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Short communication

Isotherms for Malachite Green onto rubber wood (*Hevea brasiliensis*) sawdust: Comparison of linear and non-linear methods

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Abstract

Comparison of linear least-squares method and a trial and error non-linear method of estimating the isotherm parameters was examined to the experimental equilibrium data of Malachite Green, a basic dye onto rubber wood sawdust. The experimental data were fitted to Langmuir, Freundlich and Redlich–Peterson isotherms. The four different linearized forms of Langmuir isotherms are also discussed. Langmuir isotherm parameters obtained from the four Langmuir linear equations are different but they are the same by using non-linear Langmuir equation. The best-fitting isotherms are Langmuir and Redlich–Peterson. Present investigation showed that the non-linear method is more appropriate method to determine the isotherm parameters. Langmuir is a special case of Redlich–Peterson when the constant ‘*g*’ equals to unity.

Keywords: Sorption; Equilibrium; Malachite Green; Rubber wood sawdust; Isotherms; Linear method; Non-linear method

1. Introduction

The removal of color from dye-bearing effluents is one of the major problems due to the difficulty in treating such wastewaters by conventional treatment methods. The most commonly used methods for color removal are biological oxidation and chemical precipitation. However, these processes are effective and economic only in the case where the solute concentration is relatively high. Currently sorption process is proved to be one of the effective and attractive processes for the treatment of these dye-bearing wastewaters [1–4]. Also this method will become inexpensive, if the sorbent material used is of inexpensive material and does not require any expensive additional pretreatment step. In the present study of rubber wood sawdust, a waste bio-material obtained from sawmill and wood processing industries has been used as an adsorbent for the removal of Malachite Green from its aqueous solution. Malachite Green has wider applications, which include coloring paper, coloring leather products, dyeing cottons, wools, etc. Malachite Green is selected as a model compound in order to evaluate the capacity of rubber wood sawdust for the removal of dye Malachite Green from its aqueous solutions.

2. Materials and methods

The main interest of present study is to investigate the sorption of Malachite Green onto rubber wood sawdust. The sawdust was obtained from local sawmill.

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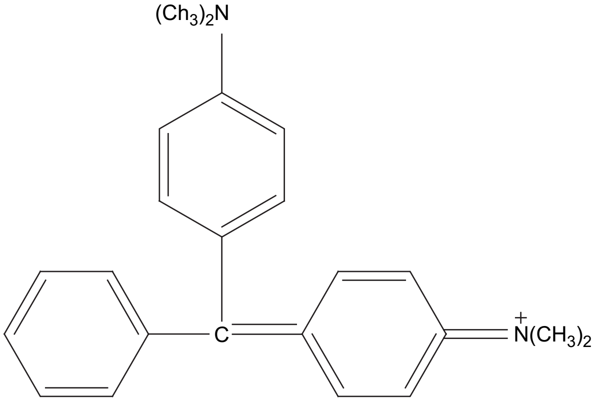
The obtained sawdust was washed with distilled water several times, till the wash water contains no color. The sawdust was then dried in hot air oven at 60 °C for 48 h. The dried materials were then sieved to obtain particle size in the range of 0.177–0.149 mm for sorption tests.

The dye used in all the experiments was Malachite Green (C.I. 42000). The dye Malachite Green was obtained from Ranbaxy chemicals, Mumbai, 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.

Equilibrium experiments were carried out by contacting weighed amount of sawdust particles with 50 mL of Malachite Green solution of initial dye concentration 100 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. After shaking the sorbent was removed from the solution by centrifugation. The left out concentration in the supernatant solution was analyzed using UV spectrophotometer. All the experiments were carried out at a constant solution temperature of 305 K.

3. Sorption isotherms

The analysis and design of sorption separation process require the relevant sorption equilibrium, which is the most important piece of information in understanding the sorption process. 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 sorbent.

In the present study, the sorption capacity and equilibrium isotherm for Malachite Green onto rubber wood sawdust were estimated using three equilibrium models: Freundlich, four different linearized forms of Langmuir isotherm equations and Redlich–Peterson isotherm equation.

