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What is the correct form of BET isotherm for modeling liquid phase adsorption?

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Abstract In this work subtleties of application of BET isotherm for liquid phase adsorption is presented. It has been shown that direct use of the classical BET equation (which was developed for gas phase adsorption) to liquid phase adsorption leads to ambiguous and erroneous results. Some cases of misuse of BET equation for liquid phase adsorption have been revisited. By close examination of the development of the classical equation, the causes of misunderstandings were elucidated and the suitable form of the BET equation for liquid phase adsorption was developed. As case studies, the classical form of the BET equation along with the correct form of the equation for liquid phase have been applied for modeling liquid phase adsorption of methyl tert-butyl ether (MTBE) on perfluorooctyl alumina, phenol on activated carbon and pentachlorophenol on carbonized bark. It has been shown that direct application of the classical BET isotherm to liquid phase adsorption results in poor and erroneous estimation of the equation parameters. For example, in aqueous phase adsorption of MTBE on perfluorooctyl alumina, the monolayer adsorption capacity of the adsorbent was calculated as 9.7 mg/g instead of 3.3 mg/g or the saturation concentration of MTBE in water was calculated as 1212 mg/L instead of 42000 mg/L.

Keywords BET isotherm · Liquid phase adsorption · Multilayer adsorption

1 Introduction

BET isotherm developed by Brunauer et al. (1938) is one of the most successful isotherm models to express adsorption phenomena. This equation has a sound theoretical basis and provides a good understanding about the nature of adsorption phenomena. Multilayer adsorption behavior, monolayer adsorption capacity and heat of adsorption at various adsorption layers are among the parameters of adsorption that can be determined using this isotherm model. Mainly because of these powerful features, BET isotherm model has found widespread application in determination of surface area and pore size distribution of adsorbents and catalysts. The most familiar form of the BET isotherm model is:

$$\frac{q}{q_m} = \frac{cx}{(1-x)(1-x+cx)}$$

or in linear form:

$$\frac{x}{q(1-x)} = \frac{1}{q_m c} + \left(\frac{c-1}{q_m c}\right)x$$

In the classical form of the BET equation which was originally developed for gas phase adsorption, the gas phase concentration was expressed as relative concentration, i.e. the ratio of the partial pressure of the adsorbate to its saturation partial pressure at the system temperature ($x = P/P^S$). In this case, the equation has two degrees of freedom in the form of two parameters of q_m and c which are found by linear regression analysis of the experimental adsorption data.

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When applying BET equation to liquid phase adsorption; one may simply substitute liquid phase concentration, C for partial pressure of the adsorbate, P in the classical BET equation. However, difficulty arises in replacing the saturation partial pressure P^S, with the corresponding term in liquid phase. In the classical BET isotherm equation, P^S resembles the maximum possible concentration of the adsorbate in the gas phase. A number of researchers have simply replaced saturation concentration of the adsorbate in liquid phase $C_{S,}$ instead of P^S when applying BET equation to liquid phase adsorption, i.e. they extended the simple analogy between P and C to the case of P^S and C_S. They have taken C_S as a known constant quantity from solubility data (Parker 1995; Maurya and Mittal 2006; Khalili et al. 2000; Fu and Viraraghavan 2000; Hall et al. 2001; Ramakrishna and Viraraghavan 1997). In this case, BET equation will have two degrees of freedom and it will behave like Langmuir isotherm equation when applied to the experimental data of liquid phase adsorption. As it will be shown, the calculated monolayer adsorption capacity by both Langmuir and BET isotherms will also be similar. Maurya and Mittal obtained such results (Maurya and Mittal 2006) when applying BET equation for modeling liquid phase adsorption of Methylene Blue and Rhodamin B cationic dyes on biosorbents prepared from mushrooms and on activated carbon, F300. They concluded that BET isotherm predicted adsorption capacity similar to that using Langmuir isotherm and that there was no possibility of multilayer adsorption in their system. As it will be shown later, this conclusion may not be entirely correct.

Some other researchers have also replaced C_S instead of P^S, but they used C_S as an adjustable parameter and have calculated it by fitting the BET isotherm equation to the experimental data (Edgehill and (Max) Lu 1998; Vazquez et al. 2007). In this case, the BET isotherm equation will have three degrees of freedom and contrary to the case of considering C_S as a known constant; a good fit of the experimental data will be obtained. However, in this approach the calculated liquid phase saturation concentration C_S, does not agree with the actual solubility data in the literature. It is obvious that one cannot determine the solubility of a solute in a liquid solvent by merely studying adsorption behavior of the solute on a solid adsorbent in the solvent. This contradiction forced some authors to interpret the calculated C_S value as the liquid phase concentration at which the adsorbent is saturated with adsorbate (Miller and Clump 1970), or as the liquid phase concentration at which upward curvature of the BET isotherm is observed (Al-Futaisi et al. 2007). These conclusions have been reached because of the particular trend of the BET equation. The mathematical form of the classical BET equation is such that when C approaches C_S, i.e. $x \to 1$, the predicted amount of adsorption q, tends to increase rapidly towards infinity.

