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ScienceDirect
Dyes and Pigments 74 (2007) 590–594
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Batch adsorber design for different solution volume/adsorbent mass ratios using the experimental equilibrium data with fixed solution volume/adsorbent mass ratio of malachite green onto orange peel

K. Vasanth Kumar [a,*], K. Porkodi [b]

[a] *Department of Chemical Engineering, A.C. Tech, Anna University, Chennai 600 025, TN, India*
[b] *Department of Chemistry, PSG College of Technology, Coimbatore, TN, India*

Received 27 August 2005; received in revised form 15 December 2005; accepted 28 March 2006
Available online 11 July 2006

Abstract

Equilibrium studies were carried out at 305 K for the sorption of malachite green onto orange peel for a fixed operating line condition (solution volume/adsorbent mass ratio or *V*/*M* ratio). The experimental data were fitted to the Freundlich, Langmuir and Redlich–Peterson isotherms by non-linear method. The best fitting isotherm was found to be the Langmuir and Redlich–Peterson isotherm. Redlich–Peterson is a special case of Langmuir isotherm when the constant g equals unity. A single stage batch adsorber was designed for different operating line (*V*/*M*) ratios using the Redlich–Peterson isotherm. Equilibrium data were obtained from the Langmuir isotherm at different *V*/*M* ratios using the mass balance equation for the batch adsorber system. A simple linear expression relating the parameters involved in the batch adsorber design was proposed for the studied system.

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 color from dye wastewaters [1,2]. The analysis and design of adsorption process require information on the equilibrium adsorption isotherms [1,2]. The most common way to obtain isotherm parameters for any adsorbate/adsorbent system is by carrying out equilibrium studies at different solution volume or at different adsorbent mass or by varying the initial dye concentrations. The effect of volume of solution to the adsorbent mass ratio (*V*/*M*) on the equilibrium uptake of dye solution at different initial concentrations is an important factor to be considered in adsorber design. However, this requires an extensive experimental work to determine the isotherm parameters for different *V*/*M* ratios and also at different initial dye concentrations. In the present study, an attempt has been made to determine the equilibrium data at different *V*/*M* ratios using the experimental equilibrium data of malachite green onto orange peel obtained from a single *V*/*M* ratio. The three widely used isotherms Freundlich, Langmuir and Redlich–Peterson were used to design the batch adsorber for different *V*/*M* ratios of malachite green/orange peel system. Non-linear method was used to estimate the parameters involved in the isotherm process. The dye malachite green is selected as a model compound in order to evaluate the capability of orange peel to remove dye from wastewaters.

2. Experimental

The orange peel used in the present study was obtained from the university canteen. The obtained orange peel was

* Corresponding author. Tel./fax: +91 9884651332.
E-mail address: vasanth_vit@yahoo.com (K.V. Kumar).

0143-7208/$ - see front matter
doi:10.1016/j.dyepig.2006.03.024

cut into small pieces using scissors. Then the orange peels were sun dried for 48 h. The dried materials were then ground using a domestic Sumeet mixer. The ground materials were then directly used as adsorbents without any pretreatment. The particle size distribution of the orange peel used in present investigation is given as follows: >1 mm: 5.342%; 1–0.75 mm: 4.489%; 0.75–0.92 mm: 40.46%; 0.92–0.335 mm: 31.22%; 0.335–0.215 mm: 7.487%; < 0.180 mm: 11% by weight.

The dye used in all the experiments was malachite green, a basic (cationic) dye. Synthetic dye solutions were prepared by dissolving weighed amount of malachite green in 1 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) with dye concentration ranging from 200 mg/L to 50 mg/L was taken in 100 mL capped conical flasks. Accurately weighed 0.009 g of orange peel was added to the solution. Then the flasks were agitated using a water bath shaker at a constant agitation speed of 95 strokes/min. The contact was made for 24 h, which is more than the sufficient time required to reach equilibrium. After shaking, the samples were then centrifuged to separate the orange peel from the solution. The left out concentration in the supernatant dye solution was analyzed using UV spectrophotometer.

