Statistical Evaluation of Non-Linear Parameter Estimation Procedures for Adsorption Equilibrium Models

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ABSTRACT: Adsorption equilibrium is a fundamental concept in the adsorption science and relates the equilibrium between the quantity of the adsorbed material and its concentration in the bulk phase. Several models have been proposed for prediction of adsorption equilibrium and all models depend on parameters whose values must be estimated from available experimental data. Although linear parameter estimation procedures can be used for model fitting, through transformation of available experimental data and model parameters, non-linear parameter estimation procedures lead to more reliable results and allow for direct comparison of results obtained with different adsorption equilibrium models. The main objective of this work is to present and compare different non-linear procedures for parameter estimation of adsorption equilibrium models, based on theoretical arguments and also on the numerical estimation of adsorption equilibrium parameters, using available experimental data for adsorption of methylene blue onto activated carbon. The results obtained indicate that the best parameter estimation procedure is the one that relies on available equilibrium concentrations in the bulk phase as a function of the fluid volume, adsorbent mass and initial concentrations in the bulk phase, without transformation of measured experimental values and model parameters. Besides, it is shown that parameter estimates should be obtained through proper minimization of weighted least-squares objective function, in accordance with maximum likelihood procedures.

1. INTRODUCTION

Adsorption equilibrium constitutes a fundamental concept in the adsorption science, which assumes that there is a well-defined relationship between the amount of adsorbed material and the concentration in the bulk phase (Dabrowski 2001). Determination of the proper adsorption equilibrium model and respective parameter values constitutes an essential step for characterization and evaluation of adsorbents and for development and design of industrial processes, including water treatment, drying of natural and cracked gases, separation of aromatics, purification of gaseous streams and separation and purification of proteins, among many other applications (Yang 1997; Dabrowski 2001; Rodrigues et al. 2013). The commonest industrial adsorbents are activated carbon, silica gel, alumina and zeolites (Do 1998; Dabrowski 2001).

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Despite its widespread use, adsorption can involve very complex phenomena that may not be completely understood in particular applications, such as the mass transfer from fluid phase to external particle surfaces, the intra-particle diffusion of adsorbed materials and the kinetic behaviour of the adsorption process at adsorbent sites. However, determination of the adsorption equilibrium model and respective model parameters constitutes the first fundamental step during the study of the adsorption phenomena.

The adsorption equilibrium hypothesis assumes that there is a relationship between the quantity adsorbed (usually defined as $q_e$) and the equilibrium concentration in the bulk phase (usually defined as $C_e$) at a specified temperature. Development of adsorption equilibrium models can be based on the modelling of adsorption/desorption kinetics and adsorption equilibrium thermodynamics, and on empirical arguments or data (Do 1998; Foo and Hameed 2010). Most adsorption equilibrium models are represented in terms of non-linear algebraic equations, so that the estimation of model parameters must necessarily involve an iterative numerical optimization procedure (Kumar and Sivanesan 2005; Kumar 2006).

Although the use of linear regression is very common in the adsorption field (model equations are manipulated to provide a linear relationship between transformed experimental data), several works in the literature indicate that non-linear regression procedures can provide better results, for example, the performances of different adsorption equilibrium models can be compared unequivocally with each other and the statistical structure of available measurements is not modified through transformation of experimental data (Kumar and Sivanesan 2005, 2006; Kumar 2006; Bolster and Hornberger 2007; Parimal et al. 2010). Recently, Osmari et al. (2013) performed the comparison of parameter estimates obtained from linear and non-linear regression procedures based on sound statistical arguments, giving particular attention to the estimated parameter values and respective uncertainties, and showed that non-linear regression techniques present more robust performances and can provide more significant parameter estimates.

It is important to notice, however, that different non-linear procedures can be applied for estimation of parameters of adsorption equilibrium models. For this reason, the main objective of this work is to discuss and compare different non-linear procedures that can be used for estimation of adsorption equilibrium parameters to show the advantages and drawbacks of each procedure based on solid statistical arguments. In the ‘Non-Linear Parameter Estimation Procedures’ section, different non-linear parameter estimation procedures are devised and discussed, while analyzed adsorption equilibrium models are shown in the ‘Adsorption Equilibrium Models’ section. In the ‘Results and Discussion’ section, results obtained with the different non-linear parameter estimation procedures are presented and discussed. Finally, concluding remarks are presented in the ‘Conclusion’ section.

2. NON-LINEAR PARAMETER ESTIMATION PROCEDURES

2.1. Traditional Procedures

The most traditional non-linear parameter estimation procedures described in the vast majority of adsorption studies assume that $q_e$ is fitted as a function of $C_e$; that is, $C_e$ (concentration in the bulk phase in equilibrium) is the independent error-free variable and $q_e$ (transformed amount of adsorbed material in equilibrium) is the dependent variable whose deviations from available experimental data are minimized for estimation of the adsorption equilibrium parameters. Traditionally, minimization of deviations is performed through minimization of the least-squares function, as presented in equation (1):
where $S$ is the objective function value, $q_{e,i}^{\text{exp}}$ and $q_{e,i}^{\text{mod}}$ are the experimental and model calculated values of the equilibrium concentration in the solid phase, $C_{e,i}^{\text{exp}}$ is the experimental value of the equilibrium concentration in the bulk phase and $\theta$ is the vector of adsorption equilibrium parameters, whose values must be optimized during the parameter estimation procedure to achieve the best adsorption model fit. This is the commonest non-linear procedure used to determine the adsorption equilibrium parameters (Kumar and Sivanesan 2005, 2006; Kumar 2006; Bolster and Hornberger 2007; Parimal et al. 2010; Osmari et al. 2013).