It is obvious that determining the correct form of the BET isotherm model equation is essential for appropriate modeling of liquid phase adsorption phenomena. The main objective of this paper is developing an appropriate form of the BET isotherm equation for liquid phase adsorption and elucidating the sources of confusion in the literature. The developed model has been applied on liquid phase adsorption data from our research and two sets of experimental data from the literature.

2 Theory

For elucidating the source of discrepancies in using BET isotherm model for adsorption in liquid phase, a close examination of the derivation of the classical BET isotherm is essential. Similar to Brunauer et al. (1938), let $S_0, S_1, S_2, \ldots, S_i, \ldots$ represent the surface area that is covered by only $0, 1, 2, \ldots, i, \ldots$ layers of adsorbed molecules. Since at equilibrium S_0 must remain constant, the rate of adsorption on the bare surface is equal to the rate of desorption from the first layer:

$$a_1 P S_0 = (b_1 e^{-E_1/RT}) S_1 \tag{1}$$

where P is the partial pressure of adsorbate, and a_1 and b_1 are rate constants for adsorption and desorption on the first layer, respectively. E_1 is the heat of adsorption on solid surface. At equilibrium, S_1 must also remain constant. S_1 can change in four different ways: by adsorption on bare surface, by desorption from the first layer, by adsorption on the top of the first layer, and by desorption from the second layer. Thus:

$$a_2 P S_1 + (b_1 e^{-E_1/RT}) S_1 = (b_2 e^{-E_2/RT}) S_2 + a_1 P S_0 \tag{2}$$

a_2 and b_2 are adsorption and desorption rate constants corresponding to the second layer. E_2 is the heat of adsorption on the second layer.

From (1) and (2):

$$a_2 P S_1 = (b_2 e^{-E_2/RT}) S_2 \tag{3}$$

i.e., the rate of adsorption on top of the first layer is equal to the rate of desorption from the second layer. Similarly, for the second and consecutive layers we obtain

$$a_3 P S_2 = (b_3 e^{-E_3/RT}) S_3, \tag{4}$$

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$

$$a_i P S_{i-1} = (b_i e^{-E_i/RT}) S_i \tag{5}$$

a_i and b_i are rate constants of adsorption and desorption processes of the i-th layer, respectively. The total surface area is given by

$$A = \sum_{i=0}^{\infty} S_i \tag{6}$$

and the total amount of adsorbed solute is

$$q = q_0 \sum_{i=0}^{\infty} i S_i \tag{7}$$

where q_0 is the amount adsorbed on unit surface area of the adsorbent when it is covered with a complete unimolecular layer. It follows that

$$\frac{q}{Aq_0} = \frac{q}{q_m} = \frac{\sum_{i=0}^{\infty} i S_i}{\sum_{i=0}^{\infty} S_i} \tag{8}$$

Brunauer et al. made two simplifying assumptions, that the heat of adsorption is equal for all upper adsorbed layers (i.e. the layers 2, 3, 4...) and it is equal to the heat of condensation. The second assumption is that the ratio of rate constants of adsorption and desorption (a_i/b_i) are equal for these layers:

$$E_2 = E_3 = \cdots = E_i = E_L, \tag{9}$$

$$\frac{b_2}{a_2} = \frac{b_3}{a_3} = \cdots = \frac{b_i}{a_i} \tag{10}$$

Letting

$$y = P\frac{a_1}{b_1} e^{E_1/RT}, \tag{11}$$

$$x = P\frac{a_2}{b_2} e^{E_L/RT} \tag{12}$$

and

$$c = \frac{y}{x} \tag{13}$$

$S_1, S_2, \dots, S_i, \dots$ can be expressed in terms of S_0:

$$S_1 = yS_0, \tag{14}$$

$$S_2 = xS_1, \tag{15}$$

$$S_3 = xS_2 = x^2 S_1 = x^2 y S_0 = cx^3 S_0, \tag{16}$$

$$\dots\dots\dots\dots\dots\dots\dots\dots$$

$$S_i = cx^i S_0 \tag{17}$$

Substituting into (8), we obtain

$$\frac{q}{q_m} = \frac{cS_0 \sum_{i=1}^{\infty} ix^i}{S_0\{1 + c\sum_{i=1}^{\infty} x^i\}} = \frac{c\sum_{i=1}^{\infty} ix^i}{\{1 + c\sum_{i=1}^{\infty} x^i\}} \tag{18}$$

These summations are calculated as

$$\sum_{i=1}^{\infty} x^i = \frac{x}{1-x}, \quad x < 1, \tag{19}$$

$$\sum_{i=1}^{\infty} ix^i = x\frac{d}{dx}\left(\sum_{i=1}^{\infty} x^i\right) = x\frac{d}{dx}\left(\frac{x}{1-x}\right) = \frac{x}{(1-x)^2} \tag{20}$$

Substituting into (18), we obtain

$$\frac{q}{q_m} = \frac{cx}{(1-x)(1-x+cx)} \tag{21}$$

Equation (21) is the most familiar form of the BET equation and it is usually used in a rearranged form for linear regression of the experimental data:

$$\frac{x}{q(1-x)} = \frac{1}{q_m c} + \left(\frac{c-1}{q_m c}\right)x \tag{22}$$

The monolayer adsorption capacity of the adsorbent q_m, can be determined from slope and intercept of this linear equation and subsequently, specific surface area of the adsorbent can be calculated.

