

Letter to the Editor

Relation between some two- and three-parameter isotherm models for the sorption of methylene blue onto lemon peel

Abstract

Equilibrium uptake of methylene blue onto lemon peel was fitted to the 2 two-parameter isotherm models namely Freundlich and Langmuir and 3 six-parameter isotherm models namely Redlich–Peterson, Toth, Radke–Prausnitz, Fritz–Schluender, Vieth–Sladek and Sips isotherms by non-linear method. A comparison between two-parameter and three-parameter isotherms was reported. The best fitting isotherm was the Sips isotherm followed by Langmuir isotherm and Redlich–Peterson isotherm equation. Redlich–Peterson isotherm is a special case of Langmuir isotherm when the Redlich–Peterson isotherm constant g was unity. Radke–Prausnitz, Toth, Vieth–Sladek isotherm were the same when the Toth isotherm constant, n_T and the Radke–Prausnitz isotherm, m_{RP} are equal to unity and when the Vieth–Sladek isotherm constant, K_{VS} equals zero. The sorption capacity of lemon peel for methylene blue uptake was found to be 29 mg/g.

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Sorption processes using low cost sorbent materials are currently proved to be an effective process for the removal of various pollutants from wastewaters [1–8]. 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 the frequently used method to determine the most fitted isotherm [9–11]. However, previously researchers showed that depending on the way the isotherm equations are linearized, the error distribution changes either the worse or the better [9–11]. Thus, non-linear method would be a better way to obtain the equilibrium isotherm parameters. In the present study, the best fit of two-parameter isotherm models namely Freundlich [12] and Langmuir [13] and 6 three-parameter isotherm models namely Redlich–Peterson [14], Toth [15], Radke–Prausnitz [16], Fritz–Schluender [17], Sips [18] and Vieth–Sladek [19] isotherm models was compared using the experimental equilibrium data of methylene blue onto lemon peel particles. The lemon peel is a complex material containing lignin and cellulose as main constituents [20]. Methylene blue is selected as model compound in order to check the potential of lemon peel as an adsorbent. Chemical sorption may occur via the polar functional groups of lignin such as alcohols, aldehydes, ketones, acids, phenolic hydroxides and ethers as chemical bonding and ion exchange [21].

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 grinded using a domestic Sumeet mixer. The grinded materials were then sieved through –90 + 105 mesh (BSS) to get uniform

geometrical size for use. Some of the chemical characteristics of lemon peel were shown in Table 1.

The dye used in all the experiments was methylene blue, a basic (cationic) dye. Synthetic dye stock solutions were prepared by dissolving 2 g of methylene blue 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. 30 mL of dye solution of dye concentration ranging from 200 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 95 strokes per minute. 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 were analyzed using UV spectrophotometer at λ_{max} of 665 nm.

The non-linearized form of the different isotherm models were shown in Table 2. For non-linear method, a trial and error procedure, which is applicable to computer operation is developed using *solver* add-in, Microsoft spreadsheet, Microsoft Excel. Fig. 1 shows the experimental and the predicted isotherms by non-linear method for the sorption of methylene blue onto lemon peel. The calculated isotherm parameters and their corresponding coefficient of determination, r^2 , values were shown in Table 3. From Table 3, it was observed that the higher r^2 values for the three-parameter Sips, Redlich–Peterson and the two-parameter Langmuir isotherms suggests the applicability of these models to represent the equilibrium sorption of methy-

Table 1
Chemical characteristics of lemon peel [20]

Cellulose	12.72 + 0.5%
Hemicellulose	5.30 + 0.2%
Lignin	1.73 + 0.2%
Ash	1.92 + 0.2%

Table 2
Isotherms and the parameters involved in the different equilibrium sorption isotherms

Isotherm	Expression	Parameters
Freundlich [12]	$q_e = K_F C_e^{1/n_F}$	K_F, n_F
Langmuir [13]	$q_e = \frac{q_m K_L C_e}{(1 + K_L C_e)}$	K_L, q_m
Redlich–Peterson [14]	$q_e = \frac{A C_e}{1 + B C_e^g}$	A, B, g
Toth [15]	$q_e = q_m C_e (b_T + C_e^{n_T})^{-1/n_T}$	b_T, n_T, q_m
Radke–Prasunitz [16]	$q_e = \frac{K_{RP} q_m C_e}{(1 + K_{RP} C_e)^{m_{RP}}}$	K_{RP}, q_m, m_{RP}
Fritz–Schluender [17]	$q_e = \frac{K_{FS} q_m C_e}{1 + q_m C_e^{m_{FS}}}$	K_{FS}, q_m, m_{FS}
Sips [18]	$q_e = \frac{q_m (K_S C_e)^{m_S}}{1 + (K_S C_e)^{m_S}}$	K_S, q_m, m_S
Vieth and Sladek [19]	$q_e = K_{VS} C_e + \frac{q_m \beta C_e}{1 + \beta C_e} \times q$	K_{VS}, q_m, β

Table 3
Isotherm parameters for methylene blue onto lemon peel obtained by non-linear method at 305 K