It is important to observe that the use of the least-squares function can only be justified statistically when experimental deviations follow the Gaussian probability distribution function (PDF), when experimental measurements are statistically independent and the variances of all experimental measurement fluctuations are the same. In fact, assumption of the Gaussian PDF of experimental fluctuations is normally due to its simplicity, easier mathematical treatment and also to the fact that the determination of the real PDF does not constitute an easy task (Bard 1974; Ratkowsky 1990). The assumption of independent measurements is usually correct in most adsorption equilibrium experiments, as experimental runs are usually conducted in different vessels and following independent sequences of events. However, when all experiments are performed simultaneously and subjected to the same temperature control scheme, for example, small deviations of the system temperature will produce deviations in all trials and lead to correlated measurements. Despite that, the independent measurement assumption is usually very consistent. By contrast, the assumption of constant variance for all experimental measurements is hardly true.

Initially, measurements of $q_e$ at very small concentration values can be expected to be smaller than the variance of the $q_e$ measured at high concentration values. One might assume that the relative variance is constant, but the real behaviour of experimental variances should be determined experimentally through replication (and replicates are usually available in consistent adsorption studies). In this case, assuming that the experimental variances are available, the appropriate objective function that must be used is the weighted least-squares function, as shown in equation (2)

\[
S = \sum_{i=1}^{N} \left[ \frac{q_{e,i}^{\text{exp}} - q_{e,i}^{\text{mod}}(C_{e,i}^{\text{exp}}, \theta)}{\sigma_{q_e,i}^2} \right]^2
\]

where $\sigma_{q_e,i}^2$ is the variance of measured $q_e$ at the experimental condition $i$. As equation (2) takes into account the experimental precision, its use should lead to more significant and precise results, when compared with equation (1). Besides, equation (2) presents a $\chi^2$ distribution and the goodness of model fits can be readily checked through sound statistical tests (Bard 1974; Schwaab and Pinto 2007).

Despite the popularity of the procedures defined by equation (1) or (2), the primary drawback of these procedures resides in the fact that the independent variable $C_e$ is also subject to experimental deviations, because $C_e$ normally is the real measured variable (and not $q_e$). In the case of batch liquid–solid adsorption equilibrium, $q_e$ values are computed from $C_e$ measured values using equation (3), which can be derived from the mass balance of the analyzed system.

\[
q_e = \frac{V}{W}(C_0 - C_e)
\]
In equation (3), \( V \) is the volume of the liquid phase, \( W \) is the weight of the solid adsorbent and \( C_0 \) is the initial concentration in the liquid phase. It must be observed that the initial adsorbed quantity was assumed to be null (i.e. a fresh adsorbent has been used).

Considering that both \( C_e \) and \( q_e \) are subject to experimental deviations, as pointed by some works in the literature (Ko et al. 1997; Valsami et al. 2000; El-Khaiary 2008), more realistic estimation procedures can be devised, as shown in the next section.

2.2. Data Reconciliation Procedure

According to the discussion presented in the previous paragraphs, both dependent and independent variables are subject to experimental deviations, so that the objective functions defined in equations (1) and (2) lack statistical meaning. Consequently, an alternative non-linear procedure should be used. One possible alternative is the use of the error-in-variables models procedure (Kim et al. 1991; El-Khaiary 2008), also known as orthogonal distance regression or perpendicular least-squares (Ko et al. 1997; Valsami et al. 2000; El-Khaiary 2008). This procedure is, in fact, closely related to data reconciliation procedures (Prata et al. 2009, 2010) and provides more reliable interpretation of the parameter estimation problem once it takes into account experimental deviations in both dependent and independent variables that are subject to experimental fluctuations, as is the case in the determination of the adsorption equilibrium parameters, given the fact that both \( q_e \) and \( C_e \) are subject to experimental deviations. In this case, the objective function used to formulate the non-linear parameter estimation procedure can be defined as shown in equation (4). In this case, one should minimize the objective function through proper manipulation of the adsorption equilibrium parameter values, present in vector \( \theta \), and the real unknown values of \( C_{e,i}^{\text{mod}} \). Because \( q_{e,i}^{\text{mod}} \) values are computed from \( C_{e,i}^{\text{mod}} \) and \( \theta \) values through an adsorption equilibrium model, the \( q_{e,i}^{\text{mod}} \) values can be inserted implicitly in the optimization procedure.

\[
S = \sum_{i=1}^{N} \left[ \frac{q_{e,i}^{\exp} - q_{e,i}^{\text{mod}}(C_{e,i}^{\text{mod}}, \theta)}{\sigma_{q_e,i}^2} \right]^2 + \sum_{i=1}^{N} \left[ \frac{C_{e,i}^{\exp} - C_{e,i}^{\text{mod}}}{\sigma_{C_e,i}^2} \right]^2
\]  

(4)

It is important to emphasize that variables \( q_e \) and \( C_e \) present different physical units, so that the use of least-square objective functions should be avoided and use of weighted least-square functions becomes almost mandatory. When weighted least-squares are used, as defined in equation (4), all terms in the summations are dimensionless, meaning that summations are physically consistent. Besides, as in the case of equation (2), equation (4) also follows a \( \chi^2 \) distribution, allowing for proper statistical evaluation of the goodness of fit.

