

Equilibrium data, isotherm parameters and process design for partial and complete isotherm of methylene blue onto activated carbon

K. Vasanth Kumar*, S. Sivanesan

Department of Chemical Engineering, AC Tech, Anna University, Chennai, TN 600 025, India

Received 31 March 2005; received in revised form 29 October 2005; accepted 2 November 2005

Available online 25 January 2006

Abstract

Equilibrium data for the adsorption of methylene blue onto activated carbon was reported. The equilibrium data were splitted to different data sets to have an idea on the partial and complete isotherm. The equilibrium data were analyzed using Freundlich, Langmuir and Redlich–Peterson isotherm. The influence of partial isotherm and complete isotherm on the equilibrium parameters in isotherm expression were estimated. Equilibrium data covering the complete isotherm is the best way to obtain the parameters in isotherm expressions. Present investigation showed that for successful batch sorber design, equilibrium data with partial isotherm is not sufficient, instead equilibrium data that covers complete isotherm is required. Redlich–Peterson and Langmuir isotherm well represent the adsorption of methylene blue onto activated carbon. Redlich–Peterson isotherm is a special case of Langmuir when the constant ‘g’ equals unity.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Adsorption; Methylene blue; Activated carbon; Isotherm; Partial isotherm; Complete isotherm; Equilibrium data; Process design

1. Introduction

Currently adsorption process is proved to be an effective process for the removal of pollutants from wastewater [1,2]. The treatment of wastewater by adsorption technique is receiving growing attention since the standards for the quality of effluent disposal are becoming increasingly more rigid. Activated carbon is the most commonly used adsorbent and is proved to be effective for the removal of various pollutants such as phenol, acid and basic dyes, heavy metals, flavor esters from their aqueous solutions.

Adsorption process involves the selective transfer of solute onto the surface or onto the bulk of the solid material. This solute transfer process is found to occur through varied mechanisms such as external mass transfer, intraparticle diffusion and adsorption at sites. Unless extensive experimental data are available concerning the specific adsorption application, determining the rate-controlling step is impossible. Therefore, empirical design procedures based on adsorption equilibrium condition are the

most common method to predict the adsorber size and performance. Adsorption equilibrium is a dynamic concept achieved when molecules adsorb onto a surface is equal to the rate at which they desorb. The analysis and design of adsorption process requires the relevant adsorption equilibrium, which is the most important piece of information in understanding the adsorption process. The different parameter and the underlying thermodynamic assumption of these equilibrium models provide some insight into both the adsorption mechanism and the surface properties and affinity of the adsorbent. Isotherms help to determine the adsorption capacity of material and further helps to evaluate the performance of the adsorption system. Further it enables an evaluation of how an adsorption system can be improved [3].

The adsorption capacity can be obtained from the simple mass balance equation as follows:

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

So far, most of the adsorption theories have been developed for gas–solid systems because the gaseous state is better to understand than the liquid. The solid–liquid adsorption process is influenced by number of parameters such as pH, solubility of solute in the solvent, solution temperature and also the initial solute concentration. Till now the statistical theories devel-

* Corresponding author. Tel.: +91 44 23776661;

fax: +91 44 23776661; mobile: +91 9444469876.

E-mail address: vasanth_vit@yahoo.com (K. Vasanth Kumar).

oped for gas–solid system were applied to solid–liquid systems with little confidence for designing of the equipment. Some of the equilibrium isotherm equations for gas adsorption are Freundlich, Langmuir, Sips, Redlich–Peterson, Unilan, Toth, Dubinin Raduskevich isotherm in principle can be extended to solid–liquid adsorption systems. Out of them Freundlich, Langmuir and Redlich–Peterson isotherm are the most commonly used isotherm in solid–liquid adsorption systems. Earlier several researchers used these three isotherm equations the most to explain the adsorption phenomena [3–7].

In general the performance of any adsorption system or any adsorption system is designed based on the equilibrium model that well represents the experimental equilibrium data. The best-fit model was selected based on the model that showed maximum value of coefficient of determination between the experimental and the regressed values.

Previously several works have been reported in the literature explaining the adsorption isotherm for different adsorbent adsorbate systems. However, no works have been carried out to explain what the actual equilibrium curve required to design an adsorption system. In other words, no works have been concentrated on the effect of the total no of data points in a complete equilibrium curve. Careful analysis of equilibrium studies reported in the literature showed that every one used the equilibrium relation in different way to obtain the isotherm parameters, which mainly include the adsorption capacity. Some researchers explained the equilibrium models using a complete isotherm data [3,4,7–13] and some researchers used only a partial isotherm data to obtain the isotherm constants [1,6,14–19]. Some researchers used to obtain the equilibrium parameters with only three or four equilibrium data to get the constants in equilibrium relations [20–30]. The term whole adsorption curve can be explained as the equilibrium data covering from the near origin of the plot between q_e versus C_e to the $q_{e,max}$ as shown in Fig. 1. The equilibrium curve can be divided into three regions I, II and III as shown in Fig. 1. Lot researchers have a complete full isotherm to explain the adsorption isotherm [4,31,32]. In literatures some researchers have equilibrium data cover-

