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Linear and Nonlinear Two-Parameter Adsorption Isotherm Modeling: A Case-Study

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----------ABSTRACT----------

Linear and nonlinear forms of two-parameter isotherm models are generallyimplemented to describe characterize anadsorption process. Throughout the previous studies associated with adsorption process, less attention has been paid to comparison of these two methods. The current study was developed to investigate mathematical and statistical properties of these two methods and compare different statistical criteria to specify the best linear and nonlinear curves, fitted to experimental data and estimate isotherm parameters.Toward these aims, the data obtained from an empirical study on nitrate adsorption onto oyster shell coated with nanoparticle zero-valent iron (OS-nZVI) were applied. Goodness of fit (GooF) method in conjunction with an error analysis was applied to determine the best line fitted to experimental data.In this regard, eight error functions were used in the iterative method.The parameters of the model were determined by using the sum of normalized error (SNE) technique. The findings showed that linear and nonlinear models cannot create the same ranking isotherm models from the best to the worst fit line. However, for both methods, the Freundlich was found to be the best model.Comparison between linear and nonlinear analysis method shows that the adsorption capacity values calculated by the two methods were not statistically significantly different from each other.

Keywords: *Adsorption, Linear Regression, Nonlinear Regression, Error Analysis*

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I. INTRODUCTION

Isotherm is a mathematical equation describing the relationship between an amount of adsorbed adsorbate and its equilibrium concentration in bulk solution at a constant temperature. The isotherm is employed to characterize and evaluate the most important properties of adsorbent (1) such as adsorbent affinity, adsorption capacity, adsorption mechanism and quantitative distribution of adsorbate on adsorbent and bulk solution (2-5). The adsorption process is described by isotherm models of two, three, four, and even five parameters (6). To determine adsorption isotherm and its constant, experimental and calculation stages are required to be done.

In the laboratory stage, a fixed concentration of adsorbate in the same environmental conditions (pH, temperature and etc.) is subjected to different amounts of absorbent material for a period of time so-called anequilibrium time. Afterward, the concentration of the adsorbate remaining in solution is determined. The data obtained in the laboratory stage are applied in the calculations so that specification of adsorption isotherm and its parameters and constants are suited on. So far, linear and nonlinear regression methods were used to describe the two-parameter isotherm models. The simplest and easiest method to calculate isotherm parameters for two-parameters isotherm is a simple linear regression model (5, 7).For linear regression to be employed in order to determine isotherm parameters and adsorption capacity, it is first required to convert the nonlinear isotherms to linear one. After drawing a linear regression line, the isotherm parameters are calculated from the slope and intercept of the line. The least square method is used to determine isotherm parameters (4, 7, 8). The isotherm

model with the best fit for adsorption data is selected on the basis of the determination of the coefficient (R^2) value (9, 10). The model with highest R^2 has the best fitness to experimental data (3).
The most important disadvantage of linear regression is non-fixed error distribution (4, 11). Since nonlinear form of isotherm is converted to linear form, error structure and distribution are altered and this can influence error variance and normality assumption of standard least square (8, 9, 12). In addition, in case of isotherms with more than two parameters, we cannot calculate the value of unknown parameters using linear regression and graphical method (4).
Over the recent years, non-linear regression in conjunction with error analysisas an alternative to linear regression has been employed to make a model in adsorption studies (7, 9). According to most literature published, the nonlinear form of isotherm had better fit for adsorption data. For a nonlinear regression method, isotherm parameters are obtained from the main form of isotherm and there is no need to convert a nonlinear form of isotherm to linear form(13). So, The structure and distribution of errors remain unchanged (14, 15). Non-linear regression estimates the parameters of the isotherm model by minimizing error. The error can be defined by different equation. So, in adsorption studies, several error functions such as the coefficient of determination (R2) (16), hybrid fractional error function (HYBRID) (17, 18), Marquardt's percent standard deviation (MPSD) (18), the average relative error (ARE) (18), the sum of the errors squared (SSE) (18), nonlinear chi-square test ($\chi 2$), residual root mean square error (RMSE) (5), average percentage errors (APE) (6, 18), and the sum of the absolute errors (EABS) (18), have been introduced for nonlinear regression analysis.In most previous adsorption studies, only the practical aspects of the linear and nonlinear regression were taken into consideration and less attention has been paid to comparison of these two methods.
Therefore, in the present study, we are intended to examine linear and nonlinear regressions in more details and represent how to use these models to describe the adsorption phenomenon was investigated.