Because \( q_e \) is computed in accordance with equation (3), the variance of \( q_e \) is related to the variance of \( C_e \) as shown in equation (5).

\[
\sigma_{q_e,i}^2 = \left( \frac{V}{W} \right)^2 \sigma_{C_e,i}^2
\]  

(5)

if one assumes that the measurement errors of the remaining variables are negligible.

It must be observed that previous works (Ko et al. 1997; Valsami et al. 2000; El-Khaiary 2008) that have used this procedure do not take into account the experimental variances of both variables, namely, \( q_e \) and \( C_e \). Equation (5) shows that variances become equal only when the ratio \( (V/W) \) is equal to 1 in all experimental runs. Finally, it must be observed that the units of \( q_e \) and
2.3. Procedure Based only on Ce Measurements

Although the use of the data reconciliation procedures can lead to more reliable estimation procedures, once deviations in Ce and qe variables are simultaneously considered, it must be pointed out that the true experimental response variable is Ce. In fact, qe is not a measured variable, but an inferred variable from the Ce measurements.

Observing equation (3), it becomes clear that variable qe only presents some ‘experimental’ deviation due to error measurements in Ce values. Furthermore, equation (3) indicates that variables qe and Ce are not independent. In fact, the correlation between variables qe and Ce are equal to –1. Consequently, just one independently measured variable is indeed available at each experiment, so that the use of both variables in the objective function (as in the data reconciliation procedure) invalidates some of the statistical assumptions used to formulate the parameter estimation procedure.

Therefore, a third procedure must be devised, as the only dependent variable in the adsorption experiment is Ce, whereas the independent variables are V, W and C0. This procedure has already been used in previous works, assuming that the Langmuir model is appropriate to describe the isotherm experiments, as an analytical solution can be derived for this model, where Ce (or qe) is presented as a closed function of the independent variables and Langmuir adsorption equilibrium parameters (Bolster 2008; Boulinguiez et al. 2008).

When only Ce deviations are considered, the objective function can be defined in terms of the least-squares function, as in equation (6), or in terms of the weighted least-squares function, as in equation (7).

\[
S = \sum_{i=1}^{N} \left[ C_{e,i}^{\exp} - C_{e,i}^{\mod} \left(V_{i}, W_{i}, C_{0,i}, \theta \right) \right]^2
\]  
\[S = \sum_{i=1}^{N} \frac{\left[ C_{e,i}^{\exp} - C_{e,i}^{\mod} \left(V_{i}, W_{i}, C_{0,i}, \theta \right) \right]^2}{\sigma_{Ce,i}^2}
\]

The values of Ce computed from the model must be obtained as the solution of the mass balance equation (8), which is similar to equation (3), although qe represents the general adsorption equilibrium model as a function of Ce and the adsorption equilibrium parameters.

\[
\frac{V}{W} (C_{0} - C_{e}) = q_{e} (C_{e})
\]

When the Langmuir model is considered, equation (8) allows for development of a closed analytical solution. However, in the general case, a numerical procedure must be used to provide the Ce solution. As the proposed problem involves solving a single algebraic equation for which very good initial guess values are available for Ce (e.g. the experimental values), standard Newton–Raphson procedures can be used and convergence can usually be attained very fast.

It must be noted that this proposed estimation procedure can be regarded as much more reliable than the previous ones, as the actual independent variables (also called the controlled variables), V, W and C0, are used in the parameter estimation procedure and the dependent variable used for
formulation of the objective function is the actual measured experimental response. As $q_e$ is not measured, its value can be inferred with help of equation (3) or with the final parameter estimates, with help of the adsorption equilibrium model. However, $q_e$ values should not be considered for formulation of the parameter estimation problem, because these values are not real measured variables.

2.4. Computation of the Estimated Parameter Values and Its Uncertainties

All parameter estimation procedures described in the previous section are non-linear, so that numerical optimization methods must be used for minimization of the objective functions. Several numerical methods are available to perform this task, but it is important to select a method that assures that the global minimum of the objective function can be reached. A good alternative is the use of a hybrid algorithm that makes use of both stochastic optimization algorithms and derivative-based methods, leading to robust and efficient optimizations (Park and Froment 1998; Schwaab et al. 2008).

