Introductory of Microsoft Excel SOLVER Function - Spreadsheet Method for Isotherm and Kinetics Modelling of Metals Biosorption in Water and Wastewater

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ABSTRACT

This paper aims to introduce a simple method to run a complicated non-linear analysis of isotherm and kinetics models for metals biosorption based on input functions of spreadsheets. A robust method is demonstrated here to exploit the 'SOLVER' function available in Microsoft (MS) Excel spreadsheet. It is more economic and user friendly than specialized computer programmes. In this study, an iterative method was proposed to produce the optimal goodness of fit between experimental data and predicted data. This was described the implementing method of a set of real data (garden grass as biosorbent) and the predicted results were compared with linear analysis and MATLAB analysis. The R^2 values found from MS Excel spreadsheet were 0.995, 0.999 and 0.996 while being 0.997, 1.000 and 0.999 by MATLAB for copper, lead and cadmium adsorption, respectively onto garden grass. The prediction of maximum adsorption, q_m by excel (59.336, 63.663 and 42.310 mg/g) were very similar to MATLAB (59.889, 63.509 and 41.560 mg/g). The predictions of kinetics parameters were also close to MATLAB analysis. Hence, the MS Excel Spreadsheet method could be a handy tool for biosorption models.

Keywords: Solver function; Microsoft Excel spreadsheet; non-linear analysis; iteration; goodness of fit; MATLAB

1. INTRODUCTION

To explore novel biosorbents in accessing an ideal biosorption system, it is essential to establish the most proper adsorption equilibrium correlation and kinetic correlation (Srivastava et al., 2006). It is crucial for reliable prediction of adsorption parameters and quantitative comparison of adsorbent behavior for different adsorbent systems or experimental conditions (Gimbert et al., 2008; Ho et al., 2002). In the perspective, equilibrium relationships, generally known as adsorption isotherms, describe how pollutants interact with the adsorbent materials, and thus are critical for optimization

of the adsorption mechanism pathways, expression of the surface properties and capacities of adsorbents, and effective design of the adsorption systems (El-Khaiary, 2008; Thompson et al., 2001). Similarly, the kinetics parameters, generally adsorption time and pattern of metals onto biosorbents are known from the fitness of kinetic parameters.

In the past, linear least-squares method was widely used by transforming the equation into a conventional linear form to calculate or predict the isotherms/kinetics parameters or the most fitted models. Principally, the models are subjected to their goodness of fit to the experimental data with the magnitude of

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coefficients of determination that close to unity (Wong et al., 2004). On the other hand, a significant limitation related to the linearized form of isotherm/kinetics equation has recently been pointed out, which produces a vast amount of different outcomes, implicitly alter the error structure, violates the error variance and normality assumptions of standard least squares, leading to the bias of the adsorption data (Han et al., 2007; Ho, 2004; Hong et al., 2009; Tunali and Akar, 2006; Vasanth and Sivanesan, 2007). In this context, a non-linear form of the isotherm and kinetics models with error analyses and optimization techniques are needed. In addition, evaluating the accuracy and consistency in parameters prediction or estimation are also demanding. Moreover, a curve fitting is applied to describe experimental data in all fields of research. The better the fit, the more accurately the function describes the data. Over the past few decades, the exponential development of computer programming has provided scope to calculate and prediction of model parameters. The introduction of computers into research makes it straightforward to fit data with simple functions such a linear regression, but it is more difficult and complicated to fit data with non-linear functions. Most of the programs (e.g. MATLAB, C^{++}, Microcal Origin, Sigma Plot or Graph pad Prism) require special mathematical knowledge to use and provides different options such as capability of fitting user-input functions to data. In addition, these programs are expensive and significantly excess cost for simply fitting the data with non-linear functions. Additionally, these programmes cannot easily manipulate the data and tend to display data, graphs, results, and analysis in multiple windows, which can lead to confusion and figures are not useable for article publication.

An alternative method is to use Microsoft Excel to fit non-linear functions. An advantage of this method is that Excel is probably included in the computer package as part of Microsoft Office, and thus no additional cost is required. Spreadsheet programmes are among the most commonly used software, and most researchers have experience with them. Excel offers a friendly user interface, flexible data manipulation, built-in mathematical functions and instantaneous graphing of data. It contains a function, named SOLVER, which is ideally suited to fitting data with non-linear functions via an iterative algorithm (Bowen and Jerman, 1995), which minimizes the sum of the squared difference between experimental data and predicted data. The objective of this present study was to propose and describe a method of non-linear regression using the SOLVER function of Excel as well as to compare the predicted parameters for Langmuir isotherm and Pseudo-2nd-order models with the MATLAB and linear analysis.

2. METHODS

The methods illustrated in this paper are: (i) to predict the optimum values of parameters for isotherms and kinetics models, (ii) to find out higher fitness of models, and (iii) to predict the curve fitted with experimental values with MS Excel spreadsheet using Solver function. They were carried out on PC operated by Windows 2007 and MS Office 2007. This protocol explained entering the experimental data manually into Excel and preparing graphs from data. On this occasion, the formulated algorithm is carried out and the predicted curve is overlaid on the experimental data points. Degree of fitness of predictions is also calculated so that the accuracy of fit can be measured.

