

Least-squares regression of adsorption equilibrium data: Comparing the options

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Abstract

Experimental and simulated adsorption equilibrium data were analyzed by different methods of least-squares regression. The methods used were linear regression, nonlinear regression, and orthogonal distance regression. The results of the regression analysis of the experimental data showed that the different regression methods produced different estimates of the adsorption isotherm parameters, and consequently, different conclusions about the surface properties of the adsorbent and the mechanism of adsorption. A Langmuir-type simulated data set was calculated and several levels of random error were added to the data set. The results of regression analysis of the simulated data set showed that orthogonal distance regression gives the most accurate and efficient estimates of the isotherm parameters. Nonlinear regression and one form of the linearized Langmuir isotherm also gave accurate estimates, but only at low levels of random error.

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1. Introduction

Adsorption is the most commonly used technique for the treatment of industrial wastewaters. Activated carbon has been used widely for the removal of many pollutants; however, activated carbon is expensive and not easily regenerated [1]. Therefore, low-cost adsorbents that are able to bind pollutants have been extensively tested [1–3]. Equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms, usually the relationship between the quantity adsorbed and that remaining in solution at a fixed temperature. These equilibrium adsorption isotherms are important for the design of adsorption systems, and the constants of the isotherms express the surface properties and the capacities of the adsorbents. Although there are many adsorption isotherms in the literature, the most widely used by researchers are two of the oldest isotherms, namely Freundlich [4] and Langmuir [5] isotherms.

The Freundlich isotherm can be used for non-ideal adsorption on heterogeneous surfaces. It is expressed by the following

empirical equation:

$$q_e = K_F C_e^{1/n} \quad (1)$$

where K_F is the Freundlich adsorption constant ((mg/g)(L/g)ⁿ) and $1/n$ is a measure of the adsorption intensity.

The development of the Langmuir isotherm assumes monolayer adsorption on a homogenous surface. It is expressed as

$$q_e = (q_m K_a C_e) / (1 + K_a C_e) \quad (2)$$

where C_e is the equilibrium concentration (mg/L), q_e the amount adsorbed (mg/g), q_m is q_e for complete monolayer adsorption capacity (mg/g), and K_a is the equilibrium adsorption constant (L/mg).

As an alternative to the BET method, the adsorption of dyes from aqueous solution has been used to determine the specific surface area (SSA) of many substances [6,7]. Assuming that the surface is homogenous and completely covered by dye molecules, the SSA (m²/g) can then be related to the first layer adsorption density (Γ_m) as described in Eq. (3):

$$SSA = \Gamma_m N A \quad (3)$$

where N is the Avogadro's number (6.023×10^{23} molecules/mol) and A is the apparent surface area occupied by one dye

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Nomenclature

A	the apparent surface area occupied by one dye molecule (m^2)
C_0	initial concentration of methylene blue (mg/L)
C_e	equilibrium concentration of methylene blue (mg/L)
K_a	the equilibrium adsorption constant in Langmuir's equation (L/mg)
K_F	Freundlich adsorption constant ($(\text{mg/g})(\text{L/g})^n$)
K_n	the equilibrium adsorption constant of the n th layer (L/mg)
LR	linear regression
m	the weight of adsorbent
MLA	multilayer adsorption isotherm
NLR	nonlinear regression
ODR	orthogonal distance regression
q_e	amount of adsorbate adsorbed at equilibrium (mg/g)
q_m	the value of q_e for complete monolayer adsorption capacity (mg/g)
r^2	coefficient of determination
S	the sum of the squares of the residuals
SSA	specific surface area (m^2/g)
V	the volume of adsorbate solution (L)
x	the independent variable
y	the dependant variable
<i>Greek letters</i>	
β	the regression parameters vector
Γ	total adsorption density (mg/g)
Γ_m	the first layer adsorption density (mg/g)
δ_i	the error in x_i
ε_i	the error in y_i

molecule. The total multilayer adsorption capacity (Γ , mg/g) can be expressed by the following equation [8]:

$$\Gamma = (\Gamma_m K_1 C_e) / ((1 - K_2 C_e)[1 + (K_1 - K_2) C_e]) \quad (4)$$

where Γ_m is the monolayer adsorption capacity (mg/g), C_e the equilibrium MB concentration (mg/L), and K_1 and K_2 are the equilibrium adsorption constants of the first and second layers (L/mg). It is noted that in case of monolayer adsorption K_2 will

have a value of zero, and Eq. (4) is reduced to the monolayer Langmuir isotherm of Eq. (2).