Once the minimum of the objective function is reached and the estimated parameter values are obtained, the computation of the estimated parameter uncertainties is necessary to evaluate the statistical significance of the parameter estimates. For the procedures presented in the ‘Traditional Procedures’ and ‘Procedure Based only on Ce Measurements’ sections, the objective function depends only on the dependent variables ($q_e$ or $C_e$, respectively, for the ‘Traditional Procedures’ or ‘Procedure Based only on Ce Measurements’ sections), defined as $y$, and the covariance matrix of parameter estimates can be computed according to equation (9). The parameter $b_{\theta,i}$ is the sensitivity vector of model responses with respect to the model parameters at experimental condition $i$, as defined in equation (10), and $V_{y,i}$ is the covariance matrix of experimental deviations at experimental condition $i$. When experimental measurements are not correlated, $V_{y,i}$ becomes a diagonal matrix.

$$V_\theta = \left( \sum_{i=1}^{N} b_{\theta,i}^T V_{y,i} b_{\theta,i} \right)^{-1}$$

$$b_{\theta,i} = \begin{bmatrix} \frac{\partial y_{m}^{\text{mod}}}{\partial \theta_1} & \frac{\partial y_{m}^{\text{mod}}}{\partial \theta_2} & \ldots & \frac{\partial y_{m}^{\text{mod}}}{\partial \theta_{\text{NP}}} \end{bmatrix}$$

For the objective functions defined in equations (1) and (6), the experimental deviations are not considered or are unknown. In this case, an approximate value can be computed according to equation (11) and the covariance matrix can be computed with equation (12). Despite the belief that replications are unnecessary and constitute a time-consuming step, the proper evaluation of the covariance matrix of experimental fluctuations allows for rigorous statistical analysis of the results. Besides, Larentis et al. (2003) showed that the proper calculation of the experimental covariance matrix yields mechanistic information about the kinetic behaviour of the analyzed system. Given the lack of replicates, it is commonly assumed that the experimental variances are constant and can be computed with equation (11), which is indeed the model prediction variance.

$$\sigma_y^2 = \frac{\sum_{i=1}^{N} \left( y_{i}^{\text{exp}} - y_{e}^{\text{mod}}(x_{i}^{\text{exp}}, \hat{\theta}) \right)^2}{N - \text{NP}}$$

\(N - \text{NP}\)
When the procedure of the ‘Data Reconciliation Procedure’ section is considered, the computation of the covariance matrix of parameter estimate must take into account the deviations in both dependent and independent variables. In this case, the covariance matrix of parameter estimates is computed in accordance with equation (13), where matrices $R_i$ and $D_i$ are defined in equations (14) and (15) (Anderson et al. 1978; Noronha et al. 1993).

$$V_0 = \sigma_y^2 \left( \sum_{i=1}^{N} b_{\theta,i}^T V_{y,i} b_{\theta,i} - \sum_{i=1}^{N} R_i^T D_i R_i \right)^{-1}$$  \hspace{1cm} (13)

$$R_i = b_{x,i}^T V_{x,i} b_{\theta,i}$$  \hspace{1cm} (14)

$$D = \left( b_{x,i}^T V_{x,i} b_{x,i} - V_{x,i} \right)^{-1}$$  \hspace{1cm} (15)

The matrix $b_{x,i}$ is the sensitivity vector of model responses with respect to the independent variables at experimental condition $i$, as defined in equation (16).

$$b_{x,i} = \begin{bmatrix} \frac{\partial y_1}{\partial x_1} & \frac{\partial y_1}{\partial x_2} & \cdots & \frac{\partial y_1}{\partial x_N} \\ \frac{\partial y_2}{\partial x_1} & \frac{\partial y_2}{\partial x_2} & \cdots & \frac{\partial y_2}{\partial x_N} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial y_M}{\partial x_1} & \frac{\partial y_M}{\partial x_2} & \cdots & \frac{\partial y_M}{\partial x_N} \end{bmatrix}$$  \hspace{1cm} (16)

Although the computation of the covariance matrix of parameter estimates is often regarded as a hard task, the fact is that matrices involved in its computation are normally computed during the iterative minimization of the objective function when derivative-based optimization methods are used (Anderson et al. 1978; Noronha et al. 1993). For this reason, the covariance matrix of parameter estimates can be made available without significant additional numerical effort.

3. ADSORPTION EQUILIBRIUM MODELS

In this work, Langmuir, Freundlich and Sips equilibrium models are considered, because these are the commonest applied models in works dealing with adsorption of dies in liquid phase.

3.1. Langmuir Model

The Langmuir model is based on the equilibrium between the adsorption and desorption kinetics and was proposed by Langmuir (1918). It considers that the surface is homogeneous and that the adsorption energy is constant over all surface sites and does not depend on the surface coverage. Besides, the model assumes that adsorption on surface is localized and that adsorbed atoms and molecules are adsorbed at well-defined localized sites, which can accommodate only one adsorbent species (Yang 1997; Do 1998). The Langmuir model presents a behaviour that agrees with the Henry’s law for dilute concentrations (i.e. a linear equilibrium relationship) and presents a maximum value as the fluid concentration increases, defined by the monolayer coverage. The
resulting adsorption equilibrium model, presented in equation (17), has two parameters that must be estimated from experimental adsorption equilibrium data.

\[ q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \]  

(17)

The first parameter in the Langmuir model, \( q_m \), is the maximum adsorption capacity of the monolayer. As this parameter is closely related with the superficial area of the adsorbent and the affinity of the adsorbent sites with the adsorbate, its value is not a function of the temperature, but can be a function of the pH of the system, once it modifies the affinity between the adsorbent and the adsorbate (Do 1998). The second parameter of Langmuir model is the equilibrium parameter \( K_L \) that takes into account the kinetic equilibrium between adsorption and desorption.

