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Prediction of optimum equilibrium and kinetic models for U(VI) sorption onto rice husk: comparison of linear and nonlinear regression methods

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ABSTRACT

The use of empirical models in the research is a vital part of the inventions and investigations of civil and environmental engineering organizations. Linear regression is the most commonly used method for optimization and parameter estimation of different equilibrium and kinetic models for sorption. In addition, the usage of this analysis can be extended to a range of nonlinear error functions, subsequently in consent to broader mathematical approach to parameter estimation. The sorption behavior of U(VI) ions from aqueous solution was studied with untreated, treated, and immobilized rice husk by conducting batch-mode sorption experiments. The equilibrium experimental data were fitted to the Freundlich, Langmuir and Redlich–Peterson isotherms by linear and nonlinear regression methods. Kinetic modeling of U(VI) ions removal was also done using linear and nonlinear pseudo-first and second-order rate expressions. In the case of nonlinear regression method, six error functions, namely hybrid fractional error function, Marquardt's percent standard deviation, average relative error, sum of the errors squared, sum of the absolute errors, and Chi-square test were used to predict the parameters involved in the two- and three-parameter isotherms, and also to predict the optimum isotherm. The results showed that nonlinear method could be a better way to obtain the parameters and get the most suitable fitted model for equilibrium and kinetic studies.

Keywords: Uranium; Rice husk; Linear regression; Nonlinear regression; Error functions

1. Introduction

The conventional approach for parameter evaluation of non-linear equations involves linearization of the equation through transformation, followed by linear regression. The linear least-squares method with linearly transformed isotherm equations has also been widely applied to confirm experimental data and isotherms using coefficients of determination [1,2].

Linear regression is based on assumption of Gaussian distribution of the error at each data point. However, linearization of the data implicitly alters this error structure and may also violate the error variance

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and normality assumption. The main disadvantage of the linear regression technique is that it is limited to the estimation of two variables in an empirical equation. Previously researchers showed that depending on the way the isotherm equations are linearized, the error distribution changes either for the worse or the better [3]. Nonlinear optimization provides a more complex, yet mathematically rigorous, method for determining isotherm parameter values, but still requires an error function assessment, in order to evaluate the fit of the isotherm to the experimental results [4].

Biosorption has been investigated as an economical, effective method of removing pollutants from wastewaters. This is a cheap technology and has no chemical sludge generation problem. Moreover, a number of biomaterials are available in nature that have no commercial significance and can be easily used for the removal of environmental pollutants [5–12]. Equilibrium and kinetic relationships between sorbents and sorbates are described by sorption isotherms and kinetic modeling, respectively. Equilibrium and kinetic modeling are characterized by certain values which provide the capacity of a sorbent for a particular sorbate and also help in the evaluation of affinity mechanism of the sorbate onto sorbent in batch reactions [13,14]. Linear regression is frequently used to predict the best-fitting isothermal and kinetic model [1]. Research reports by Dogan Karadag [2], Adnana El Hamidi [15], Vasanth Kumar [16], and Mahdi Hadi [17] suggest that simple linear regression method is not sufficient for the optimization of equilibrium and kinetic sorption models.

Uranium water contamination resulted from the nuclear industry is a major concern, since it causes serious environmental problems due to high chemotoxicity and radiotoxicity [18,19], and there is an essential need for an efficient, economical method for the treatment of uranium wastewater. In this research report, our investigation is focused on comparison between linear and nonlinear regression methods and use of six different error functions to predict optimal isothermal and kinetic model. Two-parameter equations i.e. Freundlich and Langmuir, and three-parameter equations i.e. Redlich–Peterson, were examined for equilibrium sorption data. Moreover, pseudo-first-order and pseudo-second-order models for kinetic studies of uranium sorption onto all three forms of rice husk (untreated, treated, and immobilized) were also investigated.

