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ORIGINAL PAPER

A critical assessment of the use of a surface reaction rate equation to correlate biosorption kinetics

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Abstract A critical assessment of the use of a variable-order, power-law type surface reaction rate equation to correlate biosorption kinetics is presented. The general *n*th order rate equation with three adjustable parameters was fit to the kinetic data of lead uptake by inactivated cells of *Rhodotorula glutinis* using a genetic algorithm search method. The uptake process was fast, with apparent equilibrium reached in approximately 30 min. According to the Akaike information criterion test, the three-parameter *n*th order equation was superior to the much used pseudo second order equation with two fitting parameters. However, the strong fit of the former equation resulted in unrealistic parameter estimates. Parametric sensitivity analysis indicated that the available kinetic data with only limited information content did not allow simultaneous identification of three unknown parameters. As a result, the three-parameter *n*th order equation was found to be over-parameterized with highly correlated parameters. It was, however, possible to retrieve meaningful parameter estimates from the kinetic data when the number of fitting parameters was reduced from 3 to 2.

Keywords Akaike information criterion · Genetic algorithm · Parameter estimation · Sensitivity analysis

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Introduction

Biosorption studies with nonliving materials of biological origin such as dead or inactivated microbial biomass have shown effective uptake for toxic metal ions (Park et al. 2010). The metal sequestration mechanism of microbial biomass is attributed to the presence of a myriad of functional groups or ligands on the biomass surface which are able to interact with metal cations and anions (Naja and Volesky 2011). Most inactivated microbial cells exhibit surface binding phenomena of low specificity. This facilitates uptake of a broad range of toxic metal ions. Attempts have been made to exploit the biosorption technology to remove toxic metals at their source on a commercial scale, albeit with limited success (Volesky and Naja 2007).

Batch techniques are commonly used to characterize metal uptake by microbial cells. Experimental equilibrium and kinetic results are conveniently generated from well-agitated batch systems in the form of discrete data points. Mathematical models are used to convert such data to a form useful for process design and optimization. A number of theoretical and empirical models are available in the literature to correlate measured biosorption data (Haerifar and Azizian 2013; Liu and Shen 2008a; Qiu et al. 2009). For example, to correlate kinetic data from batch systems, both mass transfer and surface reaction-based models may be used. Generally, surface reaction models are preferred by most practitioners because the models are available in the form of simple equations, many of which can be linearized to allow the estimation parameters by linear regression. Notable examples of such surface reaction models are the so-called pseudo first order and second order equations. Examples of the use of these two equations abound in the biosorption literature (Lang et al. 2013; Zamani et al. 2013).

Although popular, these simplistic pseudo reaction equations have recently encountered criticisms on two fronts. First, using linearized forms of these equations for parameter estimation is fraught with statistical deficiencies. As pointed out by McCuen and Surbeck (2008), a widely used linearized form of the pseudo second order equation suffers from the problem of ratio regression analysis, i.e., the time variable t appears on both sides of the linearized equation, resulting in highly inflated goodness-of-fit statistics.

Second, some investigators have argued that it makes no modeling sense to restrict the reaction order to either one or two. In accordance with the convention of chemical reaction kinetics, the reaction order may be a noninteger and should be treated as a fitting parameter in correlating batch kinetic data (Liu and Shen 2008b; Liu and Wang 2008; Morais et al. 2007; Özer 2007). Accordingly, they advocate using a general nth order equation for kinetic modeling rather than the simplistic pseudo first order and second order equations. Note that an even more advanced form of the nth order equation incorporating the concept of fractal kinetics has been proposed by Brouers and Sotolongo-Costa (2006). It seems that an ever increasing assortment of surface reaction models is being promulgated today. With this development, more sophisticated and presumably more accurate surface reaction models are now available for correlating biosorption kinetic data. A description of the aforementioned surface reaction models has been presented in a review by Plazinski et al. (2009). From a practical standpoint, it is important to select an accurate kinetic equation which is often embedded within a dynamic process model (e.g., batch and fixed bed models) for design or optimization studies. The performance of such dynamic process models would be impaired if an imprecise kinetic equation is used.

With the reaction order n being a fitting parameter, the nth order equation with three adjustable parameters is expected to exhibit higher correlative power relative to the pseudo first order and second order equations with two fitting parameters. However, it is not clear whether any improvement in fit is significant enough to justify inclusion of an additional adjustable parameter. To explore this question, in the present study, we compare the three-parameter nth order equation with the two-parameter pseudo second order equation using the Akaike information criterion (AIC) statistical test. The AIC is a model discrimination technique that considers both model accuracy and complexity in an objective manner. In addition, we conduct parametric sensitivity analysis to assess the identifiability of the three parameters of the nth order rate equation. This contribution provides, for the first time, an in-depth analysis of the strengths and weaknesses of the nth order rate equation in correlating biosorption kinetic data.

Batch kinetic data used in this study were obtained from lead uptake experiments with inactivated yeast cells (*Rhodotorula glutinis*) as the biosorbent. *R. glutinis* has attracted some attention in recent years as a promising metal biosorbent (Bai et al. 2010; Cho and Kim 2003; Cho et al. 2011a, b; Suazo-Madrid et al. 2011).

