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Optimum sorption isotherm by linear and non-linear methods for malachite green onto lemon peel

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Abstract

Equilibrium studies were carried out at 305 K for the sorption of malachite green onto lemon peel. The equilibrium data were fitted to the Freundlich, Langmuir and Redlich–Peterson isotherms by linear and non-linear methods. Non-linear method is a better way to obtain the isotherm parameters. The best fitting isotherm was found to be the Langmuir and Redlich–Peterson isotherm. Redlich Peterson is a special case of Langmuir when the constant g equals unity.

Keywords: Adsorption; Malachite green; Orange peel; Operating line; Adsorber design; Isotherms

1. Introduction

Adsorption process is proved to be an effective process for the removal of colour from dye wastewaters [1]. Activated carbon is the most commonly used adsorbent for the removal of various pollutants from wastewaters. However, due to the high cost and the loss involved in regeneration, there is a continuous search for low cost adsorbents as an alternate to activated carbon. In the present research, lemon peel, a waste generated from juice manufacturing industry was used as an adsorbent. The analysis and design of adsorption process require information on the equilibrium adsorption isotherms [1]. The three widely used isotherms were the Freundlich [2], Langmuir [3] and Redlich–Peterson [4] expressions. Linear regression by the method of least squares was the most commonly used method to estimate the isotherm parameters [1,5]. However, linearization of non-linear isotherm expressions may alter the error distributions and violate the normality assumptions of the least square method [1,5]. In the present study both linear non-linear methods were used to estimate the isotherm parameters of malachite green onto lemon peel. The dye malachite green is selected as a model compound in order to evaluate the capability of lemon peel to remove dye from wastewaters.

The lemon peel used in the present study was obtained from the university canteen. The obtained lemon peel was cut into small pieces using scissors. Then the lemon peels were dried at 100 °C for 24 h using hot air oven. The dried materials were then ground using a domestic Sumeet mixer. The ground materials were then sieved through $-90+105$ mesh to get uniform geometrical size for use.

The dye used in all the experiments was malachite green, a basic (cationic) dye. Synthetic dye stock solutions were prepared by dissolving 2 g of malachite green in 2 L of double distilled water. All working solutions were prepared by diluting the stock solution with distilled water.

Batch sorption experiments were carried out at 305 K. Dye solution (30 mL) of dye concentration ranging from 200 mg/L to 25 mg/L was taken in 100 mL capped conical flasks. Accurately weighed 0.05 g of lemon peel was added to the solution. Then the flasks were agitated using a water bath shaker at a constant agitation speed of 180 rpm. The contact was made for 24 h, which is more than sufficient time required to reach equilibrium. After shaking, the samples were then centrifuged to separate the lemon peel from the solution. The left out concentration in the supernatant dye solution was analyzed using UV spectrophotometer.

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Table 1
Isotherms and their linear forms

Isotherm		Linear form	Plot	Reference
Freundlich	$q_e = K_F C_e^{1/n}$	$\mathrm{Log}(q_e) = \mathrm{Log}(K_F) + 1/n\,\mathrm{Log}(C_e)$	$\mathrm{Log}(q_e)$ vs. $\mathrm{Log}(C_e)$	[2]
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	[3]
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. $\ln(C_e)$	[4]

q_m: mg/g; K_a: L/mg; K_F: (mg/g)(L/g)^n; A: L/g; B: L/mg$^{1-1/A}$.

2. Results and discussions

The non-linear and the linearized expressions of the Freundlich [2], Langmuir [3] and Redlich–Peterson [4] isotherms are shown in Table 1. From Table 1 it was observed that Langmuir isotherm can be linearized to at least four different types. The Freundlich isotherm parameters can be obtained from the plot between Log q_e and Log C_e. Similarly, the Langmuir isotherm parameters for type 1, type 2, type 3 and type 4 Langmuir can be obtained from the plots between C_e/q_e and C_e, $1/q_e$ and $1/C_e$, q_e and q_e/C_e and q_e/C_e and q_e, respectively. The way to obtain the isotherm parameters is explained in Table 1. For Redlich–Peterson isotherm the parameters can be evaluated from the plot between Log$(AC_e/q_e - 1)$ and Log C_e. However, this is not possible as it contains three parameters. Thus a trial and error procedure was adopted to estimate the parameter A by maximizing the r^2 value using the *Solver* add-in, Microsoft Excel. The obtained isotherm parameters by linear method are shown in Table 2. From Table 2, it was observed that the best fitting linear expressions were the type 1 Langmuir, type 2 Langmuir and the Redlich–Peterson isotherms. The very low r^2 value for Freundlich isotherm suggests that it is not appropriate to use Freundlich isotherm to explain the equilibrium sorption phenomena of malachite green onto lemon peel. From the r^2 values, it was observed that the determined isotherm parameters (Table 2) from the four linearized Langmuir isotherms and the r^2 values vary for the four different types of linearized forms of Langmuir isotherm expressions. The adsorption capacity was found to be 3.03 mg/g and 43.45 mg/g for type 3 and type 4 Langmuir isotherms. The different outcomes show the real complexities and problems in estimating the isotherm parameters by linear method. The different outcomes for different linearized forms of equations are due to the fact that the error structure will get varied upon linearizing the non-linear equation. This is because the way the isotherm is linearized the error distribution may change either to the worse or to the better [1,5]. Thus non-linear method would be a better way to obtain the isotherm parameters which would be avoiding such errors.