2. Materials and methods

2.1. Reagents

All chemicals used throughout this study were of analytical grade which were mainly purchased from Fluka chemicals. They are $UO_2(NO_3)_2.6H_2O$, Arsenazo III Dye, DTPA, H_2SO_4, Sodium dodecyl sulphate (SDS), and sodium alginate.

2.2. Collection of sorbent

Rice husk used in this work was collected from M/s Ayesha Rice Mill, Chiniot, Pakistan. After extensive washing with distilled water, the dried biomass was sieved (OCT-DIGITAL 4527-01) and stored in plastic containers for experiments.

2.3. Preparation of SDS-treated and immobilized rice husk

SDS-treated rice husk was prepared by mixing with water (1.0 g SDS/100 mL) in a flask and shaking for 2 h. After filtration, the treated biomass was washed with distilled water, dried in oven (50°C), sieved, and stored in plastic bags for further use. Immobilization of the rice husk was carried out by sodium alginate [20].

2.4. Analytical determination of uranium

Estimation of uranium contents in sample solution was done using Arsenazo III spectrophotometric (CECIL CE 7200 spectrophotometer) method [21].

2.5. Equilibrium study

The effect of changing metal ion concentration on uranium sorption was studied in the range of 10–100 mg/L by keeping the other parameters (pH 4, biosorbent dose 0.05 g, temperature 30°C and particle size of 300 μm at 125 rpm) constant. The two most widely used sorption isotherms i.e. Langmuir, Freundlich and Redlich–Peterson were used to determine the uranium biosorption mechanism from linearized and nonlinearized forms as shown in Table 1.

2.6. Kinetic study

The experiments were conducted to determine the time required by the untreated, treated, and immobilized biomass (0.05 g) to bind the metal ions. Synthetic metal ion solution (50 mL having pH 4 for untreated and immobilized and pH 5 for treated) was taken into each conical flasks. The solution was agitated on an orbital shaking incubator at 125 rev/min at 30°C. Kinetic analyses were performed by withdrawing the flasks at selected time intervals ranging from 5 to 720 min. The samples were filtered through filter paper and uranium concentration was determined.

Table 1
Isothermal and kinetic models and their linear and nonlinear forms

	Nonlinear form	Linear form	Plot	Reference
Isothermal model				
Langmuir	$q_\mathrm{e} = \frac{q_\mathrm{m} K_\mathrm{a} C_\mathrm{e}}{1+K_\mathrm{a} C_\mathrm{e}}$	$\frac{C_\mathrm{e}}{q_\mathrm{e}} = \frac{1}{q_\mathrm{m}} C_\mathrm{e} + \frac{1}{K_\mathrm{a} q_\mathrm{m}}$	$\frac{C_\mathrm{e}}{q_\mathrm{e}}$ vs. C_e	[13]
Freundlich	$q_\mathrm{e} = K_\mathrm{F} C_\mathrm{e}^{1/n_\mathrm{F}}$	$\log(q_\mathrm{e}) = \log(K_\mathrm{f}) + 1/n_\mathrm{F} \log(C_\mathrm{e})$	$\log q_\mathrm{e}$ vs. $\log C_\mathrm{e}$	[14]
Redlich–Peterson	$q_\mathrm{e} = \frac{A C_\mathrm{e}}{1+B C_\mathrm{e}^{g}}$	$\ln(A\frac{C_\mathrm{e}}{q_\mathrm{e}} - 1) = g\ln(C_\mathrm{e}) + \ln(B)$	$\ln(A\frac{C_\mathrm{e}}{q_\mathrm{e}} - 1)$ vs. $\ln C_\mathrm{e}$	[15]
Kinetic model				
Pseudo first order	$q_\mathrm{t} = q_1(1 - e^{-k_1 t})$	$\log(q_\mathrm{e} - q_\mathrm{t}) = \log(q_\mathrm{e}) - \frac{q_1}{2.303} t$	$\log q_\mathrm{e} - q_t$ vs. t	[16]
Pseudo second order	$q_\mathrm{t} = \frac{q_{eK_2}^2 t}{1+q_{eK_2} t}$	$\frac{t}{q_\mathrm{t}} = \frac{1}{K.q_\mathrm{e}^2} + (\frac{1}{q_\mathrm{e}})t$	$\frac{t}{q_\mathrm{e}}$ vs. t	[17]