There is no linear transformation for the multilayer adsorption (MLA) isotherm, but Freundlich isotherm can be linearized by taking the logarithm of both sides of Eq. (1), and also Langmuir isotherm can be linearized to at least three different linear forms as shown in Table 1 [9]. Linear regression has been the most commonly used technique to determine the adsorption isotherm parameters for Freundlich and Langmuir isotherms for many years. Linear regression was the easy and practical way when it was first suggested several decades ago, but it has become a custom principle nowadays [10] and is still widely used in spite of the availability of micro-computers and advanced statistical software. The mathematical linearization of nonlinear isotherm models leads to biased estimates of the isotherm parameters [11–16], and therefore, some researchers apply iterative nonlinear regression to determine the best fitting isotherm model and to evaluate its parameters [17–19]. However, nonlinear regression is also not statistically correct because there are experimental errors in both the dependent and the independent variables in the isotherm equations.

1.1. Least-squares regression

Least squares is arguably the most common method for fitting data to a model when there are errors in the observations [20]. For example, given the data pairs (x_i, y_i) ; $i = 1, 2, \dots, n$, where x_i is the independent variable and y_i is the dependent variable, suppose that x_i and y_i are related by a smooth, possibly nonlinear function f , i.e.,

$$y_i = f(x_i; \beta) \quad (7)$$

where β is the regression parameters vector. If the function is linear, the relationship takes the form

$$y_i = \beta_0 + \beta_1 x \quad (8)$$

The above equations state that if y and x could be measured with no errors in either x_i or y_i , they would be exactly related. Typical examples where this might be thought to be the case occur in the physical sciences when the variables are related by fundamental physical laws [21]. In classical least squares, it is assumed that x_i is known exactly and y_i is observed with error. Although it is often the case that x_i have errors, these errors can be safely ignored if they are much smaller than the corresponding

Table 1
Linearized forms of Freundlich and Langmuir isotherms

Isotherm	Nonlinear form	Linear form	Plot
Freundlich	$q_e = K_F C^{1/n}$	$\log(q_e) = \log(K_F) + \frac{1}{n} \log(C_e)$	$\log(q_e)$ vs. $\log(C_e)$
Langmuir-I		$\frac{C_e}{q_e} = \frac{1}{K_a q_m} + \frac{1}{q_m} C_e$	$\frac{C_e}{q_e}$ vs. C_e
Langmuir-II	$q_e = \frac{q_m K_a C_e}{1 + K_a C_e}$	$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_a q_m} \frac{1}{C_e}$	$\frac{1}{q_e}$ vs. $\frac{1}{C_e}$
Langmuir-III		$\frac{q_e}{C_e} = K_a q_m - K_a q_e$	$\frac{q_e}{C_e}$ vs. q_e

errors in y_i . Thus, taking the error in y_i to be given by ε_i , we write

$$y_i + \varepsilon_i = f(x_i; \beta) \quad (9)$$

We now seek the values of the parameters β that minimize the sum of the squares of the residuals (S):

$$S = \sum_{i=1}^n (y_i - f(x_i; \beta))^2 \quad (10)$$

This can be interpreted as minimizing the sum of the squares of the vertical distances from the data points to the fitted curve.

If $f(x)$ is linear in parameters, the solution is simple and reduces to a system of linear equations. However, when $f(x)$ is not linear in parameters, the solution is either performed as a general unconstrained optimization problem, or by an iterative algorithm that is developed especially to solve least squares problems [22], such as the Gauss–Newton algorithm or the Levenberg–Marquardt algorithm.

Based on the Gauss–Markov theorem, least-squares regression makes various assumptions about the errors in a regression model. The basic assumptions are [20,23]:

- (1) The error, ε , is uncorrelated with x , the independence assumption.
- (2) The error has the same variance (S^2) across the different levels of x , i.e. the variance of ε is homoskedastic and not heteroskedastic.
- (3) The values of ε are independent of each other, i.e. not auto-correlated or serially correlated.
- (4) The error is normally distributed.
- (5) The independent variable x is fixed, i.e. there is no measurement error in x .

If these assumptions are met, then the estimates of the regression constant and the regression coefficients are unbiased and efficient. Violation of one or more of these assumptions may lead to biased and/or inefficient estimates.

