

On the use of linearized pseudo-second-order kinetic equations for modeling adsorption systems

Mohammad I. El-Khaiary^a, Gihan F. Malash^a, Yuh-Shan Ho^{b,c,*}

^a Chemical Engineering Department, Faculty of Engineering, Alexandria University, El-Hadara, Alexandria 21544, Egypt

^b Water Research Centre, Asia University, Taichung 41354, Taiwan

^c Department of Environmental Sciences, Peking University, Beijing, 100871, China

ARTICLE INFO

Article history:

Received 26 August 2009

Received in revised form 11 February 2010

Accepted 25 February 2010

Available online 26 March 2010

Keywords:

Pseudo-second-order

Adsorption kinetics

Non-linear regression

Least squares

ABSTRACT

Simulated pseudo-second-order kinetic adsorption data were analyzed by different methods of least-squares regression. The methods used were non-linear regression and four linearized forms of the pseudo-second-order equation. The simulated data were compromised with three different homoskedastic and heteroskedastic error distributions. In the presence of all types of error distributions, non-linear regression was the most robust method and provided the most accurate and efficient estimates of the kinetic parameters.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Adsorption is the most commonly used technique for the treatment of industrial wastewaters. For practical applications of adsorption such as process design and control, it is important to model the adsorption rate and to establish the time dependence of adsorption systems under various process conditions. Many mechanistic models have been suggested to describe the adsorption kinetics. Two-resistance models, such as the film-solid model [1], the film-pore model [2], and the branched pore model [3], give detailed analysis of the adsorption dynamics. However, these models are presented as partial differential equations and their solution needs dedicated computer programs and extensive computer time. Therefore, it is impractical to use these models in industrial-plant simulations because in industry it is preferred to have more simple relations that can be solved quickly and easily. Even in the area of research, most researchers prefer to use simple lumped kinetic-models to analyze their experimental results. At the present time, Boyd's film-diffusion [4] and Weber's intraparticle-diffusion [5] are the two most widely used models for studying the mechanism of adsorption. However, in spite of their apparent simplicity, the application of both the film-diffusion and the intraparticle-diffusion models often suffers from uncertainties caused by the multi-linear nature of their plots [6].

Another approach to the modelling of adsorption kinetics is the use of pseudo-kinetic models that simulate the overall rate of adsorption. In recent years, Ho presented a model that described

adsorption, which provided a novel idea to the second-order equation called a pseudo-second-order (PSO) rate expression [7,8]. The PSO kinetic equation of Ho based on adsorption capacity may be expressed in the form:

$$\frac{dq_t}{dt} = k(q_m - q_t)^2 \quad (1)$$

Table 1

Pseudo-second-order kinetic model linearized forms.

Type	Linearized form	Plot	Effects of linearization
Linear 1	$\frac{t}{q} = \frac{1}{kq_m^2} + \frac{1}{q_m}t$	t/q vs. t	- Reversal of relative weights of data points because of $1/q$ in the dependent variable - t in both dependent and independent variables, leading to spurious correlation
Linear 2	$\frac{1}{q} = \frac{1}{q_m} + \left(\frac{1}{kq_m^2}\right)\frac{1}{t}$	$1/q$ vs. $1/t$	- Reversal of relative weights of data points because of $1/q$ in dependent variable - Independent variable is $1/t$, leading to distortion of error distribution
Linear 3	$q = q_m - \left(\frac{1}{kq_m}\right)\frac{q}{t}$	q vs. q/t	- q in both dependent and independent variables, leading to spurious correlation - The presence of q in the independent variable (q/t) introduces experimental error, violating a basic assumption in the method of least squares - $1/t$ in independent variable, leading to distortion of error distribution
Linear 4	$\frac{q}{t} = kq_m^2 - kq_mq$	q/t vs. q	- q in both dependent and independent variables, leading to spurious correlation - The presence of q in the independent variable introduces experimental error, violating a basic assumption in the method of least squares

* Corresponding author. Department of Environmental Sciences, Peking University, Beijing, 100871, PR China. Tel.: +86 6 4 2332 3456x1797; fax: +86 6 4 2330 5834.

E-mail address: ysho@asia.edu.tw (Y.-S. Ho).

Table 2
Definition of the measurement-error models used.

Measurement-error model	Definition
MEM-I	Independent random error in q with constant variance
MEM-II	Independent random error in C with variance proportional to C
MEM-III	Error in q dependant on error in C according to Eq. (5) Independent random error in C with constant variance Error in q dependent on error in C according to Eq. (5)

where k is the rate constant of pseudo-second-order adsorption ($\text{g mg}^{-1} \text{min}^{-1}$), q_m is the amount of solute adsorbed at equilibrium (mg g^{-1}), and q_t is the amount of solute adsorbed at time t (mg g^{-1}). Integrating Eq. (1) for boundary conditions $t=0$ to $t=t$ and $q_t=0$ to $q_t=q_t$ gives:

$$q_t = \frac{q_m^2 kt}{1 + q_m t} \quad (2)$$

Table 3
Percentage errors in estimated values of q_m and k obtained from linear and non-linear regression calculations. Synthetic kinetic data were obtained by adding independent random errors to ideal pseudo-second-order q and C values. (MEM-I). ϵ_q : % error in estimated value of q_m , ϵ_k : % error in estimated value of k .

Error variance (% of q_m)		Non-linear		Linear 1		Linear 2		Linear 3		Linear 4	
		ϵ_q	ϵ_k	ϵ_q	ϵ_k	ϵ_q	ϵ_k	ϵ_q	ϵ_k	ϵ_q	ϵ_k
2	Mean	0.29	-1.60	-0.14	1.50	-71.18	2.55	1.75	-6.02	-1.13	2.97
	Standard deviation	0.92	3.99	1.39	7.77	217.7	67.37	2.39	11.76	3.06	12.68
	Variance	0.84	15.89	1.93	60.31	47,407	4539	5.69	138.4	9.38	160.7
	Median	0.34	-2.36	-0.26	1.78	1.97	3.43	1.42	-1.42	-1.36	5.40
5	Mean	0.25	-0.58	3.70	11.08	-21.79	15.73	7.25	-35.48	-3.86	8.09
	Standard deviation	1.45	7.25	18.32	54.19	252.7	106.4	8.78	55.73	8.03	27.16
	Variance	2.11	52.51	335.6	2937	63,855	11,311	77.15	3105	64.50	737.8
	Median	0.45	0.31	-0.05	4.93	7.29	24.91	4.32	-12.08	-1.64	6.93
10	Mean	0.30	-1.33	0.27	65.36	10.37	34.81	9.81	-50.46	-3.48	1.96
	Standard deviation	2.20	10.27	5.90	236.5	170.6	607.5	6.66	50.58	10.36	34.54
	Variance	4.83	105.4	34.83	55,964	29,099	3.69×10^5	44.38	2559	107.3	1193
	Median	-0.03	0.09	-0.38	2.69	28.47	-50.38	9.96	-42.76	-0.62	2.50
20	Mean	-1.19	5.48	-13.07	3.74	53.84	-113.9	15.53	-113.3	-8.61	11.14
	Standard deviation	3.23	13.11	48.60	81.88	81.21	212.0	10.11	126.8	15.95	41.22
	Variance	10.41	171.9	2362	6704	6596	44,927	102.3	16,076	254.3	1699
	Median	-1.36	7.56	-2.80	17.10	41.40	-155.2	16.41	-78.41	-5.59	18.59