To understand the controlling mechanism of biosorption, the commonly used pseudo-first-order and pseudo-second-order kinetic models were used to interpret the experimental data assuming that measured concentrations are equal to cell surface concentrations. The pseudo-second-order model is based on the assumption that biosorption follows a second-order mechanism. So, the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites. Linear and nonlinear forms of pseudo-first-order and pseudo-second-order expressions used in this study are presented in Table 1.

2.7. Statistical analysis

Each experiment was conducted in duplicate to ensure the reproducibility of results. All data represent the mean of two independent experiments. Statistical analysis for nonlinear regression was performed using the statistical functions of R. version 2.15.1.

3. Results and discussion

3.1. Equilibrium modeling

The design and operation of sorption processes require equilibrium sorption data for use in mass transfer models which can then be used to predict the performance of the sorption contact processes under a range of operating conditions [12]. Graphs of the resulting equilibrium data correlating the variation of solid-phase concentration (q_e), or the amount of solute adsorbed per unit mass of solid, to the variation of equilibrium solution phase concentration (C_e) are termed as sorption isotherms. The most commonly used sorption isotherms are discussed below in detail for both linear and nonlinear regression methods.

3.1.1. Langmuir isotherm

Langmuir [22] developed a theoretical equilibrium isotherm model that is widely used in industry and research; both linear and nonlinear forms are presented in Table 1, where q_e is the amount of uranium ions biosorbed on the biomass (mg/g) at equilibrium, C_e is the equilibrium concentration of uranium ions, q_m is the maximum biosorption capacity describing a complete monolayer adsorption (mg/g) and K_a is the adsorption equilibrium constant (L/mg) that is related to the free energy of biosorption. The values of Langmuir sorption isotherm parameters calculated by linear and nonlinear methods are given in Table 2.

The data used were from batch study performed to evaluate the sorption of U(VI) onto untreated, treated, and immobilized rice husk. The results presented in Table 2 show that R^2 values of the linear regression were 0.997, 0.991, and 0.994, respectively, for untreated, treated, and immobilized forms of rice husk. The experimental values of maximum sorption capacity obtained for untreated, treated and immobilized forms are 38.9, 42.4, and 38 mg/g, respectively. The maximum sorption capacity values calculated by Langmuir for untreated, treated and immobilized forms of rice husk are 45.24, 47.16, and 40 mg/g and are close to the experimental values. The criteria of R^2 and closeness of experimental and calculated values of model suggest good fitness of Langmuir adsorption isotherm to the sorption equilibrium data of U(VI) for untreated and modified forms of rice husk. The value of R_L helps in estimating the nature of the sorption process.

R_L value	Nature of biosorption mechanism
$R_\mathrm{L} > 1$	Unfavorable
$R_\mathrm{L} = 1$	Linear
$0 < R_\mathrm{L} < 1$	Favorable
$R_\mathrm{L} = 0$	Irreversible

Table 2
Isothermal parameters optimization by linear and nonlinear regression methods

Isothermal parameters	Linear regression method			Nonlinear regression method		
	Untreated	Treated	Immobilized	Untreated	Treated	Immobilized
Langmuir						
q_m (mg/g)	45.24	47.16	40	38.66	46.68	48.519
K_a (L/mg)	0.099	0.129	0.212	0.2135	0.1038	0.1298
R_L	0.1009	0.079	0.0498	0.0494	0.0967	0.0796
R^2	0.997	0.991	0.994	0.992	0.975	0.947
Freundlich						
K_F	7.186	9.594	1.183	9.259	11.025	13.149
n	2.25	2.579	3.32	2.76	2.915	3.816
R^2	0.9435	0.982	0.9699	0.964	0.985	0.947
Redlich–Peterson						
A (L/g)	4.4	12.5	19	5.811	15.031	13.936
B (dm^3/mg)^g	0.0707	0.552	1.435	0.198	0.834	1.853
g	1	0.834	0.708	0.900	0.772	0.797
R^2	0.9941	0.9976	0.9976	0.995	0.996	0.961