Surface reaction rate equations

A general nth order rate equation based on surface reaction mechanism and governed by a single rate coefficient takes on the following form:

$$\frac{\mathrm{d}q}{\mathrm{d}t} = k_n(q_\mathrm{e} - q)^n \qquad (1)$$

where q is the biosorbent phase concentration at time t, k_n is the nth order rate coefficient, q_e is the equilibrium biosorbent phase concentration, and n is the reaction order which may be a noninteger. The solution to Eq. (1) for the initial condition of $q = 0$ at $t = 0$ can be written as follows (Özer 2007):

$$q = q_\mathrm{e} - \left(q_\mathrm{e}^{(1-n)} + k_n(n-1)t\right)^{1/(1-n)} \qquad (2)$$

Equation (2) has three adjustable parameters, k_n, n ($n \neq 1$), and q_e, which cannot be estimated by using standard linear regression.

When $n = 2$, Eq. (1) reduces to the much used pseudo second order equation:

$$\frac{\mathrm{d}q}{\mathrm{d}t} = k_2(q_\mathrm{e} - q)^2 \qquad (3)$$

where k_2 is the pseudo second order rate coefficient and all other variables are as defined above. Equation (3) has the following analytical solution:

$$q = \frac{q_\mathrm{e}^2 k_2 t}{1 + q_\mathrm{e} k_2 t} \qquad (4)$$

Of course, Eq. (4) may be recovered from Eq. (2) by setting $n = 2$. According to Kumar (2006), Eq. (4) was first proposed by Blanchard et al. (1984), albeit in a different mathematical form. Equation (4) has two adjustable parameters, q_e and k_2, which may be estimated from the following widely used linearized form (Ho 2006):

$$\frac{t}{q} = \frac{1}{k_2 q_\mathrm{e}^2} + \frac{1}{q_\mathrm{e}} t \qquad (5)$$

As noted above, the validity of Eq. (5) for the estimation of q_e and k_2 by linear regression has been called into question because t appears on both sides of the equal sign, resulting in grossly inflated goodness-of-fit statistics and erroneous parameter estimates. The speciousness of Eq. (5) for parameter estimation has been discussed at some length by McCuen and Surbeck (2008).

Materials and methods

Microorganism and biosorbent preparation

The organism used in this study was *R. glutinis* KCTC (Korean Collection for Type Cultures) 7989. The growth medium consisted of 10 g/L of glucose, 3.0 g/L of yeast extract, 3.0 g/L of malt extract, and 5.0 g/L of peptone. The cells were grown in 500-mL Erlenmeyer flasks containing 100 mL of the growth medium. Cultures were incubated at 25 °C on an orbital shaker at 150 rpm. At the end of exponential growth phase, i.e., after 30 h of incubation, the biomass was harvested by centrifugation at 10,000 *g* for 10 min. After washing twice with deionized water, the harvested cells were dried in an oven at 70 °C for 24 h which led to the formation of clumps. The clumps were broken up by grinding using a mortar and pestle to obtain biomass particles for use in the lead uptake experiments described below.

Lead uptake experiments

The lead solutions used were prepared by dilution from a 1,000 mg/L stock solution. All experiments were performed at 25 °C and pH 6 using a biosorbent dosage of 2 g/L and three different initial lead concentrations (50, 200, and 300 mg/L). Both metal-free and biomass-free control solutions were also prepared. During the experiments, the mixture was shaken at 150 rpm in an orbital shaker, and at selected time intervals, flasks were removed from the shaker for centrifugation and analysis of solution phase lead concentration using an atomic absorption spectrophotometer (Varian AA-220FS, USA). The uptake on the biosorbent was calculated by material balance. Each kinetic experiment was repeated five times. The experimental work reported here was conducted in 2010 in Seoul, Korea.

Fitting of rate equations and goodness-of-fit indicators

A genetic algorithm optimization method implemented in Microsoft Excel was used for parameter estimation. The genetic algorithm is a type of stochastic global optimization method based on an iterative procedure that mimics the process of biological evolution. While gradient-based nonlinear regression generally requires initial parameter estimates that lie in the vicinity of the optimal values in order to avoid convergence difficulties, the genetic algorithm is able to optimize a nonlinear model within search ranges that vary over several orders of magnitude, so good initial estimates are not required. The genetic algorithm optimization method has been successfully applied to a variety of parameter estimation problems in biosorption research (Chu et al. 2011a, b).

To conduct parameter identification using the genetic algorithm, optimal parameters of a particular rate equation with respect to a given set of data were determined by minimizing the sum of the squared errors (SSE) between measured and calculated values. The parameter identification process for each case was repeated several times. The final solution consistently converged to the same parameter estimates. In this study, two statistical indicators, the coefficient of determination (R^2) and the Akaike information criterion (AIC), were used to assess the goodness of fit of a rate equation to measured data. These two indicators are defined in the next section.

Results and discussion

Correlation of biosorption kinetics

Figure 1 depicts the kinetic profiles of lead uptake by *R. glutinis* cells for three different initial concentrations (C_i = 50, 200, and 300 mg/L). As shown, lead uptake in each case was fast, with apparent equilibrium reached in approximately 30 min. As expected, at a fixed biosorbent