2.1 Models and assumptions

The Langmuir adsorption isotherm is perhaps the best known of all isotherms describing adsorption. The Langmuir model is obtained under the ideal assumption of a totally homogenous adsorption surface (Bilgili, 2006)

and represented as follows (Langmuir, 1918):

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

where C_e is the equilibrium concentration (mg/l), q_e is the amount of metal ion adsorbed (mg/g), q_m is the q_e for a complete monolayer (mg/g), and K_L is the constant related to the affinity of the binding sites and the energy of adsorption (l/mg).

The pseudo-second-order model proposed by Ho and McKay (1998) is based on the assumption that the adsorption follows second order adsorption. The linear form can be written as follows:

$$q_t = \frac{K_2 q_e^2 t}{(1 + q_e k_2 t)} \qquad (2)$$

where q_e (mg/g) and q_t (mg/g) are the adsorption amount at equilibrium and time t (min) respectively and K_2 (g/mg·min) is the rate constant of adsorption.

The modelling of the models is formulated on the basis of some essentially important assumptions. The following are the assumptions:

(i) The equilibrium concentration, C_e (mg/l) for equilibrium isotherm and contact time, t (min) is considered as an 'independent' variable.

(ii) The amount of metal ion adsorbed, q_e (mg/g) and the adsorption amount at any time t (min), q_t (mg/g) are assumed as 'dependent' variables.

(iii) The maximum monolayer adsorption capacity, q_m (mg/g) and Langmuir constant K_L (l/mg) are presumed as predictable variables based on the best fitted condition of isotherm model.

(iv) The adsorption amount at equilibrium, q_e (mg/g) and the rate constant of adsorption, K_2 (g/mg·min) are assumed as predictable variables based on the best fitted condition of kinetics model.

2.2 Goodness of fit

Goodness of fit is an essentially important parameter that estimates how well the curve (i.e. the prediction) pronounces the experimental data. Generally least squares method is used to measure of the goodness of fit. It is based on the theory that the scale of the difference between the experimental data points and the prediction curve is a good measure of how well the curve fits the data. For the purposes the least squares fit method will be demonstrated by linear regression where 'independent' and 'dependent' variables are used.

In the past, non-linear data would be changed into a linear form and consequently analysed by the least squares fit method. This analysis could yield inaccurate measurements and predictions of the data and may alter the experimental error or alter the relationship between the 'independent' and 'dependent' variables. It is presumed that this method is erroneous and old fashioned which should not be operated. For data not describable by a linear function, it is crucial to apply a protocol that will fit a non-linear function to the data. A suitable method for this procedure is called iterative nonlinear least squares fitting. This process will fulfill the same goal as used for linear regression, i.e. minimizing the value of the sum of squared of the difference between data and prediction. However, it is still different from linear regression in a way that it is an iterative process based on algorithm. Initial parameters are estimates based on previous experience of the data and on a sensible guess based on knowledge of the function used to fit the data. The following parameters are measured and judged the goodness of fit:

(i) The sum of squares (SS)

The best fit of the data is judged by the sum of squares (SS) and the smallest value for the sum of squares (SS) is the best fitted data of the model. This is described by the function:

$$SS = \sum_{i=1}^{n} \left[q_{exp} - q_{model} \right]^2 \qquad (3)$$

where, q_{exp} is the experimental data, q_{model} is the value predicted by the models for curve at corresponding C_e. The first iteration calculates the SS value based on the initial parameters and the second iteration involves varying the parameter values by a small amount and recalculates the SS. This process is repeated several times until a smallest possible value of SS is achieved. Only a single iteration is required for linear regression to get the lowest value of the SS, because the second and higher derivatives of the function are zero. Conversely, the second and higher derivatives are not zero for non-linear regression, and thus an iterative process is required to calculate the optimal parameter values.

Several algorithms use in non-linear regression including the Gauss-Newton, the Marquardt-Levenberg, the Nelder-Mead and the steepest descent methods (Johnson, 1992). SOLVER, which is based on the robust and reliable generalized reduced gradient (GRG) method can be used as an easy iteration protocol. A comprehensive explanation of the evolution and operation of this code can be found in literature (Lasdon et al., 1978; Smith and Lasdon, 1992). All algorithms have similar properties, require input initial parameters and use these values to get a better estimation of the parameters used in iterative process.

(ii) The coefficient of determination (R^2)

The coefficient of determination, R^2, is practical as it gives the proportion of the variance of one variable that is predictable from the other variable. It is a measure that allows verifying how certain one can be in making predictions from a certain model. The coefficient of determination is such that $0 < R^2 < 1$, and denotes the strength of the linear association between 'experimental data, $q_{e.exp}$'

and 'prediction data, $q_{e.model}$'. The coefficient of determination represents the percent of the experimental data that is the closest to the line of best fit/prediction. The models fitness is signified by the coefficient of determination (R^2) and the following expression is used to determine the R^2 (Hossain et al., 2012b):

$$R^2 = 1 - \frac{\sum_{n=1}^{n} \left(q_{e.exp.n} - q_{e.model.n} \right)^2}{\sum_{n=1}^{n} \left(q_{e.exp.n} - \overline{q_{e.exp.n}} \right)^2} \qquad (4)$$

where, $q_{e.exp}$ is the equilibrium sorption capacity found from the batch experiment, $q_{e.model}$ is the prediction from the isotherm model for corresponding to C_e and n is the number of observations.