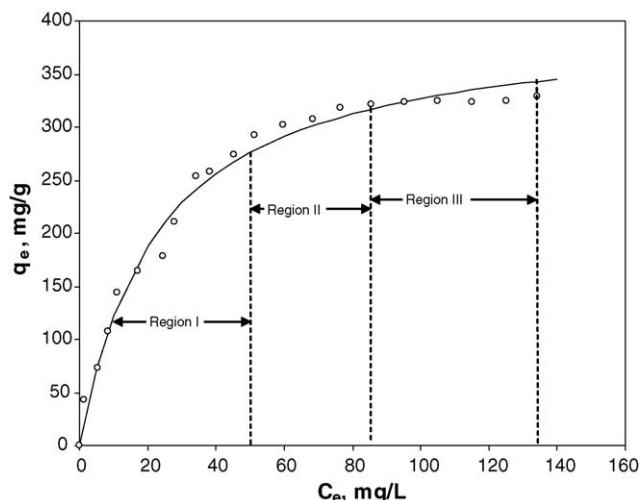


Fig. 1. Complete isotherm for methylene blue onto activated carbon.

ing the regions I and II and obtained the isotherm parameters [33]. Some researchers use the experimental equilibrium data covering the regions II and III of complete isotherm to obtain isotherm parameters [34,35]. Some researchers have obtained the isotherm parameters from the experimental equilibrium data covering the regions I and III of the complete isotherm [36,37]. Some researchers reported the equilibrium data covering only the I region alone to explain the isotherm model [38]. These different approaches reported by several researchers to explain the adsorption isotherm makes difficult to understand the actual adsorption isotherm concept. In general the adsorption isotherm can be obtained by three methods as follows:

- (i) By varying the initial concentration, C_0 in Eq. (1) and keeping the remaining V, M as constant
- (ii) By varying the volume of solution, V in Eq. (1) and keeping the remaining C_0, M as constant
- (iii) By varying the mass of adsorbent M in Eq. (1) and keeping the remaining V, C_0 as constant

Whatever may be the method applied to obtain adsorption isotherm, the most important point to be considered is to have an idea on complete isotherm which include the regions I–III as shown in Fig. 1.

As said earlier some researchers used equilibrium data covering the complete isotherm curves, some used only a partial equilibrium data to explain the isotherm curve. The aim of the present communication is to bring out the influence of experimental equilibrium data points in the complete isotherm and in a partial isotherm on the equilibrium parameters, which mainly include the adsorption capacity of the adsorbent material. The study was carried out using the experimental equilibrium data of methylene blue onto activated carbon at a constant temperature of 305 K.

2. Sorption isotherms

The equilibrium data were analyzed using the three most commonly used isotherms Freundlich, Langmuir and Redlich–Peterson isotherm equations which are explained as follows:

2.1. Freundlich isotherm

Herbert Max Finley Freundlich [39], a German physical chemist, presented an empirical adsorption isotherm for non ideal adsorption on heterogeneous surfaces as well as multi-layer adsorption and is expressed by the equation:

$$q_e = K_F C_e^{1/n} \quad (2)$$

where C_e (mg/L) is the solute concentration in the liquid at equilibrium, q_e (mg/g) the amount of dye sorbed at equilibrium, K_F (mg/g)(L/g) $^{1/n}$ and $1/n$ are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

The Freundlich isotherm has been derived by assuming an exponentially decaying adsorption 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.

2.2. Langmuir isotherm

Irving Langmuir [40], 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 and no further adsorption takes place. Theoretically, therefore, a saturation value is reached beyond which no further adsorption takes place. Also these equations can reduce to Henry's law at lower initial concentrations. Alternatively at higher concentrations, it predicts a monolayer adsorption capacity. The saturated monolayer adsorption capacity can be represented by the expression:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

where C_e is the equilibrium concentration (mg/L), q_e the amount of dye sorbed (mg/g), q_m is q_e for a complete monolayer (mg/g); K_L is the adsorption equilibrium constant (L/mg).

2.3. Redlich–Peterson isotherm

The Redlich–Peterson isotherm has three parameters and has the features of both the Freundlich and Langmuir isotherm equation. It can be described as [41]:

$$q_e = \frac{AC_e}{1 + BC_e^g} \quad (4)$$

where A is the Redlich–Peterson isotherm constant (L/g), B 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:

$$q_e = \frac{AC_e}{1 + BC_e} \quad (5)$$

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

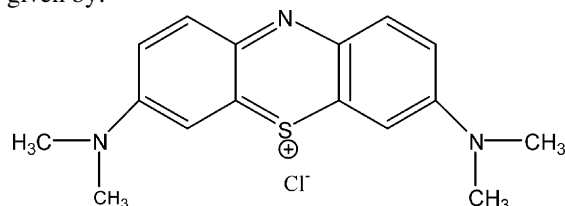
$$q_e = \frac{AC_e}{1 + B} \quad (6)$$

The isotherm constants in Eqs. (2)–(4) was solved by a trial and error non-linear method using solver add-in with Microsoft's spreadsheet, Microsoft excel. The best-fit model was selected based on the value of coefficient of determination.

3. Materials and methods

3.1. Sorbate

The dye used in all the experiments was methylene blue, a basic (cationic) dye. Synthetic dye solutions were prepared by dissolving weighed amount of methylene blue in 1 L of double distilled water. The structure of methylene blue (C.I.: Basic Blue 9) is given by:



The stock solution of methylene blue was prepared by dissolving 1 g of methylene blue in 1 L of distilled water. All working solutions were prepared by diluting the stock solution with distilled water.

3.2. Sorbent

The powdered activated carbon used in the present study was obtained from E-Merck Limited, Mumbai. The obtained activated carbon was directly used as adsorbents without any pre-treatment. Some of the specifications of the activated carbon used in the present study as supplied by the manufacturer are given by: substances soluble in water $\leq 1\%$, substances soluble in HCl $\leq 3\%$, Cl $\leq 0.2\%$, and $\text{SO}_4^{2-} \leq 0.2\%$. Heavy metals as lead (Pb) $\leq 0.005\%$, Iron (Fe) $\leq 0.1\%$, and incomplete carbonization: passes test, loss on drying $\leq 10\%$, and residue on ignition $\leq 5\%$.