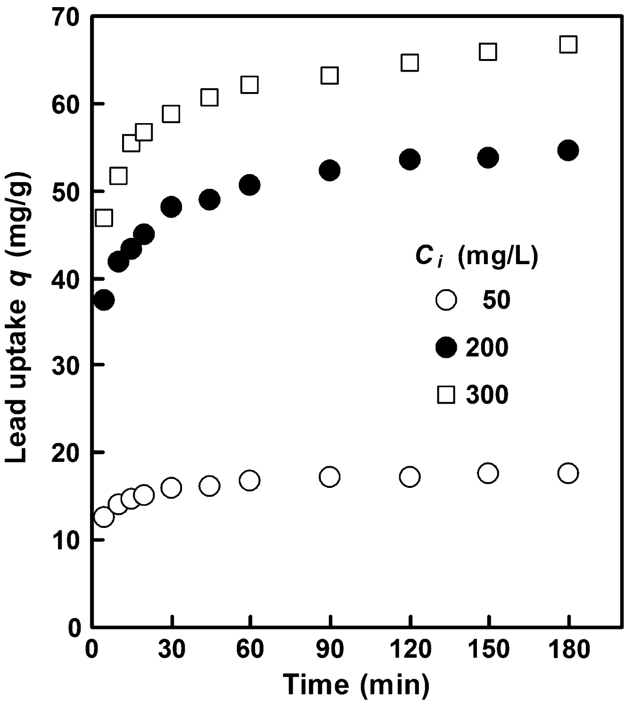

Fig. 1 Experimental lead uptake by *R. glutinis* biomass showing effect of initial metal concentration (C_i) on the uptake kinetics

Table 1 Parameter estimation in the pseudo second order and three-parameter *n*th order equations

C_i (mg/L)	Pseudo second order equation		Three-parameter *n*th order equation		
	k_2 (g/mg min)	q_e (mg/g)	k_n $[(\text{mg/g})^{1-n}/\text{min}]$	n	q_e (mg/g)
50	0.0244	17.42	7.6E−5	4.23	20.30
200	0.0069	53.40	3.2E−11	6.74	74.85
300	0.0066	65.05	9.6E−8	4.81	78.75

dosage of 2 g/L, the final equilibrium uptake value at large times increased with an increase in C_i. For the $C_i = 300$ mg/L data set, the biosorbent achieved an equilibrium uptake value of about 65 mg/g. A previous equilibrium isotherm study reported that under similar experimental conditions, the Langmuir maximum sorption capacity of *R. glutinis* for lead was 73.5 mg/g (Cho and Kim 2003).

The two-parameter pseudo second order and three-parameter *n*th order equations were fit to the Fig. 1 data sets. Listed in Table 1 are the optimal parameter estimates from the genetic algorithm search method. For the pseudo second order equation, the optimal rate coefficient k_2 decreased with increasing C_i. The optimal equilibrium parameter q_e, as expected, increased with an increase in C_i and corresponded well to the experimental equilibrium value at large times for each data set (see Fig. 1). As for the three-parameter *n*th order equation, Table 1 shows that the optimal rate coefficient k_n for $C_i = 50$ mg/L was very small compared to the optimal k_2 value for the same C_i. k_n decreased significantly when C_i was increased from 50 to 200 mg/L. However, a further increase in C_i to 300 mg/L caused a significant increase in this parameter. The optimal reaction order n also did not show a consistent trend. When C_i was changed from 50 to 200 mg/L, n increased from 4.23 to 6.74. It then decreased to 4.81 when C_i was increased further to 300 mg/L. Furthermore, the optimal equilibrium parameter q_e was noticeably larger than the corresponding experimental equilibrium value for each data set at large times, contradicting the definition of q_e.

To compare the fits of the two models in visual terms, Fig. 2 shows a parity plot for the $C_i = 200$ mg/L data set. For the pseudo second order fit denoted by open circles, it is seen that calculated values of $q > 50$ mg/g agreed well with the observed q values, as indicated by their closeness to the 1:1 line. By contrast, except for one data point calculated values of $q < 50$ mg/g demonstrated noticeable discrepancy with the corresponding observed q values. This is especially obvious for the first data point, showing a deviation of more than 10 %. This suggests that the pseudo second order equation with the single rate coefficient k_2 was unable to track well the shape of the ascending part of the kinetic profile at small times, i.e., small q values. At large times the pseudo second order equation effectively reduces to $q = q_e$ $[q_e k_2 t \gg 1$ in the denominator of Eq. (4)], it is thus not surprising that Eq. (4) can fit accurately the plateau part of the kinetic profile, i.e., large q values.

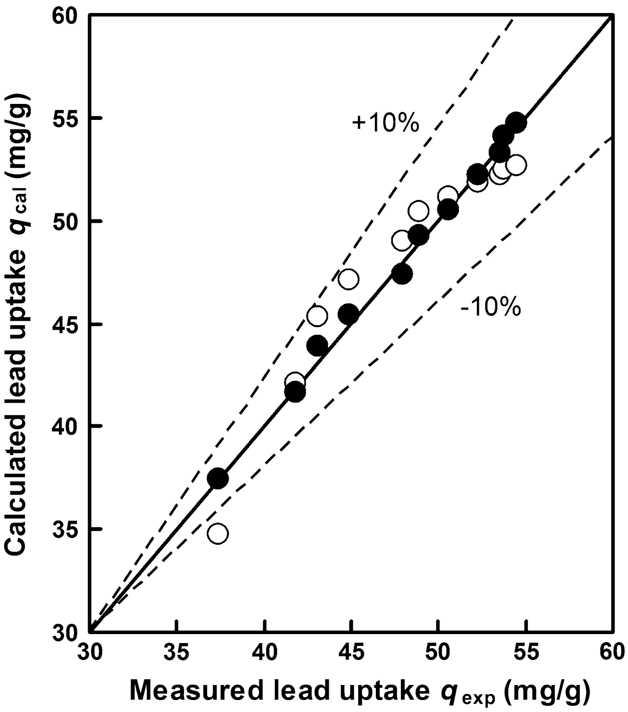

Fig. 2 Comparison between the uptake data for $C_i = 200$ mg/L and q calculated from the pseudo second order equation (*open circles*) and three-parameter *n*th order equation (*filled circles*) with the parameter estimates listed in Table 1

For the three-parameter *n*th order fit, Fig. 2 shows that all calculated q values, denoted by filled circles, lie on or very close to the 1:1 line, indicating excellent agreement with the observed q values. It is evident that the *n*th order equation with three adjustable parameters possesses very high correlative power, enabling it to track the entire data range accurately. Model parameters extracted from bench-scale experiments may be used to optimize investigations involving pilot-scale biosorption systems or design full-scale systems. Using suboptimal parameters in these tasks would result in unacceptable levels of imprecision and uncertainty.