(iii) Residual root mean square error (RMSE) and the chi-square test (χ^2)

Non-linear error functions such as the residual root mean square error (RMSE) and the chi-square test (χ^2) are used to judge the equilibrium model with the optimal magnitude. The standard equations are as follows (Hossain et al., 2012b):

$$RMSE = \sqrt{\frac{1}{n-1} \sum_{n=1}^{n} \left(q_{e.exp.n} - q_{e.model.n} \right)^2} \qquad (5)$$

$$\chi^2 = \sum_{n=1}^{n} \frac{\left(q_{e.exp.n} - q_{e.model.n} \right)^2}{q_{e.exp.n}} \qquad (6)$$

where, '$q_{e.exp}$' is the equilibrium adsorption capacity found from the batch experiment, '$q_{e.model}$' is the prediction from the isotherm model for corresponding to 'C_e' and 'n' is the number of observations. The small values of RMSE and χ^2 indicate the better model fitting and the similarity of model with the experimental data respectively (Ho et al., 2002).

(iv) The normalized standard deviation (NSD) and average relative error (ARE)

The kinetics model is verified and optimised

by the coefficient of determination (R^2), by two non-linear errors: the normalized standard deviation (NSD) and average relative error (ARE). The standard equations are defined as (Gu et al., 2006; Hossain et al., 2012b):

$$R^2 = 1 - \frac{\sum_{N=1}^{N}\left(q_{t.exp.N} - q_{t.model.N}\right)^2}{\sum_{N=1}^{N}\left(q_{t.exp.N} - \overline{q_{t.exp.N}}\right)^2} \quad (7)$$

$$NSD = 100 \times \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}\left[\frac{q_{t.exp.N} - q_{t.model.N}}{q_{t.exp.N}}\right]^2} \quad (8)$$

$$ARE = \frac{100}{N}\sum_{i=1}^{N}\left[\frac{q_{t.exp.N} - q_{t.model.N}}{q_{t.exp.N}}\right] \quad (9)$$

where, $q_{t.exp}$ and $q_{t.model}$ (mg/g) are experimental ('exp') and model ('model') predicted amount of adsorptions capacity at time 't' and 'N' is the number of observations. The smaller values of NSD and ARE imply the better fitted model.

2.3 Algorithm and configuring the spreadsheet for non-linear models

The following process illustrates how to use the SOLVER function in Excel to fit data with user-input non-linear functions. The procedure by which the data fit proceeds is called iterative non-linear least squares regression. To execute non-linear regression analysis using the Langmuir isotherm and Pseudo-2nd-order kinetics models, the following procedure must be formulated prior to proceed:

a) Enter experimental data onto a spreadsheet in two columns, the A column containing the 'equilibrium concentration, C_e (mg/l)', and the B column containing the 'equilibrium capacity, q_e (mg/g)' for Langmuir isotherm; and 'equilibrium concentration at t, C_t (mg/l)' in A column

and 'equilibrium capacity at t, q_t (mg/g)' in B column for Pseudo-2nd-order kinetics models. This is shown in Figure 1 for isotherm model and Figure 2 for kinetics models.

b) Plot the data from cells A2 to A17 as X axis and cells B2 to B17 as Y axis in a scatter plot. The data points are displayed as filled squares.

c) Enter labels in cells G1 to G8 to depict the contents of the next adjacent cells H. In cell G1 enter q_m, which will describe the maximum adsorption capacity in cell H1. Similarly, for cells G2 to G8, K_L Mean of Exp. q_e, df (degree of freedom), S.E. (standard error) of Exp. q_e, R^2. Critical t and CI (confidence interval), respectively.

d) For Kinetics model, Enter q_e in cell G1 and K2 in cell G2 and rest of cell G (G3 to G8) are same as point 3.

e) Enter Langmuir Isotherm equation (eq.1) in column C (C2 to C17) which gives the predicted values of equilibrium adsorption capacity, q_e for the corresponding equilibrium concentration, C_e. The Excel recognized form of the equation is:

= (H1*H2*A2)/(1+ (H2*A2))

f) For kinetics equation (eq.2) enter the excel form function in column C (C2 to C15) which give the predicted values of equilibrium adsorption capacity, q_t for the corresponding equilibrium time, t. The Excel recognized form of the equation is:

= (H2*(H1^2)*A2)/(1+H1*H2*A2)

g) The mean value of q_e for equilibrium isotherm and q_t for kinetics adsorption are calculated from the data at column B. The excel recognized form of the equation is need to be entered in cell H3 and the form is:

= AVERAGE (B2:B17)

h) Enter the df (degree of freedom) function

in cell H4 and the excel form is:

= COUNT (B2:B17) − COUNT (H1:H2)

i) The Standard Error (S.E) of experimental q_e is measured from the values in column B by Equation (3). Formulate the S.E. equation in excel function and enter in the column H5. As this is an array, it needs to be pressed ctrl+alt+enter together and the excel form is:

= {SQRT (SUM((B2:B17 − C2:C17)^2)/H4)}

j) The value of R^2 is determined by Equation (4) for Langmuir isotherm and Equation (7) for Pseudo-2nd-order kinetics model. It is calculated by entering the following formula in H6 and expressing it as an array formula as described below:

= {1-(SUM((B2:B17–C2:C17)^2)/ SUM((B2:B17 - H3)^2))}

k) In order for the confidence interval of the fit to be calculated, the critical t value at a significance level of 95% is calculated by entering the following formula in H7.

