Mehdinejadiani, B., Amininasab, S.M., Manhooei, L., (2018), Linear and non-linear methods for estimating the isotherm parameters of nitrate adsorption onto modified wheat straw pp. 64-70. In Gastescu, P., Bretcan, P. (edit, 2018), *Water resources and wetlands*, 4th International Conference Water resources and wetlands, 5-9 September 2018, Tulcea (Romania), p.312

Available online at http://www.limnology.ro/wrw2018/proceedings.html

4th International Conference Water resources and wetlands, 5-9 September 2018, Tulcea (Romania)

LINEAR AND NON-LINEAR METHODS FOR ESTIMATING THE ISOTHERM PARAMETERS OF NITRATE ADSORPTION ONTO MODIFIED WHEAT STRAW

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Abstract

This paper compared linear and non-linear methods for estimating the parameters of four isotherm models including Langmuir, Freundlich, Temkin and Dubinin-Radushkevich. Each model was fitted individually to equilibrium experimental data of nitrate adsorption onto modified wheat straw using the linear and non-linear methods. A detailed analysis was conducted to study the effect of the various error criteria on the estimated values of the parameters and to determine the best error function in the non-linear method. The results indicated that hybrid fractional error function was the most appropriate error function to estimate the parameters of the Langmuir, Freundlich and Temkin isotherm models while chi-square function was the best one to obtain the parameters of the Dubinin-Radushkevich isotherm model. The values of error functions and determination coefficients revealed that the non-linear method estimated more accurately the parameters of isotherm models, compared to the linear method. Also, Comparison of isotherm models indicated that, both for linear and non-linear methods, the Langmuir model provided the best fit to the experimental data. Overall, the non-linear method overcomes the drawbacks of the linear method and can determine efficiently the most optimum error function, the most set of parameters and the best-fit isotherm model.

Keywords: Adsorption, Error function, Isotherm models, Optimization, "Solver" add-in in Excel™

1 INTRODUCTION

Contamination of surface and ground waters by nitrate, which is mainly resulted from agricultural activities, is a serious worldwide environmental problem. The high concentration of nitrate in water imperils health of human and animals drinking these waters and leads to eutrophication of water bodies. Among the various methods used for nitrate removal from water, adsorption approach has received an increasing attraction as an attractive and promising alternative because of simplicity, easy operation, satisfactory results, regeneration and affordability (Loganathan et al., 2013).

Equilibrium adsorption experiments are utmost important in investigating adsorption processes because they provide useful information to understand the adsorption processes. Mathematical models of equilibrium adsorption, generally known as adsorption isotherms, are priceless tools to explain mobility of adsorbate from solution to solid phase adsorbent (Krishni et al., 2014). The adsorption isotherms are critical in designing adsorption systems, providing an insight into adsorption mechanism, determining adsorption capacity of adsorbents and assessing performance of adsorption system (Krishni et al., 2014; Shahmohammadi-Kalalagh et al., 2015; Nebaghe et al., 2016). Therefore, the determination of the most appropriate adsorption isotherm for describing experimental equilibrium data and the accurate estimation of its parameters are essential to design adsorption systems.

Linear regression method (i.e. the linearization of the adsorption isotherms) has been widely used to estimate the parameters of the adsorption isotherms and to evaluate the quality of fits and performance of adsorption because of its simplicity and software availability (Chowdhury et al., 2011; Bartoňová et al., 2017). However, several previous works have demonstrated that the linear regression method may not be a proper approach to estimate the parameters and to determine the most suitable adsorption isotherm (e.g., Kumar et al., 2008; Zhang et al., 2015; Nebaghe et al., 2016). This stems from this fact that the linearization of the adsorption isotherms may implicitly change the error structure and violate the normality assumption of the linear method (Bartoňová et al., 2017). Therefore, in recent years, non-linear regression method has been recommended to estimate the parameters of the adsorption isotherms and to evaluate the quality of fits (Bartoňová et al., 2017). The non-linear method minimizes error distribution between the experimental equilibrium data and the predicted values by adsorption isotherm (Nebaghe et al., 2016). To this end, the non-

linear method utilizes a non-linear optimization technique which requires a more complex mathematical method (Chowdhury et al., 2011; Tran et al., 2017). The main superiority of the non-linear method to the linear one is that the problems resulted from the linearization can be avoided. In addition, the non-linear method provides a more reliable comparison between adsorption isotherms because the experimental equilibrium data and the predicted values by adsorption isotherms are in the fixed x and y axes (Kumar et al., 2008).