Langmuir q_m (mg/g) = 33.17016779 $K_L = 0.055839012$ $r^2 = 0.989302007$	Freundlich $K_F = 4.476458$ $1/n_F = 0.436197$ $r^2 = 0.945912$
Redlich–Peterson $A = 1.852191677$ $B = 0.055838996$ $g = 1$ $r^2 = 0.989302007$	Toth isotherm m (mg/g) = 29.96222 $b_T = 14.30358$ $n_T = 1$ $r^2 = 0.965315$
Radke–Prasunitz q_m (mg/g) = 29.96344751 $K_{RP} = 0.069898492$ $m_{RP} = 1$ $r^2 = 0.965314825$	Fritz–Schluender q_m (mg/g) = 51.00181 $K_{FS} = 6.548796$ $m_{FS} = 0.69381$ $r^2 = 0.965315$
Sips q_m (mg/g) = 29.54032617 $K_S = 0.073989054$ $m_S = 1$ $r^2 = 0.996289057$	Vieth–Sladek q_m (mg/g) = 29.96357 $K_{VS} = 0$ $\beta = 0.069898$ $r^2 = 0.965315$

lene blue by Lemon peel particles. In addition to Sips, Langmuir and Redlich–Peterson isotherm the equilibrium methylene uptake by lemon peel was reasonably well represented by Toth, Radke–Prasunitz and Vieth–Sladek isotherms with r^2 values of 0.9635. The value of Sips isotherm constant m_S and the Redlich–Peterson isotherm constant g equal to unity suggests that the isotherm is approaching the Langmuir isotherm and not Freundlich isotherm. The lower r^2 values for Freundlich and Fritz–Schluender isotherm shows it is not appropriate to use these models to represent the uptake of methylene blue by lemon peel at equilibrium. From Fig. 1, it was observed that

the Langmuir isotherm exactly overlapped the Redlich–Peterson isotherm with same coefficient of determination (Table 3). Thus Langmuir is a special case of Redlich–Peterson when the constant g equals unity. Similarly from Fig. 1, it was observed that the three-parameter isotherms Toth, Radke–Prasunitz and Vieth–Sladek isotherms overlapped each other with same r^2 values (Table 3). This suggests Toth, Radke–Prasunitz and Vieth–Sladek are the same when the Toth isotherm constant, n_T , Radke–Prasunitz isotherm constant, m_{RP} , equals unity and the Vieth–Sladek isotherm constant, K_{VS} equals zero. The four best-fit three-parameter isotherms Sips, Toth, Radke–Prasunitz and Vieth–Sladek suggests that the sorption capacity of lemon peel to uptake methylene blue to be 29 mg/g. Table 4 shows the sorption capacity of other low cost material to uptake methylene blue from aqueous solutions for comparison. From Table 4, it was observed that methylene blue sorption capacity of lemon peel was found to be relatively higher than the other low cost materials. Thus the low cost material lemon peel can be used as an adsorbent for the removal of dye bearing wastewaters.

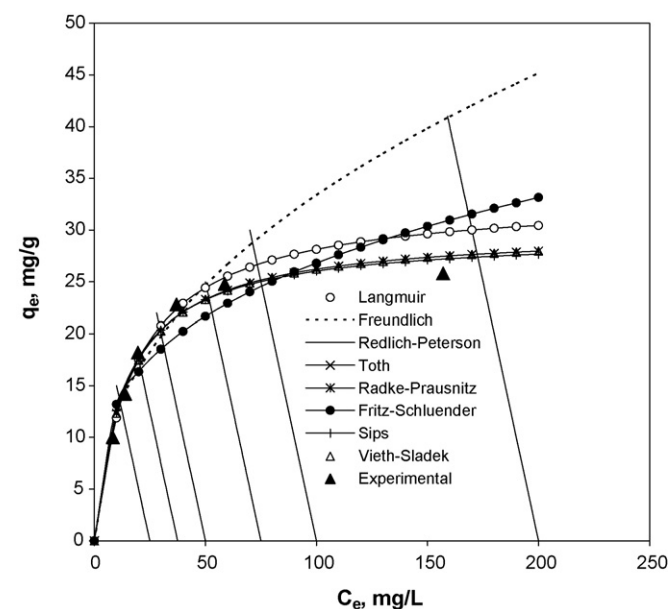


Fig. 1. Equilibrium data, operating line ($-V/X = 0.03 \text{ L}/0.05 \text{ g}$) and isotherms for methylene blue onto lemon peel at 305 K.

Table 4
Sorption capacities of several low cost adsorbents for the uptake of methylene blue from its aqueous solutions

Sorbent	Sorption capacity	Reference
Fe(III)/Cr(III) hydroxide	22.8	[22]
Fly ash	0.687 mg/g	[23]
Orange peel	18.6 mg/g	[24]
Chitosan	29.8 mg/g	[25]
Neem leaves powder	8.6 mg/g	[26]
Magenta PODMP	4.13 mg/g	[27]
Neem saw dust	2.1–3.6 mg/g	[28]
Aspergillus niger	15.5 mg/g	[29]
Clay	6.3–5 mg/g	[30]
Coal fly ash	5.718 mg/g	[31]
Lemon peel	29 mg/g	This study

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