= TINV (0.05, H4)

l) The confidence interval is defined as q_{emodel}* Critical t*S.E. of Exp. q_e. Thus in H8 enter = Critical t*S.E. of Exp. q_e

= H7 * H5

m) Enter the following formula in D2 and copy it down to D17. This calculates the upper confidence limits (95%) of the model prediction.

= C2 + CI = C2 + H8

n) Similarly, enter = C2 − CI = C2 − H8 in E2 and copy down to E17. This calculates the lower confidence limits (95%) of the model prediction.

o) The S.E. of the exp. q_e values, R^2 and CI are automatically calculated: 1.407, 0.995 and 3.017, respectively for Langmuir isotherm.

p) Similarly, the S.E. of the exp. q_t values, R^2 and CI are automatically calculated: 3.481, 0.995 and 7.584, respectively for Pseudo-2nd-order kinetics model.

q) Insert initial estimates (e.g. 40 and 2, respectively) of the parameters q_m/q_e and constant K_L/K_2 into cells H1 and H2, respectively for isotherm and kinetics model before running the algorithm.

r) Now execute the SOLVER to calculate and fit the data.

s) Graph Columns C, D and E versus Column A such that they are displayed as continuous lines on the graph as illustrated in Figures 4 and 5. These lines show the fitted lines after running the algorithm, but before running algorithm it may be shown different type of lines. The following section describes manipulations that allow SOLVER to improve the fit.

2.4   Operation of SOLVER and controls

Open the SOLVER function from the Tools menu. The dialogue box showed in Figure 3A appears the SOLVER. If SOLVER is not in this menu it should be installed, and use help from Excel for installation procedure if needed. The above procedure sets up the excel sheet that SOLVER requires in order to fit a data to the experimental data for non-linear function. Simply enter the suitable parameter values in Column H and the function in a form that Excel recognizes in Column C.

Figure 1   The experimental data are entered into Column A and B with all Excel functions into spreadsheet template for non-linear regression of Langmuir Isotherm


Figure 2   The experimental data are entered into Column A and B with all Excel functions into spreadsheet template for non-linear regression of Pseudo-2nd-order kinetics model