The values of R_L obtained in the present study are in the range of 0–1 (Table 2), describing that the biosorption process is favorable for uranium removal from wastewater using rice husk. Both linear and nonlinear regression show high suitability of the Langmuir model for all forms of rice husk in the following order:

Untreated > Immobilized > Treated

The value of coefficient of determination for nonlinear regression was evaluated by th following formula [16]

$$R^2 = \frac{q_{e,\mathrm{meas}} - \overline{q_{e,\mathrm{calc}}}}{\sum(q_{e,\mathrm{meas}} - \overline{q_{e,\mathrm{calc}}})^2 + (q_{e,\mathrm{meas}} - q_{e,\mathrm{calc}})^2} \qquad (1)$$

The R^2 value obtained by nonlinear regression is in the following order: 0.992, 0.975, and 0.947 for untreated, treated, and immobilized forms respectively. Equilibrium data of all three forms of rice husk is fitted to the Langmuir model in the following order: untreated > treated > immobilized by nonlinear regression methods;on the basis of R^2 and closeness of experimental and model sorption capacity, the values are as shown in Fig. 1(a–c).

3.1.2. Freundlich isotherm

The Freundlich isotherm [23] was developed to describe heterogeneous systems and exponential decay of energy distribution on sorption sites but it lacks the fundamental thermodynamics as not reduce to Henry's law at low concentration. The wellknown forms of the Freundlich model are given in Table 2, where K_F ((mg)g) (L/g)nF) and n are Freundlich constants, related to sorption capacity and sorption intensity of the sorbent, respectively. The values of K_F and $1/n$ are calculated from the intercept and slope, respectively, in linear regression method. The values of the parameters calculated by linear and nonlinear methods are given in Table 2. The magnitude of the Freundlich sorption capacity, n, gives an indication of favorability of adsorption. The value range of 2–10 indicates good adsorption capacity, 1–2 indicates moderate adsorption capacity, and less than 1 indicates poor adsorption capacity. The values of n obtained from linear method are 2.25, 2.579, and 3.32 for untreated, treated, and immobilized, respectively. These values suggest the favorability of the studied sorption process for the U(VI) wastewater treatment.

The R^2 values obtained from linear regression method, 0.943, 0.982 and 0.9699 suggest that Freundlich model also presents good fitness for the uranium sorption onto rice husk but the Langmuir is more suitable according to linear method. The maximum sorption capacity calculated from Freundlich model by linear regression method are 36.22, 40.92 and 35.31 mg/g for untreated, treated, and immobilized rice husk. The criteria of closeness between calculated and experimental q_e values favor suitability of Freundlich model more as compared to Langmuir by linear method.