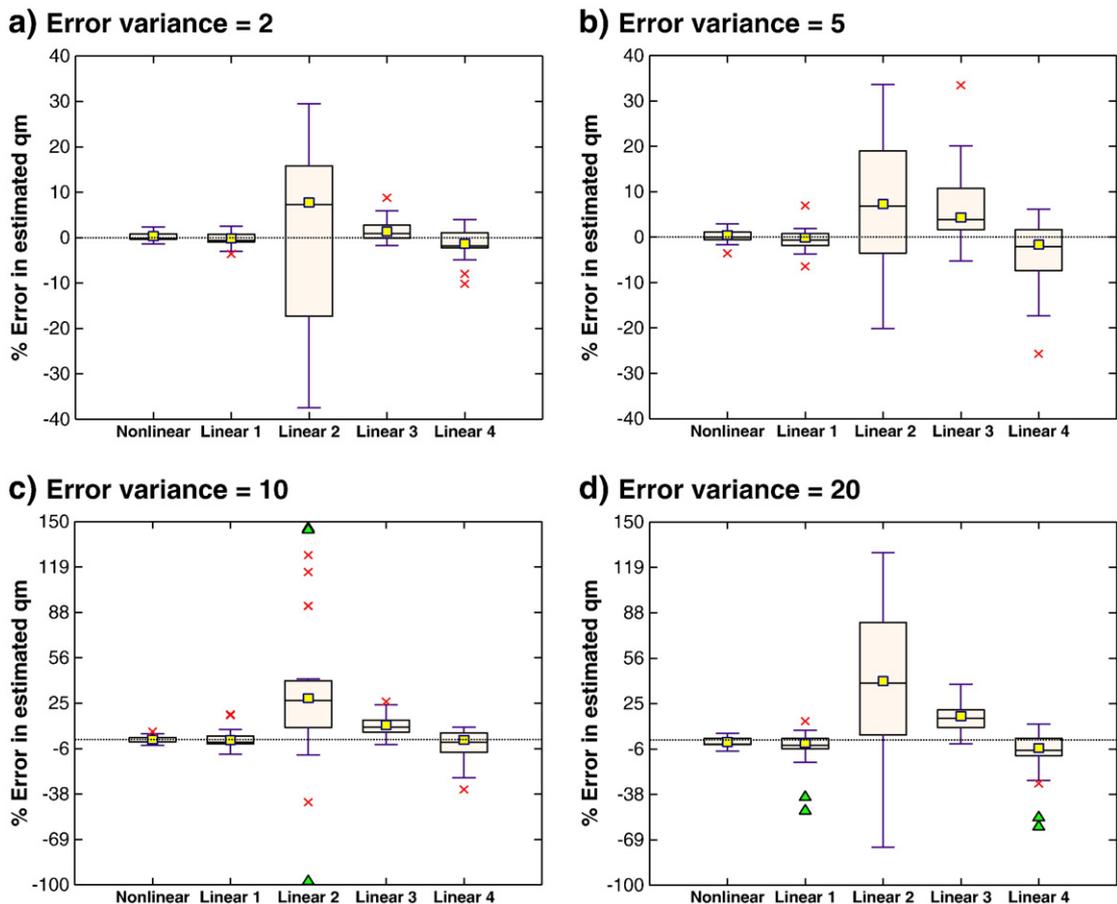


Fig. 1. Box plots for the percentage error in estimation of q_m by different methods of regression of synthetic PSO data at different levels of error variance. Synthetic kinetic data were obtained by adding independent random errors to ideal pseudo-second-order q and C values. (MEM-I).

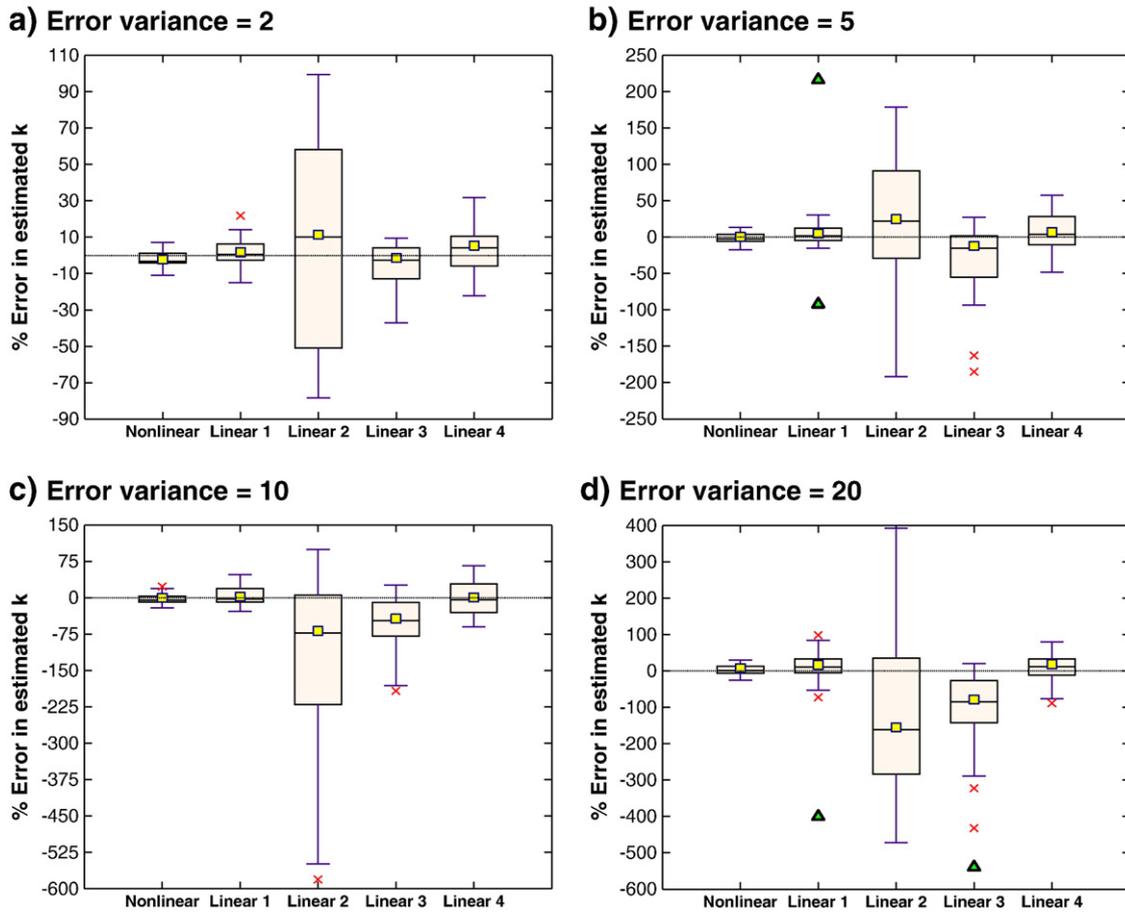


Fig. 2. Box plots for the percentage error in estimation of k by different methods of regression of synthetic PSO data at different levels of error variance. Synthetic kinetic data were obtained by adding independent random errors to ideal pseudo-second-order q values. (MEM-1).