The present study aims to compare the linear and non-linear regression methods in estimating the parameters of Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models for nitrate adsorption onto modified wheat straw (MWS). Furthermore, the paper investigates the applicability of five error functions, including sum square error (ERRSQ), hybrid fractional error function (HYBRID), Marquardt's percent standard deviation (MPSD) and Chi-square (χ^2) to evaluate the fitness quality of the isotherm models.

2 MATERIALS AND METHODS

2.1 Adsorbate and adsorbent

All chemicals utilized in this study were bought from Merck (Germany) and used without any purification. Nitrate ion and chemically modified wheat straw (MWS) were used as adsorbate and adsorbent, respectively. Nitrate stock solution was prepared by dissolving potassium nitrate (KNO_3) in deionized water and the nitrate solutions with desirable concentrations were obtained by serial dilution of the stock solution. The wheat straw (WS) was collected from a local field in Dehgolan, Kudristan province, Iran. The WS was mechanically grinded and modified using 3-chloro propyl trimethoxysilane (CPTMS) and (1,4-diazabicyclo[2.2.2]octane) (DABCO). The detailed about modification steps are given in Mehdinejadiani et al. (2018).

2.2 Equilibrium adsorption experiments

Batch equilibrium adsorption experiments were conducted at initial nitrate concentration of 20, 40, 60, 80, 100 and 150 mg L^{-1} under operational conditions of initial pH of solution=7, amount of MWS=0.1 g, agitation period=10 min, agitation rate=120 rpm and volume of solution=50 mL. Subsequently, to separate the adsorbent from aqueous solution, samples were filtered through Whatman #42 paper. Finally, the residual nitrate concentration in each filtrate sample was measured spectrophotometrically. Each batch experiment was carried out triplicate to ensure reproducibility of results that only average values are presented here. The adsorbed nitrate amount onto unit mass of MWS (nitrate adsorption capacity onto MWS) at equilibrium, q_e (mg g^{-1}) was calculated by:

$$q_e = \frac{C_i - C_e}{m} \times V \quad (1)$$

where C_i and C_e are the initial nitrate concentration and the residual nitrate concentrations at equilibrium (mg L^{-1}), respectively; V is the solution volume (L^3) and m is the MWS mass (g).

2.3 Adsorption isotherm models

The four most common isotherm models (i.e. Langmuir, Freundlich, Temkin and Dubinin-Radushkevich) were used to describe the experimental equilibrium data of nitrate/MWS system. Table 1 presents the non-linear and linear forms of the isotherm models used. The Langmuir isotherm is based on the assumptions of the structurally homogeneous adsorbent and the monolayer adsorption. The first assumption implies this fact that all adsorption sites are identical and energetically equivalent. However, the second one suggests that when an adsorbate molecule adsorbs on a site, no further adsorption can occur at that site (Foo and Hameed 2010; Chowdhury et al., 2011; Tran et al., 2017). The Freundlich isotherm can describe multilayer adsorption. It assumes that the adsorbent surface is heterogeneous with non-uniform distribution of adsorption heat and affinity over the surface (Foo and Hameed 2010). By ignoring very low and large concentrations, the Temkin isotherm assumes that adsorption heat of all molecules decrease linearly instead of logarithmic with coverage (Foo and Hameed 2010). The Dubinin-Radushkevich (D-R) isotherm is usually used to account for the porous structure effect of the adsorbent and to distinguish the physical and chemical adsorption of metal ions by analyzing free energy of each adsorbate molecule (Foo and Hameed 2010; Tran et al., 2017).