For the specific case of the Langmuir model, equation (8) provides a closed analytical solution, presented in equation (18). Boulinguiez et al. (2008) presented a similar analytical solution, but with respect to \( q_e \) and not \( C_e \).

\[ C_e = -\left(q_m K_L \frac{W}{V} + 1 - K_L C_0\right) + \sqrt{\left(q_m K_L \frac{W}{V} + 1 - K_L C_0\right)^2 + 4 K_L C_0} \]  

(18)

3.2. Freundlich Model

The Freundlich model was the first adsorption equilibrium model proposed in the literature, describing adsorption in heterogeneous surfaces (Freundlich 1906). Although this model is usually considered empirical, a theoretical development can be obtained under appropriate assumptions (Do 1998). It is important to notice that this model does not follow the Henry’s law for dilute concentrations and does not reach a maximum asymptotic value as the concentration in the fluid phase increases. The Freundlich model is defined in equation (19) and presents two parameters: \( K_F \) and \( 1/n \). The parameter \( 1/n \) is positive and less than 1.

\[ q_e = K_F C_e^{1/n} \]  

(19)

3.3. Sips Model

The Sips model (Sips 1948) is a combined form of the Langmuir and Freundlich models. At low adsorbate concentrations, it can be reduced to the Freundlich model, whereas at high concentrations it is limited by the monolayer adsorption capacity, which is characteristic of the Langmuir model. Moreover, the Sips model can be considered as an extension of the Langmuir model, taking into account that an adsorbate molecule can be adsorbed onto more than one specific adsorption site. This deviation is defined by the parameter \( n \). The Sips model, presented in equation (20), has three parameters. The \( q_m \) parameter, as for Langmuir model, is the maximum adsorption capacity of the monolayer. The parameter \( K_S \) can be regarded as an equilibrium parameter and \( n \) is a parameter that indicates the affinity between the adsorbate and the adsorbent and also the number of adsorption sites occupied by each adsorbate molecule.

\[ q_e = \frac{q_m \left(K_S C_e\right)^n}{1 + \left(K_S C_e\right)^n} \]  

(20)
Although the Sips model presents a maximum asymptotic value at high concentrations, this model does not follow the Henry’s law for dilute concentrations. When the estimated n value is higher than 1, the adsorption is not favourable at low concentration, but becomes favourable at higher concentrations. When the estimated n value is lower than 1, the adsorption is also favourable at lower concentrations, as observed with the Freundlich model.

4. METHODOLOGY
4.1. Experimental Methods

A stock solution was prepared by dissolving 1 g of methylene blue (VETEC, Rio de Janeiro, Brazil) in 1 l of distilled water. All adsorption equilibrium experiments were performed by diluting the stock solution with distilled water. The activated carbon used in this work was obtained from VETEC and used as received. Adsorption experiments were performed in an agitated thermostatic bath at 30 °C, where closed flasks containing 25 ml of a methylene blue solution and activated carbon were placed. Experiments were performed for 4 days, to assure that the equilibrium conditions had been reached. The equilibrium concentration in the liquid phase was determined with the help of a UV–visible spectrometer (Shimadzu, model UV-1800). The initial concentrations of the methylene blue solution used in the experiments were 50, 125 and 200 mg/l and the masses of activated carbon were equal to 10 and 100 mg, depending on the desired final concentration values. The six experimental conditions were replicated five times, to allow for evaluation of the experimental variances.

4.2. Parameter Estimation Procedures

To evaluate the performances of the non-linear regression procedures, the obtained experimental data of adsorption of methylene blue onto activated carbon were used. Non-linear regressions were performed with a hybrid optimization method that combines the particle swarm optimization method with a Gauss–Newton procedure in a software package called ESTIMA (Noronha et al. 1993), as described by Schwaab et al. (2008). For each parameter estimate, the confidence intervals (CIs) were computed with a confidence level of 95%, using the t-student distribution. The variances of the estimated parameter values were compared to each other with the variance ratio method, using the F distribution for confidence levels of 2.5% and 97.5% (giving an interval of 95% of confidence level). Five different non-linear procedures were used, as defined by the objective functions presented in equations (1), (2), (4), (6) and (7). The nomenclature used for each of the non-linear regression procedures is presented in Table 1.

For the regression procedures defined as LS_Ce and WLS_Ce, a numerical solution of equation (8) is necessary to obtain the values of Ce as functions of the independent variables (V, W, C0) and adsorption equilibrium parameters. For the Langmuir equilibrium model, the analytical solution presented in equation (18) was used. For the other adsorption equilibrium models, a one-dimensional Newton–Raphson procedure was used, using the analytical derivatives of equation (8) with respect to Ce.