II. MATERIAL AND METHODS

2.1 Adsorption experiments

Adsorption experiments were conducted in 1 L glass Erlenmeyer flask as the reaction vessel. The content of the flask was agitated by a magnetic stirrer during the experiment's time. The pH of the solution was adjusted at the 7 by adding a few drops of 0.1 M NaOH or 0.1 M HCl solution, if necessary into the flask. The temperature was kept at 25℃ as room temperature. For determination of adsorption isotherms, 0.25, 0.5, 0.75, 1, and 1.5 g of OS-nZVI was inserted into 5 flasks with the same concentrations of nitrate (10 mg/L). After pH adjustment, the content of flasks was agitated (50 rpm) by a magnetic stirrer for 120 min. At the end of equilibrium time, the samples were taken from the flask, the liquid was separated from the adsorbent and final concentration of nitrate was determined with UV/VIS spectrophotometer model Perkin Elmer Lambda at wavelength of 220 nm.
The amount of adsorbed nitrate or the adsorption capacity of adsorbent was calculated using the following equation (19-21).

$$q_e = \frac{(C_0 - C)V}{M} \qquad (1)$$

Where q_e is amount of adsorbed nitrate onto OS-nZVI (mg/g), C_0 is initial concentration of nitrate (mg/L), C is final concentration of nitrate (mg/L), V is the volume of the solution (L), and M is the mass of OS-nZVI (g).

2.2Optimum Adsorption isotherm

2.2.1 Linear regression

The simple linear regression is a method to model the relationship between a scalar dependent variable and one independent variable. The best-fitting line is the line that minimizes the sum of the squared errors (SSE) of prediction. The strength of the linear association between two variables is quantified by the square of the correlation coefficient (*R*) whichis calledthe determination of the coefficient(R^2).Additionally, eight error functions were used to determine the linear relationship strength.The higher R^2 value and lower values of error functions indicate a stronger linear relationship.In this study, linear form of four two-parameter isotherm models (Freundlich, Langmuir, Tempkin, and Dubinin-Radushkevich) were fitted for a description of adsorption processes at the equilibrium point.
R^2 and eight error functions were applied to discussthe fitness of isotherm models and select the best one of them which is fitted to experimental data. Detailed information about isotherm models and error functions were presented in **Tables** 1 and 2, respectively.

Table 1: Linear and nonlinear forms of adsorption isotherm models

Isotherm	Nonlinear form	Linear form	Linear plot	Parameters	Eq.	Ref.
Langmuir	$q_e = \frac{Q_0 b C_e}{1+bC_e}$	$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0C_e}$	$\frac{1}{q_e}$ vs. $\frac{1}{C_e}$	$Q_0 = \frac{1}{intercept}$ $b = \frac{1}{(slop/intercept)}$	2	(8, 22, 23)
Frundlich	$q_e = K_F C_e^{1/n}$	$\ln(q_e) = \ln(K_F) + \frac{1}{n}\ln(C_e$	$\log(q_e)$ vs. $\log(C_e)$	$n = \frac{1}{slop}$ $K_F = \exp(intercept)$	3	(1, 9, 24)
Tempkin	$q_e = \frac{RT}{b_T}\ln A_T C_e$	$q_e = \frac{RT}{b_T}\ln A_T + \frac{RT}{b_T}\ln C_e$	q_e vs. $\ln C_e$	$b_T = \frac{RT}{slop}$ $A_T = \exp(\frac{intercep}{slop})$	4	(25-27)
Dubinin–Radushkevich	$q_e = (q_s)\exp(-k_{ad}\varepsilon^2$	$\ln(q_e) = \ln(q_s) - k_{ad}\varepsilon^2$	$\ln(q_e)$ vs. ε^2	$q_s = \exp(intercept)$ $k_{ad} = -slop$	5	(4, 28)

Table 2: Error functions and their equations

Error function	Abbreviation	formula	Eq.	Ref.
Sum of the squares of the errors	ERRSQ	$\sum_{i=1}^{n}(q_{e,calc} - q_{e,exp})_i^2$	6	(29)
Hybrid fractional error function	HYBRID	$\frac{100}{n-p}\sum_{i=1}^{n}(\frac{q_{e,exp} - q_{e,calc}}{q_{e,exp}})_i$	7	(25)
Average relative error	ARE	$\frac{100}{n}\sum_{i=1}^{n}\left\lvert\frac{q_{e,exp} - q_{e,calc}}{q_{e,exp}}\right\rvert$	8	(8)
Sum of absolute error	EABS	$\sum_{i=1}^{n}\lvert q_{e,exp} - q_{e,calc}\rvert$	9	(18)
Marquardt's percent standard deviation	MPSD	$100\sqrt{(\frac{1}{n-p}\sum_{i=1}^{n}(\frac{q_{e,exp} - q_{e,calc}}{q_{e,exp}})_i^2}$	10	(8)
Nonlinear chi-square test	X^2	$\sum_{i=1}^{n}\frac{(q_{e,calc} - q_{e,exp})^2}{q_{e,exp}}$	11	(13)
Residual Root Mean Square Error	RMSE	$\sqrt{(\frac{1}{n-2}\sum_{i=1}^{n}(q_{e,exp} - q_{e,calc})_i^2}$	12	(30)
Average Percentage Errors	APE	$\frac{\sum_{i=1}^{n}\left\lvert\frac{q_{e,exp} - q_{e,calc}}{q_{e,exp}}\right\rvert_i}{p}\times 100$	13	(31)

2.2. 2 Nonlinear regression

Nonlinear regression can be a powerful alternative to linear regression because it offers the most flexible curve-fitting functionality. For nonlinear model, sum of square must be minimized by an iterative method. The nonlinear regression line is the line that minimizes the sum of squared deviations of prediction (also called the sum of squares error). The standard error of the estimate (S) is the square root of the average squared deviation. This parameter measures the accuracy of predictions. The smaller the standard error of the estimate indicates the

more accurate prediction. In nonlinear regression, Good of fitness method (GooF) is used after error analysis. The best set of parameters for each isotherm is selected using sum of normalized error (SNE). The following sections (2.2.2.1 and 2.2.2.2) introduce error analysis, GooF, and SNE method.