A   **B**
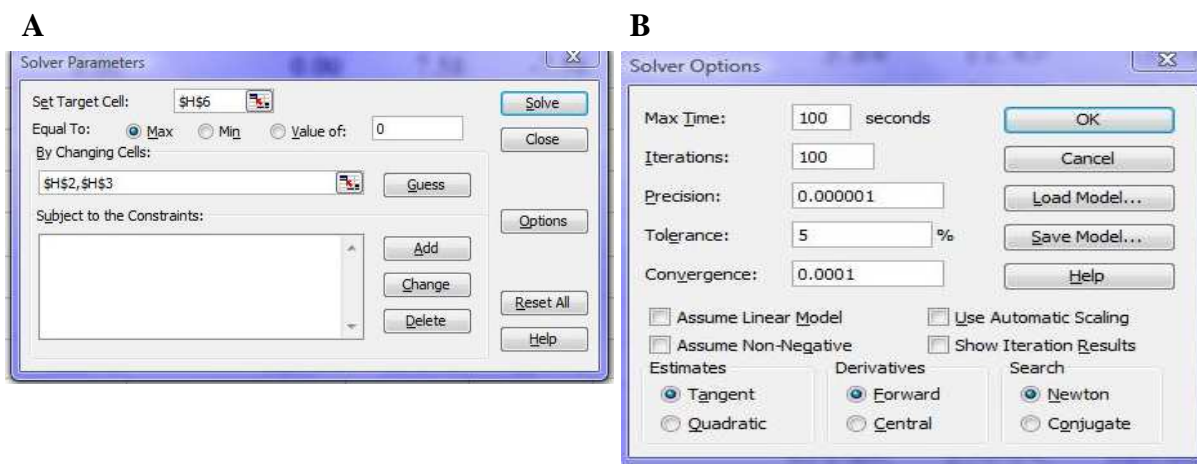
Figure 3   The built-in 'Solver' functions for running the setup algorithm and advance option. **A:** The 'Solver' dialogue box used as an interface between the 'Solver' function and data on the spreadsheet. **B:** The control and fine tune of algorithms using the 'Solver Options' dialogue box
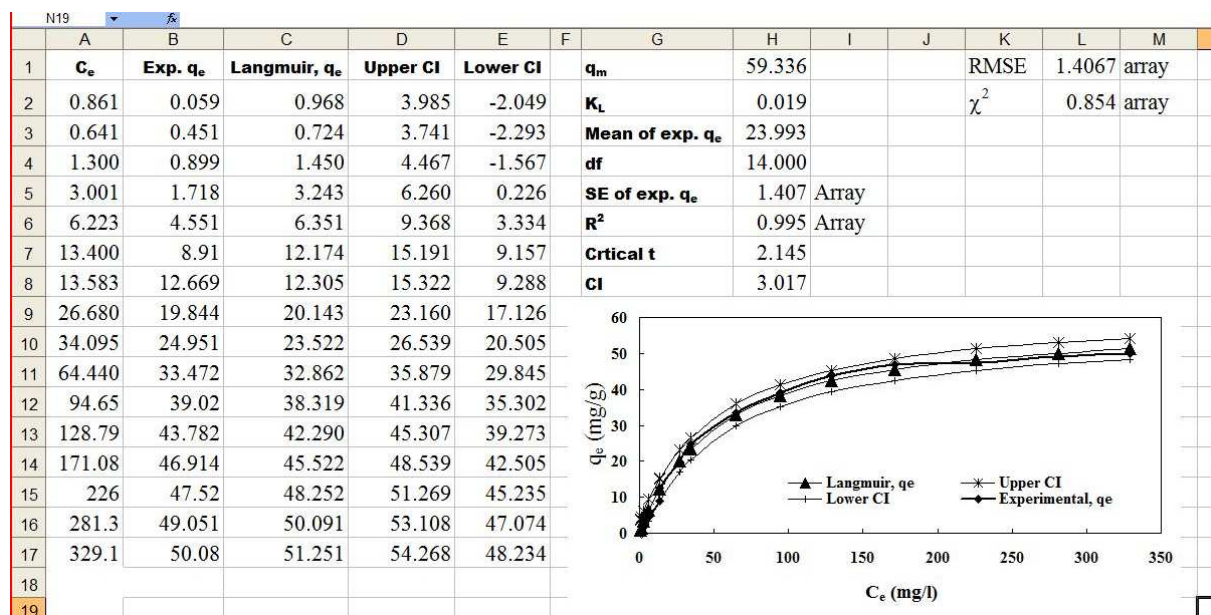
Figure 4   The excel sheet after executed the algorithm for Langmuir isotherm model with predicted parameters and fitted data curve with experimental data curve
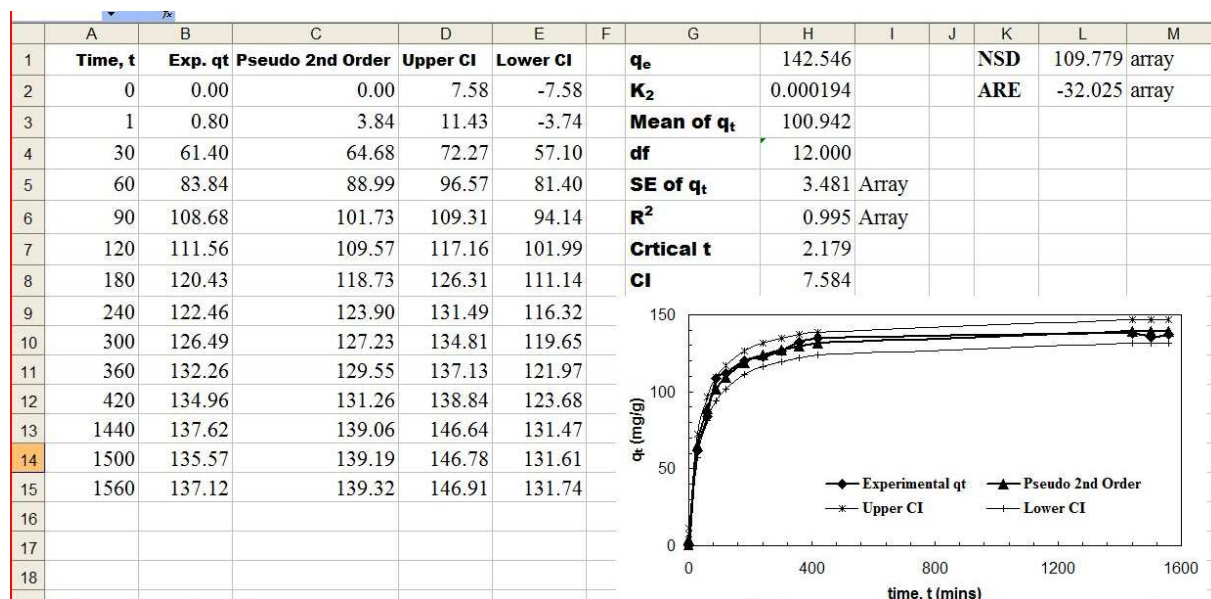
Figure 5   The excel sheet after executed the pseudo-2nd-order kinetics model with predicted parameters and fitted data curve with experimental data curve

After open the SOLVER, set the 'target cell' to H6, 'equal to' max and 'by changing cells' to H2, H3. Now execute 'Solve' in the right corner (Figure 3A) and the value will change. These changes will be displayed on the spreadsheet template (Figures 4 and 5). The optimal values of q_m/q_e and K_L/K_2 are 59.336/142.546 and 0.019/0.00019, respectively. The maximal value of R^2 is 0.995/0.995 for isotherm and kinetics model, respectively. The continuous thick line in Figures 4 and 5 with Δ marker illustrates the best fit and it is

clear that it is an improvement over the fit provided by the initial parameter values. Additionally, the confidence intervals around the fit have been reduced.

The default solver settings can be changed by opening the Solver Options (Figure 3B). Normally, the default setting is appropriate for most situations but that can be changed into required targets. The most relevant to the protocol in this paper are described as below.