5. RESULTS AND DISCUSSION

The experimental data for the adsorption of methylene blue onto activated carbon at six different experimental conditions, with five replications at each condition, are shown in Figure 1. The
Dashed lines represent the transient trajectory, according to equation (3), starting at $C_0$ values and with angular coefficient equal to $-V/W$. It can be noticed that the experimental fluctuations of the data are lying on these lines, showing clearly that variables $q_e$ and $C_e$ are not independent. This evidence has been completely neglected in previous works. This behaviour and the statistical observations presented in the ‘Non-Linear Parameter Estimation Procedures’ section lead to the conclusion that the use of only $C_e$ variable as function of the independent variables $V$, $W$ and $C_0$ is the more appropriate non-linear procedure for estimation of adsorption equilibrium parameters. It can also be seen in Figure 1 that the experimental fluctuations can be very high, although this does not invalidate our analysis, as these experimental data are helpful to show the obvious dependence of variables $q_e$ and $C_e$. In fact, replication has been hardly reported in previous works. When replication is carried out, normally only the average values are presented and the experimental variances are neglected. As a consequence, the uncertainties associated with the experimental measurements at the different experimental conditions cannot be taken into account during the parameter estimation procedure, leading to unreliable parameter estimates that cannot be explained with rigorous statistical analysis.

In Table 2, the averages and the standard deviations are presented for measured concentrations at the six analyzed experimental conditions. It can be noticed that the experimental fluctuations, as observed with the standard deviation values, change significantly in the different experimental conditions. It is interesting to observe that the magnitude of the $q_e$ standard deviation changes dramatically when the mass of the activated carbon is changed. Consequently, the assumption of

| Nomenclature | Objective function | Regression variable |
|--------------|--------------------|--------------------|
| LS_qe        | Equation (1)       | $q_e$              |
| WLS_qe       | Equation (2)       | $q_e$              |
| DR_Ceqe      | Equation (4)       | $C_e$ and $q_e$    |
| LS_Ce        | Equation (6)       | $C_e$              |
| WLS_Ce       | Equation (7)       | $C_e$              |

Figure 1. Experimental data obtained in six experimental conditions with five replications.
constant experimental error in all experimental conditions cannot be supported by the experimental observations and the use of the least-squares function for parameter estimation cannot be supported by statistical arguments.

Despite the fact that the least-squares procedure cannot be supported by the available experimental values, all five non-linear procedures were used for estimation of the adsorption equilibrium parameters in the ‘Adsorption Equilibrium Models’ section. Figures 2(a–c) show the experimental data and the fitted Langmuir, Freundlich and Sips models using the five different non-linear procedures.

Although it could be expected that the weighted least-squares procedure would provide a better response than the least-squares procedure, it was not observed, as shown in Figures 2(a–c). It is clearly noticed that the WLS_qe procedure provides a discordant fit for all adsorption equilibrium models. This can be explained by the fact that the experimental data obtained for low concentration values of C_e and q_e are the ones that present very low values of the standard deviation, when compared with the data obtained at high concentration values. Consequently, the model fit is dominated by these low error data, so that the data with high standard deviation are not very relevant for parameter estimation. It is important to observe that the data at low equilibrium concentrations are not very precise, as large deviations in the C_e values can be observed, although the deviations in q_e values are not large. Consequently, when the WLS_qe procedure is used, despite the fact that this seems to be a more statistically grounded procedure, erroneous results are obtained because of neglecting the deviation in the C_e values.

It can be observed that the non-linear procedures DR_Ceqe and WLS_Ce provide almost the same results for all adsorption equilibrium models. This indicates the importance of taking into account the deviations in both variables and also shows that considering only C_e as the dependent variable (and its experimental deviation) is enough to provide a good representation of the experimental data.

It can also be noticed that the least-squares procedures (LS_qe and LS_Ce) present fits with significant deviations from fits obtained with the weighted least-squares procedures (despite the WLS_qe). This can be regarded as the effect of neglecting the experimental measurement precision.

In Tables 3–5, the regression results for the Langmuir, Freundlich and Sips models are presented. As observed in Figures 2(a–c), the procedure WLS_qe provides erroneous results, because of neglecting deviations in the variable C_e; consequently, the estimated parameter values are meaningless.

With respect to the Langmuir model, whose results are shown in Table 3, the estimated q_m values cannot be considered statistically different in the four regression procedures (excluding WLS_qe, according to the previous observations), as can be observed through the 95% confidence limits. By contrast, the q_m variances in these four regressions are not equivalent, as indicated in
Figure 2. (a) Langmuir, (b) Freundlich and (c) Sips model fits to the methylene blue equilibrium data using five different non-linear parameter estimation procedures.
### TABLE 3. Estimated Parameter Values and Respective Uncertainties for All Non-Linear Regression Procedures for the Langmuir Model

| Non-linear procedure | $S_{min}$ | Parameter | Estimated value | Variance | Variance ratio | Lower CI limit | Upper CI limit |
|----------------------|-----------|-----------|----------------|----------|----------------|---------------|---------------|
| LS_qe                | 14,481.6  | $q_m$     | 128.71         | 109.46   | 6.360          | 107.28        | 150.14        |
|                      |           | $K_L$     | 85.82          | 762.07   | 0.548          | 29.27         | 142.36        |
| WLS_qe               | 3858.3    | $q_m$     | 15.92          | 0.05     | 0.003          | 15.47         | 16.37         |
|                      |           | $K_L$     | 22.058         | 5,603,541| 4029           | 17.209        | 26,907        |
| DR_Ceqe              | 32.16     | $q_m$     | 125.80         | 14.89    | 0.865          | 117.90        | 133.71        |
|                      |           | $K_L$     | 132.09         | 1234.79  | 0.888          | 60.11         | 204.07        |
| LS_Ce                | 753.17    | $q_m$     | 131.33         | 44.04    | 2.559          | 117.74        | 144.93        |
|                      |           | $K_L$     | 91.70          | 716.27   | 0.515          | 36.87         | 146.52        |
| WLS_Ce               | 26.86     | $q_m$     | 126.45         | 17.21    | 1.000          | 117.95        | 134.95        |
|                      |           | $K_L$     | 121.77         | 1390.87  | 1.000          | 45.37         | 198.16        |

Note: Bold values indicate a significant difference between variance values.