and the initial rate of adsorption, h , is:

$$h = kq_m^2 \tag{3}$$

A theoretical analysis of the PSO model was reported by Azizian [9]. The advantage of Azizian's derivation is that when the initial concentration of a solute is low, the adsorption process obeys the pseudo-second-order model. The PSO equation has the following advantages [10]:

It does not have the problem of assigning an effective adsorption capacity; the adsorption capacity, rate constant of pseudo-second-order, and the initial adsorption rate can all be determined from the equation without initially knowing any parameter. On using the PSO model, it should be kept in mind that it does not correspond to any specific physical models; it simply approximates well the behaviors predicted by many different theoretical approaches [11].

Due to its simplicity and its good fitting many adsorption systems, the PSO model has been extensively used in the modeling of numerous adsorption systems [8]. Because the PSO as expressed by Eq. (2) is non-linear, estimating the values of q_m and k requires fitting the equation to experimental data by non-linear regression using numerical optimization techniques. A common alternative to non-linear regression is to use linearized versions of the equation which allows for the calculation of the two parameters, q_m and k , by linear regression on transformed data (Table 1) [12].

Because linear regression is convenient, requires little understanding of the data fitting process, and is easily done in spreadsheets such as Microsoft® Excel™, this method is commonly used for estimating the pseudo-second-order parameters. A limitation to this linearization

approach, however, is that the transformation of data required for linearization can result in modifications of error structure, introduction of error into the independent variable, and alteration of the weight placed on each data point [13]. These limitations often lead to differences in fitted parameter values between linear and non-linear versions of the PSO model [12]. In Table 1 we summarize the effects of different linearizations on the least squares regression results. Linear 1

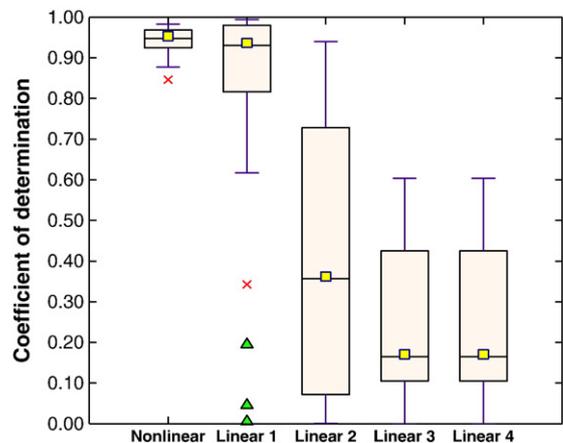


Fig. 3. Box plots for the r^2 values of the different methods of regression of synthetic PSO data. Synthetic kinetic data were obtained by adding independent random errors to ideal pseudo-second-order q values. (MEM-1).

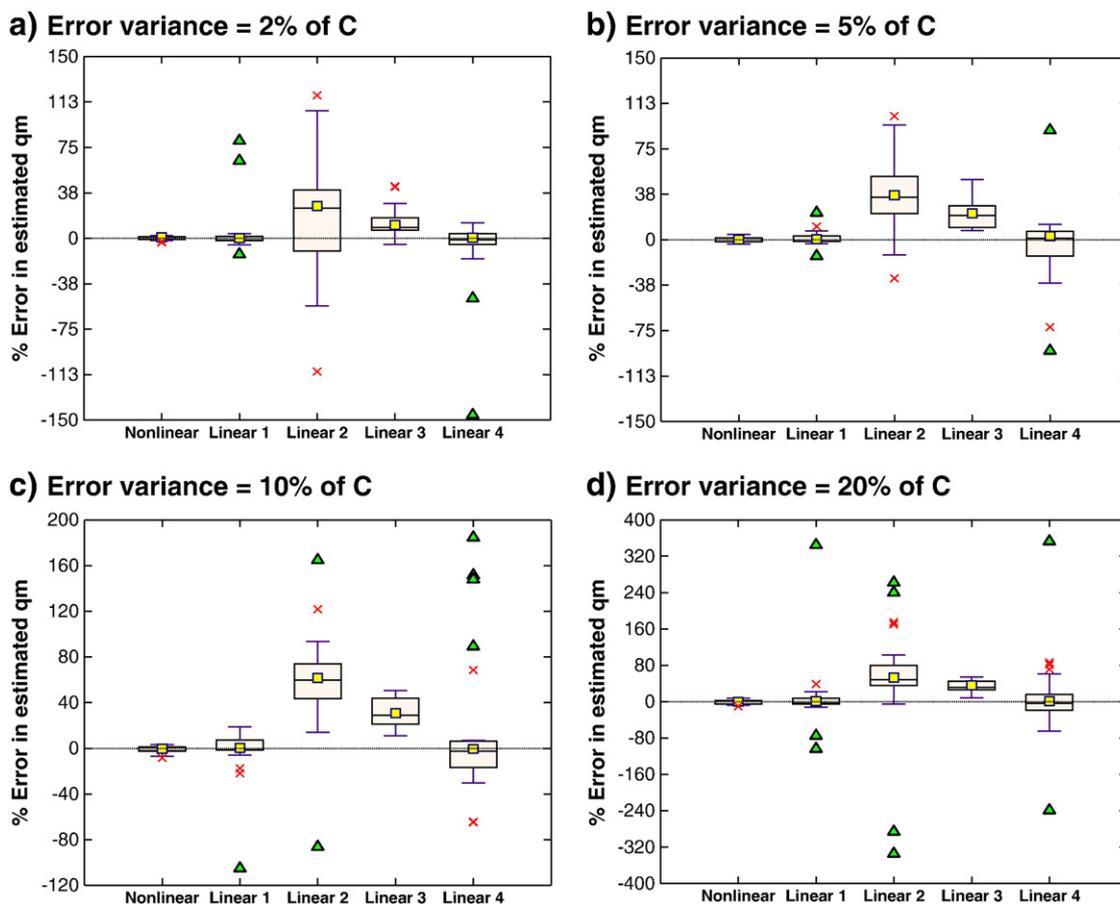


Fig. 4. Box plots for the percentage error in estimation of q_m by different methods of regression of synthetic PSO data at different levels of error variance. Synthetic kinetic data were obtained by adding a random error proportional to C in ideal pseudo-second-order data, then calculating q from Eq. (5) (MEM-II).