3.1. Freundlich isotherm

Herbert Max Finley Freundlich [5], a German physical chemist, presented an empirical sorption isotherm for non-ideal sorption on heterogeneous surfaces as well as multilayer sorption and is expressed by the equation:

$$q_e = K_F C_e^{1/n} \qquad (1)$$

where, C_e (mg/dm^3) is the left out solute concentration at equilibrium, q_e (mg/g) is the amount of dye sorbed at equilibrium, K_F (mg/g)(L/g)$^{1/n}$ and $1/n$ are the Freundlich constants related to sorption capacity and sorption intensity, respectively. The term q_e in Eq. (1) can be calculated from the simple mass balance equation as follows:

$$q_e = \frac{(C_0 - C_e)V}{M} \qquad (2)$$

where, C_0 is the initial dye concentration (mg/L), C_e is the dye concentration at equilibrium (mg/L), V is the volume of solution (L), and M is the mass of sorbent (g).

The linearized form of Eq. (1) can be obtained by taking log on both sides:

$$\log(q_e) = \log(K_F) + 1/n \log(C_e) \qquad (3)$$

The Freundlich isotherm has been derived by assuming an exponentially decaying sorption site energy distribution. Freundlich equation suffers by the limitation like it does not follow the fundamental thermodynamic basis since it does not reduce to Henry's law at lower concentrations.

3.2. Langmuir isotherm

Irving Langmuir [6], an American chemist developed a theoretical equilibrium isotherm relating the amount of solute sorbed on a surface to the concentration of solute. This equation is derived from simple mass action kinetics, assuming chemisorption. This model is based on two assumptions that the forces of interaction between sorbed molecules are negligible and once a molecule occupies a site no further sorption takes place. Theoretically therefore a saturation value is reached beyond which no further sorption takes place. Also these equations can reduce to Henry's law at lower initial concentrations. Alternatively at higher concentrations, it predicts a monolayer sorption capacity. The saturated monolayer sorption capacity can be represented by the expression:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{4}$$

where, C_e is the equilibrium concentration (mg/dm^3), q_e is the amount of dye sorbed (mg/g), q_m is q_e for a complete monolayer (mg/g), and K_L is sorption equilibrium constant (L/mg).

Eq. (4) can be linearized to at least four different forms [7]. The different linearized forms of Langmuir equations are given in Table 1.

3.3. Redlich–Peterson isotherm

The Redlich–Peterson isotherm has three parameters and has the feature of both the Freundlich and Langmuir isotherm equations. It can be described as [8]:

$$q_e = \frac{A C_e}{1 + B C_e^g} \tag{5}$$

where, A is the Redlich–Peterson isotherm constant (L/g), B is the Redlich–Peterson isotherm constant (L/mg$^{1-1/A}$) and g is the exponent, which lies between 0 and 1. It has two limiting cases, which can be explained as follows:

When the exponent $g = 1$, the Langmuir equation results, given by

$$q_e = \frac{A C_e}{1 + B C_e} \tag{6}$$

When $g = 0$, Redlich–Peterson isotherm equation transforms to Henry's law equation

$$q_e = \frac{A C_e}{1 + B} \tag{7}$$

Eq. (5) can be rearranged as follows:

$$A\frac{C_e}{q_e} - 1 = B C_e^g \tag{8}$$

Eq. (8) can be transformed to a linear equation by taking logarithms:

$$\ln\left(A\frac{C_e}{q_e} - 1\right) = \ln(B) + g\ln(C_e) \tag{9}$$

The Redlich–Peterson constants can be obtained by plotting the left hand side of Eq. (9). However, this is not possible as Eq. (9) 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 Eq. (9) and the experimental data.

4. Results and discussions

4.1. Linear method

Linear regression was frequently used to determine the most fitted isotherm, and the method of least squares has been used for finding the parameters of the isotherms. The Freundlich constant K_F and Freundlich exponent $1/n$ were calculated from the intercept and slope of Eq. (3). Table 2 shows the calculated K_F, $1/n$ values and their corresponding linear regression coefficients of determination at a solution temperature of 305 K. From Table 2, it was observed that the coefficient of determination for Freundlich isotherm equation was found to be 0.947232. This relatively lower coefficient of determination suggests that the equilibrium data does not follow the Freundlich isotherm equation.