2.4 Estimation of isotherm parameters

In the linear regression method, the parameters of the isotherm models were determined using various plots of q_e versus C_e (see Table 1). However, in the non-linear regression method, the parameters were estimated by minimizing one of the error functions presented in Table 1. To this end, the ***Solver add-in***", Microsoft Office Excel (2016 version) (Tran et al., 2017) was used. To select the most optimum set of each isotherm parameters among the obtained sets by minimizing each error function in the non-linear method, the sum of normalized errors (SNE) was used. The minimum value of SNE determines the most optimum set of parameters and the best error function to estimate the parameters (Gimbert et al., 2008). The values of the error functions which resulted in the minimum value of SNE along with the corresponding coefficient of determination (r^2) were utilized to determine the most optimum isotherm and compare the linear and non-linear regression methods. The r^2 value was calculated using the following equation (Tran et al., 2017):

$$r^2 = 1 - \frac{\sum_{i=1}^{n} (q_{e,\exp} - q_{e,cal})_i^2}{\sum_{i=1}^{n} (q_{e,\exp} - \overline{q}_{e,\exp})_i^2} \quad (2)$$

where $\overline{q}_{e,\exp}$ is the average of measured values of q_e and the other variables are defined in Table 2.

3 RESULTS AND DISCUSSION

3.1 Linear method

Table 2 gives the parameters of the linear isotherm models and the corresponding error functions. Based on the values of ERRSQ, HYBRID, MPSD, χ^2 and r^2, the linear form of the Langmuir isotherm model better describes the equilibrium experimental data of nitrate adsorption onto MWS in comparison with the other linear isotherm models. As can be seen in Table 2, the Langmuir isotherm model is followed by Temkin, Dubinin-Radushkevich and Freundlich, respectively. Figure 1a also confirms these findings.

3.2 Non-linear method

Table 2 also presents the parameters of the non-linear isotherm models together with the values of the error functions and SNE. Bold values represent the minimum values of SNE for relevant error function. According to Table 2, the lowest value of SNE was obtained using the HYBRID function for the Langmuir, Freundlich and Temkin isotherm models. Therefore, the sets of parameters resulted from the application of this error function are the best ones for these three models. It is necessary to mention that ability of the HYBRID function to estimate isotherm parameters has been reported in several previous studies (e.g., Gunay 2007; Gimbert et al., 2008; Millar et al., 2016). For the Dubinin-Radushkevich isotherm model, the chi-square function (χ^2) yields the minimum value of SNE and, therefore, the most optimum set of parameters. Considering the values of the error functions related to the minimum SNE value and the r^2 value of each isotherm model, the Langmuir isotherm model has the lowest error for describing nitrate adsorption onto MWS. As shown in Table 2, the Langmuir isotherm model is followed by Temkin, Dubinin-Radushkevich and Freundlich, respectively. Figure 2b also verifies these findings.

As mentioned above, both the linear and the non-linear regression methods demonstrate the excellent fit of the Langmuir isotherm model. Therefore, the nitrate adsorption onto MWS is monolayer and the MWS is structurally is homogeneous.

Table 1. List of studied isotherm models and used error functions in this work

Isotherm	Non-linear form	Linear form	Plot of linear form	References
Langmuir	$q_e = \frac{q_{\max} b C_e}{1 + b C_e}$	$\frac{C_e}{q_e} = \frac{1}{b q_{\max}} + \frac{C_e}{q_{\max}}$	$\frac{C_e}{q_e}$ vs C_e	Tran et al., 2017
Freundlich	$q_e = K_F C_e^{1/n_F}$	$\log q_e = \log K_F + \frac{1}{n_F} \log C_e$	$\log q_e$ vs $\log C_e$	Foo and Hameed, 2010
Temkin	$q_e = \frac{RT}{B_T} \ln(A_T C_e)$	$q_e = \frac{RT}{B_T} \ln A_T + \frac{RT}{B_T} \ln C_e$	q_e vs $\ln C_e$	Foo and Hameed, 2010
Dubinin-Radushkevich	$q_e = q_{DR} \exp(-K_{DR} \varepsilon^2)$	$\ln q_e = -K_{DR} \varepsilon^2 + \ln q_{DR}$	$\ln q_e$ vs ε^2	Tran et al., 2017

Error function	Expression	
Sum squares errors	$\sum_{i=1}^{n} (q_{e,\exp} - q_{e,cal})_i^2$	Chowdhury et al., 2011
Hybrid fractional error function	$\frac{100}{n-p} \times \sum_{i=1}^{n} \left[\frac{(q_{e,\exp} - q_{e,cal})^2}{q_{e,\exp}} \right]_i$	Chowdhury et al., 2011
Marquardt's percent standard deviation	$100 \times \sqrt{\frac{1}{n-p} \cdot \sum_{i=1}^{n} \left(\frac{q_{e,\exp} - q_{e,cal}}{q_{e,\exp}} \right)_i^2}$	Foo and Hameed, 2010
Chi-square	$\sum_{i=1}^{n} \left[\frac{(q_{e,\exp} - q_{e,cal})^2}{q_{e,cal}} \right]_i$	Tran et al., 2017