2.2.2.1 Error analysis and GooF method

In this study, eight non-linear error functions, as presented in **Table 2**were examined to model isotherm and to determine isotherm parameters by minimizing the respective error function across the studied concentration range.

The iterative nonlinear regression analysis is conducted by using the solver Add-Ins of Microsoft Excel® which employs minimization of the error functions and maximization of R^2 to produce the best fitness to experimental data and to estimate the coefficients of the isotherm models.

The optimum isotherm was selected using good of fitness (GooF) method. In GooF method,given error functionwas calculated for all of isotherm models and the isotherm model with the lowest value of that error function was selected as the best model to describe experimental data. The results of other error functions weretaken into account to classify isotherm modelsfrom the best to worst.

2.2.2.2 Sum of the normalized error (SNE)

Different error functions may produce a different set of parameters for each isotherm(13, 18). In this study, the best set of parameters for each isotherm was selected according to normalization/optimization method. In this method, the sum of the normalized error (SNE) was calculated and applied to select the parameters. To obtain SNE value, one isotherm and one error function were selected and the isotherm parameters were determined based on trial and error method using solver Add-Ins in Microsoft Excel and the obtained parameters minimized the selected error function. Next, the values of the other error functions for isotherm parameters set were computed. Two previous steps were conducted for each isotherm and other error functions. Then, each parameter set was selected and the ratio of its associated error functions to largest associated error function was calculated.To produce sum of the normalized error (SNE), obtained ratios for that parameter set were summed. Finally, the parameter set with the minimum SNE was selected as the best set of parameters for that isotherm.

III. Results and discussion

3.1 Linear regression

The linear isotherm plots for the sorption of nitrate onto OS-nZVIweredepicted in Figure 1. Furthermore, Values of isotherm parameters and error functions were presented in **Table 3.**On the basis of R^2 value presented, although Freundlich,Langmuir, and Temkin isotherm have almost the same and high coefficient of determination when compared to Dubinin–Radushkevich isotherm, the Freundlichmodel has the highest R^2 value and therefore, it was selected as the best isotherm for a description of nitrate adsorption onto OS-nZVI based on this criterion.

Since the R^2 values are close to each other on three models (Freundlich, Langmuir, and Tempkin), the other criterion, Akaike Information Criterion (AIC), was applied to choose the best linear isotherm model. AIC approximates the quality of each model relative to other models between a certaincollection of models for the data. In the other word, the AIC is a method to choosethe best model among a set of models that minimizes the Kullback-Leibler distance between the model and the truth. The AIC is calculated by the following equation:

$AIC = 2K - 2(\ln(L))$(15)

Where K indicates the number of parametersand L indicatesa probability of the data given a model (likelihood). In this study, the least amount of AIC belongs to the Langmuir model. After Langmuir,the Freundlich is placed in the next rank with minimum AIC.Therefore, According to this criterion, Langmuir is the best model to describe the adsorption data. This ranking is different from that obtained based on R^2 value. Linear regression line of isotherm models was depicted in **Figure 1.**