The equilibrium data were further analyzed using the four linearized forms of Langmuir equations [7]. The different forms of Langmuir isotherms are shown in Table 1. The Langmuir constants corresponding to type 1 Langmuir linear equation can be obtained from the plot between C_e/q_e and C_e. For type 1 linear form, the Langmuir constants, monolayer sorption capacity q_m, and K_L were calculated from the slope and intercept of the plot between C_e/q_e and C_e. Similarly, the q_m and K_L values for the other linearized forms of Langmuir equations type 2, type 3, and type 4 can be obtained 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 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. The experimental equilibrium data

Table 1
Different linearized forms of Langmuir equation [13]

Linear regression	Plot	Parameters
Type 1: $C_e/q_e = (1/K_L q_m) + (C_e/q_m)$	C_e/q_e vs C_e	K_L = slope/intercept, q_m = 1/slope
Type 2: $1/q_e = (1/q_m) + (1/K_L q_m C_e)$	$1/q_e$ vs $1/C_e$	K_L = intercept/slope, q_m = 1/intercept
Type 3: $q_e = q_m - (q_e/K_L C_e)$	q_e vs q_e/C_e	K_L = −1/slope, q_m = intercept
Type 4: $q_e/C_e = K_L q_m - K_L q_e$	q_e/C_e vs q_e	K_L = −slope, q_m = −intercept/slope

Table 2
Isotherm constants for Malachite Green onto rubber wood sawdust

	Type 1	Type 2	Type 3	Type 4
Langmuir isotherm constants (linear method)				
q_m (mg/g)	33.25033	25.30619	32.10867	33.77159
K_L (L/mg)	0.210481	0.613571	0.215517	0.183049
r^2	0.995395	0.763099	0.84935	0.84935
Freundlich isotherm constants (linear method)				
K_F (mg/g)(L/g)^n	10.8822			
$1/n$	0.268567			
r^2	0.947232			
Redlich–Peterson isotherm constants (linear method)				
A (L/g)	14.97771			
B (L/mg$^{1-1/A}$)	0.971818			
g	0.810227			
r^2	0.991554			
Langmuir isotherm constants (non-linear method)				
q_m (mg/g)	36.45996			
K_L (L/mg)	0.142758			
r^2	0.955047			
Freundlich isotherm constants (non-linear method)				
K_F (mg/g)(L/g)^n	9.227175			
$1/n$	0.342447			
r^2	0.96277			
Redlich–Peterson isotherm constants (non-linear method)				
A (L/g)	5.204864			
B (L/mg$^{1-1/A}$)	0.142755			
g	1			
r^2	0.955047			

and the predicted values from the four types of Langmuir isotherms by linear method are shown in Fig. 1. From Fig. 1, it was observed that the predicted values were different for each type of linearized Langmuir equation. The calculated Langmuir constants and their corresponding r^2 values for the four linearized forms of Langmuir isotherm equations are shown in Table 2. From Table 2, it was observed that the coefficient of determination values for all the four linearized forms of Langmuir isotherm equations were different. This is because the error distribution gets altered either the worse or better upon linearizing an equation. Further from Table 2, it was observed that the r^2 value for type 1 Langmuir isotherm showed a better fit than the remaining linearized forms. This shows that the type 1 expression is the best-fitting linear Langmuir equation for the present study. The adsorption capacity of sawdust was found to be 33.250 mg/g (based on the type 1 Langmuir isotherm). This shows that the low cost rubber wood sawdust can be used as an adsorbent for the removal of Malachite Green from its aqueous solution. A list showing the adsorption capacity of different materials for the sorption of different dye materials from their aqueous solutions is given in Table 3. From Table 3, it was observed that the adsorption capacity of rubber wood sawdust for dye uptake is comparable with other low cost adsorbents.

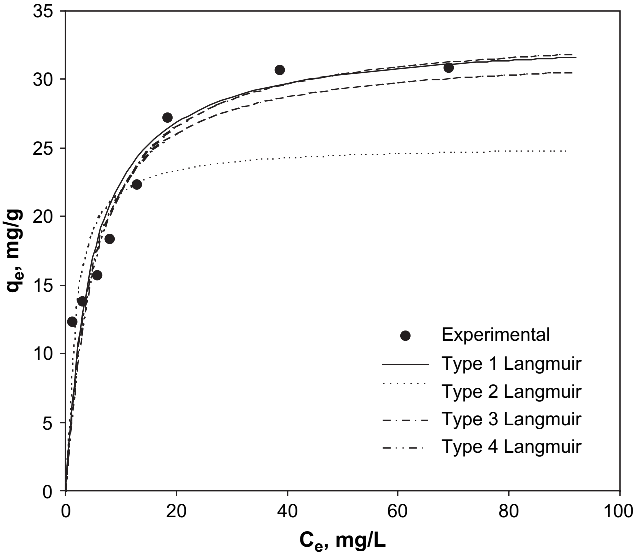


Fig. 1. Langmuir isotherm for Malachite Green onto rubber wood sawdust at 305 K.

