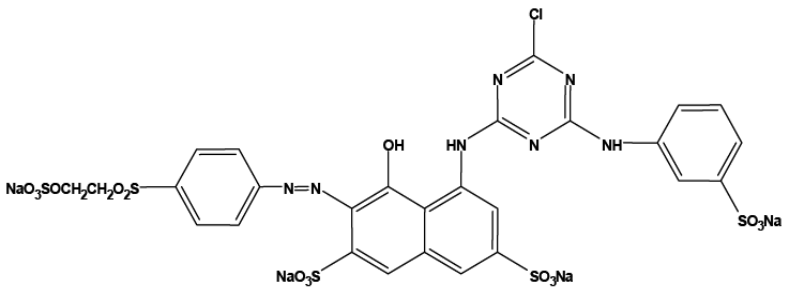

Fig. 1. The general chemical structure of Remazol Red (C.I. 18221).

Table 1. Mathematical equation of the used single component isotherm models.

Isotherm	Equation	Linear expression	Plot	Reference
Type 1 Langmuir	$q_e = \frac{q_m K_a C_e}{1+K_a C_e}$	$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_a q_m}$	$\frac{C_e}{q_e}$ vs. C_e	Langmuir [18]
Type 2 Langmuir		$\frac{1}{q_e} = (\frac{1}{K_a q_m})\frac{1}{Ce} + \frac{1}{q_m}$	$\frac{1}{q_e}$ vs. $\frac{1}{Ce}$	
Type 3 Langmuir		$q_e = q_m - (\frac{1}{K_a})\frac{q_e}{Ce}$	q_e vs. $\frac{q_e}{Ce}$	
Type 4 Langmuir		$\frac{q_e}{C_e} = K_a q_m - K_a q_e$	$\frac{q_e}{C_e}$ vs. q_e	
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. $\log(C_e)$	Freundlich [19]
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. $\ln(C_e)$	Redlich [20]

However, this is not possible as the linearized form of Redlich-Peterson isotherm equation (Table 1) contains three unknown parameters: *A*, *B,* and *g*. Because of this, 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 [20]. 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 0.90 shows that it is appropriate to use Redlich-Peterson isotherm for the adsorption of Remazol Red onto pistachio shell.

The present investigation suggests that the linear least squares method as a reasonable approach to determine the optimum isotherm and also for estimating the isotherm parameters. The predicted isotherm constants for Remazol Red and its corresponding R^2 values by the linear method are shown in Table 2. However, comparing the R^2 values of the four types of linearized Langmuir isotherms with Freundlich and Redlich-Peterson isotherm alone will produce different outcomes.

In the case of Remazol Red/pistachio shell system, the higher R^2 value of type 1 or 4 Langmuir isotherm suggest that Langmuir isotherm was found to be the best-fitting isotherm, followed by Redlich-Peterson and Freundlich. The lower R^2 value of types 2 and 3 Langmuir isotherm suggest that the Redlich-Peterson isotherm is the best-fit isotherm followed by Freundlich and Langmuir isotherm for Remazol Red/pistachio shell systems. For the Remazol Red onto pistachio shell system, the R^2 values for types 1 and 4 isotherm suggest that Langmuir is the best-fitting isotherm, followed by the Redlich-Peterson and Freundlich isotherms. The lower R^2 value of types 2 and 3 Langmuir isotherm suggest that the Redlich-Peterson is the best-fit for Remazol Red onto pistachio shell, followed by Freundlich and Langmuir. Similarly, different outcomes were observed for the sorption of Remazol Red onto pistachio shell. These different out-comes show the real complexities in estimating the isotherm parameters using the linearization technique. The different outcomes further suggest that the better fit of a set of experimental data in a particular isotherm model over another model alone is not sufficient to predict the sorption mechanism. The difference between the predicted and experimental equilibrium data by different linear expressions can be due to the problems with the transformation of non-linear to linear expression, which will distort the experimental error and also the normality assumptions of the least squares method. Further, the linear method does not test whether the experimental data are linear.

Table 2. Isotherm parameters obtained using linear method.