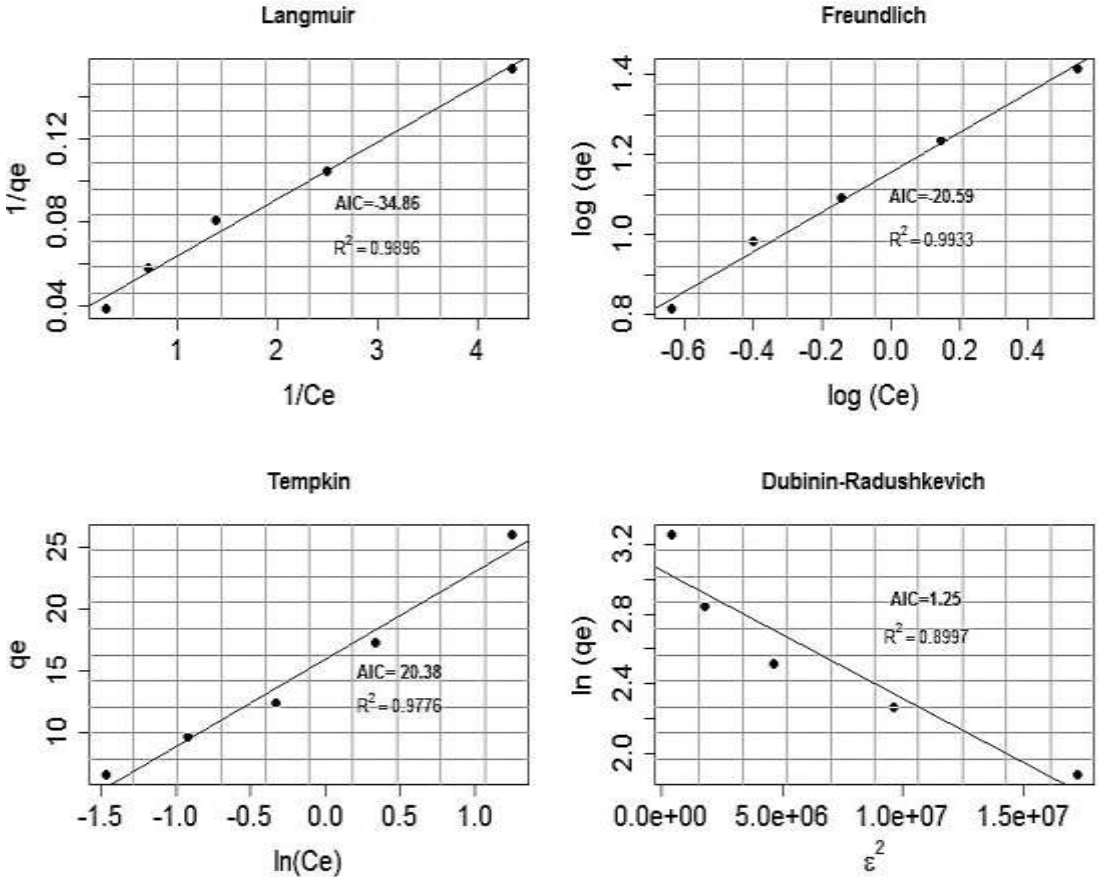


Figure1: Linear regression line for two-parameter isotherm (Langmuir, Freundlich, Tempkin, and Dubinin-Radushkevich)models, qe: adsorption capacity (mg/g), Ce: equilibrium concentration (mg/L)

Table 3: Isotherm constants obtained by linear regression modeling

	Langmuir		**Freundlich**		**Tempkin**		**Dubinin-Radushkevich**	
parameter	**Q_0**	**b**	**K**	**n**	**b_T**	**A_T**	**k_{ad}**	**q_s**
	25.39	**1.746**	**14.41**	**2.16**	**396.14**	**12.39**	**6.2(10^{-8})**	**21.04**
R^2	0.9896		0.9933		0.9776		0.8997	
RMSE	2.148		0.591		1.316		2.062	
□²	0.587		0.078		0.398		41.621	
ERRSQ	13.841		1.046		5.194		68.725	
HYBRID	19.580		2.592		13.268		19.838	
MPSD	9.470		5.053		11.357		13.421	
ARE	5.409		3.436		7.503		11.056	
EABS	5.292		2.081		4.676		33.553	
APE	13.522		8.589		19.542		0.257	

3.2 Nonlinear regression

3.2.1 Error analysis

The parameters of the different isothermsobtained by minimizing each error functionand maximizing R^2in an iterative method and the corresponding values of the other error functions were shown in **Table 4.**To judge the fit of the model with experimental data, the coefficient of determination (R^2) was employed. As can be seen from the **Table 4,** for Langmuir isotherm, modeled adsorption capacity (modeled q_e) curves obtained by minimizing the RMSE, χ^2, ERRSQ, and HYBRID error functions have the same and the most consistency with experimental adsorption capacity points (experimental q_e).Next match ratings awarded to MPSD error function.

The minimum agreement exists when ARE, EABS,and APE error functionswereapplied to obtain the modeled adsorption capacities and isotherm constants.

The constants for Freundlich isotherm obtained by nonlinear regression analysis are shown in **Table 4.** All of fitted non-linear curves for Freundlich isotherm obtained by minimizing different error functions have the same R^2 value (RMSE= ERRSQ= HYBRID = χ^2 = MPSD = EABS = APE=ARE).

For Tempkin isotherm, on the basis of R^2values obtained by error analysis, RMSE= ERRSQ, χ^2=HYBRID, APE= ARE=MPSD= EABS were ranked from 1 to 3, respectively. The number 1 represents the best and number 3 represents the worst error function for modeling of data and obtaining the constants of the isotherm.

According to **Table 4**, the non-linear regression lines of Dubinin-Radushkevich fitted the experimental data were falling into two categories. Frist category with higher R^2values includeslines when RMSE, χ^2, ERRSQ and HYBRID error functions were minimized. The MPSD, ARE, EABS, and APE error functionsproducedthe second group of lines with lower R^2 values.

As discussed above, for all two-parameter isotherm equations, RMSE and ERRSQ error function are the best error function for optimizing non-linear regression model. For almost these isotherms, the APE, EABS, and ARE error functions fall in the low end as well.