Indicators of model fits

To compare the fits of the two rate equations in quantitative terms, we use the following coefficient of determination (R^2) as an indicator of model fit (Anderson-Sprecher 1994):

Table 2 Comparison of R^2 and $\mathrm{AIC_c}$ statistics for the pseudo second order equation and three-parameter *n*th order equation

C_i (mg/L)	R^2		$\mathrm{AIC_c}$	
	Pseudo second order equation	Three-parameter *n*th order equation	Pseudo second order equation	Three-parameter *n*th order equation
50	0.944	0.997	−12.1	−40.7
200	0.914	0.995	19.3	−7.4
300	0.935	0.997	18.4	−8.9

$$R^2 = 1 - \frac{\sum_{j=1}^{m}\left(q_{\mathrm{exp},j} - q_{\mathrm{cal},j}\right)^2}{\sum_{j=1}^{m}\left(q_{\mathrm{exp},j} - \bar{q}_{\mathrm{exp}}\right)^2} \tag{6}$$

where j is an index, m is the number of observations, $q_{\mathrm{cal},j}$ is the model-calculated q value for observation j, $\bar{q}_{\mathrm{exp}}$ is the mean of measured q values, and $q_{\mathrm{exp},j}$ is the measured q value for observation j. An R^2 of 1 indicates a perfect fit to the data. The two surface reaction equations may thus be ranked on the basis of R^2 statistics, with the one having the highest R^2 being the best.

R^2 statistics computed for the three Fig. 1 data sets are shown in Table 2. Discernible differences exist between the R^2 scores of the two surface reaction models. The three-parameter *n*th order equation with R^2 values >0.99 for all three data sets consistently outperformed the pseudo second order equation with R^2 scores ranging from 0.914 to 0.944. There is no doubt that the three-parameter *n*th order equation is a clear winner in fitting the Fig. 1 kinetic data, as indicated by the parity plot of Fig. 2 and the R^2 statistics of Table 2. However, it should be borne in mind that a model will always improve fit to some degree by adding more adjustable parameters. Consequently, the three-parameter *n*th order equation has an unfair advantage over the two-parameter pseudo second order equation. Comparing models with different numbers of adjustable parameters on the basis of goodness-of-fit statistics alone is therefore a naïve approach.

Several statistical tests that address the trade-off between gain in fit and addition of parameters have been developed in a branch of statistics called model selection (Burnham and Anderson 2002). A commonly implemented test is the corrected Akaike information criterion ($\mathrm{AIC_c}$) which can be written as follows:

$$\mathrm{AIC_c} = m \ln\left(\frac{\mathrm{SSE}}{m}\right) + 2(w+1)\left(1 + \frac{w+2}{m-w-2}\right) \tag{7}$$

where SSE is the sum of the squared errors between measured and calculated q values, m is the number of data points, and w is the number of adjustable parameters. Note that the first term on the right in Eq. (7) has the units of q^2, while the second term is dimensionless (Motulsky and Christopoulos 2004). Because the $\mathrm{AIC_c}$ value for a single model can be manipulated by changing the units of q, and hence, SSE, using Eq. (7) to compute $\mathrm{AIC_c}$ for a set of candidate models should be based on consistent SSE units. The $\mathrm{AIC_c}$ is used for model discrimination when the sample size is small, i.e., when $m/w < 40$ (Burnham and Anderson 2002). Bolster and Hornberger (2007) recommend $m - w \geq 5$ to ensure meaningful model comparison. Practitioners in sorption research have recently employed the $\mathrm{AIC_c}$ tool as a basis for model comparison (Chu et al. 2011b; Pipíška et al. 2010; Praus and Turicová 2007; Usunoff et al. 2009).

In Eq. (7), the first term measures fit, while the second term penalizes complex models, i.e., models with more adjustable parameters. Given a data set, multiple models with different numbers of fitting parameters may be ranked according to their $\mathrm{AIC_c}$, with the one producing the lowest value being the best. The two surface reaction models are ranked according to $\mathrm{AIC_c}$ statistics computed from Eq. (7) for the three Fig. 1 data sets, as shown in Table 2. Given the data sets, the $\mathrm{AIC_c}$ test suggests that the three-parameter *n*th order equation having the lowest scores is clearly the best model.