Max time: This is the amount of time in seconds that 'Solver' will be allowed to run the iteration process before stopping. The default value is 100 s.

Iterations: It is the number of iterations that 'Solver' will carry out the calculation before stopping. The default value is 100 and it will provide the optimal solution before either of these limits is reached and will present the results.

Precision: It is determined how the calculated values are precise to meet a target or satisfies a lower or upper bound. The default value is 0.000001. The higher the precision, the more time is taken to reach a solution.

Tolerance: This option is appropriate only to problems with integer constraints. The percent value by which the target cell of a solution will fulfill the integer constraints and it can differ from the true optimal value; however, it still be considered acceptable. A lower tolerance tends to slow up the solution process and the default value is set at 5.

Convergence: It tells the 'Solver' when to stop the iterative process. The 'Solver' stops after five iterations, if the calculated value in 'target cell' is less than the number in the 'Convergence box'. The smaller the convergence value, the more time 'Solver' takes to reach a solution and the default value is 0.001.

Assume Linear Model: This analysis is non-linear regression, so leave the box unchecked. It could be checked only if the model is solved in linear.

Use Automatic Scaling: This option can be used for automatic scaling when inputs and outputs have large differences in magnitude. It is recommended that this box keep checked for all 'Solver' models.

Assume Non-Negative: No constraints have been used for all adjustable cells to get a lower limit of 0 for all adjustable cells.

Show Iteration Results: Set to have 'Solver' pause to show the results for every iteration.

Estimates: It determines subsequent estimates of the basic variable values at the outset of each one-dimensional search.

Tangent: It uses linear extrapolation from a tangent vector. The Tangent choice is slower but more accurate.

Quadratic: This option extrapolates the minimum (or maximum) of a quadratic fitted to the function at its current point.

Derivatives: This option denotes the difference used to estimate partial derivatives of the objective and constraint functions in the models.

Forward: The previous iteration is used in conjunction with the current point by this option. It saves the recalculation time for finite differencing, which can account for up to half of the total solution time.

Central: Central difference depends only on the present point and disturbs the decision variables in opposite directions from that point. Although this engrosses more recalculation time, it may provide better result to choose a direction when the derivatives are rapidly changing, and hence fewer total iterations.

Search: It specifies the algorithm used for each iteration to find the direction to search.

Newton: The default choice is Newton that requires more memory but less iteration than does the Conjugate gradient method.

Conjugate: It requires less memory than the Newton method but typically needs more

iteration to reach a particular level of accuracy.

Load Model: It allows loading a previously saved fitted routine with newly data.

Save Model: This option allows the user to save the preferable fitting routine for future use.

3. RESULTS AND VALIDATION OF THE MODELS

The spreadsheet based models were executed with the experimental data of copper(II), lead(II) and cadmium(II) adsorption on garden grass. The parameters of Isotherm and kinetics model from the predictions were compared with linear analysis and MATLAB modelling (procedure details is not provided in this paper) parameters.

3.1 Verification of models data

Some conventional programmes and modelling are designed based on the standard error of the parameters for non-linear regression, but these values are not always considered valuable (Motulsky and Ransnas, 1987). As these errors are neither additive nor symmetrical, and exact confidence limits cannot be estimated by non-linear functions (Motulsky and Ransnas, 1987). This Excel based program is designed with the built-in functions and the coefficient of determination (R^2) is used instead of standard error of the parameters for non-linear regression. It is assumed that an appropriate function is used to describe the experimental data and it is informed that how accurately the function describes or fits the data. The R^2 value is named as the coefficient of determination and its value represents the fraction of the overall variance of the 'predicted model' data that is explained by the 'experimental data'. It is calculated from the sum of the squares of the residuals captured the error between the model prediction and the

experimental data. The goodness of fit of the model prediction to the experimental data were evaluated by R^2 and RMSE and χ^2 for Langmuir model; and NSD and ARE for Pseudo-2nd-Order model (Hossain et al., 2012a; Wang et al., 2004). The R^2 values also calculated from linear regression and MATLAB analysis to judge of the best fit and compared. Normally the sum of the squares of regression computes how far the predicted values differ from the overall mean of actual values, and is equivalent to the sum of the squares, the denominator of Equation (4) for Isotherm and Equation (7) for Kinetics model. After using 'Solver' analysis, the united values of the parameters for Langmuir isotherm and Kinetics model with linear and MATLAB analyses are presented in Tables 1 and 2.

The model analysis process and after analysis with 'Solver' are shown in Figures 1 and 4 respectively. The model fitting statistics of the Langmuir and Kinetics model from Excel Spreadsheet, Linear and MATLAB program were used to explain 'predicted maximum or equilibrium adsorption' with 'experimental adsorption' relationships (Table 1). According to the R^2 values (Table 1), the experimental data for copper(II), lead(II) and cadmium(II) adsorption on garden grass were highly fitted with Langmuir isotherm prediction. It is apparent that the linear analysis showed low fitness with experimental data as R^2 values of 0.382, 0.700 and 0.142 for copper(II), lead(II) and cadmium(II) adsorption on garden grass respectively. Conversely, the Excel Spreadsheet and MATLAB program analysis demonstrated high R^2 with prediction for experimental data for copper(II), lead(II) and cadmium(II) adsorption on garden grass as the values were 0.995 and 0.997 for copper(II), 0.996 and 1.00 for lead(II) and 0.996 and 0.999 for cadmium. It is revealed that both analyses systems predicted similar data which were close to the experimental data. Furthermore, the Excel Spreadsheet and MATLAB program