3.3. Process

Batch adsorption studies were carried out by contacting 0.01 g of activated carbon with 50 ml of dye solution of known initial dye concentration in 125 ml capped conical flasks. The contact was made using water bath shakers at a constant agitation speed of 95 strokes with a stroke length of 1.5 cm at a constant solution temperature of 305 K. The contact was made for 48 h, which is more than sufficient time to attain equilibrium. After 48 h, the dye solutions were separated from the adsorbent by centrifugation. The concentration in the supernatant solution was analyzed using a UV Spectrophotometer.

4. Results and discussion

Fig. 1 shows the equilibrium plot between q_e versus C_e using the whole adsorption isotherm curve for methylene blue onto activated carbon. From Fig. 1 it was observed that there are totally 20 experimental equilibrium data points between C_e and q_e covering the entire adsorption data. The isotherm curve in Fig. 1 can be splitted to atleast three regions I–III. Where the regions covering I–III separately contribute the partial isotherm, further any isotherm which include any two of the regions in I–III

Table 1
Equilibrium data for complete and partial isotherm of methylene blue onto activated carbon at 305 K

C_0 (mg/L)	C_e (mg/L)	q_e (mg/g)	DS1	DS2	DS3	DS4	DS5	DS6	DS7	DS8	DS9	DS10	DS11	DS12	DS13	DS14	DS15
0	0	0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
10	1.4	43	A	–	–	–	–	A	A	A	A	A	–	A	–	–	–
20	5.4	73	B	–	–	–	–	B	B	B	B	–	B	–	B	–	–
30	8.5	107.5	C	C	–	–	–	C	C	C	C	C	–	–	C	–	–
40	11.1	144.5	D	D	–	–	–	D	D	D	D	–	D	–	D	–	–
50	17.2	164	E	E	E	–	–	E	E	E	E	E	–	–	–	–	–
60	24.4	178	F	F	F	–	–	F	F	F	–	–	F	F	–	–	–
70	27.9	210.5	G	G	G	G	–	G	G	G	–	G	–	–	–	G	–
85	34.3	253.5	H	H	H	H	–	H	H	H	–	–	H	–	–	H	–
90	38.4	258	I	I	I	I	I	I	I	I	–	I	–	–	–	I	–
100	45.2	274	J	J	J	J	J	J	J	J	–	–	J	–	–	J	–
110	51.4	293	K	K	K	K	K	K	K	K	–	K	–	K	–	–	–
120	59.6	302	L	L	L	L	L	L	L	L	–	–	L	–	–	–	–
130	68.4	308	M	M	M	M	M	M	M	M	M	M	–	–	–	–	–
140	76.4	318	N	N	N	N	N	N	N	N	N	N	–	–	–	–	–
150	85.6	322	O	O	O	O	O	O	O	–	O	O	–	–	–	–	–
160	95.2	324	P	P	P	P	P	P	P	–	P	–	P	–	–	–	–
170	105	325	Q	Q	Q	Q	Q	Q	–	–	Q	Q	–	–	–	–	Q
180	115.2	324	R	R	R	R	R	R	–	–	R	–	R	–	–	–	R
190	125	325	S	S	S	S	S	–	–	–	S	S	–	–	–	–	S
200	134.2	329	T	T	T	T	T	–	–	–	T	–	T	T	–	–	T

leaving the third one also can be represented as a partial isotherm curve. A full isotherm is one, which has all the three regions in an isotherm curve. In the present study, the isotherm parameters for both full and partial equilibrium isotherm data were reported and discussed.

For the present case, the experimental equilibrium data are named as A, B and C for data point 1, 2 and 3, respectively, and similarly upto T for the 20th experimental data point. The details are shown in Table 1.

In order to observe the effect of leaving the I region alone in the complete isotherm, the equilibrium curve were plotted by leaving the data points in the initial region (I) of the equilibrium curve. To make a careful observation instead of completely leaving the equilibrium data in the I region, the first two equilibrium data points A and B were deleted as shown in DS2 and the next two points in DS3 and similarly deleted the first 6 and 8 points as shown in DS4 and DS5, respectively. Where DS2, DS3, DS4, DS5 and DS6 represents the experimental equilibrium data set 2, experimental equilibrium data set 3, experimental equilibrium data set 4, experimental equilibrium data set 5 and experimental equilibrium data set 6, respectively. The details are shown in Table 1. All the experimental data set points in Table 1 except the DS1, DS10, DS11 represents the partial isotherm.

Similarly the influence of leaving experimental data points of the final (III) portion and the II portion in the complete isotherm curve can be obtained by leaving the data in these regions. The probable conditions to have a partial isotherm by leaving the experimental data in the region III are given in DS6, DS7 and DS 8 (Table 1). Similarly the probable condition to have a partial isotherm by leaving the experimental data in the region II is given in DS9 (Table 1).

Apart from studying the partial and complete isotherm curve, it is planned to estimate to find out whether the total number of experimental data points in a full isotherm curve has any effect

on the isotherm parameters. For this, two more data set points were obtained and represented by DS10 and DS11 as shown in Table 1. The DS10 was obtained by leaving the even data points in DS1, i.e., by leaving the 2nd, 4th, 6th and upto the 20th experimental point. DS11 was obtained by leaving the odd data points in DS1, i.e., by leaving 1st, 3rd, 5th and upto 19th experimental point.