An alternative $\mathrm{AIC_c}$-based indicator for comparing candidate models is the difference in $\mathrm{AIC_c}$ values, as follows:

$$\Delta\mathrm{AIC}_{\mathrm{c},j} = \mathrm{AIC}_{\mathrm{c},j} - \mathrm{AIC}_{\mathrm{c,min}} \tag{8}$$

where $\Delta\mathrm{AIC}_{\mathrm{c},j}$ is the difference between the $\mathrm{AIC_c}$ value for model j ($\mathrm{AIC}_{\mathrm{c},j}$) and the smallest $\mathrm{AIC_c}$ value among all candidate models ($\mathrm{AIC}_{\mathrm{c,min}}$). Note that Eq. (8) removes the effects of SSE units on the $\mathrm{AIC_c}$ formula [Eq. (7)]. As a rough rule of thumb (Burnham and Anderson 2002), if the absolute value of $\Delta\mathrm{AIC}_{\mathrm{c},j}$ is >10, model j receives no support from the data and is deemed inferior to the model with the smallest $\mathrm{AIC_c}$. If $\Delta\mathrm{AIC}_{\mathrm{c},j} \leq 2$, there is no evidence from the data to indicate that model j is inferior to the model with the smallest $\mathrm{AIC_c}$. If $3 \leq \Delta\mathrm{AIC}_{\mathrm{c},j} \leq 7$, model j receives less support from the data relative to the model with the smallest $\mathrm{AIC_c}$. Letting the pseudo second order equation be model j and the *n*th order equation the model with the smallest $\mathrm{AIC_c}$, $\Delta\mathrm{AIC}_{\mathrm{c},j}$ values computed for the $C_\mathrm{i} = 50$, 200, and 300 mg/L data sets are, respectively, 28.6, 26.7, and 27.3. It is immediately apparent that these values are bigger than 10. Consequently, it can be concluded that there is overwhelming evidence in the data to suggest that the three-parameter *n*th order equation is superior to the pseudo second order equation.

While the AIC$_c$ test endorses the use of the three-parameter *n*th order equation to correlate the Fig. 1 data, the optimal parameter estimates, as shown in Table 1, are somewhat tricky to interpret. As previously mentioned, the k_n estimates were exceedingly small compared to the k_2 estimates and both the k_n and n values exhibited erratic trends with increasing C_i. More importantly, the q_e estimates were noticeably larger than the corresponding observed equilibrium values at large times. Notwithstanding the fact that it is possible to obtain unique estimates of k_n, n, and q_e using the genetic algorithm search method, all these incongruities point to the possibility that the three fitting parameters are highly correlated.

Parametric sensitivity analysis

A parametric sensitivity analysis can provide useful information about the identifiability of the three fitting parameters of the *n*th order equation. Many of the methods available for conducting sensitivity analyses have been summarized by Saltelli et al. (2008). Here, we use a 'local' sensitivity test based on partial differentiation of the *n*th order equation. The sensitivity coefficient for a particular parameter is obtained from the partial derivative of the *n*th order equation with respect to the parameter, as follows:

$$\frac{\partial q}{\partial q_e} = 1 - q_e^{-n}\left(q_e^{(1-n)} + k_n(n-1)t\right)^{n/(1-n)} \quad (9)$$

$$\frac{\partial q}{\partial k_n} = t\left(q_e^{(1-n)} + k_n(n-1)t\right)^{n/(1-n)} \quad (10)$$

$$\frac{\partial q}{\partial n} = -\exp\left[\frac{\ln\left(q_e^{(1-n)} + k_n(n-1)t\right)}{1-n}\right] \times \left[\frac{\ln\left(q_e^{(1-n)} + k_n(n-1)t\right)}{(1-n)^2} + \frac{k_n t - q_e^{(1-n)}\ln q_e}{(1-n)\left(q_e^{(1-n)} + k_n(n-1)t\right)}\right] \quad (11)$$

To remove the effects of units and facilitate comparison, the partial derivative is multiplied by the ratio of the parameter value (p) to the observed maximum q value ($q_{\max}$) for a given data set to obtain the following dimensionless sensitivity coefficient (S_p):

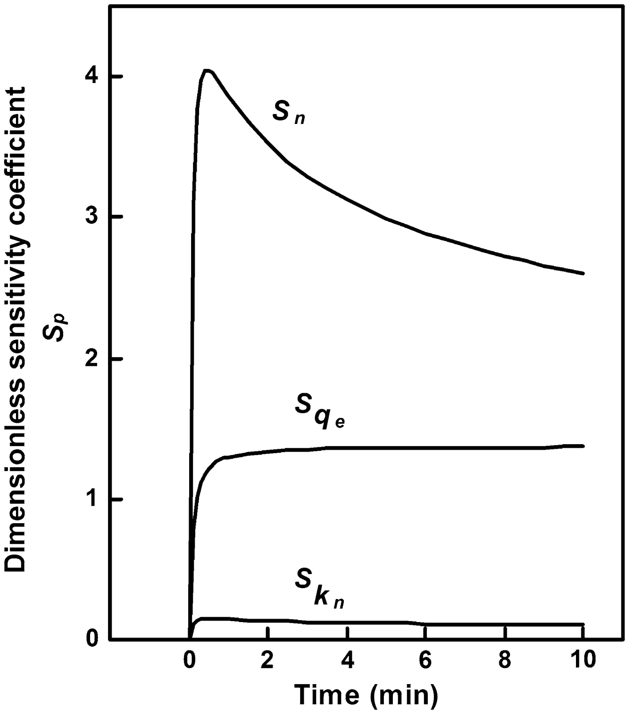

Fig. 3 Dimensionless sensitivity coefficient profiles calculated for the three-parameter *n*th order equation with the parameter estimates for $C_i = 200$ mg/L given in Table 1

$$S_p = \left(\frac{p}{q_{\max}}\right)\left(\frac{\partial q}{\partial p}\right) \quad (12)$$

In the sensitivity analysis presented here, the $C_i = 200$ mg/L data set is used as an example. Using the fitted values of the three parameters (Table 1) and taking the final data point measured at 180 min as $q_{\max}$, the dimensionless sensitivity coefficient is plotted as a function of time for each parameter to form a sensitivity curve, as shown in Fig. 3. It can be seen that the decreasing order of the maximum dimensionless sensitivity values of the three parameters is as follows: $S_n > S_{q_e} > S_{k_n}$. Also, both S_n and S_{k_n} reached their maximum values within the first few minutes. Generally, the likelihood for a parameter to be identified is directly proportional to the magnitude of its dimensionless sensitivity coefficient. Consequently, the numerical dominance of S_n over S_{k_n} practically eliminates the possibility of identifying k_n from the data. Additionally, the sensitivity equations for k_n and q_e are nearly proportional over most of the kinetic profile, resulting in parameter estimations that are highly correlated.