Table 4: The constants of two-parameter isotherm obtained by different error function and their R^2 value

Isotherm	Parameter	RMSE	□²	ERRSQ	HYBRID	MPSD	ARE	EABS	APE	R^2
	Q_0	33.82	31.93	33.82	31.93	29.77	25.39	25.39	25.39	33.82
	K_L	0.86	0.98	0.86	0.98	1.14	1.50	1.50	1.50	0.86
	RMSE	**1.16**	1.26	1.16	1.26	1.56	2.74	2.74	2.74	1.16
	□²	0.36	**0.31**	0.36	0.31	0.37	0.89	0.89	0.89	0.36
	ERRSQ	4.07	4.74	**4.07**	4.74	7.31	22.50	22.50	22.50	4.07
Langmuir	HYBRID	12.11	10.47	12.11	**10.47**	12.27	29.78	29.78	29.78	12.11
	MPSD	11.39	9.27	11.39	9.27	**8.52**	11.05	11.05	11.05	11.39
	ARE	7.71	7.01	7.71	7.01	6.28	**5.07**	5.07	5.07	7.71
	EABS	4.32	4.63	4.32	4.63	4.95	5.56	**5.56**	5.56	4.32
	APE	19.28	17.51	19.28	17.51	15.70	12.67	12.67	**12.67**	19.28
	R^2	0.98	0.98	0.98	0.98	0.97	0.90	0.90	0.90	**0.98**
	K	14.39	14.33	14.39	14.33	14.31	14.44	14.44	14.44	14.39
	n	2.10	2.05	2.10	2.05	2.00	2.13	2.13	2.13	2.09
	RMSE	**0.45**	0.48	0.45	0.48	0.60	0.47	0.47	0.47	0.450
	□²	0.08	**0.07**	0.08	0.07	0.08	0.09	0.09	0.09	0.076
	ERRSQ	0.61	0.69	**0.61**	0.69	1.09	0.66	0.66	0.66	0.606
Freundlich	HYBRID	2.55	2.32	2.55	**2.32**	2.65	3.02	3.02	3.02	2.545
	MPSD	5.94	5.30	5.94	5.30	**5.04**	6.64	6.64	6.64	5.943
	ARE	3.14	3.33	3.14	3.33	3.49	**3.01**	3.01	3.01	3.142
	EABS	1.46	1.77	1.46	1.77	2.14	1.23	**1.23**	1.23	1.465
	APE	7.86	8.32	7.86	8.32	8.71	7.53	7.53	**7.53**	7.856
	R^2	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	**0.997**
Tempkin	b_T	350.6	372.9	350.6	372.9	396.2	396.2	396.2	396.2	350.62
	A_T	9.5	10.7	9.5	10.7	11.9	11.6	11.6	11.6	9.52
	RMSE	**1.32**	372.9	350.6	372.9	396.2	396.2	396.2	396.2	350.62
	□²	0.40	**0.34**	0.40	0.34	0.39	0.40	0.40	0.40	0.398
	ERRSQ	5.19	6.02	**5.19**	6.02	8.57	9.05	9.05	9.05	5.194
	HYBRID	13.27	11.23	13.27	**11.23**	12.86	13.33	13.33	13.33	13.270
	MPSD	11.36	8.83	11.36	8.83	**8.13**	8.31	8.31	8.31	11.360
	ARE	7.50	6.09	7.50	6.09	5.20	**5.06**	5.06	5.06	7.504
	EABS	4.68	4.51	4.68	4.51	4.48	4.35	**4.35**	4.35	4.676

Table 4 cont.: The constants of two-parameter isotherm obtained by different error function and their R^2 value

Isotherm	Parameter	RMSE	□²	ERRSQ	HYBRID	MPSD	ARE	EABS	APE	R^2
	APE	18.76	15.23	18.76	15.23	13.01	12.65	12.65	**12.65**	18.761
	R^2	0.98	0.97	0.98	0.97	0.96	0.96	0.96	0.96	**0.978**
Dubinin-Radushkevich	k_{ad}	7.3×10^{-8}	7.3×10^{-8}	7.3×10^{-8}	7.3×10^{-8}	6.2×10^{-8}	6.2×10^{-8}	6.2×10^{-8}	6.2×10^{-8}	7.34×10^{-8}
	q_s	21	21	21	21	21	21	21	21	21.0376
	RMSE	**3.65**	3.65	3.65	3.65	4.02	4.02	4.02	4.02	4.016
	□²	0.05	**0.05**	0.05	0.05	0.06	0.06	0.06	0.06	0.057
	ERRSQ	39.95	39.95	**39.95**	39.95	48.38	48.38	48.38	48.38	48.384
	HYBRID	1.80	1.80	1.80	**1.80**	1.89	1.89	1.89	1.89	1.887
	MPSD	0.52	0.52	0.52	0.52	**0.52**	0.52	0.52	0.52	0.521
	ARE	13.30	13.30	13.30	13.30	17.85	**17.85**	17.85	17.85	17.851
	EABS	10.74	10.74	10.74	10.74	13.16	13.16	**13.16**	13.16	13.163
	APE	33.25	33.25	33.25	33.25	44.63	44.63	44.63	**44.63**	44.627
	R^2	0.83	0.83	0.83	0.83	0.79	0.79	0.79	0.79	**0.791**

3.2.2 Selecting the best isotherm model

The results of the isotherm models ranking were shown in **Table 5**. The first rank is awarded to the isotherm with the least amount of considered an error function. As can be seen from the table, based on the APE, EABS and ARE error functions, the best to worst order of isotherm models are in respect Freundlich, Tempkin, Langmuir and Dubinin-Radushkevich. According to HYBRID, MPSD, and χ^2 error functions, ranking from the best to worst models are Dubinin-Radushkevich, Freundlich, Tempkin, and Langmuir. Based on ERRSQ and RMSE error functions, Freundlich is the best model and Langmuir, Tempkin, and Dubinin-Radushkevich are ranked following.In the overall ranking (highlighted column), the Freundlich, Tempkin, Langmuir, and Dubinin-Radushkevich models ranked from 1 to 4 based on the highest number of view of each isotherm per each row. Finally, Freundlich isotherm model was chosen as the best fitted nonlinear model for data.