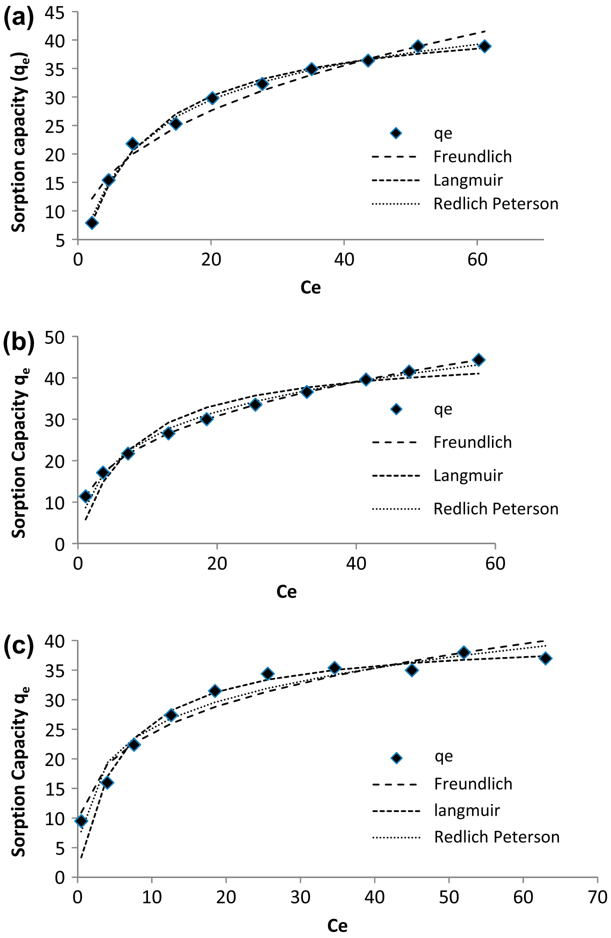

Fig. 1. Comparison of different isotherms for sorption of U(VI) onto rice husk (a) untreated, (b) treated, and (c) immobilized.

According to nonlinear method, the R^2 values for untreated, treated, and immobilized are 0.964, 0.975, and 0.949, respectively. The results also present the favorability of sorption process explanation by Freundlich model but the Fig. 1(a–c) obtained from nonlinear regression shows that experimental data are not very close to the Freundlich model data.

3.1.3. Redlic–Peterson isotherm

Redlich and Peterson [24] proposed an empirical three-parameter equation, which may be used to represent adsorption equilibria over a wide concentration range. This equation reduces to a linear isotherm at low surface coverage and to the Langmuir isotherm when $g = 1$. The exponent g lies between 0 and 1. Thus, when $g = 1$, the Redlich–Peterson equation becomes the Langmuir equation, and when $g = 0$, the equation presents the Henry's law. Linear and nonlinear forms of the Redlich and Peterson sorption isotherm are given in Table 2, where A, B, and g are the Redlich–Peterson parameters. The two models considered so far have all been two-parameter equations that employed linear transformation in order to determine and evaluate the quality of the model constants. The experimental data used to evaluate this model is identical to that used for the Freundlich and Langmuir isotherm evaluation.

The results given in Table 2 and Fig. 1(a–c) show that Redlich and Peterson equation is more suitable as compared to Freundlich and comparable with Langmuir isotherm.

3.1.4. Error analysis for optimization of sorption isotherms

The optimization procedure requires the selection of error functions in order to evaluate the best-fit isotherm to explain the experimental equilibrium data [25]. In this study, six non–linear error functions were examined and in each case a set of isotherm parameters were determined by minimizing the respective error function across the concentration range studied. The error functions employed were as follows:

The sum of the squares of the errors (SSE) [26]

$$\sum_{\mathrm{i}=1}^{n} (q_{\mathrm{e,exp}} - q_{\mathrm{q,calc}})_i^2 \tag{2}$$

A composite fractional error function (HYBRD) [27]

$$\frac{100}{n-p} \sum_{\mathrm{i}=1}^{n} \left[\frac{q_{\mathrm{e,exp}} - q_{\mathrm{q,calc}}}{q_{\mathrm{e,exp}}} \right]_i \tag{3}$$

Average relative error (ARE) [28]

$$\frac{100}{n} \sum_{\mathrm{i}=1}^{n} \left[\frac{q_{\mathrm{e,exp}} \; q_{\mathrm{q,calc}}}{q_{\mathrm{e,exp}}} \right]_i \tag{4}$$

Sum of absolute error (SSE) [29]

$$\sum_{i=1}^{n} |q_{\mathrm{e,exp}} - q_{\mathrm{q,calc}}| \tag{5}$$

Marquardt's percent standard deviation (MPSD) [30]

$$\sum_{\mathrm{i}=1}^{N} \left| \frac{q_{\mathrm{e,exp}} - q_{\mathrm{q,calc}}}{q_{\mathrm{e,exp}}} \right|_i \tag{6}$$