$q_{\max}$ (mg g^{-1}) is the maximum adsorption capacity of adsorbent; b (L mg^{-1}), K_F (mg g^{-1} (mg $L^{-1})^{-1/n_F}$), B_T (J mol^{-1}), A_T (L mg^{-1}), and q_{DR} (mg g^{-1}) are the constants of the Langmuir, Freundlich, Temkin and Bubinin–Radushkevich isotherm models, respectively; n_F (dimensionless) and K_{DR} (mol^2 kJ^{-2}) are the exponents of the Freundlich and Bubinin–Radushkevich isotherm models, respectively; R is the universal gas constant (8.314 J mol^{-1} K^{-1}); T is the absolute temperature (K); $\varepsilon = RT \ln(1 + C_e^{-1})$; $q_{e,\exp}$ is each value of q_e experimentally measured; $q_{e,cal}$ is each value of q_e predicted by the fitted model; n is the number of measurement points and p is the number of the fitted model parameters.

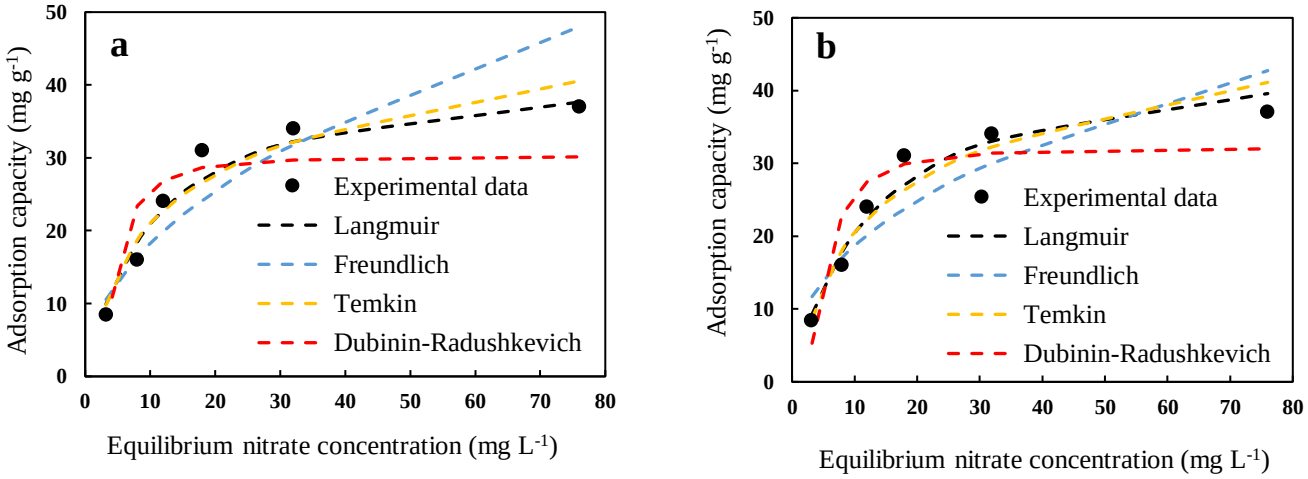

Figure 1. Experimental data and the fitted isotherm models for nitrate adsorption onto MWS, (a) Linear forms of isotherm models and (b) Non-linear forms of isotherm models

Table 2. Parameters of isotherms with error analysis for nitrate adsorption onto MWS