and Linear 2 models both have t/q and $1/q$ in the Y axis, which yields numerically small values of Y when q is large, thus reversing the relative weights (and leverage) of data points by giving greater weights to point of small q values. The distribution of experimental errors in both t and q will change if the axis is the reciprocal ($1/t$ or $1/q$), as seen in Linear 2 and Linear 3. There is also the problem of spurious correlation in Linear 1, Linear 3 and Linear 4. (i.e. the observed correlation is a “mathematical artifact” without a real statistical meaning), it often occurs when the ratios between variables are used to build parametric relationships between the variables themselves [14,15]. Many experimental procedures have negligible errors in measuring t , but when the X axis is q/t or q , as in Linear 3 and Linear 4, an experimental error is introduced in the X variable.

Although it is commonly assumed that linearized versions of the PSO model provide poorer fits and less accurate parameter estimates than the non-linear equation [12], this assumption may not be always true. However, it is not appropriate to use the linear regression analysis for comparing the best-fitting of linear models. Non-linear analysis could be a better method. The most accurate PSO equation for regression will depend on the error structure of the data because a major assumption in least squares analyses is that the variance of the errors remains constant [16]. Therefore, if a transformation improves the constancy of the error variance, then the associated linear equation will provide more accurate parameter estimates than the non-linear equation [17]. For example, studies on the Langmuir isotherm showed that while the non-linear equation provides the most accurate parameter estimates when the error variance remains constant [13,18–21] but linearized versions of the Langmuir equation have been shown to provide slightly

better parameter estimates than the non-linear equation when the error variance increases linearly with the independent variable [22].

When the experimental errors in the data are small, the choice of which linearized, or non-linear, equation used for regression has a minor effect on the estimated PSO parameter values. However, when experimental errors are large, it would be useful to know which equation gives the most accurate estimates.

The objectives of this paper are to demonstrate the differences in estimated PSO parameters arising from the application of linear and non-linear regression methods to kinetic adsorption data, and to assess the accuracy of predictions from different regression methods. In order to assess the accuracy of each regression method in the presence of measurement errors, simulated PSO type data were calculated then errors were added to the data set. The simulated data were subsequently analyzed by linear and non-linear regression methods and the accuracy of predicted PSO parameters were compared.

2. Simulations

2.1. Measurement-errors in kinetic adsorption experiments

In the present study, the concentrations, C , were assumed to be compromised by measurement errors, while true adsorption times, t , were assumed to be error free. It should be noted that this assumption of error-free adsorption times is not always correct. It is only justified when the time needed for separating the solid adsorbent from the solution is very short in comparison to the

adsorption period. Therefore, the measurement error in adsorption time may be safely ignored in cases such as:

Very quick separation, like in the case of granular adsorbent, where simply pipetting instantaneously separates a solution sample from the solid.

Data points taken at long adsorption times, thus diminishing the relative error introduced by the finite time needed for separation.

If the errors in measuring adsorption times are appreciable, then we will have at hand an error-in-variables problem [23], which is outside the scope of the present study.

2.2. Errors in q values

The PSO equation is a relationship between q (the dependant variable) and t (the independent variable). There is no practical method to measure q directly; its value is calculated by the equation:

$$q = \frac{(C_0 - C)V}{m} \tag{4}$$

where C_0 is the initial concentration of adsorbate (mg dm^{-3}), V is the volume of adsorbate solution in the adsorption experiment (dm^3), and m is the weight of adsorbent (g). From Eq. (4) it can be seen that the error in q is a result of error propagation from measuring C , C_0 , V , and m .

2.3. Measurement error models for q values

2.3.1. Measurement-error model I (MEM-I)

If errors in measuring C , C_0 , V , and m are all appreciable, then the measurement-error in q will be independent of the measurement error in C .

2.3.2. Measurement-error models II and III (MEM-II and MEM-III)

The situation may be simplified if we assume that errors in measuring C_0 , V , and m are very small compared to errors in measuring C . This assumption may be justified in many cases on the basis of the methods of experiment and measurement; C_0 accurately measured by direct weighting and dilution, V by direct pipetting, and m by direct weighting. On the other hand, the measurement of C is much more complex because it involves preparation of solutions for calibration curve, construction of calibration curve and modeling its equation (straight line or polynomial), dilution of experimental samples before measurement, measurement of absorbance in spectrophotometer, and also prediction uncertainty from using the equation of the calibration curve.

In this case the error in q and Δq , is correlated to the error in C and ΔC , by the equation:

$$\Delta q = \frac{C_0 - (C + \Delta C)V}{m} - q. \tag{5}$$

The variance of Δq will depend primarily on the variance of ΔC . If the error variance of ΔC is proportional to C , it can be easily seen in Eq. (5) that the term $C_0 - (C + \Delta C)$ is not sensitive to errors in C if C is small, but