Nonlinear chi-square test (χ^2) [31]

$$\sum_{i=1}^{n} \frac{(q_{\mathrm{e,calc}} - q_{\mathrm{q,exp}})^2}{q_{\mathrm{e,exp}}} \tag{7}$$

If the data from the model are similar to the experimental data, errors will be a small number; if they are different, error will be a large number. The subscripts "exp" and "calc" show the experimental and calculated values, and N is the number of observations in the experimental data. The smaller the error values, the better they are for curve fitting.

The general procedure to find an adequate model by means of the error functions is to calculate the error function for all isotherms and make a comparison of the values obtained by different error functions for each isotherm. Overall optimum parameter set is difficult to identify directly; hence, trying to make a comparison between the values of error functions can lead to meaningful results.

The error functions for the untreated rice husk are in the following increasing order

ERRSQ/SSE	Frendlich > Langmuir > R-P
EABS	Frendlich > Langmuir > R-P
ARE	Freundlich > R-P > Langmuir
HYBRID	Freundlich > R-P > Langmuir
MPSD	Freundlich > R-P > Langmuir
χ^2	Freundlich > R-P > Langmuir

The results obtained from error function for equilibrium biosorption studies of U(VI) removal from aqueous showed that both Langmuir and Redlich–Peterson have good correlation with the experimental values as shown in Fig. 1(a). There is a minor difference between error function values of these two isotherms but overall trend of results favors Langmuir isotherm sorption process for U(VI) onto untreated rice husk.

The error function for the treated rice husk increase in the following order for each isotherm

ERRSQ/SSE	Langmuir > Frendlich > R-P
EABS	Langmuir > Frendlich > R-P
ARE	Langmuir > Frendlich > R-P
HYBRID	Langmuir > Frendlich > R-P
MPSD	Langmuir > Frendlich > R-P
χ^2	Langmuir > Frendlich > R-P

For treated biomass, the trend of error functions is in strong favor of Redlich and Peterson sorption isotherm. This same trend is also clear from the equilibrium curve in Fig. 1(b) obtained from the nonlinear regression for all three isotherms.

For immobilized rice husk

ERRSQ/SSE	Langmuir > Frendlich > R-P
EABS	Freundlich > R-P > Langmuir
ARE	Langmuir > Frendlich > R-P
HYBRID	Langmuir > R-P > Frendlich
MPSD	Langmuir > R-P > Frendlich
χ^2	Langmuir > Frendlich > R-P

The trend of error functions for sorption isotherm for immobilized rice husk is complicated and visual estimation of the above shown trend is not sufficient. If we see the values of error in Table 3, very small values of the errors for Redlich–Peterson are present as compared to Freundlich and Langmuir isotherm. So, it is concluded that equilibrium data of the U(VI) sorption onto immobilized rice husk best fitted to the Redlich–Peterson sorption isotherm.

3.2. Kinetic studies

The kinetic study determines how a reaction proceeds between uranium ions and sorbent by following an appropriate pathway with the passage of time. A number of models have been proposed in order to

Table 3
Sorption isotherm optimization by error functions

Error function	Untreated			Treated			Immobilized		
	Freundlich isotherm	Langmuir isotherm	Redlich-Paterson isotherm	Freundlich isotherm	Langmuir isotherm	Redlich-Paterson isotherm	Freundlich isotherm	Langmuir isotherm	Redlich-Paterson isotherm
ERRSQ/SSE	35.969	8.162	5.233	16.969	28.524	4.282	43.142	44.948	33.498
EABS	14.663	7.268	6.010	11.462	14.721	5.281	17.811	13.426	16.226
ARE	9.060	2.917	3.062	5.671	7.378	1.762	7.427	9.100	7.377
HYBRID	35.966	4.051	3.910	12.785	21.316	1.726	21.738	53.038	22.991
MPSD	19.669	4.185	5.351	10.557	13.429	2.356	10.435	23.187	11.740
Chi-Sq/χ^2	2.877	0.324	0.274	1.023	1.705	0.121	1.739	4.243	0.274

estimate the removal rate and the kinetic parameters to evaluate the mechanism of the process.