Table 5: The ranking of isotherm models based on SNE method

Error function								Most visited
RMSE	□²	ERRSQ	HYBRID	MPSD	ARE	EABS	APE	
*FR	D-R	FR	D-R	D-R	FR	FR	FR	FR
LA	FR	LA	FR	FR	TE	TE	TE	TE
TE	LA	TE	LA	TE	LA	LA	LA	LA
D-R	TE	D-R	TE	LA	D-R	D-R	D-R	D-R

*FR=Freundlich, LA=Langmuir, TE=Tempkin, D-R=Dubinin-Radushkevich

3.2.3 Determination of optimal parameter values by SNE method

Table 4 shows the coefficients of fitted isotherm models of the nitrate adsorption on OS-nZVI, which are obtained by minimizing the various error functions. The optimal values of the parameters for each isotherm obtained from the standardized normal error method are shown in highlighted columns. As can be seen from the **Figure 2**, in case of Langmuir and Freundlich adsorption isotherm, the optimal parameters are obtained by minimizing EABS error function, for the Tempkin adsorption by ERRSQ error function, and for the Dubinin-Radushkevich adsorption isotherm, the optimal parameter value can be derived from each of the HYBRID, ERRSQ, $\chi2$, and RMSE error functions. Isotherm adsorption curves for different models were shown in Figure 3. As seen in these curves, the Freundlich model has the highest fit on experimental data.

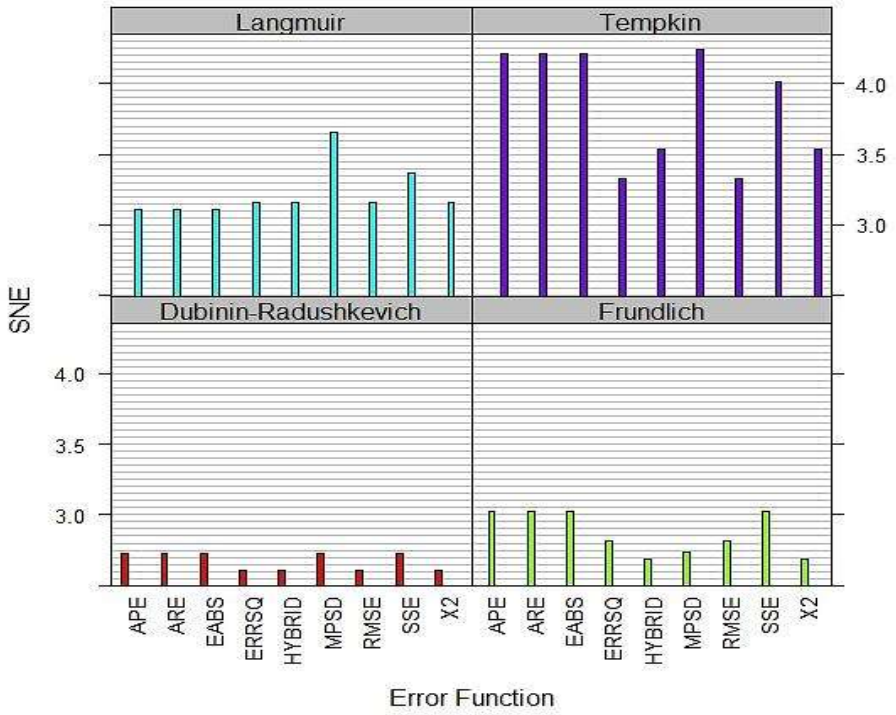


Figure 2: The level of different standard normalized error (SNE)for isotherm models

After choosing the overall best error method for determining the parameters of the isotherm models, the plots of different nonlinear isotherm modelswith optimized values of the constants were presented in **Figure 3**. As can be seen from the **Figure 3**, the curves of Freundlich and Tempkin have the most consistent with experimental data. The least consistency is related to Dubinin-Radushkevich isotherm.