Figs. 2–4 show the predicted equilibrium curves using non-linear method for the three equilibrium isotherm models Freundlich, Langmuir and Redlich–Peterson, respectively, at 305 K. For non-linear method, a trial and error procedure, which is

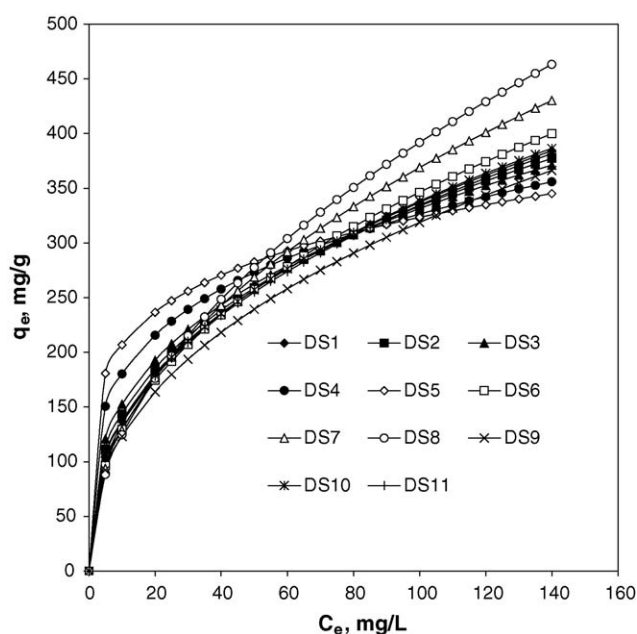


Fig. 2. Predicted Freundlich isotherm for methylene blue onto activated carbon.

Table 2

Isotherm parameters for methylene blue onto activated carbon (q_m (mg/g); K_L (L/mg); K_F (mg/g)(L/g) $^{1/n}$; A (L/g); B (L/mg $^{1-1/A}$))

	DS1	DS2	DS3	DS4	DS5	DS6	DS7	DS8	DS9	DS10	DS11
Langmuir											
q_m	400.9724	522.5552	409.4512	391.03	376.4123	419.2317	426.1511	440.1231	390.9081	401.5892	401.0283
K_L	0.044165	0.016064	0.040417	0.049933	0.061733	0.038712	0.038402	0.035961	0.047064	0.043915	0.043931
r^2	0.983464	0.927448	0.947068	0.940963	0.937892	0.98173	0.985371	0.983799	0.993053	0.988475	0.975851
Freundlich											
K_F	55.86837	61.91768	70.14918	99.56312	132.2336	48.49297	45.00659	39.65823	47.48155	54.63975	55.14142
$1/n$	0.390228	0.365712	0.337176	0.25783	0.194161	0.426943	0.456828	0.497422	0.413474	0.395879	0.391523
r^2	0.927712	0.903483	0.868116	0.866665	0.871683	0.91426	0.962061	0.975019	0.969445	0.942816	0.906158
Redlich–Peterson											
A	17.7095	17.37686	16.54877	19.52898	23.23828	16.99573	16.36478	15.82694	18.39765	17.6352	17.61832
B	0.044167	0.043102	0.040418	0.049946	0.061737	0.041419	0.038401	0.03596	0.047064	0.043914	0.043933
g	1	1	1	1	1	1	1	1	1	1	1
r^2	0.983464	0.971986	0.947068	0.940963	0.937892	0.977383	0.985371	0.983799	0.993053	0.988475	0.975851

applicable to computer operation, was developed to determine the isotherm parameters by minimizing the respective the coefficient of determination between experimental data and isotherms using the *solver* add-in with Microsoft's spreadsheet, Microsoft excel.

The calculated isotherm parameters and the corresponding coefficient of determination r^2 values were shown in Table 2, it was observed that for all the data sets (from DS1 to DS11).

In the case of Langmuir isotherm, it was observed that the maximum adsorption capacity q_m was found to be 522.53, 409.43, 391.03 and 376.41 mg/g at DS2, DS3, DS4 and DS5, respectively. This shows that by simultaneously leaving the experimental data in the region I of the complete isotherm curve will show a decreased value in the maximum adsorption capacity. Whereas for DS6, DS7 and DS8, it was observed that the maximum adsorption capacity was found to increase by simultaneously leaving the data point in the region III of the complete isotherm curve. In the case of DS9, it was observed

that the maximum adsorption was found to be 390 mg/g, which is less than q_m value at 400.972 mg/g for DS1. This suggests that leaving the experimental equilibrium data in the region II will give a decreased value in the maximum adsorption capacity of the adsorbent material. A similar observation was noticed with Langmuir constant K_L , which has a direct relation with the energy of adsorption. From Table 2 it was observed the K_L value was found to decrease from DS2 to DS5 and was found to increase from DS6 to DS8. Further from Table 2 it was observed that, the q_m and K_L values for DS2–DS9 doesn't match with the Langmuir constants obtained from the complete isotherm curve data (DS1). This suggests that, it is simply incorrect to predict the isotherm parameters by having a partial adsorption isotherm.