3. Results and discussions

The Freundlich [3], Langmuir [4] and Redlich–Peterson [5] isotherm expressions are given by Eqs. (1)–(3), respectively

$$q_e = KC_e^{1/n} \tag{1}$$

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \tag{2}$$

$$q_e = \frac{AC_e}{1 + BC_e^g} \tag{3}$$

where C_e is the equilibrium concentration (mg/L); q_e is the amount of dye sorbed (mg/g); K is the Freundlich isotherm constant, (mg/g)(L/g)^n; n is the Freundlich exponent; q_m is q_e for a complete monolayer (mg/g); K_L is sorption equilibrium constant (L/mg); 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.

The parameters involved in the isotherm expressions were obtained by 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 maximizing 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 orange peel

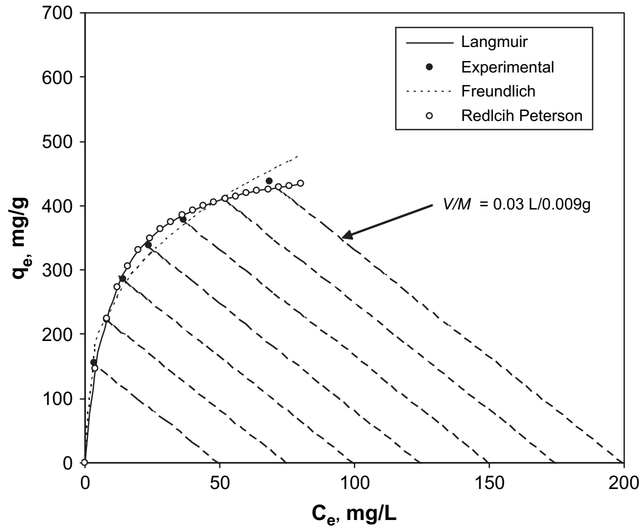

Fig. 1. Experimental and predicted isotherms for malachite green onto orange peel at 305 K.

at 305 K, respectively. The obtained isotherm parameters are listed in Table 1. From Table 1 it was observed that the coefficient of determination (r^2) values were found to be 0.98 for all the three isotherms studied. The higher r^2 values for all the three isotherms studied confirm the applicability of these isotherms. The higher q_m values of 483.63 mg/g confirm that the orange peel can be effectively used as an adsorbent for the removal of malachite green from its aqueous solution. Fig. 1 shows that the Langmuir and Redlich–Peterson isotherms overlapped each other with the same coefficient of determination values (Table 1). Thus the Redlich–Peterson is a special case of Langmuir when the Redlich–Peterson isotherm constant g equals unity. A similar observation was previously reported by our research group for safranin/activated carbon systems.

The essential characteristics of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor or equilibrium parameter, R_L, given by [6]

$$R_L = 1/(1 + K_L C_0) \tag{4}$$

The parameter R_L indicated the shape of isotherm as follows:

Value of R_L	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

Table 1
Isotherm parameters by non-linear method for malachite green onto orange peel

Langmuir isotherm		Freundlich isotherm		Redlich–Peterson isotherm	
q_m	483.6323	$1/n$	0.322987	A	52.27661
K_L	0.108082	K_F	115.7596	B	0.108094
r^2	0.983281	r^2	0.983826	g	1
				r^2	0.983281

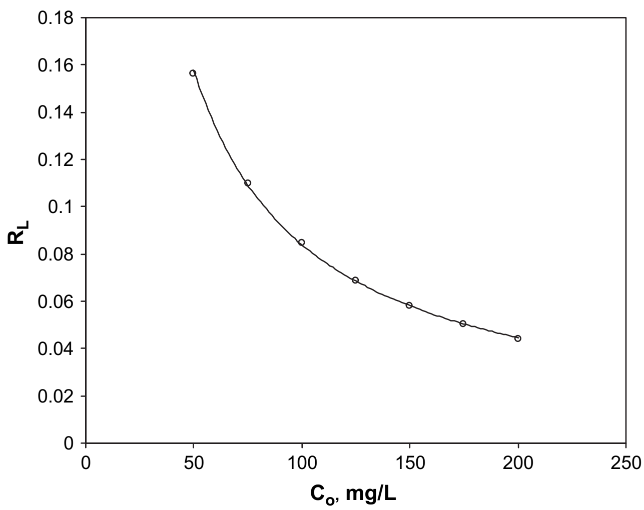

Fig. 2. Plot of separation factor versus initial dye concentration.