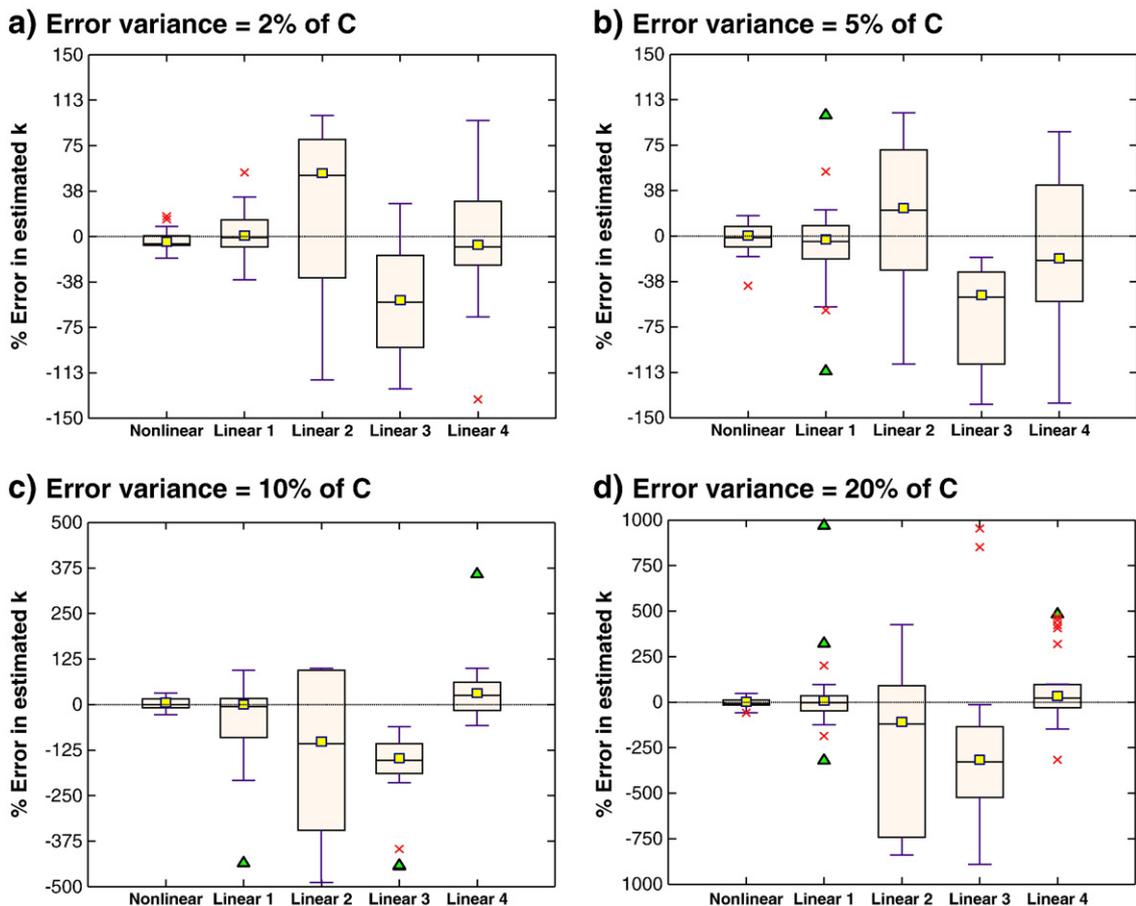


Fig. 5. Box plots for the percentage error in estimation of k by different methods of regression of synthetic PSO data at different levels of error variance. Synthetic kinetic data were obtained by adding random error proportional to C in ideal pseudo-second-order data, then calculating q from Eq. (5) (MEM-II).

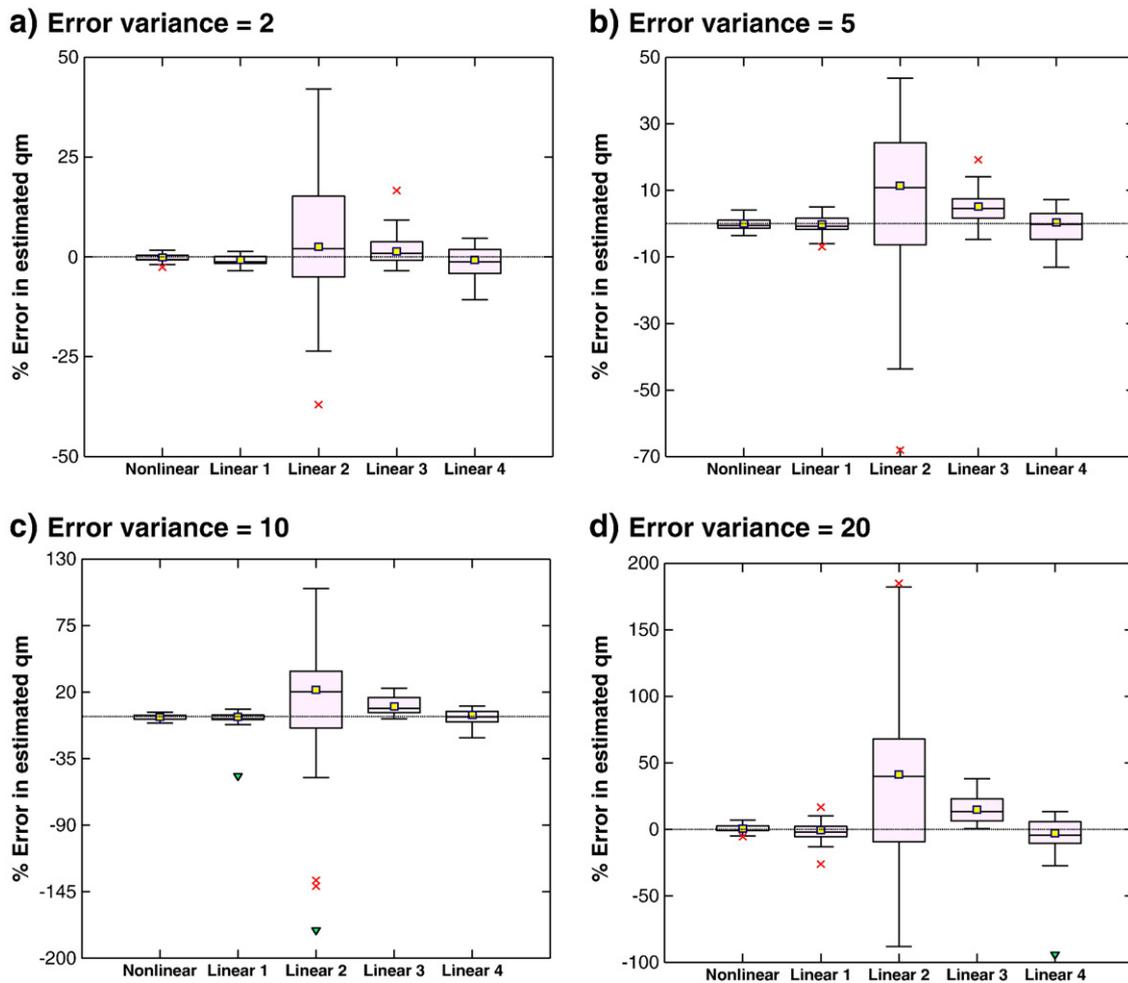


Fig. 6. Box plots for the percentage error in estimation of q_m by different methods of regression of synthetic PSO data at different levels of error variance. Synthetic kinetic data were obtained by adding a random error of constant variance to C in ideal pseudo-second-order data, then calculating q from Eq. (5) (MEM-III).

as C approaches C_0 , the value of $C_0 - (C + \Delta C)$ may change significantly. Therefore Δq will be more sensitive to errors in C at the beginning period of adsorption. This will be called henceforth measurement-error model II (MEM-II). On the other hand, if the error variance of ΔC is constant, then Δq will be more sensitive to measurement-errors in C when C is small, i.e. the longer the adsorption period, the greater Δq will be, thus giving rise to measurement-error model III (MEM-III). The three measurement-error models defined above are summarized in Table 2.