If the number of adsorbed layers cannot exceed some finite number n, then the summations in (18) are to be carried out up to n terms only, and not to infinity, i.e.

$$\sum_{i=1}^{n} x^i = \frac{x(1-x^n)}{1-x}, \tag{23}$$

$$\sum_{i=1}^{n} ix^i = x\frac{d}{dx}\left(\sum_{i=1}^{n} x^i\right) = x\frac{d}{dx}\left(\frac{x(1-x^n)}{1-x}\right) = \frac{x[1-(n+1)x^n + nx^{n+1}]}{(1-x)^2} \tag{24}$$

Replacing (23) and (24) into (18), we obtain:

$$\frac{q}{q_m} = \frac{cx\{1-(n+1)x^n + nx^{n+1}\}}{(1-x)\{1+(c-1)x - cx^{n+1}\}} \tag{25}$$

It should be noted that (25) has a more general form and the assumption of $x < 1$ is not made in this equation. If $x < 1$ and we let $n \to \infty$ (25) will be reduced to (21).

From (1) and (3–5) we obtain the following equations for the equilibrium constants of the first and consecutive layers. Equilibrium constant of adsorption for the first layer:

$$K_S = \frac{a_1}{b_1} e^{E_1/RT} \tag{26}$$

Equilibrium constant of adsorption for upper layers:

$$K_L = \frac{a_2}{b_2} e^{E_L/RT} \tag{27}$$

And so

$$c = \frac{K_S}{K_L} \tag{28}$$

E_1 and E_L are heat of adsorption of the first layer on the solid surface and heat of condensation of the adsorbate, respectively.

Brunauer et al. made another important assumption that q will be infinite when the partial pressure of the adsorbate equals its saturation pressure ($P = P^S$) in gas phase, i.e. the adsorbate will condense on the surface. This assumption led to the point that x must be equal to 1 when $P = P^S$.

$$x(P^S) = 1 \Rightarrow P^S \frac{a_2}{b_2} e^{E_L/RT} = 1 \Rightarrow P^S = \frac{b_2}{a_2} e^{-E_L/RT} \tag{29}$$

$$\Rightarrow x = P \frac{a_2}{b_2} e^{E_L/RT} = \frac{P}{P^S} \tag{30}$$

Brunauer et al. made this critical assumption (Brunauer et al. 1938) mainly for the purpose of reducing the number of parameters of the model to two by eliminating K_L from the equations and expressing the isotherm model in a linear form (21). This was justified because using a linear equation for fitting the experimental data was much easier than fitting a nonlinear equation with a complex form.

From (27) and (29) we obtain:

$$P^S = 1/K_L \tag{31}$$

and from (28) and (31):

$$c = \frac{K_S}{K_L} = K_S P^S \tag{32}$$

For $n = 1$ the (25) reduces to the Langmuir isotherm equation:

$$\frac{q}{q_m} = \frac{cx}{1 + cx} = \frac{K_S P}{1 + K_S P} \tag{33}$$

In fact, the Langmuir isotherm is a special case of the more general BET isotherm model.

As it is shown, the inverse of the equilibrium constant of the upper layer adsorptions, $1/K_L$, has been replaced by P^S in the classical BET equation (21). In addition, the constant c in BET isotherm equation is the ratio of the equilibrium constant of the first layer to that of the upper layers. Replacing $1/K_L$ by P^S in the classical BET equation is the direct result of assuming that q will be infinite when $P = P^S$ in the gas phase. One should note that a similar assumption is not necessarily valid in liquid phase adsorption, i.e. one cannot assume that q will be infinite when $C = C_S$. In liquid phase adsorption, no layers may be adsorbed even at $C = C_S$ if the surface has no affinity for the adsorbate molecules; and in contrary, the amount of adsorption can be very high even at concentrations much lower than the maximum solubility of the adsorbate when the affinity of the surface is high for the adsorbate molecules.

From another point of view, one should note that in gas phase multilayer adsorption the adsorbate molecules from the gas phase adsorb on similar molecules and a condensation-like phenomenon occurs. The heat of adsorption of these layers, E_L, is equivalent to the heat of condensation and (29) is consistent with the Clausius-Clapeyron equation for vapor pressure ($\ln P^S = (-E_L/RT) + \text{const}$). One can relate K_L and P^S by (27), (29), and (31). In other words, the critical assumption of Brunauer et al. is a realistic assumption only for gas phase adsorption. Nevertheless, in liquid phase adsorption; the adsorbate molecules in bulk phase are in liquid state and the heat of adsorption of upper layers, E_L, is not equivalent to the heat of condensation and a similar relation between K_L and C_S cannot be assumed.