3.2.1. Pseudo-first-order model

The pseudo-first-order model [31], based on solid capacity, expresses the mechanism of removal as a sorption preceded by diffusion through a boundary. It considers that the sorption is partially first order depending on the concentration of free sites. Pseudo-first-order kinetic model is based on the fact that the change in uranium ions concentration with respect to time is proportional to the power one. Linear and nonlinear forms of pseudo-first-order model used for kinetic study of the U(VI) onto rice husk biomasses are given in Table 1, where q_e and q_t are the amount of uranium adsorbed (mg/g) at equilibrium and at time t (min), respectively, and k_1 (min^{-1}) is the pseudo-first-order rate constant. Values of k_1 are calculated from the plots of $\log(q_e - q_t)$ vs. t (Fig. 2(a–c)). The R^2 values obtained for untreated, treated, and immobilized rice husk biomass are presented in Table 4. The results showed relatively very small R^2 and the experimental q_e values do not agree with the values calculated from the linear plots. So, the first-order kinetic model is not fitted well for the whole data range of contact time. The values of R^2 calculated by nonlinear method also show that the model is not a good fit to the kinetic sorption data of untreated, treated and immobilized rice husk; however; the calculated and experimental maximum sorption capacity values are in good agreement.

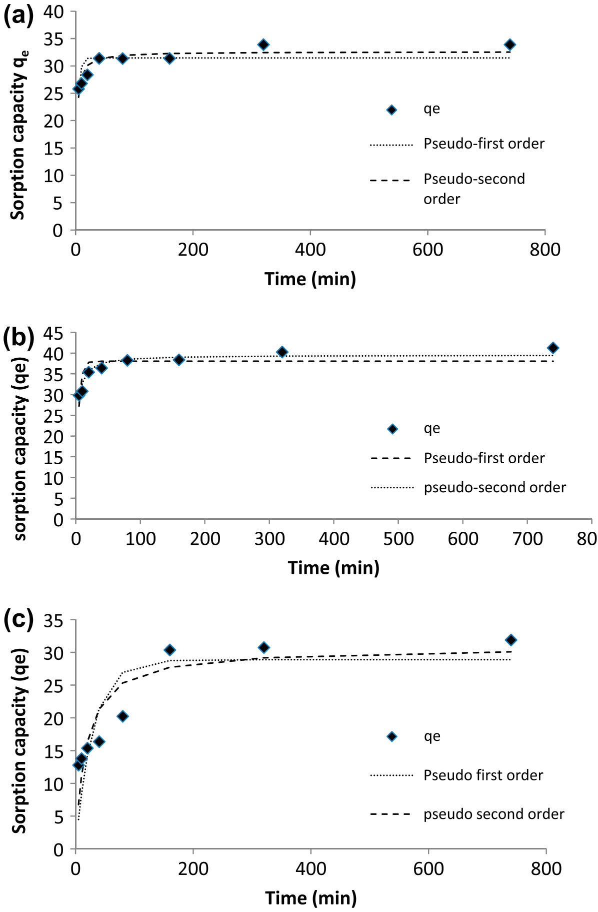

Fig. 2. Comparison of different kinetic models for sorption of U(VI) onto rice husk (a) untreated, (b) treated and (c) immobilized.