The calculated R_L values at different initial malachite green concentrations at 305 K are shown in Fig. 2. From Fig. 2 it was observed that sorption was found to be more favorable at higher initial dye concentrations. Also the value of R_L in the range of 0–1 at all initial dye concentrations confirms the favorable uptake of malachite green in the sorption process [6].

Generally sorption process proceeds through varied mechanisms such as external mass transfer of solute onto adsorbent followed by intraparticle diffusion. Unless extensive experimental data are available concerning the specific sorption application, determining the rate-controlling step is impossible. Therefore, empirical design procedures based on sorption equilibrium conditions are the most common methods to predict the adsorber size and performance. Previously, sorption isotherm relations have been used to predict the design of single stage batch adsorption systems [2,7,8]. A schematic diagram of a single stage batch adsorber is shown in Fig. 3. The design objective is to reduce the dye solution of volume V (L) from an initial concentration of C_0 to C_1 (mg/L). The amount of adsorbent is M and the solute loading changes from q_0 (mg/g) to q_1 (mg/g). At time $t=0$, $q_0=0$ and as time proceeds the mass balance equates the dye removed from the liquid to that picked up by the solid. The mass balance equation for the sorption system in Fig. 3 can be written as

$$V(C_0 - C_1) = M(q_0 - q_1) = Mq_1 \quad (5)$$

At equilibrium conditions, $C_1 \rightarrow C_e$ and $q_1 \rightarrow q_e$ (6)

Since the sorption isotherm studies confirm that the equilibrium data for malachite green onto orange peel fitted well in Langmuir isotherm, Langmuir isotherm equation can be used for q_1 in equation batch adsorber design.

Eq. (6) can be rearranged as

$$\frac{M}{V} = \frac{(C_0 - C_e)}{q_1} = \frac{(C_0 - C_e)}{q_e} = \frac{(C_0 - C_e)}{\left(\frac{q_0 K_L C_e}{1 + K_L C_e}\right)} \quad (7)$$

Eq. (7) can be rearranged as follows:

$$q_e = \frac{q_0 K_L C_e}{1 + K_L C_e} = -\frac{V}{M}C_e + \frac{V}{M}C_0 \quad (8)$$

The equilibrium sorption capacity q_e for any initial dye concentration can be obtained from the operating line (V/M) and the Langmuir isotherm. Fig. 1 shows the Langmuir isotherm and the series of operating lines with the slope of 0.03 L malachite green/0.009 g orange peel. From Fig. 1, it was observed that the equilibrium sorption capacities evaluated from the Langmuir isotherm and from the experiments are reasonable. Similarly the q_e values for different orange peel masses can be obtained from Langmuir isotherm by projecting a series of operating lines with varying slope values. Figs. 4–7 show the Langmuir isotherm and the generated

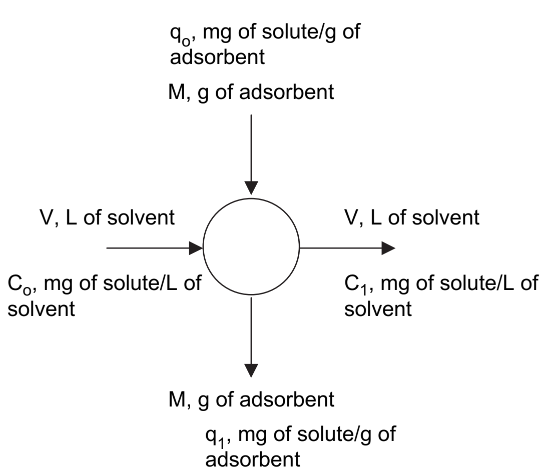

Fig. 3. Single stage batch adsorber design.