1.2. Effect of linearization

Linearization is used extensively in least-squares regression and model testing of experimental data, possibly because regression analysis of linear models can be carried out graphically and also because linear regression software is readily available. Another reason that explains the affinity to linear models is the simplicity of statistical estimation and hypothesis testing. Algorithms for estimating parameters of linear models are straightforward, direct solutions are available, and iteration is not required.

Unfortunately, linearization may lead to false conclusions [9–13,24–25], and the statistical tests used to check the goodness of fit will often not detect that the parameters are incorrect. In other words, statistical tests performed to check the quality of the fit between the data and the calculated curve can be meaningless if they are performed using transformed data. Nonlinear transformation distorts the experimental error. Linear regression assumes that the vertical scatter of points around the line

follows a normal distribution, and that the standard deviation is the same at every value of x . These assumptions are usually not true with the transformed data. A second problem is that some transformations alter the relationship between x and y . Since the assumptions of linear regression are violated, the results of linear regression are incorrect. The values derived from the slope and intercept of the regression line are not the most accurate determinations of the variables in the model [25].

1.3. Dealing with errors in the independent variable x

It is not widely appreciated in the adsorption community that a special treatment of the least squares problem is required when there is more than one observation having error per equation of condition. This is commonly referred to as the measurement error model or the errors-in-variables problem. Failure to formulate the problem correctly may result in an asymptotically biased estimator, even when fitting a straight line.

Orthogonal distance regression provides one method for fitting these error-in-variables models. If the error in x_i cannot be ignored and δ_i denotes the error in x_i , then Eq. (9) becomes

$$y_i + \varepsilon_i = f(x_i + \delta_i; \beta) \quad (11)$$

and it is reasonable to approximate the parameter β by minimizing the sum of the squares of the orthogonal distances from the data points to the curve $y_i = f(x_i; \beta)$. As shown by Boggs et al. [26] this gives rise to the orthogonal distance regression (ODR) problem given by

$$\min_{\beta, \delta} \frac{1}{2} \sum_{i=1}^n [(f(x_i + \delta_i; \beta) - y_i)^2 + \delta_i^2] \quad (12)$$

Note that ODR is easily seen to be equivalent to

$$\min_{\beta, \delta, \varepsilon} \frac{1}{2} \sum_{i=1}^n \varepsilon_i^2 + \delta_i^2 \quad (13)$$

subject to

$$y_i + \varepsilon_i = f(x_i + \delta_i; \beta), \quad i = 1, \dots, n \quad (14)$$

from which it is easy to see that ODR is, indeed, minimizing the sum of the squares of the orthogonal distances. In ordinary least squares, we try to minimize the sum of the vertical squared distances between the observed points and the fitted line. In ODR, we try to fit a line which minimizes the sum of the squared distances between the observed points and the fitted line, as measured perpendicular to that line.

In 1996, Schulthess and Dey published an article that describes a nonlinear least-squares regression analysis of the Langmuir equation that is based on minimizing the sum of the normal distance of the data to the isotherm [27]. The authors have noted that this regression method yields different Langmuir constants when compared with linear and nonlinear regression methods. However, they just pointed out that their regression method should be less biased than linear and nonlinear regression methods and they did not give recommendation for using one method of regression, quoting “None of the regressions are

endorsed per se since they should all agree if the isotherm is Langmuirian". This subject has not been investigated again, and the work of Schulthess and Dey is rarely referenced in adsorption literature.

The objectives of this paper are (1) to demonstrate the differences in estimated isotherm parameters arising from the application of different regression methods to the adsorption equilibrium data, (2) to discuss the causes of these differences, and (3) to systematically assess the accuracy of predictions from different regression methods. For demonstration, the adsorption of Methylene Blue (MB) onto Water Hyacinth (WH) is considered. The methods applied are linear regression, nonlinear regression, and orthogonal distance regression. A comparison of the best fitting model and the predicted parameter values obtained from each method is presented. In order to assess the accuracy of each regression method in the presence of measurement errors, simulated Langmuir-type data were simulated then random errors were added to the data set, the simulated data were subsequently analyzed by different least-squares regression methods, and the accuracy of predict isotherm parameters were compared.

2. Materials and methods

2.1. Adsorbent preparation

Live WH was collected from El-Mahmoudeya Canal, Alexandria, Egypt. Live WH consists of 94–95% water and barely contains 50–60 g total solid/kg [28]. The plants were thoroughly washed with water, the roots were cut out and disposed, and then the leaves and stems were left to dry in the sun for 14 days. In a recent publication, the sun-dried WH of El-Mahmoudeya Canal near Alexandria was analyzed [29]. It was found to contain 19% crude fiber, 18.2% ash, 21.1% crude protein, 1.0% crude lipids, and 40.7% nitrogen-free extract. In the present study, the sun-dried WH was subjected to washing, sulfonation, and chemical treatment with nitric acid to remove soluble compounds and to alter the surface properties.