2.4. Simulation of kinetic data

A simulated ideal data set was defined with 16 adsorption times for a PSO adsorption process having $q_m = 100 \text{ mg g}^{-1}$ and $k = 0.001 \text{ g mg}^{-1} \text{ min}^{-1}$. The sampling times were 0.5, 1, 2, 3, 4, 5, 10, 15, 20, 25, 30, 40, 50, 60, 70, and 100 min. The total experiment time of 100 min corresponds to $q = 90.9 \text{ mg g}^{-1}$, i.e. 90.9% of the equilibrium value. One criterion for the goodness of fit is the ability of the regression method to accurately estimate the correct value of q_m which is extrapolated beyond the range of data. Simulated experimental data (with random errors corresponding to each measurement-error model) were generated. The levels of error variance studied in cases of MEM-I and MEM-III were 2, 5, 10, and 20 $\text{mg}^2 \text{ g}^{-2}$. In case of MEM-II the equivalent levels of error variance were 2%, 5%, 10%, and 20% of C . This data was subsequently analyzed by the different linearized and the non-linear PSO models. This step was repeated 30 times for each combination of

MME and error variance, and then the distribution of estimated q_m and k were studied.

2.5. Estimation of regression parameters

All calculations were performed using Microsoft Excel®. Linear regression for each linearized PSO equation was done by the conventional least-squares method, while the coefficient of determination, r^2 , was calculated by the built-in Excel function RSQ. The regression parameters were also estimated by non-linear regression using the Excel add-in Solver.

2.6. Evaluation of estimation quality

Since the true values of q_m and k are known, the errors in the estimated values of q_m and k were calculated as:

$$\% \text{Error} = \frac{E_e - E_t}{E_t} \times 100\% \quad (6)$$

where E_e is estimated value, E_t is true value.

3. Results

The estimates of q_m and k from the four linearized PSO models and from the non-linear model were compared for different

measurement-error-models. The regression results are graphically presented as Box plots and the corresponding numerical results are listed in Tables S1–S3 in the supporting information section. It should be mentioned that in order to keep the scale of Box Plots within reasonable limits, some severe outliers are not shown.

Box plots express the accuracy and precision of the estimates. The top and bottom of the box are the 25th and 75th percentiles (Q1 and Q3, respectively). The length of the box is thus the interquartile range (IQR). Accordingly, the box represents the middle 50% of the data. The IQR is a measure of spread. A “square” symbol and a line are drawn through the box at the median, Q2, (the 50th percentile). The median is a measure of the variable's location (center), it is defined as the numeric value separating the higher half of a sample, a population, or a probability distribution, from the lower half. The median can be used as a measure of location when a distribution is skewed, when end values are not known, or when one requires reduced importance to be attached to outliers. The upper adjacent value is the largest observation that is less than or equal to the 75th percentile plus 1.5 times IQR. The lower adjacent value is the smallest observation that is greater than or equal to the 25th percentile minus 1.5 times IQR. The adjacent values are displayed as T-shaped lines that extend from each end of the box. Values outside the upper and lower adjacent values are called outside values. Values that are under three IQRs from the 25th and 75th percentiles are called mild outliers and plotted with

“x” symbols. Those outside three IQRs are called severe outliers and plotted with triangle symbols.

3.1. Data having independent random errors in q and C (MEM-I)

Table 3 shows the distribution of the percentage error in estimating q_m and k values from the non-linear and the linearized PSO equations by the method of least squares for data having independent random errors in both C and q . It is obvious that the linearized equation Linear 2 provides the worst estimates. It can be seen in Figs. 1 and 2 that the estimates from Linear 2 varied wildly, even at the smallest level of error variance investigated. This is because this equation is a relationship between $1/q$ vs. $1/t$, and therefore, extremely big weight is given to data points at the beginning of the adsorption period. Thus, the slope and intercept of the line are greatly sensitive to errors in q at early periods of adsorption, leading to biased estimates.

The linearized equations Linear 3 and Linear 4 perform reasonably at low levels of error variance, but as the error variance increased, both the accuracy and precision of estimates from Linear 3 deteriorated much more than estimates from Linear 4. This is interesting because, as shown in Fig. 3, the r^2 values obtained from both equations are exactly the same. This demonstrates the ineffectiveness of comparing models based on r^2 values of linearized (transformed) equations. Mathematically, both equations

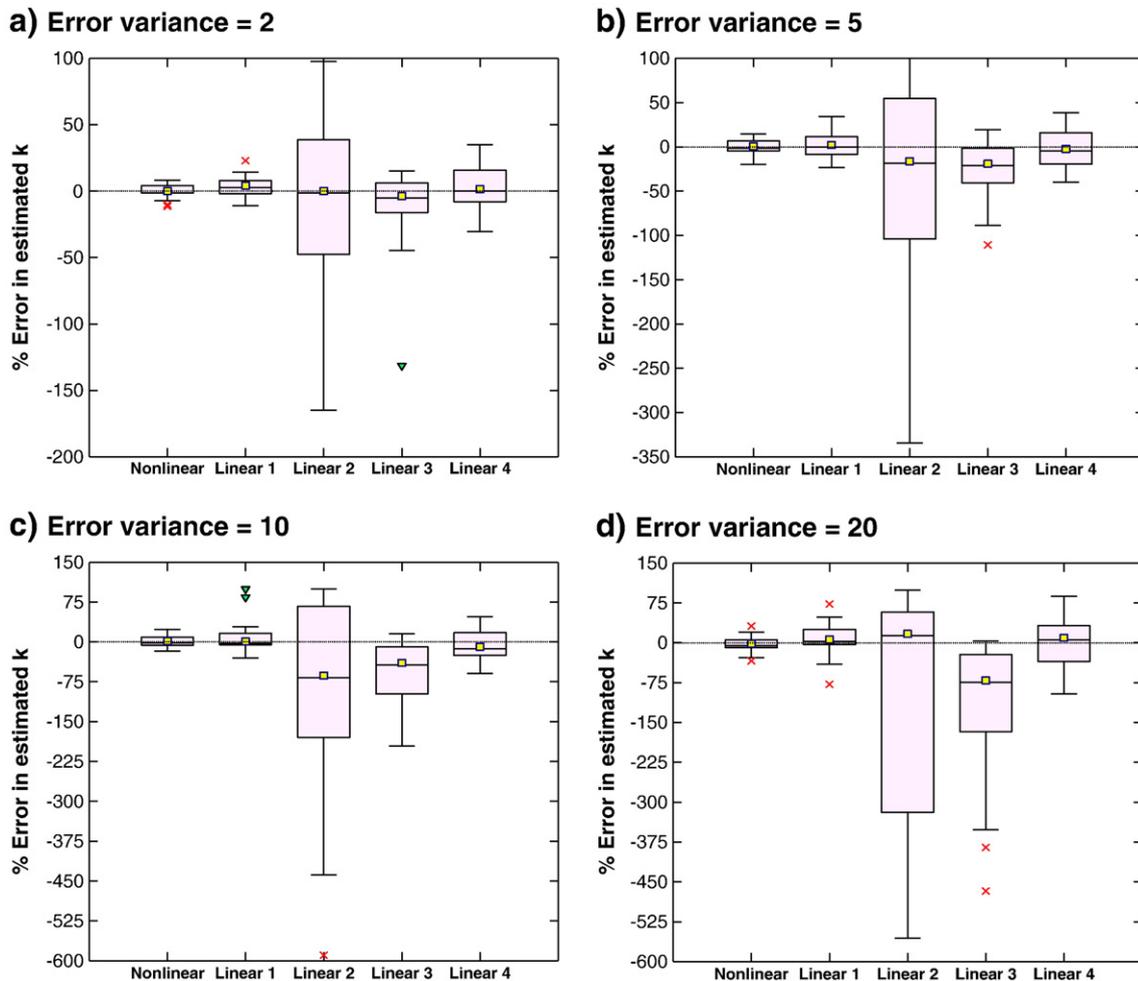


Fig. 7. Box plots for the percentage error in estimation of k by different methods of regression of synthetic PSO data at different levels of error variance. Synthetic kinetic data were obtained by adding random error of constant variance to C in ideal pseudo-second-order data, then calculating q from Eq. (5) (MEM-III).