	Linear form	ERRSQ	HYBRID	MPSD	χ^2
Langmuir					
q_{max}	42.92	44.51	46.24	47.95	46.40
b	0.09	0.09	0.08	0.07	0.08
ERRSQ	29.56	**26.46**	29.65	36.43	28.73
HYBRID	33.41	32.37	**27.78**	30.29	28.32
MPSD	14.01	14.40	11.20	**10.40**	11.86
χ^2	1.33	1.22	1.15	1.29	**1.128**
r^2	0.96	0.96	0.96	0.95	0.96
SNE	-	3.67	**3.34**	3.66	3.36
Freundlich					
K_F	6.05	9.49	7.28	5.81	8.28
n_F	2.09	2.97	2.45	2.11	2.61
ERRSQ	195.69	**107.22**	129.05	178.53	118.55
HYBRID	155.80	161.38	**126.79**	146.96	139.77
MPSD	24.41	37.26	26.40	**23.39**	31.59
χ^2	5.97	5.10	5.29	6.69	**4.82**
r^2	0.72	0.85	0.81	0.74	0.83
SNE	-	3.36	**3.01**	3.54	3.10
Temkin					
B_T	255.36	255.36	241.91	239.00	236.88
A_T	0.86	0.86	0.73	0.70	0.72
ERRSQ	46.76	**46.76**	48.98	50.38	50.36
HYBRID	46.04	46.01	**41.19**	41.59	42.25
MPSD	15.18	15.17	12.31	**12.14**	12.59
χ^2	1.83	1.83	1.71	1.74	**1.66**
r^2	0.93	0.93	0.93	0.93	0.93
SNE	-	3.93	**3.61**	3.66	3.67

Dubinin-Radushkevich					
q_{DR}	30.23	32.18	30.97	28.04	32.14
K_{DR}	2.98	3.73	3.74	2.89	3.96
ERRSQ	135.03	**101.12**	113.03	179.12	102.54
HYBRID	145.99	141.19	**135.40**	159.13	138.89
MPSD	27.01	29.66	28.69	**25.71**	30.39
χ^2	5.04	3.86	3.98	6.79	**3.57**
r^2	0.81	0.85	0.84	0.74	0.85
SNE	-	3.03	3.01	3.85	**2.97**

3.3 Linear method versus non-linear method

As can be seen in Table 2 and Figure 1, the error function values for the non-linear method are generally lower than those for the linear method at each studied isotherm model, especially in the case that the minimum SNE value is obtained. The similar results have been reported in previous studies (e.g., Chowdhury et al., 2011; Shahmohammadi-Kalalagh et al., 2015; Nebaghe et al., 2016). The less accuracy of the linear method can be attributed to variation in error structure distribution and violation of theories behind the isotherm resulted from different axial settings (Chowdhury et al., 2011). Moreover, the linear method assumes that the error distribution at every value of independent variable (the x-axis) is uniform and the distribution of the scatter vertical points around the line is normal. These assumptions are usually incorrect because the isotherm models generally are non-linear (Chowdhury et al., 2011). Also, in the non-linear method, several sets of parameters are obtained by minimizing the various error functions for each isotherm model which one can select the most optimum set according to SNE values. Therefore, the non-linear is more flexible than the linear method which only yields a set of parameters for each model.

Despite the superiority of the non-linear method, both methods confirm that the Langmuir method is the best-fit isotherm model to describe nitrate adsorption onto MWS. The q_{max} values obtained from two methods is nearly close to each other (see Table 2). Also, both methods give the exponent value of the Freundlich isotherm (n_F) in the range of 1 to 10 which demonstrates the nitrate adsorption process onto MWS is favorable (Chen et al., 2014). Therefore, both methods describe well governing mechanism on adsorption process. However, the non-linear method is more capable to determine the most suitable error function, the most optimum set of parameters and the best-fit isotherm model.

4 CONCLUSION

In this study, the equilibrium experimental data of nitrate adsorption onto MWS were fitted to the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models and the parameters of the models were individually estimated using linear and non-linear regression methods. The results showed that the non-linear method estimated more accurately the parameters in comparison with the linear method. In addition, the non-linear analyses indicated that the HYBRID function yielded the most optimum sets of parameters for the Langmuir, Freundlich and Temkin isotherm models while the chi-square function (χ^2) resulted in the most optimum set of parameters for the Dubinin-Radushkevich isotherm model. Notwithstanding the superiority of the non-linear method, both methods indicated that the nitrate adsorption onto MWS followed the Langmuir isotherm model and the adsorption process was favorable. In a nutshell, the non-linear method overcomes the limitations of the linear method and can be used as a robust method to determine the most appropriate error function, to estimate the parameters of the isotherm models and to select the most optimum isotherm model.

ACKNOWLEDGMENT

The authors would like to thank University of Kurdistan for the financial support in this work.

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