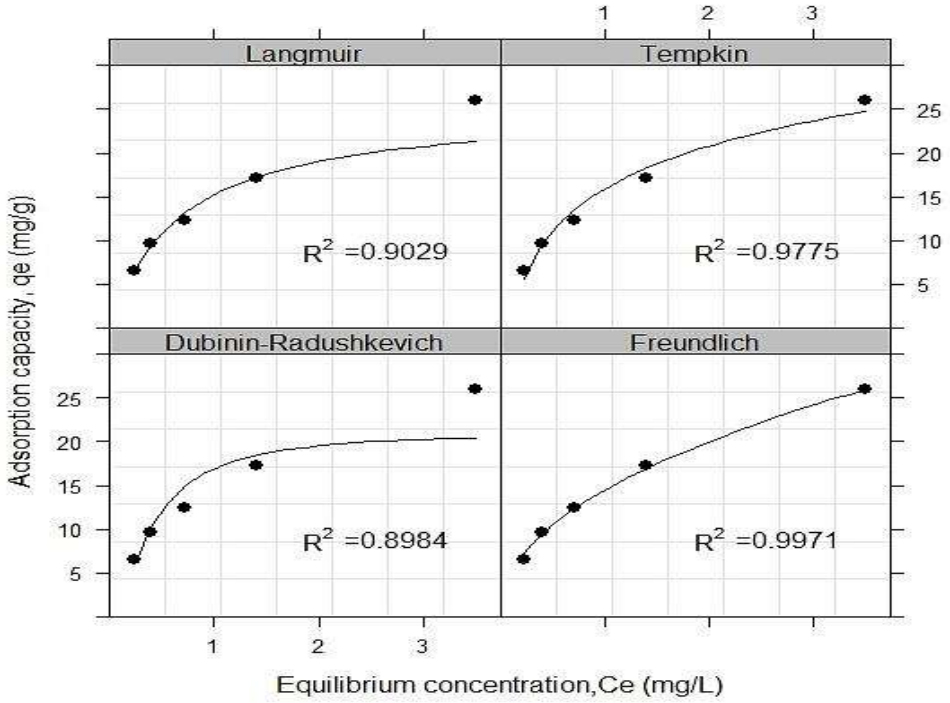


Figure 3: Nonlinear adsorption isotherm curve (-: predicted, ●: observed), Langmuir based on EABS, Tempkin based on ERRSQ, Dubinin-Radushkevich based on RMSE ‹HYBRID ‹ERRSQor □², and Freundlich Based on EABS

3.3 Comparative analysis of linear and nonlinear model

The obtained parameters of isotherm models from linear and nonlinear regression were shown in **Table 6**.As can be seen from the table, different error functions produce different constants. For Langmuir model, Q_0produced by minimizing ARE, EABS, and APE are the same as linear method. Other error functions produce higher value for Q_0 in comparison with linear method. The other parameter of Langmuir isotherm (b) is significantly different in nonlinear method and linear method. There is no error function which produces similar $Q_0$and b to linear method.

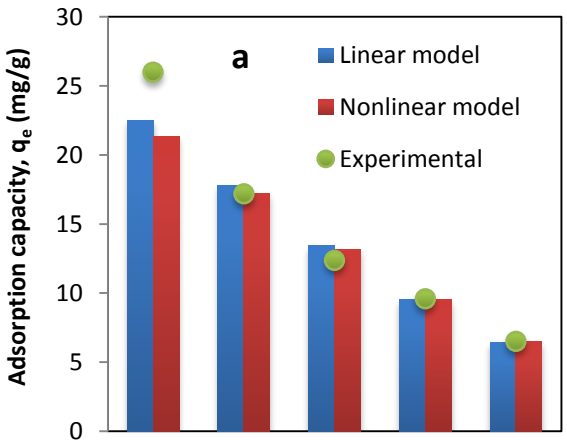
For Freundlich, two parameters (K, n) are very similar for all error functions and are also very close to those obtained by the linear method. The greatest difference between the parameters obtained by the nonlinear method was found to be in the Tempkin model.

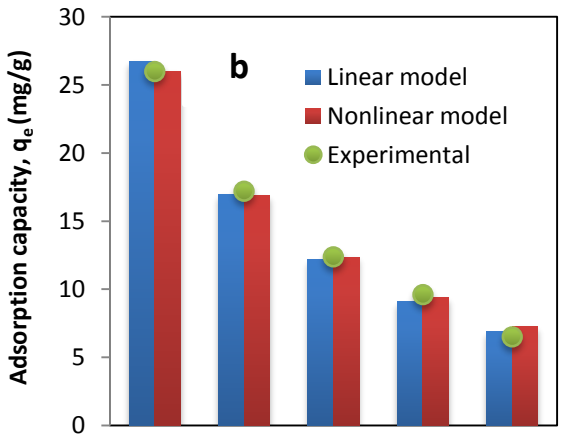
The least variability in the parameter values is related to the Dubinin-Radushkevich isotherm. For this isotherm MPSD, ARE, EABS, and APE produce parameters the same as linear method.

Adsorption capacity (q_e) for different equilibrium concentrations obtained by linear and optimized constants from nonlinear method were shown in **Figure 4.** As can be seen from this figure, there is no significant difference between q_e from linear and nonlinear method.