The sun-dried WH was soaked in 2 M nitric acid for 24 h. The ratio of nitric acid solution to WH was 10 mL/g. It was then washed repeatedly with hot distilled water until the filtrate was free of nitrate. Sulfonated WH was obtained by heating at 70 °C for 3 h with a solution containing 19 g/L sodium bicarbonate and 168 g/L sodium sulfite [30]. The ratio of sulfonation solution to WH was 10 mL/g. After sulfonation, it was washed repeatedly with hot 0.1 M HCl solution until the supernatant was free of sulfate and magnesium. Washed WH was prepared by washing the sun-dried WH repeatedly with hot distilled water at 80 °C until the supernatant was free from magnesium. All types of treated WH were subsequently dried at 105 °C for 24 h, then ground and sieved to particle size 0.20–0.315 mm, and stored in a desiccator.

2.2. Methylene blue

Methylene blue ($C_{16}H_{18}N_3Cl \cdot 3H_2O$) was purchased from Sigma–Aldrich and used without further purification. All MB

solutions used in this study were prepared by weighing and dissolving the required amounts MB in distilled water.

2.3. Isotherm experiments

Adsorption isotherms of MB at 40 °C were obtained at different solution concentrations of MB and at the natural pH. The MB solution was not buffered during isotherm experiments to avoid the effect of buffering chemicals on the surface properties of WH and on the solution chemistry. All isotherm experiments were conducted in 100 mL polyethylene bottles containing 0.1 g of WH and 50 mL of MB solution, which were placed in a thermostatically controlled shaker operating at 150 rpm for 3 h. Initial experiments showed that 3-h shaking is enough to reach the equilibrium state in all cases. The initial concentration of MB was altered from 50 to 1000 mg/L. The residual MB concentration in solution after equilibrium was analyzed using Novaspec II spectrophotometer (Pharmacia LKB) at wavelength of 655 nm.

2.4. Numerical regression calculations

Linear, nonlinear, and orthogonal distance regression computations were carried out using the statistical software DATAPLOT [31] developed by NIST, the American National Institute for Statistics and Technology. DATAPLOT supports orthogonal distance regression using the ODRPACK library [27,32]. ODRPACK uses a trust region Levenberg–Marquardt method. The Levenberg–Marquardt method starts the calculations with the steepest descent method, and then gradually changes to Newton's method when approaching the solution. A major advantage of ODRPACK is that its scaling algorithm automatically accommodates poorly scaled problems, in which the model parameters and/or unknown errors in the independent variables vary widely in magnitude.

3. Results and discussion

3.1. Regression analysis of experimental isotherm data

3.1.1. Nitric acid treated water hyacinth (NWH)

The experimental equilibrium data for the adsorption of MB at 40 °C were fitted to Freundlich isotherm, Langmuir isotherm, and the multilayer adsorption Langmuir isotherm. The fitting of experimental data to the isotherms was performed by the methods of linear regression (LR), nonlinear regression (NLR), and ODR. The different regression methods resulted in different estimates of the parameters of adsorption isotherms as shown in Table 2 and Figs. 1 and 2.

The values of the K_f parameter of Freundlich isotherm estimated from LR, NLR, and ODR are 32.636, 47.612, and 83.085, respectively. Also the values of the n parameter are 2.706, 3.553, and 5.485, respectively. It is obvious that the differences in K_f and n are large and if it is required to use the Freundlich isotherm for modeling the equilibrium of adsorption in the system MB–NWH, then it must be decided which regression method to choose for prediction of the isotherm parameters. By comparing the values of the coefficient of determination, r^2 , it is found that

Table 2

Isotherm parameters estimated by different methods of regression for the system MB-NWH at 40 °C