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 coefficients of determination between experimental data and isotherms using the *Solver* add-in with Microsoft's spreadsheet, Microsoft Excel. Fig. 1 shows the experimental equilibrium data and the predicted isotherms using non-linear method for malachite green onto lemon peel at 305 K, respectively. The obtained isotherm parameters are listed in Table 1. From Table 1, it was observed that the coefficients of determination, i.e. r^2 values were found to be 0.99 for all the three isotherms studied, showing the applicability of these models. Further the r^2 values for Freundlich isotherm by non-linear method were found to be very high (= 0.99) when compared to the r^2 values of Freundlich isotherm by linear method (= 0.82). This shows that the error distribution changes to

Table 2
Isotherm parameters for malachite green onto lemon peel at 305 K

	Type 1	Type 2	Type 3	Type 4
Langmuir isotherm constants (linear method)				
q_m (mg/g)	43.45684	51.41801	3.031433	3.158113
K_L (L/g)	0.083853	0.055813	16.03917	14.88719
r^2	0.997696	0.99042	0.928177	0.928177
Freundlich isotherm constants (linear method)				
K_F (mg/g)(L/g)^n	7.784133			
$1/n$	0.373698			
r^2	0.849926			
Redlich–Peterson isotherm constants (linear method)				
A	2.724444			
B	0.037335			
g	1.088417			
r^2	0.994897			
Langmuir isotherm constants (non-linear method)				
q_m (mg/g)	51.73459			
K_L (L/g)	0.05848			
r^2	0.99891			
Freundlich isotherm constants (non-linear method)				
K_F (mg/g)(L/g)^n	6.104755			
$1/n$	0.489962			
r^2	0.994593			
Redlich–Peterson isotherm constants (non-linear method)				
A	3.025473			
B	0.058481			
g	1			
r^2	0.99891			

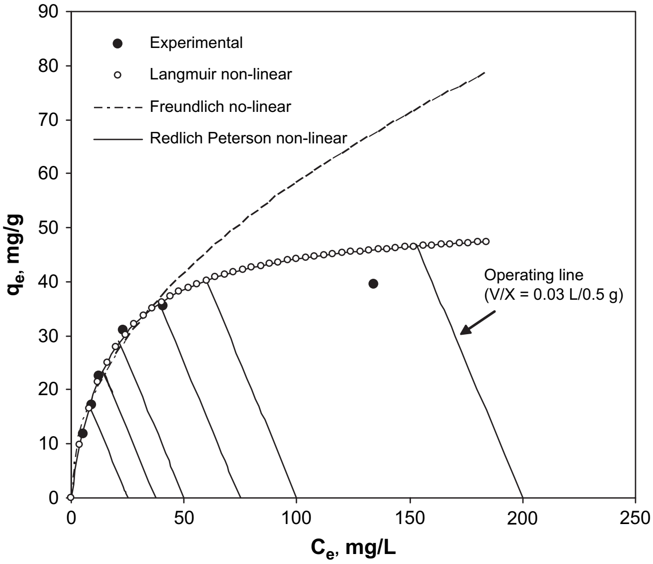

Fig. 1. Isotherms for malachite green onto lemon peel at 305 K.

the worse while fitting the experimental data of malachite green onto lemon peel in Freundlich isotherm. In addition the higher monolayer sorption capacity, q_m, value of 51.73 mg/g suggests that lemon peel can be used as an adsorbent for the removal of malachite green onto lemon peel. Fig. 1 shows that the Langmuir and Redlich–Peterson isotherms overlapped each other with the same coefficient of determination values (Table 2). Thus the Redlich–Peterson is a special case of Langmuir when the constant *g* equals unity confirming our previously reported findings [5].

3. Conclusions

The present study shows that the waste material, lemon peel, can be effectively used as an adsorbent for the removal of the malachite green from its aqueous solution. The equilibrium data were found to be well represented by the Freundlich, Langmuir and Redlich–Peterson isotherms. Non-linear is the more appropriate method to obtain the isotherm parameters. Redlich–Peterson is a special case of Langmuir when the constant *g* equals unity.

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