In the case of DS10 and DS11, it was observed that the Langmuir constant q_m and K_L were found to be similar to that for DS1. This shows that, whatever may be the total number of experimental data points in a isotherm curve, if the data is sufficient

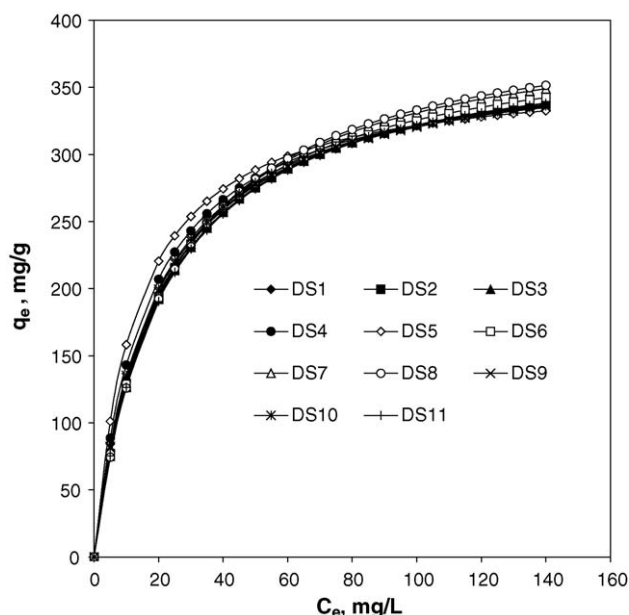


Fig. 3. Predicted Langmuir isotherm for methylene blue onto activated carbon.

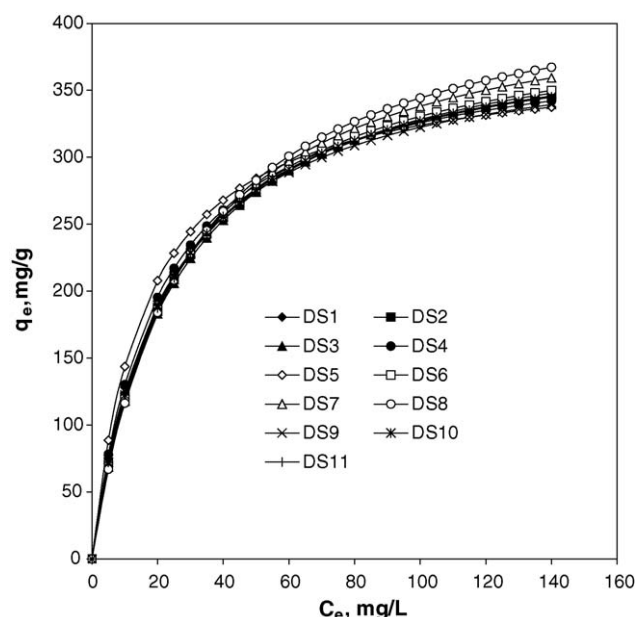


Fig. 4. Predicted Redlich–Peterson isotherm for methylene blue onto activated carbon.

enough to represent a complete isotherm curve, then it will give the isotherm constants more accurately. Further the r^2 values for all the different set of experimental data points was found to be higher in the range of 0.9274–0.9931. These very higher r^2 values show that the present system may follow the Langmuir isotherm equation.

In the case of Freundlich isotherm constants, from Table 2 it was observed that the Freundlich constant K_F was found to increase from 61.92, 70.15, 99.56 and 132.23 for DS2, DS3, DS4 and DS5, respectively. This suggests that leaving the experimental data points simultaneously in the region I of the complete isotherm curve show an increasing K_F value. From Table 1, it was further observed that the $1/n$ value gets decreased from 0.36, 0.34, 0.26 and 0.19 for DS2, DS3, DS4 and DS5, respectively. This suggests that leaving the experimental equilibrium points in the region I of the complete isotherm curve will affect the Freundlich exponent $1/n$, which is related to the adsorption intensity, which will have a direct error in the batch adsorber design.

A completely reversible approach was observed when leaving the experimental equilibrium data point in the region III of the complete isotherm. In this case K_F value was found to decreased when simultaneously leaving last two points in the III region to the first two points in the last (III) region. From Table 2, further it was noticed that, by leaving the data points in the II region of the complete isotherm showed a decrease in K_F value and increase in $1/n$ value when compared to K_F and $1/n$ value for DS1. For DS10 and DS11, it was observed that the both K_F and $1/n$ values were seemed to be more or less equal to that of DS1, this once again suggests that irrespective of the total number of experimental equilibrium data get altered much if the data are sufficient enough to represent a complete isotherm curve. From Table 2, it was further observed that for all the experimental data sets the coefficient of determination r^2 was found to be lower than the r^2 of Langmuir isotherm equation. Thus Freundlich equation cannot be used for the design of batch adsorber for the present solute and sorbate system studied.

For the three parameter Redlich–Peterson isotherm equation, it was observed that the constants A and B were found different for different experimental data sets from DS2 to DS9 (Table 2). The constant A value was found to get varied when leaving the experimental points in the regions I and III of the complete isotherm. However, the constant g was found to be unity and was found to be unchanged. This may be due to the fact that, irrespective of the experimental equilibrium data, whether partial or complete isotherm, the adsorption process approaching the Langmuir isotherm and not the Freundlich. The more or less equal value of A and B of DS10, DS11 with Redlich–Peterson constant for DS1 once again suggests that irrespective of the

Table 3a
Langmuir isotherm parameters for the adsorption of methylene blue onto activated carbon (q_m (mg/g); K_L (L/mg))

	DS1	DS12	DS13	DS14	DS15
q_m	400.9724	368.3779	220.0659	510.7495	343.1231
K_L	0.044165	0.060628	0.127596	0.026442	0.157569
r^2	0.983464	0.986498	0.735654	0.915748	0.997522

Table 3b
Process design for methylene blue onto activated carbon for conditions: C_0 , 100 mg/L; C_e , 20 mg/L