Isotherm model	Regression results	Isotherm model	Regression results
Freundlich LR		Langmuir-III	
K_F (mg/g)(L/g) ⁿ	32.636 (23.681–44.978)	q_m (mg/g)	222.78 (122.41–323.15)
n	2.706 (2.184–3.554)	K_a (L/mg)	0.106 (0.0358–0.176)
r^2	0.9587	R^2	0.7512
Isotherm model	Regression results	Isotherm model	Regression results
Freundlich NLR		Langmuir NLR	
K_F (mg/g)(L/g) ⁿ	47.612 (23.09–72.136)	q_m (mg/g)	248.48
n	3.553 (2.306–4.780)	K_a (L/mg)	0.0524
r^2	0.9431	r^2	0.9712
SS	2667	SS	1348.2
Isotherm model	Regression results	Isotherm model	Regression results
Freundlich ODR		Langmuir ODR	
K_F (mg/g)(L/g) ⁿ	83.085 (41.174–124.94)	q_m (mg/g)	266.63 (248.00–285.25)
n	5.482 (2.720–8.244)	K_a (L/mg)	0.0327 (0.0198–0.0455)
SS _y	668	SS _{total}	170.3
		SS _y	65.7
Isotherm model	Regression results	Isotherm model	Regression results
Langmuir-I		MLA NLR	
q_m (mg/g)	257.43 (244.32–271.96)	Γ_m (mg/g)	215.47
K_a (L/mg)	0.0758 (0.0347–0.128)	K_1 (L/mg)	0.0747
r^2	0.9978	K_2 (L/mg)	0.000330
		r^2	0.9805
		SS	915.3
Isotherm model	Regression results	Isotherm model	Regression results
Langmuir-II		MLA ODR	
q_m (mg/g)	147.43 (94.139–339.72)	Γ_m (mg/g)	266.29 (247.57–285.01)
K_a (L/mg)	0.239 (0.188–0.330)	K_1 (L/mg)	0.0328 (0.0197–0.0458)
r^2	0.9463	K_2 (L/mg)	2.4×10^{-6}
		SS _{total}	170.7
		SS _y	66.5

Values in parenthesis are 95% confidence interval of the estimate.

the LR method has an r^2 value of 0.9587, which is higher than r^2 of NLR, 0.9431. This might suggest that LR fits the experimental data better than NLR, but the comparison here is not correct because in case of LR the r^2 values are calculated from the residuals of $\log q_e$ while in NLR the residuals of q_e are used to calculate r^2 value. Similarly, r^2 cannot be used to compare NLR and ODR because ODR has residuals in both x and y directions. Therefore, the goodness of fit in case of ODR is presented in Table 2 by means of the total sum of squared residuals, SS_{total} (x direction + y direction) and also by SS_y in the y direction, i.e. sum of q_e residuals. It is observed in Table 2 that SS_y values from NLR (2667) is much higher than SS_y from ODR (668) which indicates that the method of ODR gives predictions that fits the experimental data better than NLR. A visual inspection of Fig. 1 shows that although the regression of the linearized form of Freundlich isotherm results in a higher r^2 value than NLR, the predicted curve obtained from NLR passes closer to the experimental results, especially at the higher end of C_e where the curve from LR deviates significantly from the experimental results. It

is also observed in Fig. 1 that the predicted curve from ODR fits the experimental results better than LR and NLR, especially at high values of C_e .

Table 2 and Fig. 3 show the regression results of the three linearized forms of Langmuir isotherm along with NLR and ODR of experimental data on Langmuir isotherm. It is seen in Table 2 that LR of the experimental data on the three linearized forms of Langmuir isotherm, Langmuir I, II, and III, predicts different values for q_m , 257.43, 147.43, and 222.78 mg/g, respectively. In addition, the predicted values of K_a from Langmuir I, II, and III are 0.0756, 0.239, and 0.106 L/mg, respectively. It is also noticed that the 95% confidence intervals are quite different; Langmuir II has the widest confidence interval of q_m (94.139–339.72 mg/g) which demonstrates the high uncertainty of the estimate. The r^2 values are 0.9978, 0.9463, and 0.7512 for Langmuir I, II, and III, respectively, but it is not appropriate to compare the goodness of fit solely on the basis of r^2 because the three linearized forms involve different transformations of the x and y axis, leading to changes of the relative weights of data points and also to distor-