The isotherm constants for the sorption of Malachite Green onto rubber wood sawdust particles for the linearized form of Redlich–Peterson equation can be obtained from the plot of $\ln(AC_e/q_e - 1)$ vs $\ln(C_e)$. The calculated Redlich–Peterson constants and their corresponding coefficients of determination are shown in Table 2. The very higher r^2 value of 0.9916 showed that in addition to Langmuir isotherm the sorption process can also be represented by Redlich–Peterson isotherm. In addition, it can be seen that the value of g is unity that means the isotherm is approaching the Langmuir but not Freundlich isotherm.

4.2. 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 minimizing the respective coefficient of determination between experimental data and isotherms using the *solver* add-in with Microsoft's spreadsheet, Microsoft Excel.

Fig. 2 shows the experimental data and the predicted values by non-linear method. The determined isotherm constants by non-linear method are shown in Table 2. In the case of Langmuir isotherm, the results from the four Langmuir linear equations are the same. By using non-linear method there is no problem with transformations of non-linear Langmuir isotherm equation to linear forms, and also they are in the same error structures. From Table 2, it was observed that the Langmuir and Freundlich isotherm constants calculated by linear and non-linear methods varied a little. But the difference between Redlich–Peterson isotherm constants predicted by linear and non-linear methods was very high. From Fig. 2, it was observed that the predicted Langmuir and Redlich–Peterson isotherms overlapped each other.

Table 3
Adsorption capacities of different low cost adsorbent for the uptake of different dyes from its aqueous solutions

Adsorbent	Solute	Adsorption capacity (mg/g)	Reference
Pear millet husk carbon	Methylene Blue	66	[1]
Iron humate	Methylene Blue	32.978	[2]
Raw kaolin	Methylene Blue	27.5	[9]
Pure kaolin	Methylene Blue	91.9	[9]
Calcined raw kaolin	Methylene Blue	13.4	[9]
Calcined pure kaolin	Methylene Blue	56.3	[9]
Neem sawdust	Methylene Blue	3.62	[10]
Clay	Methylene Blue	6.3	[11]
Aspergillus niger	Methylene Blue	54.67	[12]
Fe (III)/Cr (III) hydroxide	Direct Red 12B	5	[13]
Fe (III)/Cr (III) hydroxide	Methylene Blue	22.8	[13]
Coir pith activated carbon	Congo Red	6.7	[14]
Biogas residual slurry	Congo Red	9.5	[15]
	Acid Violet	137.9	
Banana pith	Congo Red	20.2	[15]
	Rhodamine B	8.5	
	Acid Violet	13.1	
	Acid Brilliant blue	4.3	
Orange peel	Acid Violet	19.8	[15]
	Congo Red	22.4	
	Rodamine B	3.2	
Coir pith	Acid Violet	1.6	[15]
	Acid Brilliant blue	16.6	
	Rhodamine B	203.2	
Carbonized coir pith	Acid Violet	8.1	[15]
	Rhodamine B	2.6	
Chitin	Acid Blue 25	48.8	[15]
	Basic Blue 69	52.4	
Chitosan	Acid Blue 25	212.6	[15]
	Basic Blue 69	162.1	
Hard wood	Astrazone Blue	88.7	[15]
Rubber wood sawdust	Malachite Green	36.45	This study