Data sets	DS1	DS2	DS3	DS4	DS5	DS6	DS7	DS8	DS9	DS10	DS11	DS12	DS13	DS14	DS15
V (L)	M (g)	M (g)	M (g)	M (g)	M (g)	M (g)	M (g)	M (g)	M (g)	M (g)	M (g)	M (g)	M (g)	M (g)	M (g)
1	0.425388	0.629596	0.437096	0.409452	0.384672	0.437292	0.432148	0.434494	0.422069	0.426021	0.426533	0.396267	0.505981	0.452818	0.307137
2	0.850777	1.259193	0.874191	0.818904	0.769345	0.874583	0.864297	0.868988	0.844138	0.852041	0.853066	0.792534	1.011961	0.905635	0.614274
3	1.276165	1.888789	1.311287	1.228357	1.154017	1.311875	1.296445	1.303483	1.266207	1.278062	1.279599	1.188802	1.517942	1.358453	0.921411
4	1.701553	2.518385	1.748382	1.637809	1.53869	1.749167	1.728593	1.737977	1.688276	1.704082	1.706132	1.583069	2.023922	1.811271	1.228548
5	2.126942	3.147982	2.185478	2.047261	1.923362	2.186459	2.160742	2.172471	2.110345	2.130103	2.132666	1.981336	2.529903	2.264089	1.535685
6	2.55233	3.777578	2.622573	2.456713	2.308035	2.62375	2.59289	2.606965	2.532414	2.556123	2.559199	2.377603	3.035883	2.716906	1.842822
7	2.977718	4.407174	3.059669	2.866165	2.692707	3.061042	3.025038	3.041459	2.954483	2.982144	2.985732	2.77387	3.541864	3.169724	2.149938
8	3.403107	5.036771	3.496764	3.275618	3.077379	3.498334	3.457187	3.475953	3.376552	3.408164	3.412265	3.170138	4.047844	3.622542	2.457095
9	3.828495	5.666367	3.93386	3.68507	3.462052	3.935626	3.889335	3.910448	3.798621	3.834185	3.838798	3.566405	4.553825	4.075359	2.764232
10	4.253883	6.295963	4.370955	4.094522	3.846724	4.372917	4.321483	4.344942	4.22069	4.260205	4.265331	3.962672	5.059805	4.528177	3.071369
11	4.679272	6.92556	4.808051	4.503974	4.231397	4.810209	4.753632	4.779436	4.64276	4.686226	4.691864	4.358939	5.565786	4.980995	3.378506
12	5.10466	7.555156	5.245147	4.913426	4.616069	5.247501	5.18578	5.21393	5.064829	5.112246	5.118397	4.755207	6.071766	5.433813	3.685643
13	5.530049	8.184752	5.682242	5.322879	5.000742	5.684703	5.617928	5.648424	5.486898	5.538267	5.544931	5.151474	6.577747	5.88663	3.99278
14	5.955437	8.814349	6.119338	5.732331	5.385414	6.122084	6.050076	6.082919	5.908967	5.964287	5.971464	5.547741	7.083727	6.339448	4.299917
15	6.380825	9.443945	6.556433	6.147783	5.770087	6.559376	6.482225	6.517413	6.331036	6.390308	6.397997	5.944008	7.589708	6.792266	4.607054
16	6.806214	10.07354	6.993529	6.551235	6.154759	6.996668	6.914373	6.951907	6.753105	6.816328	6.82453	6.340275	8.095688	7.245084	4.914191
17	7.231602	10.70314	7.430624	6.960688	6.539431	7.433959	7.346521	7.386401	7.197243	7.242349	7.251063	6.736543	8.601669	7.697901	5.221328
18	7.65699	11.33273	7.86772	7.37014	6.924104	7.871251	7.77867	7.820895	7.597574	7.668369	7.677596	7.13281	9.107649	8.150719	5.528465
19	8.082379	11.96233	8.304815	7.779592	7.308776	8.308543	8.210818	8.255389	8.019312	8.09439	8.104129	7.529077	9.61363	8.603537	5.835602
20	8.507767	12.59193	8.741911	8.189044	7.693449	8.745835	8.642966	8.689884	8.441381	8.52041	8.530662	7.925344	10.11961	9.056354	6.142739