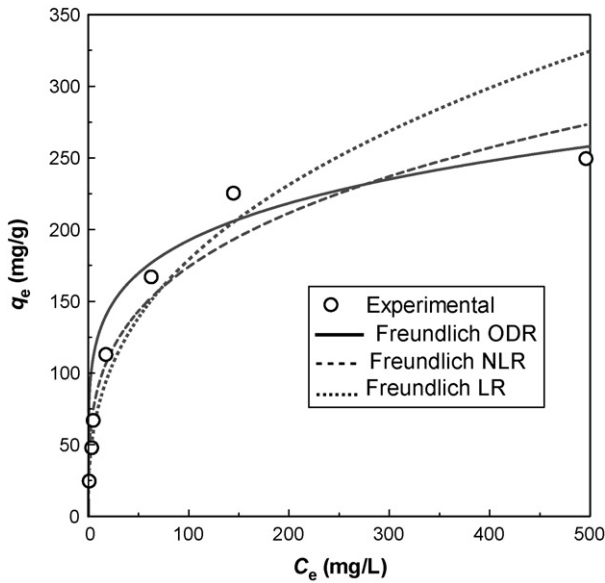


Fig. 1. Comparison of Freundlich isotherms estimated by different methods of regression for the system MB-NWH at 40 °C (pH 4.1–4.5; NWH dosage: 2 g/L; initial MB concentration: 50–1000 mg/L; agitation rate: 150 rpm).

tion of the correlation. By visual inspection of Fig. 2 it is seen that the curve predicted from the linearized Langmuir I gives a better fit to the experimental results than Langmuir II and III. It is interesting here to notice that although Langmuir III has the lowest value of r^2 (0.7512), its predicted curve passes much closer to the experimental data points than the curve predicted from Langmuir II ($r^2 = 0.9463$).

These discrepancies can be understood by examining the effects of the three linearization methods. In Langmuir I linearization, C_e/q_e is plotted against C_e so the x and y axis in the plot are not independent, leading to strengthening of

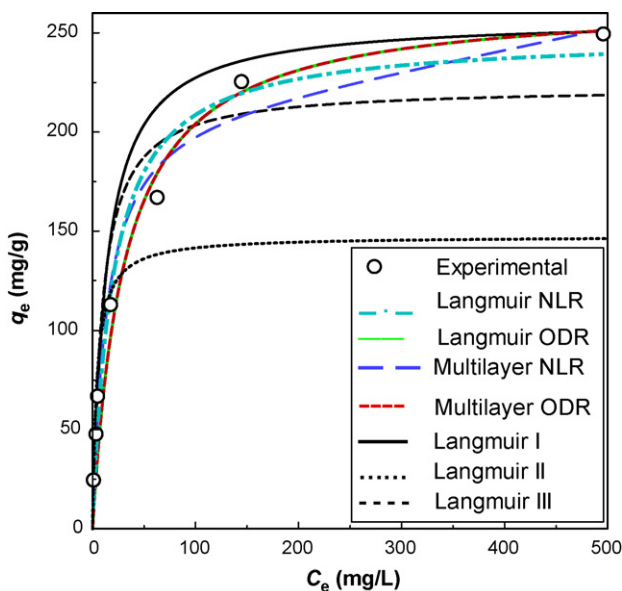


Fig. 2. Comparison of Langmuir and MLA isotherms estimated by different methods of regression for the system MB-NWH at 40 °C (pH 4.1–4.5; NWH dosage: 2 g/L; initial MB concentration: 50–1000 mg/L; agitation rate: 150 rpm).

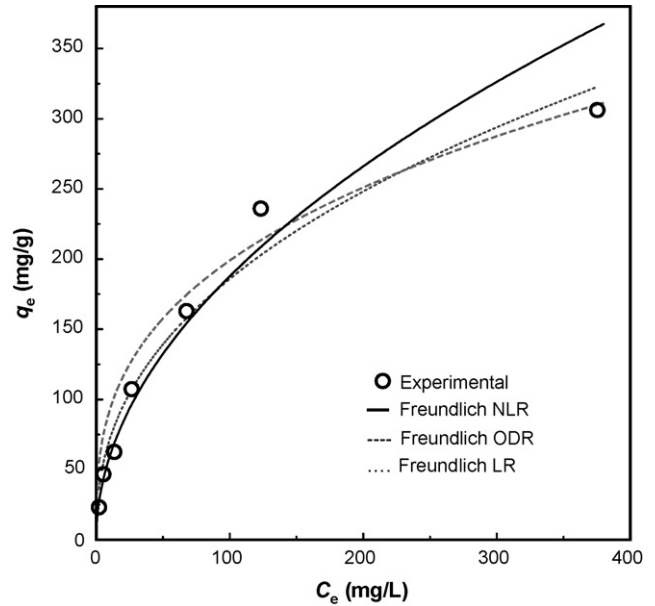


Fig. 3. Comparison of Freundlich isotherms estimated by different methods of regression for the system MB-WWH at 40 °C (pH 3.9–4.2; WWH dosage: 2 g/L; initial MB concentration: 50–1000 mg/L; agitation rate: 150 rpm).