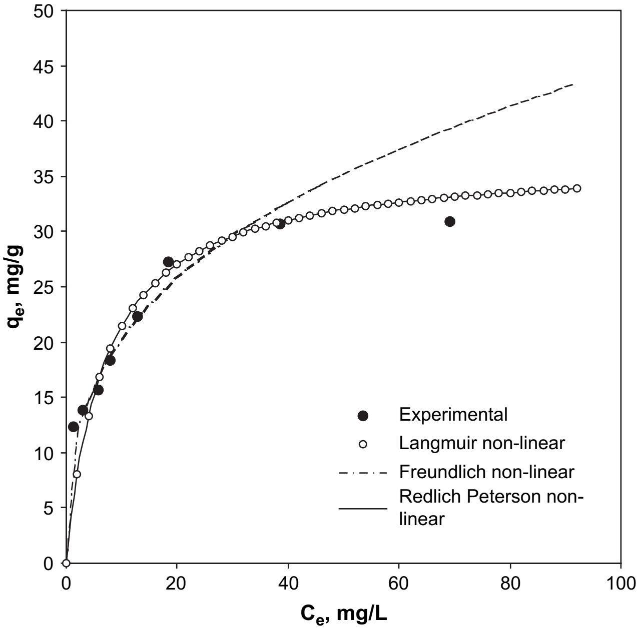


Fig. 2. Sorption isotherms by non-linear method for Malachite Green onto rubber wood sawdust.

Further from Table 2, it was observed that the r^2 value remains the same for both Langmuir and Redlich–Peterson isotherms. Thus, Redlich–Peterson is a special case of Langmuir when the constant g is unity. Thus, both the Langmuir and Redlich–Peterson isotherms well represent the sorption of Methylene Blue onto rubber wood sawdust. As the non-linear method avoids the variation in error distribution due to linearization and also as all the parameters are fixed in the same axis, non-linear method will be a more appropriate method to determine optimum sorption isotherm.

4.3. Comparison of linear and non-linear methods

The r^2 values obtained from linear method and non-linear method for the three-isotherm equation suggests that in some cases linear method showed a better fit and in some cases non-linear method shows better fit to the experimental data with a higher coefficient of determination. In case of Redlich–Peterson, the r^2 value by linear method was higher than the r^2 value obtained from non-linear method. This suggests that linear method is more appropriate method in predicting the Redlich–Peterson isotherm constants for the present system. In case of Langmuir isotherm, the r^2 value calculated by type 1 linear equation was higher than the r^2 value obtained by non-linear method. However, r^2 value by non-linear method was found to be higher than the r^2 values of type 3 and type 4 Langmuir isotherm. In Table 2, the coefficient of determination values for type 1 Langmuir isotherm equation was greater than the r^2 value for Freundlich isotherm suggesting that the Langmuir isotherm is an appropriate model in estimating the adsorption parameters. Whereas comparing the r^2 value for Freundlich isotherm with r^2 value for the Langmuir-2, Langmuir-3 and Langmuir-4 isotherm expressions, it can be concluded that Freundlich isotherm is an appropriate model to explain the present system. The observations, especially from the Langmuir isotherm equation, show the mathematical complexities associated with using linear method in estimating the rate parameters. The different r^2 values for different linearized forms of Langmuir isotherm equations are due to the variation in distribution of error structure for different linear equations. Transforming the non-linear equation to a linear equation and then fitting the experimental data into the transformed equation using least squares is not a valid approach unless the transformed data satisfy the assumption appropriate to least squares. It is simply wrong to linearize the non-linear equation to a linear form and applying the least squares method. Instead, it is better to predict the form of linear equation that best fits the wide range of experimental data with a higher coefficient of determination.

However, in the present study, it is strongly evident that type 1 Langmuir form has a higher r^2 value when compared to Freundlich isotherm equation. But type 3 and type 4 showed a lower r^2 value than Freundlich isotherm, this suggests that Freundlich isotherm is more appropriate model to describe the sorption equilibrium data. This observation makes clear that even the search for a best fit linear model is not an appropriate technique in estimating the isotherm parameters, as the different linearized forms of a single non-linear equation produce various observations. It will be an inappropriate method to get isotherm parameters by fitting the experimental data to the 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.

5. Conclusions

The present study showed that the low cost material rubber wood sawdust can be used as an adsorbent for the removal of Malachite Green from its aqueous solutions. It is not appropriate to use the coefficient of determination of linear regression method for comparing the best fitting of isotherms. Non-linear method could be a better way to obtain the parameters. It was clear that both two-parameter Langmuir and three-parameter Redlich–Peterson isotherms were the best-fitting models for the adsorption of Malachite Green onto rubber wood sawdust. Langmuir is a special case of Redlich–Peterson isotherm when constant g was unity.

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