In the classical BET equation, if we replace $1/P^S$ with the equilibrium constant of upper layers K_L, and P with the liquid phase equilibrium concentration C_{eq}, the BET isotherm equation can be modified for liquid phase adsorption as:

$$q = q_m \frac{K_S C_{eq}[1 - (n+1)(K_L C_{eq})^n + n(K_L C_{eq})^{n+1}]}{(1 - K_L C_{eq})\left[1 + \left(\frac{K_S}{K_L} - 1\right)K_L C_{eq} - \left(\frac{K_S}{K_L}\right)(K_L C_{eq})^{n+1}\right]} \tag{34}$$

for $n = \infty$

$$q = q_m \frac{K_S C_{eq}}{(1 - K_L C_{eq})(1 - K_L C_{eq} + K_S C_{eq})} \tag{35}$$

for $n = 1$

$$q = q_m \frac{K_S C_{eq}}{1 + K_S C_{eq}} \quad \text{(Langmuir)} \tag{36}$$

It is obvious that in case of liquid phase adsorption the BET isotherm equation has three degrees of freedom (q_m, K_S, K_L), while it has two degrees of freedom (q_m, c) in the case of gas phase adsorption.

In fact, Brunauer et al. fixed one of the three parameters of the equation (q_m, K_S, K_L) by expressing the adsorbate concentration in the form of relative concentration (by equating $1/K_L = P^S$) and reduced the number of parameters to two (q_m, c) for the purpose of developing the equation in linear form for ease of linear regression of the experimental data.

The BET isotherm equation for liquid phase adsorption can also be derived directly by a method similar to the development of the classical BET equation. Gritti and Guiochon used a similar approach for liquid phase adsorption (Gritti and Guiochon 2003). By referring to the original derivation of the BET equation for gas phase, one can clarify the physical significance of P^S and K_L in the BET equation. This prevents misuse of C_S (solubility of the solute) instead of

P^S (saturation partial pressure of the adsorbate) when applying BET equation to liquid phase adsorption.

Equation (25) has three parameters (q_m, c, n) that should be determined using experimental data. As a result, it is impossible to convert this equation to a linear form. According to Brunauer et al., to determine the number of maximum adsorbed layers (n) in the (25), one should evaluate c and q_m by fitting the $n = \infty$ form of the equation to the experimental data in the low concentration region, then use these values in the equation, to solve for the best average value of n (Brunauer et al. 1938). Nevertheless, nowadays it is possible to evaluate the three parameters of the (25) and (35) or even the four parameters in (34) by nonlinear regression calculations using available regression software packages.

3 Application of the BET isotherm to liquid phase adsorption

To clarify the differences between various approaches in using BET equation for liquid phase adsorption, three sets of liquid phase adsorption data have been modeled by different approaches in using the BET isotherm model. These data are the equilibrium adsorption data of MTBE on perfluorooctyl alumina (PFOAL) at moderate concentration range of 5–700 mg/L (Ebadi et al. 2007), adsorption of phenol on activated carbon (Miller and Clump 1970), and adsorption of pentachlorophenol (PCP) on carbonized bark (Edgehill and (Max) Lu 1998). The DataFit® (Oakdale Engineering) nonlinear regression software was used to evaluate the model parameters of the adsorption isotherm and relevant statistical parameters.

Three different approaches in using the BET isotherm equation are:

BET-Case 1: Using (21) with $x = C_{eq}/C_S$ and $C_S =$ constant (taken from solubility data)
BET-Case 2: Using (21) with $x = C_{eq}/C_S$ and C_S is taken as an adjustable parameter
BET-Case 3: Using (35) (The correct form of BET isotherm for liquid phase adsorption)

For the purpose of comparison of the results (especially with the results of BET-Case 1) the Langmuir isotherm, which is a special case of the BET isotherm, was also used to model the experimental data.

Figures 1, 2 and 3 show the trends of the experimental data and the trends predicted by different forms of the BET isotherm and Langmuir isotherm equation at low (parts a) and high (parts b) concentration ranges for the liquid phase adsorption of MTBE, phenol, and pentachlorophenol, respectively. Tables 1, 2 and 3 show the calculated parameters for each of the three cases of BET equation along with the Langmuir equation for the three adsorption systems, respectively.