Langmuir (Type 1)	$q_{max.}$ (mg·g^{-1})	70.92
	K_L (L/mg)	0.0343
	R^2	0.978
Langmuir (Type 2)	q_{max}, (mg·g^{-1})	2.11
	K_L (L/mg)	0.03
	R^2	0.58
Langmuir (Type 3)	q_{max}, (mg·g^{-1})	27.40
	K_L (L/mg)	0.02
	R^2	0.81
Langmuir (Type 4)	q_{max}, (mg·g^{-1})	50.06
	K_L (L/mg)	0.03
	R^2	0.95
Freundlich	n	0.5634
	K_F (mg·g)	13.61
	R^2	0.84
Redlich-Peterson	g	0.8282
	B (L·mg$^{1-1/A}$)	0.1647
	A (L/g)	4.319
	R^2	0.90

Table 3. Isotherm parameters obtained using the non-linear method.

Non-linear Langmuir	$q_{max.}$ (mg·g^{-1})	108.15
	K_L (L/mg)	0.006319
	R^2	0.98
Freundlich	n	1.65
	K_F (mg·g)	0.1328
	R^2	0.98
Redlich-Peterson	g	0.8282
	B (L·mg$^{1-1/A}$)	0.1647
	A (L/g)	4.319
	R^2	0.97

It assumes the experimental data were linear and predicts the slope and intercept that makes a straight line that predicts the best-fit of experimental equilibrium data. The linear method assumes that 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 form. The linear method just predicts the Y for the corresponding X. It considers only the error distribution along the Y-axis irrespective of the corresponding X-axis, resulting in the different determined parameters (Table 2) for the four different types of linearized Langmuir isotherms for the same experimental data. Thus, the experimental data were further fitted to the experimental equilibrium data of Remazol Red onto pistachio nut shell by the non-linear method.

Non-Linear Method

For the 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 coefficients of determination between experimental data and isotherms using the solver add-in with Microsoft Excel. Fig. 2 shows the experimental equilibrium data and the predicted theoretical isotherms for the sorption of Remazol Red onto pistachio shells. The calculated isotherm constants by non-linear method were shown in Table 3. From Table 3 it was observed that 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. Fig. 2 shows that the Freundlich 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.

The Freundlich model appears to fit the experimental data better than the Langmuir model as reflected with the correlation coefficients in the range of 0.98 (Table 3). Maximum adsorption capacity of pistachio shells was determined as 108.15 mg·g^{-1} at 20ºC. In the literature, the maximum adsorption capacity of Remazol Red on eggshell was found to be 46.9 mg·g^{-1} at 22ºC [11]. Besides, Gulnaz et al. found that the maximum adsorption capacities at 20ºC of native acid and alkali pretreated biomass were determined as 14.3, 26.8, and 44.2 mg·g^{-1}, respectively [2].

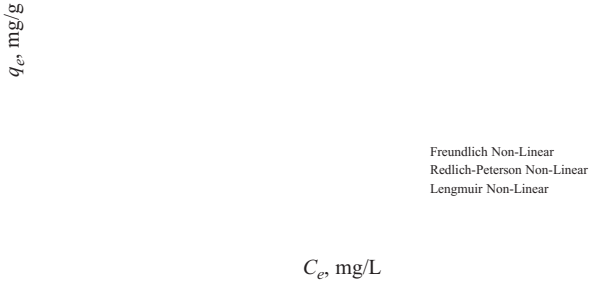

Fig. 2. Adsorption isotherm for Remazol Red onto pistachio nut shell at 293 K.

Conclusions

Present study shows that the non-linear method is a more appropriate technique to predict the optimum adsorption isotherm than the linear method. The experimental equilibrium data of Remazol Red onto pistachio shell follow Freundlich and Langmuir isotherms equally well. Langmuir is a special case of Redlich-Peterson isotherm when constant g was unity. The relatively better fit of experimental equilibrium data in the Langmuir isotherm suggests the monolayer coverage and chemisorption of Remazol Red onto pistachio shell.

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