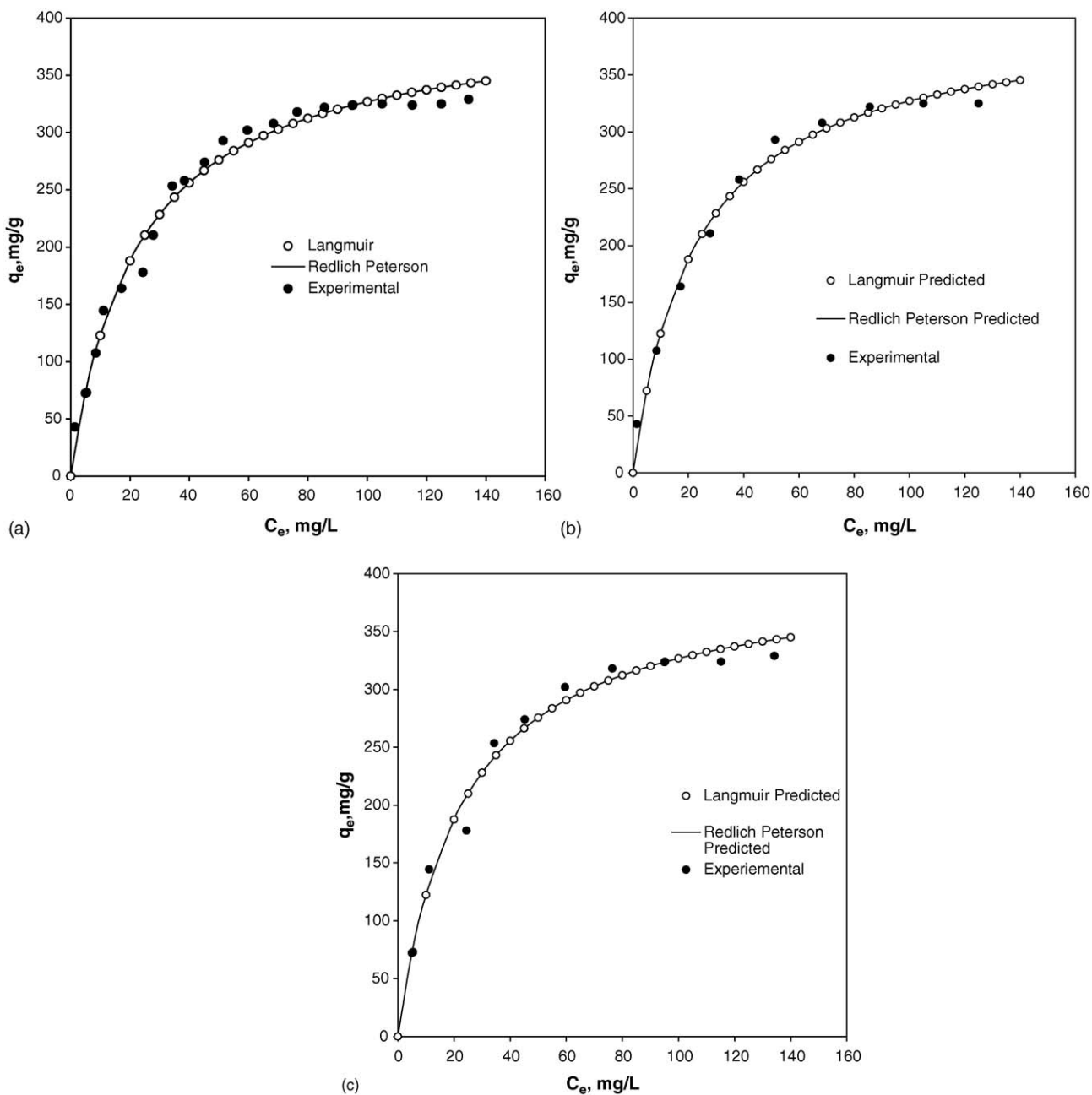


Fig. 5. (a) Comparison of Redlich–Peterson and Langmuir isotherm for methylene blue onto activated carbon for DS1. (b) Comparison of Redlich–Peterson and Langmuir isotherm for methylene blue onto activated carbon for DS10. (c) Comparison of Redlich–Peterson and Langmuir isotherm for methylene blue onto activated carbon for DS11.

experimental data points in a complete isotherm curve, the isotherm parameters doesn't get much altered. Further the r^2 values were found to be equal to the r^2 value of Langmuir isotherm equation, this suggests that for the present system, both Langmuir and Redlich–Peterson have a same error structures.

Fig. 5 (a)–(c) shows the experimental value and the predicted Langmuir and Redlich–Peterson isotherm for the data sets DS1, DS10 and DS11, respectively. From these figures it was observed that the Redlich–Peterson isotherm exactly overlapped the Langmuir isotherm. This suggests that for a full isotherm curve Redlich–Peterson is a special case of Langmuir when $g = 1$.

Previously some researchers used only three to four experimental equilibrium data alone to have a isotherm. To check whether it is a right method to determine the isotherm parameters with limited number of experimental data, four more experimental data set from DS12 to DS14 (Table 1) were made. Also the complete isotherm curve suggested the Langmuir isotherm and Redlich–Peterson isotherm are the best fitting isotherm for the present system, the isotherm parameters for Langmuir isotherm alone were estimated for DS12–DS14 and the results were compared with isotherm parameters for DS1. The four experimental points in DS12 represent the equilibrium data covering the whole adsorption isotherm, DS13 have four experimental

data covering the region I of the complete isotherm. DS14 and DS15 have four experimental equilibrium data in II and III part of the complete isotherm curve. Tables 3a and 3b lists the predicted Langmuir isotherm parameters for DS1, DS12, DS13, DS14 and DS15. From Tables 3a and 3b, it was observed that the predicted isotherm parameters for DS12–DS15 deviated very much from the isotherm parameters for DS1. This very clearly suggests that it is an inappropriate method to have isotherm parameters from an experimental equilibrium data with very limited data representing only a partial part of a partial isotherm.

5. Conclusions

From the present investigation the following points were concluded:

1. The adsorption of methylene blue onto activated carbon follows Langmuir and Redlich–Peterson isotherms.
2. It is inappropriate to obtain equilibrium parameters using equilibrium data that's represents only a partial isotherm curve.
3. Equilibrium data covering the complete isotherm is the best way to obtain the parameters in isotherm expressions.
4. For a successful batch sorber design, equilibrium data with partial isotherm is not sufficient, instead equilibrium data that covers complete isotherm is required.
5. Redlich–Peterson isotherm is a special case of Langmuir when the constant 'g' equals unity.

Acknowledgements

The valuable suggestions by the reviewer are greatly appreciated and acknowledged. The thanks are extended to the CSIR for awarding SRF to first author.