analysis indicated similar prediction for experimental data for copper(II), lead(II) and cadmium(II) adsorption on garden grass. These two analyses systems predicted the parameters for Langmuir isotherm such as q_m that were similar for the three metals adsorption. The predicted values of q_m from Excel Spreadsheet and MATLAB program analyses were 59.336 and 59.899 mg/g for copper(II), 63.663 and 63.509 mg/g for lead(II), and 42.310 and 41.560 mg/g for cadmium(II) adsorption. On the other hand, linear analysis predicted much lower values for q_m for three metals adsorption. The model constants K_L were predicted at similar values by the two analyses system but different values found by linear analysis (Table 1). A plot of predicted data (Langmuir, q_e) versus experimental data (Exp. q_e) for copper(II) adsorption onto garden grass by excel model is shown in Figure 4. As can be seen in Figure 4, Excel spreadsheet model has similar fit to measured values/experimental data of copper(II) adsorption to MATLAB analysis ($R^2 = 0.995$ compared to $R^2 = 0.997$) (Table 1). Similar R^2 values for lead(II) and cadmium(II) adsorption were predicted by both excel spreadsheet and MATLAB analysis. The error functions RMSE and χ^2 were also calculated and tabulated in Table 1. Surprisingly both errors were predicted or estimated at similar values by excel and MATLAB analysis. The results showed that overall performance of excel model was clearly equivalent to technically advanced MATLAB as shown in Table 1.

The kinetics data for copper(II), lead(II) and cadmium(II) adsorption onto garden grass were also analysed by MS Excel Solver function - spreadsheet, linear and MATLAB analysis. The MS Excel Solver function - spreadsheet process is shown in Figure 2. The analysed data are shown in Figure 5 and tabulated in Table 2. It is noticeable that the predictions of equilibrium adsorption, q_e, kinetics constant, K_2 and coefficient of deter-

mination, R^2 values by excel spreadsheet, linear and MATLAB analysis were similar (Table 2), which implies that all analysis were properly fitted with experimental data. The R^2 values for excel model, linear and MATLAB analysis were 0.995, 0.995 and 0.998 for copper(II), 0.997, 0.998 and 0.998 for lead(II), and 0.996, 0.999 and 0.998 for cadmium(II) adsorption onto garden grass.

Linear analysis was found to be equal validity to the experimental with excel model and MATLAB analysis. However, K_2 values by linear analysis were different with the prediction of other two models while K_2, by excel spreadsheet and MATLAB analyses were similar and almost equal to the experimental data (Table 2). From the above discussion, excel spreadsheet method can be reliable and useful for kinetics analysis.

3.2 Statistical significance of excel modelling

Normally, non-linear regression programs estimate of the standard error of (the) parameters. These values sometimes mislead the predictions and in non-linear functions, additive nor symmetrical errors, and exact confidence intervals cannot be computed (Bowen and Jerman, 1995; Motulsky and Ransnas, 1987). The stated standard errors are based on linearising assumptions and will always underestimate the true uncertainty of any non-linear equation and not proper to use the standard error values in further formal statistical calculations (Brown, 2001; Speers et al., 2003). Asymptotic standard errors of the parameters have been calculated, but a complex and time consuming computer program is needed to evaluate the Hessian matrix (Brown, 2001; Hong et al., 2008). Thus, an approach is adopted in this paper to estimate the standard error of the data around the prediction curve and is calculated by dividing the sum of the squares of the residuals by the degrees of

freedom to get the variance of experimental data. The square root of this value produces the standard error of the residuals and is used to calculate the confidence interval. This confidence interval is a sign of the probability that the true value/experimental data lie within the range specified by the probability formula (Brown, 2001). It commonly uses 95% confidence interval, which means there is a 95% probability that the experimental value lies within the interval. To calculate the confidence interval the Critical t-value must be calculated and it depends on the confidence interval and the degrees of freedom (Brown, 2001; Tramšek and Goršek, 2008). Excel has a built-in function (tinv) which allows calculation of the Critical t-value, thus bypassing the need to look up tables of t values. The formula in cell H7 (Figures 1 and 2) calculates this value for the desired confidence interval and degrees of freedom (Abu−Lail et al., 2012; Hong et al., 2008). Once this value has been calculated, the confidence interval is simply the best fit at all data points. It is found that the MS Excel Solver function - spreadsheet method fulfilled all the statistical measures to predict the real variance of probability of experimental data for both isotherm and kinetics adsorption of metals.