correlation. This is known as spurious correlation (i.e. the observed correlation is a “mathematical artifact” without a real statistical meaning) between originally independent variables, it often occurs when the ratios between variables and/or the log-transforms of the variables are used to build parametric relationships between the variables themselves [33,34]. On the other hand, Langmuir II linearization involves plotting $1/q_e$ against $1/C_e$ which leads to a reversal in the relative weights of data points and makes the results of LR very sensitive to errors at low values of q_e (i.e. high values of $1/q_e$), giving the data points of low q_e extreme weights, and if the experimental error is random and independent of C_e then the relative error is expected to be highest at the lowest values of q_e , leading to biased estimates from Langmuir II linearization method. The linearization method Langmuir III involves ratios between the variables like Langmuir I, in this case the LR plot is q_e/C_e against q_e , but the transformation of coordinates and the distortion of error distribution leads to weakening of correlation compared to the untransformed correlation.

The results of fitting the experimental results to the Langmuir isotherm by NLR and ODR are also shown in Table 2 and Fig. 2. By comparing SS_y it is obvious that ODR gives a better fit ($SS_y = 65.7$) than NLR ($SS_y = 1348.2$), this is confirmed from Fig. 2 where it is clear that the curve predicted from ODR passes much closer to the experimental data points than the curve predicted from NLR. It is also noticed in Table 2 that the 95% confidence intervals of the parameters estimated by ODR are much smaller than the results of NLR, indicating less statistical uncertainty in the ODR results.

By fitting the experimental results to the MLA Langmuir model, it is found that the method of ODR clearly rejects the hypothesis of multilayer adsorption because the value of the first layer adsorption capacity Γ_m (266.29 mg/g) is almost exactly the

same as q_m previously estimated by ODR (266.63 mg/g), and also because the value of the adsorption constant of the second layer, K_2 , is extremely small (2.41×10^{-6} L/mg) compared to that of the first layer, K_1 , which is estimated to be 0.0328 L/mg. On the other hand, the results of NLR suggest the occurrence of multilayer adsorption because the estimated value of K_2 is comparable to K_1 , 3.3×10^{-4} and 7.47×10^{-2} L/mg, respectively, and also the value of Γ_m (215.47 mg/g) is significantly smaller than q_m previously estimated by NLR (248.48 mg/g). These results, however, are questionable because the 95% confidence interval of K_2 contains the zero.

3.1.2. Water-washed water hyacinth (WWH)

The regression results of adsorption equilibrium in the system MB-WWH at 40 °C are presented in Table 3. Values of K_F and n estimated from the three methods of regression are quite different from each other. The curves estimated from Freundlich isotherm by LR, NLR, and ODR are shown in Fig. 3, where it can be seen that the curve obtained from ODR fits the experimental data better than the curves from LR and NLR.

The general trend of the regression results of the three linearized forms of Langmuir isotherm is similar to the case of NWH; Langmuir I gives the highest r^2 value (0.9708) among the linearized forms, while Langmuir III gives the lowest r^2 value (0.7272) but its estimated curve fits the experimental data much better than Langmuir II which has a relatively high r^2 value (0.9693), as shown in Fig. 4.

On comparing the Langmuir parameters estimated by NLR and ODR, it is found that unlike the case of NWH, the values of q_m are relatively close, 356.25 and 365.77 mg/g for NLR and ODR, respectively. Also the values of K_a are 0.0152 and 0.0139 L/mg for NLR and ODR, respectively. An inspection of Fig. 4 shows that the curves estimated by NLR and ODR are very close and almost overlap in parts, but ODR fits the data better as indicated by its low SS_y (36.45) compared to NLR ($SS_y = 932.1$). This difference comes from the deviation at low C_e values where the slope of the curve is large. The geometrical shape of the curve portion with large slope creates conditions for the vertical deviation to be much larger than the orthogonal deviation. Therefore, the minimization of SS_y in NLR was not

Table 3
Isotherm parameters estimated by different methods of regression for the system MB-WWH at 40 °C.