References

- [1] Y.S. Ho, G. McKay, *Can. J. Chem. Eng.* 76 (1998) 822–826.
- [2] G.M. Walker, L. Hansen, J.A. Hanna, S.J. Allen, *Water Res.* 37 (2003) 2081–2089.
- [3] X.S. Wang, Y. Qin, *Process Biochem.* 40 (2) (2005) 677–680.
- [4] Y.C. Wong, Y.S. Szeto, W.H. Cheung, G. McKay, *Langmuir* 19 (2003) 7888–7894.
- [5] S. Wang, Y. Boyjoo, A. Choueib, Z.H. Zhu, *Water Res.* 39 (2005) 129–138.
- [6] Y.S. Ho, *Carbon* 42 (10) (2004) 2115–2116.
- [7] E. Longhinotti, F. Pozza, L. Furlan, M.D.N.D. Sanchez, M. Klug, M.C.M. Laranjeira, V.T. Favere, *J. Braz. Chem. Soc.* 9 (5) (1998) 435–440.
- [8] Y.S. Ho, J.F. Porter, G. McKay, *Water Air Soil Pollut.* 141 (1–4) (2002) 1–33.
- [9] P. Janoš, H. Buchtová, M. Ryznarová, *Water Res.* 37 (2003) 4938–4944.
- [10] G. McKay, J.F. Porter, G.R. Prasad, *Water Air Soil Pollut.* 114 (1999) 423–438.
- [11] I. Safarik, M. Safarikova, V. Buricova, *Collect. Czech. Chem. Commun.* 60 (1995) 1448–1455.
- [12] B.S. Inbaraj, K. Selvarani, N. Sulochana, *J. Sci. Ind. Res.* 61 (2002) 971–978.
- [13] A. Gürses, S. Karaca, C. Doğan, R. Bayrak, M. Acikyildiz, M. Yalcin, *J. Colloid Interface Sci.* 269 (2004) 310–314.
- [14] B. Acemioğlu, *J. Colloid Interface Sci.* 274 (2004) 371–379.
- [15] G. McKay, *J. Chem. Technol. Biotechnol.* 32 (1982) 759–767.
- [16] Z. Aksu, T. Kutsal, *J. Chem. Technol. Biotechnol.* 52 (1991) 109–118.
- [17] M. Ottero, F. Rozada, L.F. Calvo, A.I. Garcia, A. Moran, *Biochem. Eng. J.* 15 (2003) 59–68.
- [18] S.D. Khattri, M.K. Singh, *Water Air Soil Pollut.* 120 (2000) 283–294.
- [19] D. Gosh, G. Bhattacharya, *Appl. Clay Sci.* 20 (2002) 295–300.
- [20] C. Namasivayam, R. Jeyakumar, R.T. Yamuna, *Waste Manage.* 14 (7) (1994) 643–648.
- [21] C. Namasivayam, N. Kanchana, R.T. Yamuna, *Waste Manage.* 13 (1993) 89–95.
- [22] C. Namasivayam, N. Muniasamy, K. Gayatri, M. Rani, K. Ranganathan, *Bioresour. Technol.* 57 (1996) 37–43.
- [23] C. Namasivayam, R.T. Yamuna, *Chemosphere* 30 (3) (1995) 561–578.
- [24] C. Namasivayam, K. Kadirvelu, *Carbon* 37 (1999) 79–84.
- [25] C. Namasivayam, D.J.S.E. Arasi, *Chemosphere* 34 (2) (1997) 401–417.
- [26] C. Namasivayam, R.T. Yamuna, *Environ. Pollut.* 89 (1995) 1–7.
- [27] C. Namasivayam, D. Kavitha, *Dyes Pigments* 54 (2002) 47–58.
- [28] C. Namasivayam, S. Sumithra, *J. Environ. Manage.* 74 (2005) 207–215.
- [29] C. Namasivayam, D. Sangeetha, *J. Colloid Interface Sci.* 280 (2004) 359–365.
- [30] C. Namasivayam, R. Radhika, S. Suba, *Waste Manage.* 21 (2001) 381–387.
- [31] S.J. Allen, G. McKay, J.F. Porter, *J. Colloid Interface Sci.* 280 (2004) 322–323.
- [32] M.Y. Arica, İ. Tüzün, E. Yalçın, Ö. İnce, G. Bayramoğlu, *Process Biochem.* 40 (2005) 2351–2358.
- [33] N. Bekatas, S. Kara, *Sep. Purif. Technol.* 39 (2004) 189–200.
- [34] Y.S. Ho, W.T. Chiu, C.C. Wang, *Bioresour. Technol.* 96 (2005) 1285–1291.
- [35] J.P. Chen, D. Lie, L. Wang, S. Wu1, B. Zhang, *J. Chem. Technol. Biotechnol.* 77 (2002) 657–662.
- [36] F. Banat, S. Al-Asheh, F. Mohai, *Sep. Sci. Technol.* 37 (2002) 311–327.
- [37] E. Oguz, *Colloids Surf A: Physicochem. Eng. Aspects* 252 (2004) 121–128.
- [38] M. Ozacar, I.Y. Sengil, *Bioresour. Technol.* 96 (2005) 791–795.
- [39] H.M.F. Freundlich, *Zeitschrift für Physikalische Chemie (Leipzig)* 57A (1906) 385–470.
- [40] I. Langmuir, *J. Am. Chem. Soc.* 38 (11) (1916) 2221–2295.
- [41] O. Redlich, D.L. Peterson, *J. Phys. Chem.* 63 (1959) 1024.