BET-Case 1: The results obtained for modeling the adsorption data of MTBE (Table 1 and Fig. 1), and adsorption of phenol (Table 2 and Fig. 2), and adsorption of PCP (Table 3 and Fig. 3) show that when C_S in BET isotherm is taken as the actual saturation concentration of the adsorbate in liquid phase (a constant value), the model exhibits a poor performance in expressing the experimental data ($R^2 = 0.9586$, 0.7366, and 0.9209 for adsorption of MTBE, phenol and pentachlorophenol, respectively). Prediction of the experimental data and quality of the regression is similar to that of Langmuir isotherm for adsorption of MTBE and phenol ($R^2 = 0.9579$ and 0.7363 for adsorption of MTBE and phenol, respectively; see also Figs. 1a and 2a). For adsorption of PCP, the quality of the regression is different for the BET-Case 1 and Langmuir isotherms ($R^2 = 0.9209$ and 0.8450 for BET-Case 1 and Langmuir isotherms, respectively; see also Fig. 3). The reason for this difference will be explained in the next paragraph. The q_m values calculated by BET-Case 1 equation is very close to that calculated by Langmuir isotherm for the adsorption of MTBE and phenol (9.682 mg/g vs.10.081 mg/g and 134.145 mg/g vs. 134.359 mg/g, respectively). Again, the q_m values calculated by BET-Case 1 and Langmuir equations are considerably different for adsorption of pentachlorophenol (1.489 mg/g and 4.083 mg/g by the BET-Case 1 and Langmuir equations, respectively). Figures 1b and 2b show that as the liquid phase concentration approaches the actual saturation concentration, the amount of adsorption predicted by BET-Case 1 isotherm approaches infinity while that of Langmuir isotherm remains constant. At low concentration range, the number of degrees of freedom of the BET-Case 1 equation reduces to two and from mathematical standpoint; the model behaves similar to the Langmuir isotherm which has two degrees of freedom. In other words, the model behaves similar to the Langmuir model equation at liquid phase concentrations far from the saturation level (low concentration range). The BET-Case 1 isotherm can predict the S-shaped trend at higher liquid phase concentration ranges while as shown in Figs. 1a and 2a the experimental data trend shows this S-shaped trend at lower concentration range. Maurya and Mittal obtained similar results for BET ($C_S =$ constant) and Langmuir equations in liquid phase adsorption of dyes on biosorbents (Maurya and Mittal 2006). For example according to their results, q_m values calculated by BET and Langmuir equations were 203.78 and 204.38 mg/g, respectively.

A number of authors that used BET equation with C_S as a constant value have reported a significant difference between BET and Langmuir equations in terms of saturation capacity (Fu and Viraraghavan 2000; Hall et al. 2001; Ramakrishna and Viraraghavan 1997). For the purpose of elucidating this point, we have used different values of C_S in BET-Case 1 equation for the adsorption of MTBE and

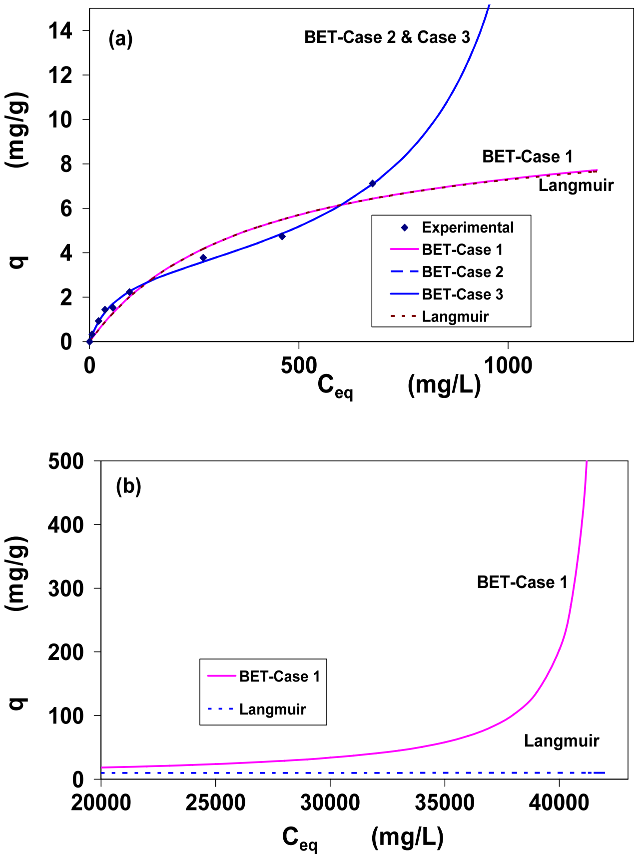

Fig. 1 Correlation of experimental data of adsorption of MTBE on PFOAL adsorbent (Ebadi et al. 2007) by various forms of BET isotherm and Langmuir isotherm (**a**) low concentration range (**b**) Extending Case 1 of BET and Langmuir equation to high concentration range