For the purpose of comparison, the dimensionless sensitivity curves for the two fitting parameters of the pseudo

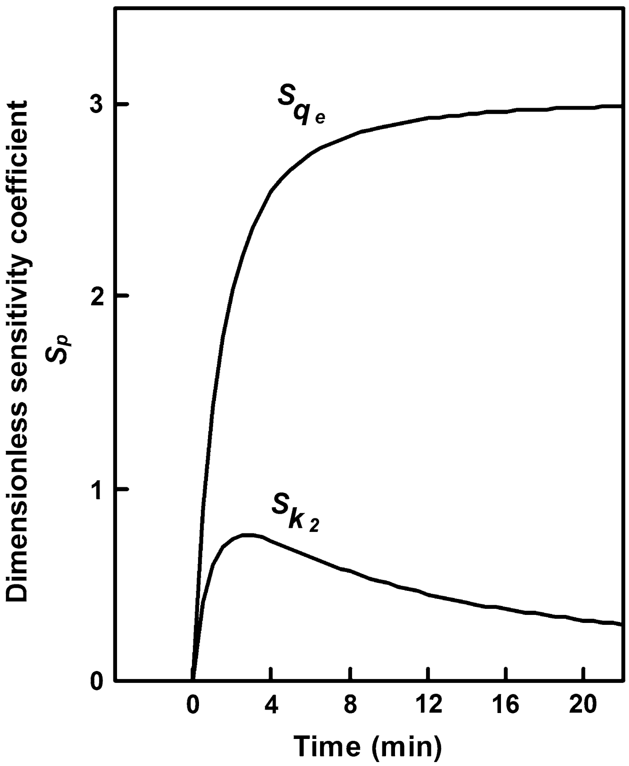

Fig. 4 Dimensionless sensitivity coefficient profiles calculated for the pseudo second order equation with the parameter estimates for $C_i = 200$ mg/L given in Table 1

second order equation are plotted in Fig. 4, using the following sensitivity equations:

$$S_{q_e} = \left(\frac{q_e}{q_{\max}}\right)\left(\frac{\partial q}{\partial q_e}\right) = \left(\frac{q_e}{q_{\max}}\right)\left(\frac{k_2 q_e t(2 + k_2 q_e t)}{(1 + k_2 q_e t)^2}\right) \tag{13}$$

$$S_{k_2} = \left(\frac{k_2}{q_{\max}}\right)\left(\frac{\partial q}{\partial k_2}\right) = \left(\frac{k_2}{q_{\max}}\right)\left(\frac{q_e^2 t}{(1 + k_2 q_e t)^2}\right) \tag{14}$$

From Fig. 4, it is seen that the effect of k_2 was transitory in nature, exerting its influence on the model output in the first few minutes and becoming less influential as equilibrium was approached. In contrast, the sensitivity equation for q_e increased rapidly within the first few minutes and thereafter tended to a maximum asymptotically. These trends are consistent with the structure of the pseudo second order equation. Although the two dimensionless sensitivity coefficients are quite different in magnitude, they are not multiples of one another. This means that the data set can constrain the parameter space created by the two fitting parameters of the pseudo second order equation, allowing unique and accurate estimates of q_e and k_2 to be retrieved from the data.

Table 3 Parameter estimation in the two-parameter *n*th order equation

C_i (mg/L)	Fitted parameters		Fixed parameter		
	k_n [(mg/g)$^{1-n}$/min]	n	q_e (mg/g)	R^2	AIC$_c$
50	0.0118	2.35	17.65	0.967	−17.8
200	0.0016	2.45	54.48	0.948	13.8
300	0.0012	2.49	66.64	0.968	10.5

Identification of unique model parameters

Although the much better fit of the three-parameter *n*th order equation relative to the pseudo second order equation is well supported by the AIC$_c$ test, it is clear that the significant improvement in fit masks the reality that the three-parameter *n*th order equation is overparameterized, making simultaneous identification of its three parameters problematic. An obvious solution to overparameterization is to reduce the number of adjustable parameters. Of the three parameters in the *n*th order equation, there is prior information in q_e which by definition is the equilibrium uptake value at large values of time. It is thus possible to fix the q_e value by assigning the observed value of uptake measured at the end of the kinetic experiments to it, thereby reducing the number of unknown parameters from three to two. Following this approach, the *n*th order equation with two unknown parameters was fit to the Fig. 1 data sets using the genetic algorithm and the converged values of k_n and n are given in Table 3. Listed also in Table 3 are the assigned values of q_e and associated R^2 and AIC$_c$ statistics.