Physical parameter units: $q_m = [\text{mg/g}]$ and $K_L = [\text{L/g}]$.

### TABLE 4. Estimated Parameter Values and Respective Uncertainties for All Non-Linear Regression Procedures for the Freundlich Model

| Non-linear procedure | $S_{min}$ | Parameter | Estimated value | Variance | Variance ratio | Lower CI limit | Upper CI limit |
|----------------------|-----------|-----------|----------------|----------|----------------|---------------|---------------|
| LS_qe                | 11,482.9  | $K_F$     | 31.82          | 23.498   | 0.185          | 21.89         | 41.75         |
|                      |           | 1/n       | 0.274          | $1.274 \times 10^{-3}$ | 0.949 | 0.201         | 0.348         |
| WLS_qe               | 3225.7    | $K_F$     | 15.40          | 0.017    | 0.0001         | 15.14         | 15.67         |
|                      |           | 1/n       | 0.228          | $0.032 \times 10^{-3}$ | 0.024 | 0.216         | 0.239         |
| DR_Ceqe              | 43.11     | $K_F$     | 66.51          | 90.546   | 0.713          | 47.02         | 86.00         |
|                      |           | 1/n       | 0.117          | $0.934 \times 10^{-3}$ | 0.696 | 0.055         | 0.180         |
| LS_Ce                | 1109.13   | $K_F$     | 33.26          | 48.115   | 0.379          | 19.05         | 47.47         |
|                      |           | 1/n       | 0.269          | $2.145 \times 10^{-3}$ | 1.598 | 0.174         | 0.364         |
| WLS_Ce               | 39.20     | $K_F$     | 64.84          | 127.051  | 1.000          | 41.75         | 87.93         |
|                      |           | 1/n       | 0.123          | $1.342 \times 10^{-3}$ | 1.000 | 0.048         | 0.198         |

Note: Bold values indicate a significant difference between variance values.

Physical parameter units: $K_F = [(\text{mg/g})/(\text{mg/l})^{1/n}]$ and $1/n = \text{[dimensionless]}$. 
TABLE 5. Estimated Parameter Values and Respective Uncertainties for All Non-Linear Regression Procedures for the Sips Model

| Non-linear procedure | $S_{\text{min}}$ | Parameter | Estimated value | Variance | Variance ratio | Lower CI limit | Upper CI limit |
|----------------------|-------------------|-----------|----------------|----------|----------------|----------------|----------------|
| LS_qe                | 11,342.4          | $q_m$     | 325.34         | 210,184  | 7070           | -615.34        | 1266.02        |
|                      |                   | $K_S$     | 1.77           | 141,327  | 0.09           | -22.62         | 26.16          |
|                      |                   | $n$       | 0.363          | 0.028    | 0.41           | 0.022          | 0.704          |
|                      |                   | $q_m$     | 1000           | 80,399,736 | 2.7 x 10^6 | -17,398        | 19,398         |
| WLS_qe               | 3240.8            | $K_S$     | 1.02 x 10^{-5} | 6.10 x 10^{-5} | 3.8 x 10^{-11} | -5.0 x 10^{-4} | 5.2 x 10^{-4} |
|                      |                   | $n$       | 0.226          | 0.480    | 7.06           | 0.181          | 0.271          |
|                      |                   | $q_m$     | 122.80         | 22.69    | 0.76           | 113.02         | 132.57         |
| DR_Ceqe              | 31.52             | $K_S$     | 136.72         | 1,038,070 | 0.64           | 70.61          | 202.83         |
|                      |                   | $n$       | 1.170          | 0.054    | 0.79           | 0.693          | 1.647          |
|                      |                   | $q_m$     | 121.71         | 38.32    | 1.29           | 109.01         | 134.41         |
| LS_Ce                | 704.85            | $K_S$     | 105.08         | 510,841  | 0.32           | 58.71          | 151.46         |
|                      |                   | $n$       | 1.586          | 0.333    | 4.90           | 0.401          | 2.770          |
|                      |                   | $q_m$     | 123.09         | 29.73    | 1.00           | 111.91         | 134.28         |
| WLS_Ce               | 26.35             | $K_S$     | 133.37         | 1,615,252 | 1.00           | 50.91          | 215.84         |
|                      |                   | $n$       | 1.163          | 0.068    | 1.00           | 0.629          | 1.697          |

Note: Bold values indicate a significant difference between variance values.

Physical parameter units: $q_m$ = [mg/g], $K_S$ = [l/g]; $n$ = [dimensionless].

the variance ratio column (bold values). In this case, the degrees of freedom are both equal to 28 and the variance ratio must lie in the range [0.47, 2.13] if the variances are statistically equivalent. Consequently, the $q_m$ variances computed with the least-squares objective function (LS_qe and LS_Ce procedures) are statistically higher than the one provided by the WLS_Ce procedure. Only the results obtained by the DR_Ceqe and WLS_Ce procedures can be considered statistically equivalent. Furthermore, these procedures provide minimum values of the objective function $S_{\text{min}}$ that can be used for model evaluation through a $\chi^2$ test, and this is another reason to prefer these procedures than the others.