Table 6: Isotherm parameters obtained by linear and nonlinear method

	Model	Parameter	RMSE	χ^2	ERRSQ	HYBRID	MPSD	ARE	EABS	APE	R^2
Langmuir	Nonlinear	Q_0	33.82	31.93	33.82	31.93	29.77	25.39	25.39	25.39	33.82
		b	0.86	0.98	0.86	0.98	1.14	1.50	1.50	1.50	0.86
	Linear	Q_0					25.39				
		b					1.75				
Freundlich	Nonlinear	K_F	14.39	14.33	14.39	14.33	14.31	14.44	14.44	14.44	14.39
		n	2.10	2.05	2.10	2.05	2.00	2.13	2.13	2.13	2.09
	Linear	K_F					14.41				
		n					2.16				
Tempkin	Nonlinear	b_T	350.6	372.9	350.6	372.9	396.2	396.2	396.2	396.2	350.62
		A_T	9.5	10.7	9.5	10.7	11.9	11.6	11.6	11.6	9.52
	Linear	b_T					396.14				
		A_T					12.39				
Dubinin-Radushkevich	Nonlinear	k_{ad}	7.3×10^{-8}	7.3×10^{-8}	7.3×10^{-8}	7.3×10^{-8}	6.2×10^{-8}	6.2×10^{-8}	6.2×10^{-8}	6.2×10^{-8}	7.3×10^{-8}
		q_s	21	21	21	21	21	21	21	21	21
	Linear	k_{ad}					$6.2\ (10^{-8})$				
		q_s					21.04				





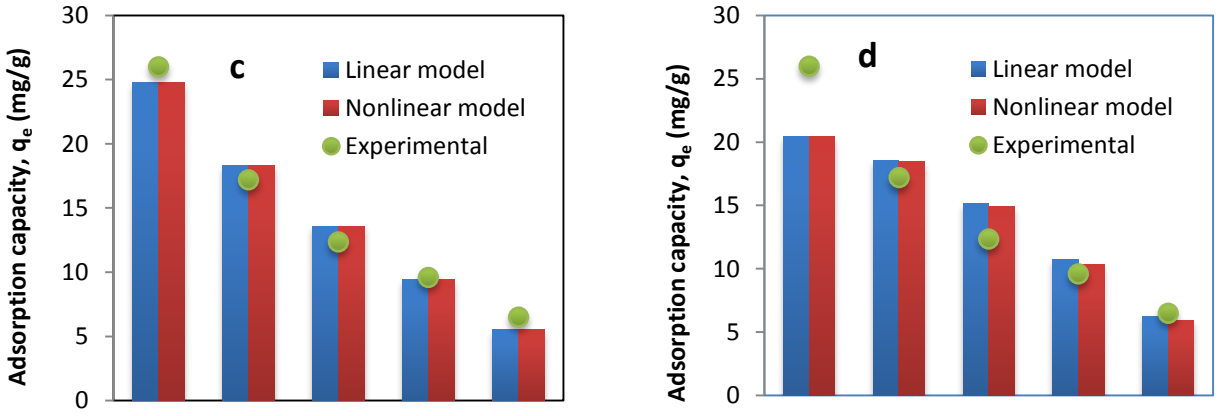


Figure 4: Comparison of adsorption capacity produced by linear and nonlinear approaches, a: Langmuir, b: Freundlich, c:Tempkin, and d: Dubinin-Radushkevich

IV. CONCLUSION

In this study different statistical criteria such as the coefficient of the determination (R^2) and Akaike Information Criterion (AIC), standard normalized error (*SNE*),and different statistical methodsinclude linear regression, nonlinear regression, error analysis, and goodness of fit (GooF) were examined to describe two-parameteradsorption isotherm models. The results indicated that AIC criterion can be used asa criterion to select the best fit linear isotherm model,especially at a time when R^2 values of models examined are very close to each other. Also, results of $R^2$are not necessarily the same as AIC.The changes in parameters of some individual model obtained with different error function are impressive and for some isotherm model, there are significant differences between linear and nonlinear parameters. Although an average adsorption capacity of linear and nonlinear model is not statistically different from each other, the values of error functions for nonlinear method are less than those for linear method. Therefore, it can be concluded that nonlinear regression is a better method than linear regression to describe the isotherm models and to obtain their parameters.

Abbreviations

Parameter	Definition	Parameter	Definition
A_T	Tempkin isotherm model equilibrium binding constant (L/g)	$q_{e,calc}$	Calculated amount of adsorbate in the adsorbent at equilibrium (mg/g)
a_e	Initial sorption rate (mMol/g min)	$q_{e,exp}$	Experimental amount of adsorbate in the adsorbent at equilibrium (mg/g)
b	Langmuir isotherm model constant (L/mg)	q_s	Theoretical isotherm saturation capacity (mg/g)
b_T	Tempkin isotherm model constant (KJ/Mol)	R	Gas constant (J/Mol K)
C	Adsorbate initial concentration (mg/L)	T	Absolute temperature(K)
C_e	Equilibrium concentration (mg/L)	V	Reactor volume (L)
k_{ad}	Dubinin–Radushkevich isotherm model constant (Mol^2/kJ^2)	ε	Dubinin–Radushkevich isotherm constant
K_F	Freundlich isotherm model constant (mg/g) related to adsorption capacity		
M	Mass of adsorbent (g).		
n	Adsorption intensity (in Freundlich isotherm model)		
n	Number of data point (in error function equations)		
p	Number of parameters within the isotherm equation		
Q_0	Maximum monolayer coverage capacities (mg/g)		
q	Amount of adsorbate in the adsorbent at equilibrium (mg/g)		

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