Comparing the R^2 and AIC$_c$ scores for the two-parameter pseudo second order, three-parameter *n*th order, and two-parameter *n*th order equations (Tables 2, 3) indicates that, for the given data, the three-parameter *n*th order equation is the best model, outperforming the other two models. The values of $\Delta\text{AIC}_{c,j}$ calculated for the pseudo second order and two-parameter *n*th order equations ranged from about 6–8. Since these values are <10, both models with the same number of parameters are well supported by the data and there is not enough evidence to confirm that

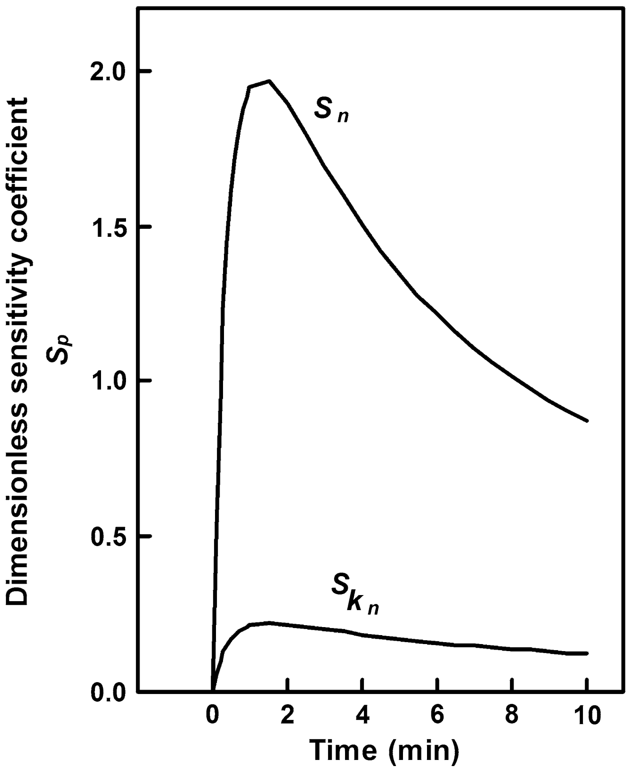

Fig. 5 Dimensionless sensitivity coefficient profiles calculated for the two-parameter *n*th order equation with the parameter estimates for $C_i = 200$ mg/L given in Table 3

one model is definitely better than the other. On the other hand, the values of $\Delta \mathrm{AIC}_{c,j}$ calculated for the two- and three-parameter *n*th order equations ranged from about 19–23, suggesting that the former model is inferior to the latter.

However, as previously mentioned, the three-parameter *n*th order equation yielded unrealistic parameter estimates. By contrast, fixing the q_e value to turn the three-parameter *n*th order equation into a two-parameter model led to very reasonable estimates of k_n and n. The estimates of k_n decreased with increasing C_i (Table 3). This is consistent with the trend observed for the estimates of k_2 obtained from the pseudo second order equation (Table 1). Furthermore, the numerical values of k_n are much more realistic when compared to the exceedingly small values obtained from the three-parameter *n*th order equation. Interestingly, the optimal estimates of n did not vary with C_i and remained essentially constant across the three data sets. Using the $C_i = 200$ mg/L data set as an example, the sensitivity equation plots for the two-parameter *n*th order equation are presented in Fig. 5. Comparing Figs. 3 and 5 indicates that the removal of q_e from the fitting procedure has the effects of decreasing the maximum sensitivity value of n and enhancing the maximum sensitivity value of k_n. The two sensitivity curves are not linearly dependent, allowing unique and accurate estimates of the two parameters to be retrieved from the data. It is evident that the kinetic data only contain enough information to constrain the *n*th order equation with up to two fitting parameters.

Conclusion

The application of a general *n*th order surface reaction rate equation with three adjustable parameters to the kinetic data of lead uptake by yeast cells was systematically investigated. The lead uptake process in each case was fast, with apparent equilibrium reached in about 30 min. The model parameters were estimated using a genetic algorithm search method. According to the Akaike information criterion test, the three-parameter *n*th order equation was well supported by the data and it outperformed the much used pseudo second order equation with two adjustable parameters. However, the numerical values of the fitted parameters exhibited erratic trends and contradicted observed data at large times when equilibrium was established.

Parametric sensitivity analysis provided valuable insights into the identifiability of the model parameters. The three parameters, rate coefficient (k_n), reaction order (n), and uptake at equilibrium (q_e), were found to exhibit strong inter-correlations and broad differences in sensitivity effects. When the q_e parameter was fixed, it was possible to obtain meaningful numerical values for k_n and n. Despite its excellent correlative power, it was surely overkill to fit the three-parameter *n*th order equation to the kinetic data of this biosorption system which simply did not contain enough information to accommodate three fitting parameters. The findings from this work indicate that the use of the superior *n*th order rate equation in biosorption modeling requires more sophisticated experimental data in order to obtain meaningful parameter estimates.

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Nomenclature

C_i	Initial solution phase concentration (mg/L)
j	Index
k_2	Pseudo second order rate coefficient (g/mg min)
k_n	nth order rate coefficient [$(\mathrm{mg/g})^{1-n}$/min]
m	Number of observations
n	Surface reaction order
p	Parameter value
q	Biosorbent phase concentration (mg/g)
$q_{\mathrm{cal},j}$	Model-calculated q value for observation j (mg/g)
q_{e}	Equilibrium biosorbent phase concentration (mg/g)
$q_{\mathrm{exp},j}$	Measured q value for observation j (mg/g)
$q_{\max}$	Observed maximum q value (mg/g)
$\bar{q}_{\mathrm{exp}}$	Average of measured q values (mg/g)
S_p	Dimensionless sensitivity coefficient
t	Time (min)
w	Number of adjustable parameters

References

Anderson-Sprecher R (1994) Model comparisons and R^2. Am Stat 48:113–117

Bai J, Yao H, Fan F, Lin M, Zhang L, Ding H, Lei F, Wu X, Li X, Guo J, Qin Z (2010) Biosorption of uranium by chemically modified *Rhodotorula glutinis*. J Environ Radioact 101:969–973