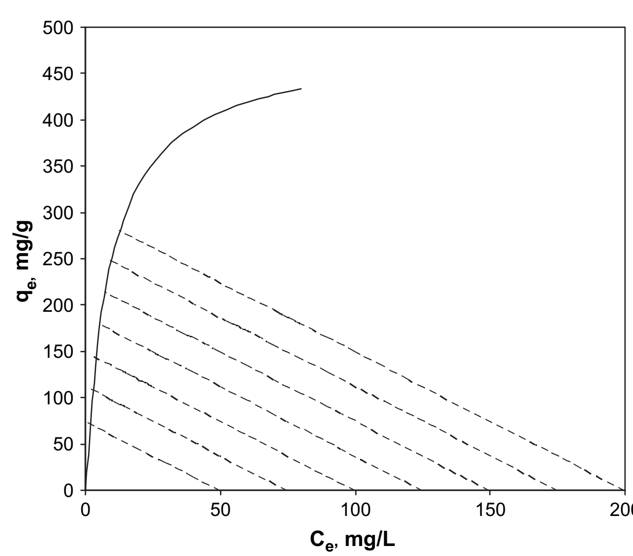

Fig. 4. Langmuir isotherm and operating lines with slope value equal to $V/M = 0.03$ L/0.02 g.

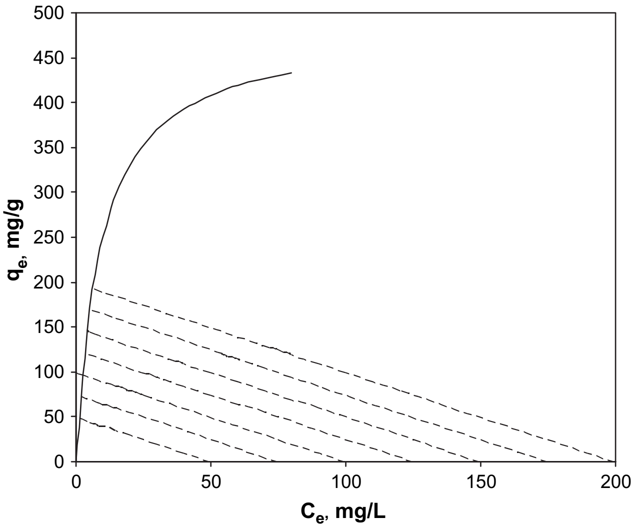

Fig. 5. Langmuir isotherm and operating lines with slope value equal to $V/M = 0.03$ L/0.03 g.

operating lines having a slope of V/M of 0.03 L/0.02 g, 0.03 L/0.03 g, 0.03 L/0.04 g and 0.03 L/0.05 g, respectively. The predicted q_e values for different initial dye concentrations at different V/M ratios are shown in Fig. 8. Fig. 8 can be used to determine the amount of dye adsorbed at equilibrium for the initial dye concentrations and V/M ratios ranging between 50 mg/L to 200 mg/L and 0.03 L/0.02 g to 0.03 L/0.05 g, respectively. The relation between the V/M ratio and the q_e values predicted from the Langmuir isotherm at different initial malachite green concentrations fit the following equation:

$$q_e = \frac{C_0 V}{0.9506M} - 2.66053 \qquad (9)$$

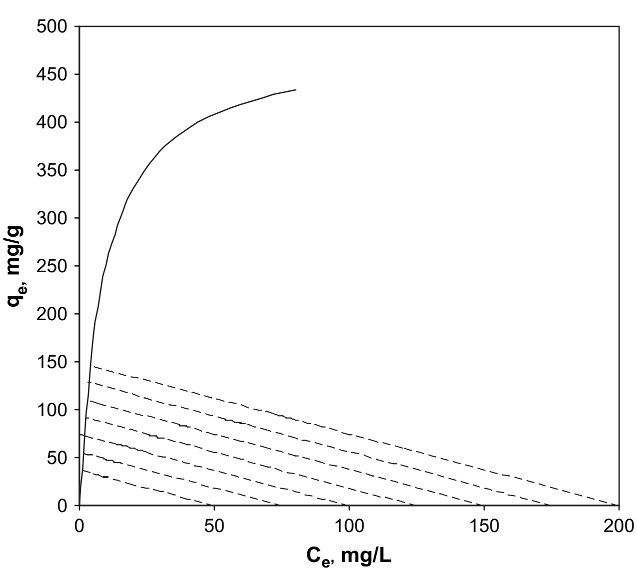

Fig. 6. Langmuir isotherm and operating lines with slope value equal to $V/M = 0.03$ L/0.04 g.

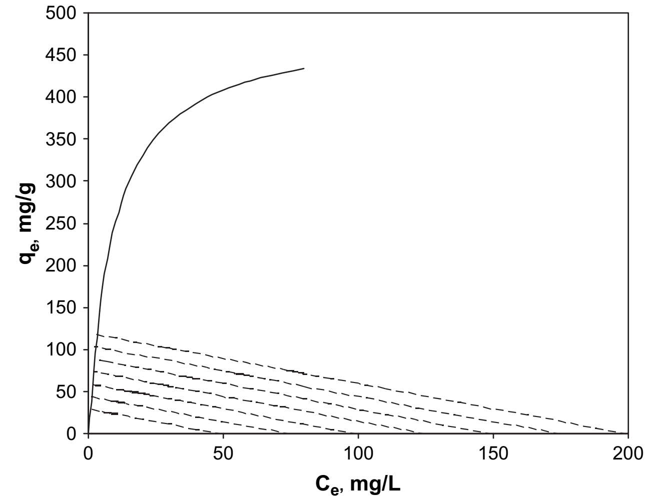

Fig. 7. Langmuir isotherm and operating lines with slope value equal to $V/M = 0.03$ L/0.05 g.

Eq. (9) can be used to design the malachite green/orange peel sorption system for any V/M ratio and for any initial dye concentration.

4. Conclusions

The present study shows that the biosorbent orange peel can be effectively used as an adsorbent for the removal of malachite green from its aqueous solution. The equilibrium data were found to be well represented by the Freundlich, Langmuir and Redlich–Peterson isotherms. Redlich–Peterson is a special case of Langmuir isotherm when the constant g equals unity. A single stage batch adsorber was designed for different V/M ratios using the experimental equilibrium data obtained at a single V/M ratio.

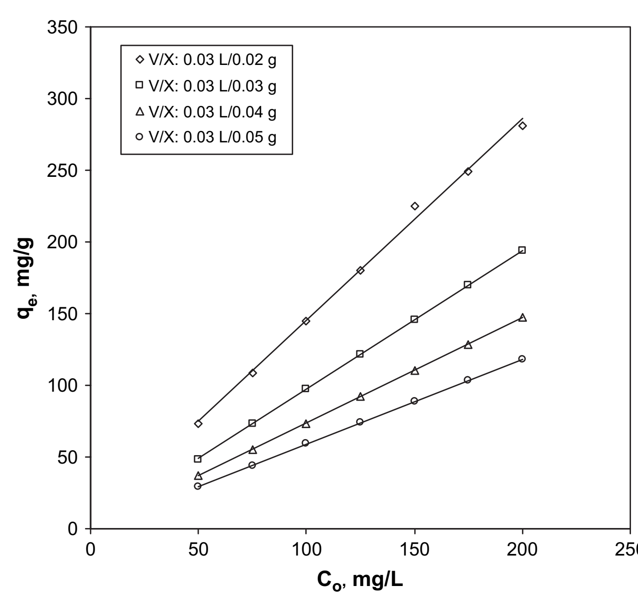

Fig. 8. Plot of q_e versus C_0 for different V/M ratios.

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