Table 4
Percentage errors in estimated values of q_m and k obtained from linear and non-linear regression calculations. Synthetic kinetic data were obtained by adding a random error proportional to C in ideal pseudo-second-order data, then calculating q from Eq. (5) (MEM-II). ϵ_q : % error in estimated value of q_m , ϵ_k : % error in estimated value of k .

Error variance (% of C_0)		Non-linear		Linear 1		Linear 2		Linear 3		Linear 4	
		ϵ_q	ϵ_k	ϵ_q	ϵ_k	ϵ_q	ϵ_k	ϵ_q	ϵ_k	ϵ_q	ϵ_k
2	Mean	0.51	-3.52	3.81	14.84	-304.5	491.0	13.25	-154.7	-12.70	-1.16
	Standard deviation	1.31	8.26	18.36	51.68	1480	2837	10.72	342.9	43.65	46.53
	Variance	1.72	68.2	337.1	2670	2.2×10^6	8.0×10^5	114.9	1.2×10^5	1905	2164
	Median	0.77	-4.20	0.20	1.16	25.84	-34.06	10.94	-66.09	0.50	-6.84
5	Mean	0.10	-1.67	-21.43	-9.24	-7.32	475.3	21.79	-153.5	-4.86	9.91
	Standard deviation	1.81	12.10	129.5	112.2	352.4	2615	11.23	490.4	29.48	131.1
	Variance	3.30	146.5	1.7×10^4	1.2×10^4	1.2×10^5	6.8×10^6	126.1	2.4×10^5	869.1	1.7×10^4
	Median	0.10	0.49	0.42	-2.64	36.81	-145.16	21.83	-160.1	2.99	-18.07
10	Mean	-1.05	4.31	-1.90	-58.14	57.92	-12313	31.33	604.7	50.60	52.96
	Standard deviation	2.97	15.71	20.39	268.7	566.1	72,887	12.69	2832	206.5	127.79
	Variance	8.79	246.7	415.6	7.2×10^4	3.2×10^5	5.3×10^9	161.0	8.0×10^6	42,647	16,330
	Median	-0.41	5.42	0.47	0.78	57.05	82.64	30.82	-144.8	-0.29	33.16
20	Mean	0.02	-2.41	8.50	28.08	51.35	821.9	36.05	461.3	80.77	76.25
	Standard deviation	4.07	25.54	66.25	204.1	111.9	4264	11.39	3881	416.4	190.9
	Variance	16.59	652.3	4389	41,676	12,509	1.8×10^6	129.7	1.5×10^7	1.7×10^5	36,441
	Median	0.03	2.08	1.36	9.24	53.21	-37.55	36.44	-319.0	1.69	34.35

are identical with Linear 4 actually being Linear 3 divided by t . This division, however, makes a vital difference when it comes to least squares regression. Linear 3 is a relationship between q vs. q/t while Linear 4 has the X and Y axis reversed, i.e. the relationship is between q/t vs. q . Reversing the axis is known to change the regression estimates because least-squares minimizes the error in the Y axis and assumes that the X values are error-free. Both equations have q (with measurement error) in the X variable, thus violating a basic assumption in the method of least-squares, and as expected, their estimates are biased and inefficient.

The linearized PSO equation Linear 1 gave estimates almost as accurate as the non-linear equation, but the non-linear estimates were more precise. In statistical terms, the regression of the non-linear equation proved to be more robust, i.e. less sensitive to measurement errors. As the error variance increased, Linear 1 resulted in more biased estimates and more outliers. Robustness is considered as a major criterion in the evaluation of models and methods of regression [24], and therefore the nonlinear method is considered superior to Linear 1 when the experimental error is distributed according to MEM1.

3.2. Data having independent random errors in C with variance proportional to C (MEM-II)

The results in Figs. 4 and 5 are generally similar to the case of MEM-I with slight differences. The non-linear equation provided the most accurate and precise estimates. Linear 1 did not perform as well as it did in case of MEM-I. With MEM-II errors, the estimates of q_m and k were generally accurate but notoriously sensitive to errors, thus giving outlier estimates even at the smallest error variance investigated. Equations Linear 3 and 4, just like in case of MEM-I, gave different estimates although the r^2 values were the same. Linear 2 provided estimates that are extremely inaccurate and scattered.

3.3. Data having independent random errors random error in C with constant variance (MEM-III)

The results in Figs. 6 and 7 are much the same as MEM-I. The non-linear equation was the most accurate and precise at all levels of error variance, the numerical values are shown in Tables 4 and 5. Linear 1

Table 5
Percentage errors in estimated values of q_m and k obtained from linear and non-linear regression calculations. Synthetic kinetic data were obtained by adding a random error with constant variance to C values in ideal pseudo-second-order data. Then calculating q from Eq. (5) (MEM-III). ϵ_q : % error in estimated value of q_m , ϵ_k : % error in estimated value of k .