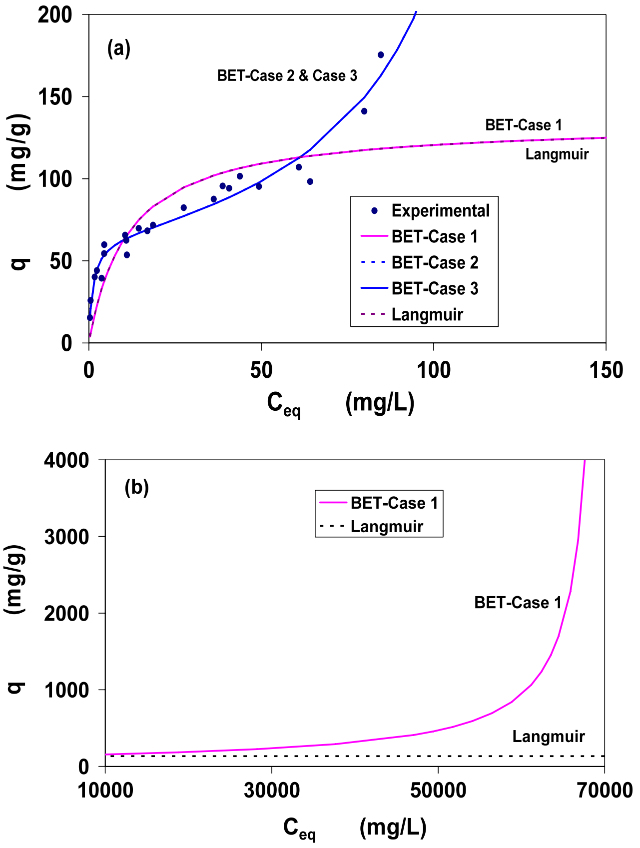

Fig. 2 Correlation of experimental data of adsorption of phenol on activated carbon (experimental data from Miller and Clump 1970) by various forms of BET isotherm and Langmuir isotherm (**a**) low concentration range (**b**) Extending Case 1 of BET and Langmuir equation to high concentration range

Table 1 Calculated parameters for isotherm models applied for adsorption of MTBE on PFOAL (experimental data from Ebadi et al. 2007)

	BET				Langmuir
	Case 1: $x = C_{eq}/C_S$ $C_S =$ constant	Case 2: $x = C_{eq}/C_S$ $C_S =$ adjustable	Case 3: $x = K_L C_{eq}$ Correct form of BET isotherm for liquid phase adsorption		
C_S (mg/L)	(42000)[a]	1212.30	K_L (L/mg)	8.25E-04	–
c	115.395	20.696	K_S (L/mg)	1.7071E-02	2.61E-03
q_m (mg/g)	9.682	3.257	q_m (mg/g)	3.257	10.081
R^2	0.9586	0.9978	R^2	0.9978	0.9579

[a] The saturation concentration of MTBE in water at room temperature (Stephenson 1992)

Table 2 Calculated parameters for isotherm models applied for adsorption of phenol on activated carbon (experimental data from Miller and Clump 1970)

	BET				Langmuir
	Case 1: $x = C_{eq}/C_S$ $C_S =$ constant	Case 2: $x = C_{eq}/C_S$ $C_S =$ adjustable	Case 3: $x = K_L C_{eq}$ Correct form of BET isotherm for liquid phase adsorption		
C_S (mg/L)	(70000)[a]	138.877	K_L (L/mg)	7.201E-03	–
c	6103.487	129.599	K_S (L/mg)	0.933	8.690E-02
q_m (mg/g)	134.145	63.835	q_m (mg/g)	63.835	134.359
R^2	0.7366	0.9585	R^2	0.9585	0.7363

[a] The saturation concentration of phenol in water at room temperature (Quintelas et al. 2006)

phenol and reported the results in Tables 4 and 5. One should note that in this case (BET-Case 1) when the used C_S is very large, $x = C_{eq}/C_S \cong 0$ and it can be ignored in the equation. As a result, BET equation approaches the Langmuir isotherm:

$$\frac{q}{q_m} = \frac{cx}{(1-x)(1-x+cx)}$$
$$\longrightarrow \frac{q}{q_m} = \frac{cx}{1+cx} = \frac{K_S C_{eq}}{1+K_S C_{eq}}$$

As it is shown in Tables 4 and 5, if the C_S is taken as a constant value (BET-Case 1) one may face with two limiting situations. If the used value of C_S is sufficiently larger than the value of $1/K_L$ then the monolayer adsorption capacity (q_m) calculated by BET-Case 1 isotherm equation will be close to the q_m value calculated by the Langmuir isotherm equation. For example, the actual saturation concentration (solubility) of MTBE and phenol in aqueous medium is 42000 mg/L (Stephenson 1992) and 70000 mg/L (Quintelas et al. 2006), respectively which are very large compared with their corresponding $1/K_L$ values (1212.30 mg/L and 138.88 mg/L, respectively). As a result, the q_m values calculated by BET-Case 1 and Langmuir equations for the adsorption of MTBE and phenol are very close (9.682 mg/g vs. 10.081 mg/g and 134.145 mg/g vs. 134.359 mg/g, respectively). If the value of C_S is close to the value of $1/K_L$, then the value of q_m calculated by BET-Case 1 equation will be considerably different from that by Langmuir isotherm equation (see Tables 4 and 5). This is the situation faced in adsorption of PCP. The saturation concentration (solubility) of PCP in water is the same order of magnitude as $1/K_L$ value (~10 mg/L vs. 5.437 mg/L). Consequently, the q_m values calculated by BET-Case 1 and Langmuir isotherms for adsorption of PCP are different (1.489 mg/g versus 4.083 mg/g).