Table 1   Comparison of equilibrium's modelling parameters from MS Excel Solver function - spreadsheet method with the analysed parameters from Linear and MATLAB analyses for Langmuir isotherm

Name of metals adsorption onto grass	Parameters from Excel modelling for Langmuir isotherm model	Parameters from Linear analysis for Langmuir isotherm model	Parameters from MATLAB analysis for Langmuir model
Copper(II)	$q_{m.Exp}$ = 50.89 mg/g $q_{m.Model}$ = 59.336 mg/g K_L = 0.019 R^2 = 0.995 RMSE = 1.407 χ^2 = 0.854	$q_{m.Exp}$ = 50.89 mg/g $q_{m.Model}$ = 9.597 mg/g K_L = 0.019 R^2 = 0.382 - -	$q_{m.Exp}$ = 50.89 mg/g $q_{m.Model}$ = 59.899 mg/g K_L = 0.0188 R^2 = 0.997 RMSE = 1.426 χ^2 = 0.768
Lead(II)	$q_{m.Exp}$ = 56.302 mg/g $q_{m.Model}$ = 63.663 mg/g K_L = 0.027 R^2 = 0.999 RMSE = 0.833 χ^2 = 13.607	$q_{m.Exp}$ = 56.302 mg/g $q_{m.Model}$ = 5.659 mg/g K_L = 2.539 R^2 = 0.700 - -	$q_{m.Exp}$ = 56.302 mg/g $q_{m.Model}$ =63.509 mg/g K_L = 0.0198 R^2 =1.00 RMSE = 0.789 χ^2 = 12.908
Cadmium(II)	$q_{m.Exp}$ = 37.64 mg/g $q_{m.Model}$ = 42.310 mg/g K_L = 0.020 R^2 = 0.996 RMSE = 1.475 χ^2 = 1.029	$q_{m.Exp}$ = 37.64 mg/g $q_{m.Model}$ = 1.199 mg/g K_L = 0.167 R^2 = 0.142 - -	$q_{m.Exp}$ = 37.64 mg/g $q_{m.Model}$ = 41.560 mg/g K_L = 0.0199 R^2 = 0.999 RMSE = 1.365 χ^2 = 1.015

Table 2 Comparison of kinetic's modelling parameters from MS Excel Solver function - spreadsheet method with the analysed parameters from Linear and MATLAB analyses for Pseudo-2nd-Order model

Name of metals adsorption onto grass	Parameters from Excel modelling for Pseudo-2nd-Order model	Parameters from Linear analysis for Pseudo-2nd-Order model	Parameters from MATLAB analysis for Pseudo-2nd-Order model
Copper(II)	$q_{e.exp}$ = 134.96 mg/g	$q_{e.exp}$ = 134.96 mg/g	$q_{e.exp}$ =134.96 mg/g
	$q_{e.model}$ =142.540 mg/g	$q_{e.model}$ = 140.845 mg/g	$q_{e.model}$ = 142.550 mg/g
	K_2 = 0.000194	K_2 = 0.00016	K_2 = 0.000123
	R^2 = 0.995	R^2 = 0.995	R^2 = 0.998
	NSD = 109.810	-	NSD = 98.055
	ARE = -32.034	-	ARE = -31.056
Lead(II)	$q_{e.exp}$ = 4.8036 mg/g	$q_{e.exp}$ = 4.8036 mg/g	$q_{e.exp}$ = 4.8036 mg/g
	$q_{e.model}$ = 4.851 mg/g	$q_{e.model}$ = 4.733 mg/g	$q_{e.model}$ = 4.863 mg/g
	K_2 = 0.286	K_2 = 2.706	K_2 = 0.289
	R^2 = 0.997	R^2 = 0.998	R^2 = 0.998
	NSD = 2.112	-	NSD = 2.567
	ARE = -0.052	-	ARE = -0.053
Cadmium(II)	$q_{e.exp}$ = 2.900 mg/g	$q_{e.exp}$ = 2.900 mg/g	$q_{e.exp}$ = 2.900 mg/g
	$q_{e.model}$ = 2.962 mg/g	$q_{e.model}$ = 2.921 mg/g	$q_{e.model}$ = 2.986 mg/g
	K_2 = 1.089	K_2 = 4.825	K_2 = 1.289
	R^2 = 0.996	R^2 = 0.999	R^2 = 0.998
	NSD = 2.547	-	NSD = 2.897
	ARE = -0.068	-	ARE = -0.078

3.3 Advantages and limitations

The above discussion indicated that although this analysis protocol could be seen as robust and reliable method for isotherm and kinetics adsorption modelling as compared to other programs, a few points should be taken in mind before formulating the models. Firstly, the SOLVER will take longer time while the number of parameters in the function is larger. Furthermore, the more constraints or increasing tolerance or precision in the function, the longer SOLVER will take. Secondly, sensible initial parameters are important and an inappropriate parameter can lead the iteration process in the wrong direction and thus wrong solution.

4. CONCLUSION

Isotherm and kinetics adsorption of metals are important models to predict and explicit the inert characters of biosorbents for researchers. In this context, non-linear modelling is a powerful technique for standardizing the experimental data. The invention of computers has made the modelling of data easier, quick and reliable for the users. This paper described the method suitable for users with basic

knowledge of excel and do not require a vast understanding of the mathematics behind the processes involved in this modelling. It is important, however, is that the users understand enough about the data to be fit to use the correct type of analysis, and to judge goodness of fit from calculated estimates. Most of the researchers might have this knowledge to execute the program and feel freed from using technically advanced and expensive computer software like MATLAB. This MS Excel Solver function-spreadsheet method showed robustness of well-fitting with experimental data which has a high degree of fitness (high R^2 values). The predicted values of parameters for isotherm and kinetics are comparable with the analysis by advanced MATLAB programme. Thus, it is reasonably helpful and user friendly for researchers who are not advanced in computer programming.

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