Using the $\chi^2$ distribution with 28 degrees of freedom (for Langmuir and Freundlich models that present two parameters) and a probability value equal to 0.975, the upper interval value for the objective function is equal to 44.5. It can be noticed in the results presented in Tables 3 and 4 that DR_Ceqe and WLS_Ce procedures always lead to objective function values lower than 44.5, indicating that both Langmuir and Freundlich models are adequate to represent the available data. For Sips model, for which the number of degrees of freedom is equal to 27, the upper interval value for the objective function is equal to 43.2 and, as presented in Table 5, the Sips model can also be considered adequate to represent the available data.

For the Freundlich model, whose results are shown in Table 4, the estimated parameter values with the LS_qe and WLS_qe are statistically different from the ones obtained with the WLS_Ce, according to the CIs of parameter estimates. Consequently, it can be concluded, based on statistical arguments, that the traditional procedure does not lead to results that are equivalent to
those obtained with the weighted least-squares based only in the Ce measurements; the latter is the statistically more adequate procedure. Besides, the K_F variances are not equivalent, as indicated in the variance ratio column (bold values). As it can be noticed, the K_F variances computed through least-squares objective function (LS_qe and LS_Ce procedures) are statistically higher than the one provided by the WLS_Ce procedure. The results obtained by the DR_Ceqe and WLS_Ce procedures can be considered statistically equivalent, and these procedures provide minimum values of the objective function S^2_min that can be used for model evaluation through a \chi^2 test, one more reason to choose these procedures than the others.

With respect to the results obtained for the Sips model, shown in Table 5, it was noticed once again that the WLS_Ce and DR_Ceqe present similar results, but different from the results obtained with the two least-squares procedures (LS_qe and LS_Ce), particularly, when the variance ratio is considered. It must be observed that the LS_qe procedure leads to parameter CIs that comprises the zero value, indicating that the parameters q_m and K_S are not statistically significant. It must also be noticed that the high values for the estimated parameter variances obtained in almost all procedures are due to the inclusion of the additional parameter n, which does not lead to any significant improvement of the model fit, leading to correlated parameters and increasing the parameter variances. For the LS_qe procedure, the confidence limit for the parameter n does not include the value 1, indicating that this parameter is statistically different from 1 and, consequently, that model fit obtained by the Sips model is different from the one obtained by the Langmuir model. However, when DR_Ceqe and WLS_Ce are considered, the CIs include the value 1, which is in good agreement with the results indicated by the \chi^2 test, where both model fits with experimental data could be considered adequate. Consequently, the results obtained by the LS_qe procedure, the most popular parameter estimation procedure in the literature, leads to erroneous conclusions, because it indicates that the Sips model present an n parameter different than 1.

The results presented in Figures 2(a–c) and Tables 3–5 indicate that the procedure based on data reconciliation (DR_Ceqe), where deviations in both variables C_e and q_e are considered, and the procedures based on the weighted least-squares objective function, taking into account only deviations in the C_e variable (WLS_Ce), provide similar results and can be used for appropriate parameter estimation of the adsorption equilibrium models. To show the advantage of the WLS_Ce over DR_Ceqe procedure more clearly, Figures 3(a and b) show the Langmuir fit to the experimental data and the model predicted values. It can be observed that the data reconciliation
procedure, as it takes into account deviations in both variables, leads to model predicted values that are not similar to the measured experimental conditions [observe the closed black circles in Figure 3(a)]. By contrast, the weighted least-squares procedure, based only in the $C_e$ variable, leads to a single predicted value for each experimental condition, because it is based on constant $V$, $W$ and $C_0$ values for all experimental conditions. It sounds reasonable to observe that replicates lead to similar predicted values, as experimental conditions were kept constant, even if the experimental responses are not the same due to the existence of experimental fluctuations.

6. CONCLUSION

In this work five different procedures for non-linear regression of adsorption equilibrium parameters were presented and compared with each other. Initially, based on statistical arguments, the analyzed procedures were proposed and evaluated. Then, using experimental data obtained for adsorption of methylene blue onto activated carbon, estimation procedures were evaluated during the estimation of the model parameters and respective variances for Langmuir, Freundlich and Sips models. It was shown that procedures based on the least-squares objective function usually lead to poor estimation of the parameter variances, distorting the statistical analysis of the precisions of the parameter estimates. The procedure based on the weighted least-squares function of variable $q_e$ provided the poorest results, as the deviations in the $q_e$ variables controlled the estimation process. It was also shown that the procedure based on data reconciliation, which takes into account error in both variables $C_e$ and $q_e$, and the procedure that considers only $C_e$ measurements in a weighted least-squares objective function lead to similar results. However, the data reconciliation procedure neglects the correlation that exists between variables $C_e$ and $q_e$ and lead to different model predictions for replicates, which are not consistent. Consequently, the procedure based only on the $C_e$ measurements is more reliable and must be used for estimation of the adsorption equilibrium parameters according with the statistical premises indicated in this work.

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