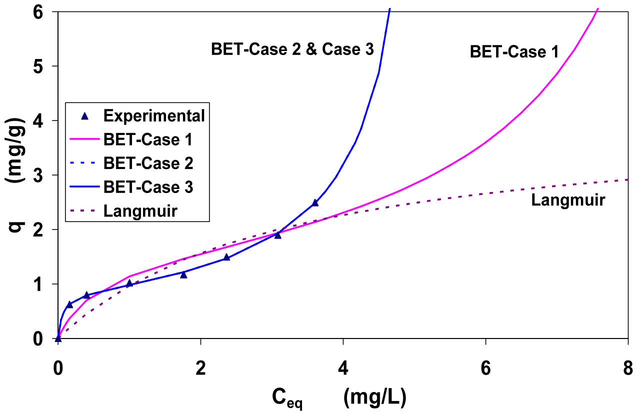

Fig. 3 Correlation of experimental data of adsorption of pentachlorophenol (PCP) on carbonized bark (experimental data from Edgehill and (Max) Lu 1998) by various forms of BET isotherm and Langmuir isotherm

In addition, one should note that monolayer and maximum adsorption capacities are the same for Langmuir isotherm because in this isotherm model it is assumed that only one layer can adsorb on the adsorbent. However, in BET isotherm equation the monolayer adsorption capacity q_m, differs from maximum adsorption capacity. The maximum adsorption capacity is not limited in (21) and (35) and it can approach infinity. In (25) and (34) the maximum adsorption capacity is limited, because it is assumed that the number of adsorbed layers cannot exceed some finite number n.

BET-Case 2: Figures 1a, 2a, and 3 show that when C_S in the classical BET isotherm is taken as an adjustable parameter (BET-Case 2), the model shows a good fit of the experimental. The model predictions do not differ from those of the correct form of the BET equation for liquid phase adsorption (BET-Case 3) and the curves for the two cases coincide exactly. The values of C_S calculated by BET-Case 2 for the three sample data are 1212.30 mg/L, 138.877 mg/L, and 5.437 mg/L, respectively which are exactly the inverse of the corresponding values of K_L (8.25E-4 L/mg, 7.20E-3 L/mg, and 0.184 L/mg) calculated by the BET-Case 3, i.e. $C_S = 1/K_L$. In addition, the calculated value of the parameter c by BET-Case 2 is equal to the ratio of K_S/K_L by BET-Case 3. These equalities are the result of using the classical form of the BET equation (developed for gas phase adsorption) directly to liquid phase adsorption and are in agreement with the theoretical results obtained in (31) and (32). The calculated monolayer adsorption capacities, q_m, are also the same for the two cases, BET-Case 2 and BET-Case 3, and

Table 3 Calculated parameters for isotherm models applied for adsorption of pentachlorophenol on carbonized bark (experimental data from Edgehill and (Max) Lu 1998)

	BET				Langmuir
	Case 1: $x = C_{eq}/C_S$ $C_S =$ constant	Case 2: $x = C_{eq}/C_S$ $C_S =$ adjustable	Case 3: $x = K_L C_{eq}$ Correct form of BET isotherm for liquid phase adsorption		
C_S (mg/L)	(10)[a]	5.437	K_L (L/mg)	0.184	–
c	19.775	88.212	K_S (L/mg)	16.224	0.312
q_m (mg/g)	1.489	0.841	q_m (mg/g)	0.841	4.083
R^2	0.9209	0.9986	R^2	0.9986	0.8450

[a] The saturation concentration of pentachlorophenol in water at room temperature (Arcand et al. 1995)

Table 4 Monolayer adsorption capacities calculated by BET isotherm at different values of C_S, when C_S is taken as a constant value (BET-Case 1), applied for adsorption of MTBE on PFOAL (experimental data from Ebadi et al. 2007)

	BET isotherm C_S (mg/L)	Case 1: $x = C_{eq}/C_S$ and C_S = constant			Langmuir
	$1212.3 = 1/K_L$	1300	2500	42000	
q_m (mg/g)	3.257	3.515	5.625	9.682	10.081
R^2	0.9978	0.9970	0.9762	0.9586	0.9579

Table 5 Monolayer adsorption capacities calculated by BET isotherm at different values of C_S, when C_S is taken as a constant value (BET-Case 1), applied for adsorption of phenol on activated carbon (experimental data from Miller and Clump 1970)

	BET isotherm C_S(mg/L)	Case 1: $x = C_{eq}/C_S$ and C_S = constant				Langmuir
	$138.876 = 1/K_L$	300	5000	30000	70000	
q_m (mg/g)	63.835	95.187	131.417	133.862	134.145	134.359
R^2	0.9585	0.8371	0.7410	0.7371	0.7366	0.7363

are considerably different from those for the BET-Case 1 and Langmuir equations (see Tables 1, 2, and 3).