Error variance (% of C_0)		Non-linear		Linear 1		Linear 2		Linear 3		Linear 4	
		ϵ_q	ϵ_k	ϵ_q	ϵ_k	ϵ_q	ϵ_k	ϵ_q	ϵ_k	ϵ_q	ϵ_k
2	Mean	-0.21	0.42	-0.77	3.71	14.93	-5.74	1.98	-9.30	-1.17	2.27
	Standard deviation	1.06	4.90	1.23	7.22	142.6	70.49	4.08	26.43	3.56	15.46
	Variance	1.12	24.04	1.51	52.12	20,335	4968	16.67	698.3	12.65	238.9
	Median	-0.13	-0.05	-0.72	4.24	0.58	0.05	1.40	-3.73	-0.80	1.43
5	Mean	0.12	-0.08	-0.31	2.82	587.92	-37.97	5.51	-24.74	-0.75	-1.03
	Standard deviation	2.05	8.77	2.71	13.43	3237	116.7	5.17	31.04	5.47	22.92
	Variance	4.21	76.85	7.32	180.3	1.0×10^7	13,606	26.69	963.8	29.94	525.5
	Median	0.00	0.84	-0.17	2.29	15.36	-16.13	5.15	-18.97	0.41	-2.21
10	Mean	-0.48	1.17	26.14	8.85	12,592	-173.7	9.26	-54.29	-0.69	-5.00
	Standard deviation	2.26	9.48	161.8	25.72	71,202	401.7	7.34	55.29	6.16	26.47
	Variance	5.13	89.95	26,188	661.7	5.1×10^9	1.61×10^5	53.85	3057	37.95	700.5
	Median	-0.62	0.97	-0.40	1.30	23.01	-89.09	8.17	-39.24	1.24	-8.98
20	Mean	0.88	-3.64	-1.21	61.88	6.37	-42.16	15.46	-114.7	-6.35	0.59
	Standard deviation	2.93	13.44	7.75	308.1	174.5	643.6	9.39	122.0	19.56	44.11
	Variance	8.59	181	60.05	94,939	30,435	4.14×10^5	88.23	14875	382.7	1945
	Median	0.66	-3.08	-0.56	6.70	39.90	14.52	14.75	-70.64	-2.94	9.69

performed well especially when the error was small. Linear 2 was the worst, and Linear 3 and 4 behaved as in case of MEM-I.

4. Conclusions

Based on the results of this study, it is not recommended to estimate the PSO parameters by the linearized versions Linear 2, Linear 3, and Linear 4. These linearized forms of the PSO equation resulted in severely biased and inefficient estimates, Linear 2 being the worst. The linearized PSO equation Linear 1 provided accurate estimates in many cases, but it occasionally produced severe outliers. The method of non-linear regression of the data on the non-linear PSO equation was shown to be the most robust method studied. No matter what type of error distribution compromised the data; non-linear regression always produced accurate and efficient estimates of the PSO parameters. Another point to consider is that the challenge for fitting of kinetic adsorption equations to data is not limited only to the choice of regression method, but also the selection of the correct kinetic model. From a statistical point of view, it is fundamentally wrong to compare the goodness of fit for models that are subjected to different transformations. Therefore, in cases where the experimental data are tentatively fitted to several kinetic equations, it is statistically wrong to compare the goodness of fit (based on r^2 or similar statistics) if the kinetic equations are linearized.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.desal.2010.02.041](https://doi.org/10.1016/j.desal.2010.02.041).

References

- [1] G. McKay, B. Al-Duri, Multicomponent dye adsorption onto carbon using a solid diffusion mass transfer model, *Ind. Eng. Chem. Res.* 30 (1991) 385–395.
- [2] B. Al-Duri, G. McKay, Pore diffusion: dependence of the effective diffusivity on the initial sorbate concentration in single and multisolute batch adsorption systems, *J. Chem. Technol. Biotechnol.* 55 (1992) 245–250.
- [3] R.G. Peel, A. Benedek, C.M. Crowe, A branched pore kinetic model for activated carbon adsorption, *AIChE J.* 27 (1981) 26–32.
- [4] G.E. Boyd, A.W. Adamson, L.S. Myers Jr., The exchange adsorption of ions from aqueous solutions by organic zeolites. II. Kinetics. *J. Am. Chem. Soc.* 69 (1947) 2836–2848.
- [5] W.J. Weber Jr., J.C. Morris, Kinetics of adsorption on carbon from solution, *J. Sanitary Eng. Div.-ASCE* 89 (1963) 31–59.
- [6] Y.S. Ho, G. McKay, The kinetics of sorption of basic dyes from aqueous solution by sphagnum moss peat, *Can. J. Chem. Eng.* 76 (1998) 822–827.
- [7] Y.S. Ho, Adsorption of heavy metals from waste streams by peat. Ph.D. Thesis, University of Birmingham, Birmingham, U.K. (1995).
- [8] Y.S. Ho, Review of second-order models for adsorption systems, *J. Hazard. Mater.* 136 (2006) 681–689.
- [9] S. Azizian, Kinetic models of sorption: a theoretical analysis, *J. Colloid Interface Sci.* 276 (2004) 47–52.
- [10] Y.S. Ho, Pseudo-isotherms using a second order kinetic expression constant, *Adsorpt. J. Int. Adsorpt. Soc.* 10 (2004) 151–158.
- [11] W. Plazinski, W. Rudzinski, A. Plazinska, Theoretical models of sorption kinetics including a surface reaction mechanism: a review, *Adv. Colloid Interface Sci.* 152 (2009) 2–13.
- [12] Y.S. Ho, Second-order kinetic model for the sorption of cadmium onto tree fern: a comparison of linear and non-linear methods, *Water Res.* 40 (2006) 119–125.
- [13] Y.S. Ho, Selection of optimum sorption isotherm, *Carbon* 42 (2004) 2115–2116.
- [14] J.A. Berges, Ratios, regression statistics and “spurious” correlations, *Limnol. Oceanogr.* 42 (1997) 1006–1007.
- [15] C. Bolster, Assessing the Accuracy of Linearized Langmuir Equations, ASA-CSSA-SSSA 2006 International Meeting, Indianapolis, USA, November 12–16 2006.
- [16] S. Weisberg, *Applied Linear Regression*, Wiley, New York, 2005.
- [17] D. Colquhoun, A comparison of estimators for a 2-parameter hyperbola, *J. R. Stat. Soc. C-Appl.* 18 (1969) 130–140.
- [18] P. Persoff, J.F. Thomas, Estimating Michaelis-Menten or Langmuir isotherm constants by weighted nonlinear least-squares, *Soil Sci. Soc. Am. J.* 52 (1988) 886–889.
- [19] L.J.A. Gerringa, P.M.J. Herman, T.C.W. Poortvliet, Comparison of the linear Van Den Berg/Ruziĉ transformation and a non-linear fit of the Langmuir isotherm applied to Cu speciation data in the estuarine environment, *Mar. Chem.* 48 (1995) 131–142.
- [20] Y.S. Ho, W.T. Chiu, C.C. Wang, Regression analysis for the sorption isotherms of basic dyes on sugarcane dust, *Bioresour. Technol.* 96 (2005) 1285–1291.
- [21] M.I. El-Khaiary, Least-squares regression of adsorption equilibrium data: comparing the options, *J. Hazard. Mater.* 158 (2008) 73–87.
- [22] G.L. Atkins, I.A. Nimmo, A comparison of seven methods for fitting the Michaelis-Menten equation, *Biochem. J.* 149 (1975) 775–777.
- [23] W.H. Jefferys, Robust estimation when more than one variable per equation of condition has error, *Biometrika* 77 (1978) 597–607.
- [24] J. Poch, I. Villaescusa, A model to describe Cr(VI) kinetics biosorption, *J. Hazard. Mater.* 175 (2010) 770–778.