Blanchard G, Maunaye M, Martin G (1984) Removal of heavy metals from waters by means of natural zeolites. Water Res 18:1501–1507

Bolster CH, Hornberger GM (2007) On the use of linearized Langmuir equations. Soil Sci Soc Am J 71:1796–1806

Brouers F, Sotolongo-Costa O (2006) Generalized fractal kinetics in complex systems (application to biophysics and biotechnology). Phys A 368:165–175

Burnham KP, Anderson DR (2002) Model selection and multimodel inference: a practical information-theoretic approach, 2nd edn. Springer, New York

Cho DH, Kim EY (2003) Characterization of Pb^{2+} biosorption from aqueous solution by *Rhodotorula glutinis*. Bioprocess Biosyst Eng 25:271–277

Cho DH, Chu KH, Kim EY (2011a) Loss of cell components during rehydration of dried *Rhodotorula glutinis* and its implications for lead uptake. Eng Life Sci 11:283–290

Cho DH, Chu KH, Kim EY (2011b) Lead uptake and potentiometric titration studies with live and dried cells of *Rhodotorula glutinis*. World J Microbiol Biotechnol 27:1911–1917

Chu KH, Feng X, Kim EY, Hung Y-T (2011a) Biosorption parameter estimation with genetic algorithm. Water 3:177–195

Chu KH, Kim EY, Feng X (2011b) Batch kinetics of metal biosorption: application of the Bohart–Adams rate law. Sep Sci Technol 46:1591–1601

Haerifar M, Azizian S (2013) Mixed surface reaction and diffusion-controlled kinetic model for adsorption at the solid/solution interface. J Phys Chem C 117:8310–8317

Ho Y-S (2006) Review of second-order models for adsorption systems. J Hazard Mater B136:681–689

Kumar KV (2006) A note on the comments by Dr. Y.S. Ho on "Nitrate removal from aqueous solution by adsorption onto various materials". J Hazard Mater B136:995–996

Lang W, Buranaboripan W, Wongchawalit J, Parakulsuksatid P, Vanichsriratana W, Sakairi N, Pathom-aree W, Siri-sansaneeyakul S (2013) Biosorption of lead from acid solution using chitosan as a supporting material for spore forming-fungal biomass encapsulation. Int J Environ Sci Technol 10:579–590

Liu Y, Shen L (2008a) From Langmuir kinetics to first- and second-order rate equations for adsorption. Langmuir 24:11625–11630

Liu Y, Shen L (2008b) A general rate law equation for biosorption. Biochem Eng J 38:390–394

Liu Y, Wang Z-W (2008) Uncertainty of preset-order kinetic equations in description of biosorption data. Bioresour Technol 99:3309–3312

McCuen RH, Surbeck CQ (2008) An alternative to specious linearization of environmental models. Water Res 42:4033–4040

Morais WA, Fernandes ALP, Dantas TNC, Pereira MR, Fonseca JLC (2007) Sorption studies of a model anionic dye on crosslinked chitosan. Colloids Surf A: Physicochem Eng Asp 310:20–31

Motulsky H, Christopoulos A (2004) Fitting models to biological data using linear and nonlinear regression: a practical guide to curve fitting. Oxford University Press, Oxford

Naja G, Volesky B (2011) The mechanism of metal cation and anion biosorption. In: Kotrba P, Mackova M, Macek T (eds) Microbial biosorption of metals. Springer, Dordrecht, pp 19–58

Özer A (2007) Removal of Pb(II) ions from aqueous solutions by sulphuric acid-treated wheat bran. J Hazard Mater 141:753–761

Park D, Yun Y-S, Park JM (2010) The past, present, and future trends of biosorption. Biotechnol Bioprocess Eng 15:86–102

Pipíška M, Horník M, Remenárová L, Augustín J, Lesný J (2010) Biosorption of cadmium, cobalt and zinc by moss *Rhytidiadelphus squarrosus* in the single and binary component systems. Acta Chim Slov 57:163–172

Plazinski W, Rudzinski W, Plazinska A (2009) Theoretical models of sorption kinetics including a surface reaction mechanism: a review. Adv Colloid Interface Sci 152:2–13

Praus P, Turicová M (2007) A physico-chemical study of the cationic surfactants adsorption on montmorillonite. J Braz Chem Soc 18:378–383

Qiu H, Lv L, Pan B-C, Zhang Q-J, Zhang W-M, Zhang Q-X (2009) Critical review in adsorption kinetic models. J Zhejiang Univ Sci A 10:716–724

Saltelli A, Ratto M, Andres T, Campolongo F, Cariboni J, Gatelli D, Saisana M, Tarantola S (2008) Global sensitivity analysis: the primer. Wiley, Chichester

Suazo-Madrid A, Morales-Barrera L, Aranda-García E, Cristiani-Urbina E (2011) Nickel(II) biosorption by *Rhodotorula glutinis*. J Ind Microbiol Biotechnol 38:51–64

Usunoff E, Winzettel P, Dietrich S (2009) Sorption of fluoride by quartz sand: batch tests. Geoacta 34:9–17

Volesky B, Naja G (2007) Biosorption technology: starting up an enterprise. Int J Technol Transf Commer 6:196–211

Zamani AA, Shokri R, Yaftian MR, Parizanganeh AH (2013) Adsorption of lead, zinc and cadmium ions from contaminated water onto *Peganum harmala* seeds as biosorbent. Int J Environ Sci Technol 10:93–102