3.2.2. Pseudo-second-order kinetic model

The biosorption mechanism over a complete range of the contact time is explained by the pseudo-second-order kinetic model [32]. It expresses the sorption as partially second order with respect to free sites. The studied equation in both linear and nonlinear forms is given in Table 1, where q_e and q_t are the amount of uranium adsorbed on adsorbent (mg/g) at equilibrium and at time t (min), respectively, and k_2 is the pseudo-second-order rate constant (g/mg min). Based on the experimental data of q_t and t, the equilibrium sorption capacity (q_e) and the pseudo-second-order rate constant (k_2) can be determined from the slope and intercept of a plot of t/q_e vs. t. It was found that the pseudo-second-order model is best fit for all three rice husk forms. Linear and nonlinear regression analysis showed the good fitness of the pseudo-second order kinetic model to the experimental kinetic data of U(VI) biosorption onto rice husk as shown in Fig. 2 (a–c), obtained from nonlinear regression method. The R^2 values obtained by nonlinear method are comparatively small as compared to linear method but agreement between calculated and experimental sorption capacity values is fantastic.

3.2.3. Error analysis for optimization of kinetic model

All the above six error functions used for sorption isotherm optimization were also used for kinetic equation optimization. The error fractions can be arranged in decreasing order for U(VI) biosorption kinetic models onto untreated rice husk from Table 5

ERRSQ/SSE	Pseudo-first order > pseudo-second order
EABS	Pseudo-first order > pseudo-second order
ARE	Pseudo-first order > pseudo-second order
HYBRID	Pseudo-first order > pseudo-second order
MPSD	Pseudo-first order > pseudo-second order
χ^2	Pseudo-first order > pseudo-second order

Table 4
Kinetic parameters determination by linear and nonlinear methods

Kinetic model	Linear regression method			Nonlinear regression method		
	Untreated	Treated	Immobilized	Untreated	Treated	Immobilized
Pseudo-first order						
K_1 (L min^{-1})	0.0000690	0.00138	0.0011	0.296	0.252	0.034
q_e calculated (mg/g)	33.9	42.25	30.9	31.4	38.037	28.883
q_e experimental (mg/g)	4.036	10.44	5.24	33.9	42.25	30.9
R^2	0.5819	0.5617	0.6699	0.507	0.607	0.606
Pseudo-second order						
K_2 (g/mg min)	0.0069	0.0064	0.000924	0.108	0.012	0.002
q_e calculated (mg/g)	33.9	42.25	30.9	32.60	39.526	30.80
q_e experimental (mg/g)	34.129	40.48	32.8	33.9	42.25	30.9
R^2	0.999	0.999	0.9968	0.828	0.888	0.775

Table 5
Kinetic model optimization by error functions

Error function	Untreated		Treated		Immobilized	
	Pseudo-first order	Pseudo-second order	Pseudo-first order	Pseudo-second order	Pseudo-first order	Pseudo-second order
ERRSQ/SSE	32.293	11.215	47.830	13.628	186.306	106.444
EABS	12.650	8.608	16.754	9.169	33.263	25.611
ARE	5.355	3.613	6.020	3.292	24.673	18.373
HYBRID	18.265	6.296	23.315	6.666	199.022	109.250
MPSD	7.916	4.632	8.325	4.463	36.671	26.742
Chi-Sq/χ^2	1.096	0.378	1.399	0.400	11.941	6.555

The same trend was observed for treated and immobilized rice husk. Due to very small values of error functions, as shown in Table 5, it is concluded that the second order kinetic model is best fitted for the U(VI) sorption onto rice husk untreated, treated, and immobilized.

4. Conclusions

The interesting features of all the above discussions can be summarized as follows:

(1) Nonlinear regression error analysis shows the closeness of the equilibrium sorption data of U (VI) removal by untreated biomass is followed by Langmuir while treated and immobilized by Redlich–Peterson sorption isotherm.
(2) Kinetic sorption mechanism of U(VI) removal by untreated, treated and immobilized biomass is followed by pseudo-second-order reaction.
(3) The comparison of linear and nonlinear regression methods shows that parameter estimation and error analysis in nonlinear regression results are more reliable in prediction of best fitted isotherm and sorption mechanism evaluation. The simple linear regression alone is not sufficient for the prediction of optimum kinetic and equilibrium model.

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