One can conclude that when C_S in the classical BET isotherm is taken as an adjustable parameter, in fact the inverse of the equilibrium adsorption constant of upper layers, $1/K_L$, is calculated instead of K_L by nonlinear regression. In other words, the C_S value calculated by BET-Case 2 is not the actual saturation concentration of the liquid phase; it is only the inverse of K_L. The large difference between the calculated values of C_S by BET-Case 2 (1212.30 mg/L and 138.88 mg/L for adsorption of MTBE and phenol, respectively) and the actual value of saturation concentration of MTBE (42000 mg/L) (Stephenson 1992) and phenol (70000 mg/L) (Quintelas et al. 2006) in water supports this argument. In an attempt to justify the difference between calculated values and actual values of C_S some authors have stated that the value of C_S calculated from the BET isotherm equation was the liquid phase concentration at which the adsorbent saturates with the adsorbate (Miller and Clump 1970) or as the concentration at which the upward curvature of the isotherm occurs (Al-Futaisi et al. 2007).

BET-Case 3: This is the correct form of the BET isotherm equation for liquid phase adsorption (35), BET-Case 3. In this case an assumption similar to the critical assumption of Brunauer and co-workers that q will be infinite when $P = P^S$ in the gas phase (Brunauer et al. 1938) does not apply for the liquid phase. As a result, the saturation concentration of the adsorbate was eliminated from the BET isotherm equation and the equilibrium constant of adsorption of upper layers (K_L) was reinstated in the equation. As shown in Figs. 1a, 2a, and 3 and Tables 1, 2, and 3 a good fit of the experimental data has been obtained. As discussed previously, the trend of prediction by BET-Case 3 coincides exactly with that of the BET-Case 2 but all of the calculated model parameters have real physical significance for the BET-Case 3. Although, in gas phase adsorption $P^S = 1/K_L$ consistent with the Clausius-Clapeyron equation for vapor pressure ($\ln P^S = -E_L/RT + \text{const}$); in liquid phase adsorption the actual saturation concentration is not equal to $1/K_L$, i.e. in liquid phase adsorption $C_S \neq 1/K_L$.

4 Conclusions

In the classical BET isotherm equation (21), developed for gas phase adsorption, the bulk phase concentration was expressed as a relative concentration, $x = P/P^S$. Some researchers applied this equation directly to liquid phase adsorption and expressed the bulk liquid phase concentration as $x = C_{eq}/C_S$. A close examination of the classical BET equation and application of this equation to liquid phase adsorption data showed that when applying BET equation to liquid phase adsorption, partial pressure of adsorbate in the BET equation should be replaced by liquid phase concentration, C_{eq}. However, applying a similar approach to replace the saturation partial pressure, P^S, in the equation with the saturation concentration of the adsorbate in liquid phase, C_S is not appropriate. This is the point of ambiguity and misunderstanding in a number of previous reports in the literature. One should note that the assumption of infiniteness of adsorption at saturation concentration made in the classical BET equation for gas phase adsorption can not be valid for liquid phase adsorption. Since both the adsorbate and solvent are in condensed form, if the adsorbent has no affinity for the adsorbate or if it has already been saturated with the adsorbate, the amount of adsorption will not increase with increasing liquid phase concentration.

When applying BET isotherm for liquid phase adsorption the adsorption equilibrium constant of upper layers, K_L, which had been taken out from the classical BET equation as a result of an assumption which can only be valid for gas phase adsorption, should be reinstated, i.e. $x = K_L C_{eq}$. In other words, the correct form of the BET isotherm for liquid phase adsorption is given by (35) and (34) instead of (21) and (25), respectively.

Nomenclature

a_1	Rate constant for adsorption on solid surface, mol/s m^2 (mg/L)
$a_2, a_3, \ldots$	Rate constant for adsorption on 2nd, 3rd, … layers, mol/s m^2 (mg/L)
b_1	Rate constant for desorption from the first layer, mol/s m^2
$b_2, b_3, \ldots$	Rate constant for desorption from 2nd, 3rd, … layers, mol/s m^2
C_{eq}	Equilibrium liquid phase concentration, mg/L
C_S	Saturation concentration of liquid phase, mg/L
c	A constant parameter in BET isotherm, $c = K_S/K_L$
E_1	Heat of adsorption on the solid surface (first layer), J/mol
E_L	Heat of liquefaction (heat of adsorption on upper layers), J/mol
K_S	Equilibrium constant of adsorption for 1st layer in Langmuir and BET isotherms, (mg/L)$^{-1}$
K_L	Equilibrium constant of adsorption for upper layers in BET isotherm, (mg/L)$^{-1}$
MTBE	Methyl *tert*-butyl ether
n	Maximum number of adsorbed layers on solid surface in BET isotherm
P	Partial pressure of adsorbate in gas phase, Pa
P^S	Saturation pressure (vapor pressure) of adsorbate in system temperature, Pa
PCP	Pentachlorophenol
PFOAL	Perfluorooctyl alumina
q	Amount of adsorbate adsorbed on the solid surface, mg/g
q_m	Amount of adsorbate corresponding to complete monolayer adsorption, mg/g
R	Universal gas constant, J/mol K
S_i	Surface area covered by i layers of adsorbed molecules, m^2/g
T	Absolute temperature, K

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