Isotherm model	Regression results	Isotherm model	Regression results
Freundlich LR		Langmuir-III	
K_F (mg/g)(L/g) ⁿ	18.515 (13.903–24.6587)	q_m (mg/g)	288.20 (170.90–405.56)
n	1.988 (1.724–2.348)	K_a (L/mg)	0.0321 (0.00949–0.0546)
r^2	0.9826	R^2	0.7272
Isotherm model	Regression results	Isotherm model	Regression results
Freundlich NLR		Langmuir NLR	
K_F (mg/g)(L/g) ⁿ	27.241 (14.276–40.206)	q_m (mg/g)	356.25 (307.95–404.56)
n	2.398 (1.873–2.993)	K_a (L/mg)	0.01521 (0.00948–0.0209)
r^2	0.9764	r^2	0.9887
SS	1950	SS	932.1
Isotherm model	Regression results	Isotherm model	Regression results
Freundlich ODR		Langmuir ODR	
K_F (mg/g)(L/g) ⁿ	42.520 (21.422–63.618)	q_m (mg/g)	365.77 (342.18–389.36)
n	2.984 (2.201–3.767)	K_a (L/mg)	0.01393 (0.01071–0.1716)
SS_{total}	702.9	SS_{total}	130.3
SS_y	381.4	SS_y	36.45
Isotherm model	Regression results	Isotherm model	Regression results
Langmuir-I		MLA NLR	
q_m (mg/g)	330.86 (282.00–400.19)	Γ_m (mg/g)	290.06 (156.01–424.10)
K_a (L/mg)	0.02507 (0.0155–0.0648)	K_1 (L/mg)	0.0215 (0.00255–0.0405)
r^2	0.9708	K_2 (L/mg)	3.905×10^{-4} (-4.7×10^{-4} to 0.00126)
		r^2	0.9903
		SS	802.5
Isotherm model	Regression results	Isotherm model	Regression results
Langmuir-II		MLA ODR	
q_m (mg/g)	175.03 (112.13–398.66)	Γ_m (mg/g)	365.76 (331.43–400.09)
K_a (L/mg)	0.0749 (0.0622–0.094)	K_1 (L/mg)	0.01393 (0.00707–0.0208)
r^2	0.9693	K_2 (L/mg)	2.69×10^{-8} (-4.84×10^{-4} to 4.84×10^{-4})
		SS_{total}	130.3
		SS_y	36.45

Values in parenthesis are 95% confidence interval of the estimate.

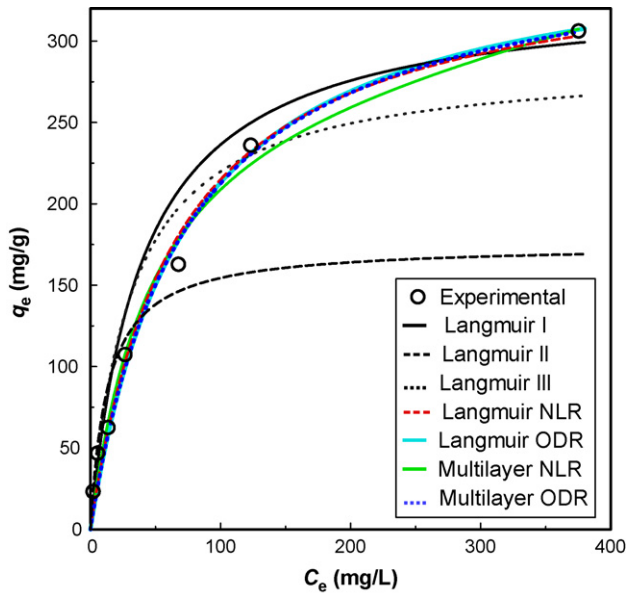


Fig. 4. Comparison of Langmuir and MLA isotherms estimated by different methods of regression for the system MB-WWH at 40 °C (pH 3.9–4.2; WWH dosage: 2 g/L; initial MB concentration: 50–1000 mg/L; agitation rate: 150 rpm).

as efficient as the minimization of $SS_y + SS_x$ in ODR because a small shift in x direction leads to a large decrease in the vertical deviation.

When NLR and ODR were used to fit the MLA model to the experimental data, the results in Table 3 show that ODR rejects the hypothesis of multilayer adsorption, while NLR estimates Γ_m to be 290.06 mg/g, much less than q_m estimated from the monolayer Langmuir isotherm to be 356.25 mg/g. Therefore, the NLR results suggest that adsorption of MB on WWH occurs by multilayer adsorption on a homogeneous surface, but this conclusion is questionable because the 95% confidence limits of K_2 includes the zero.

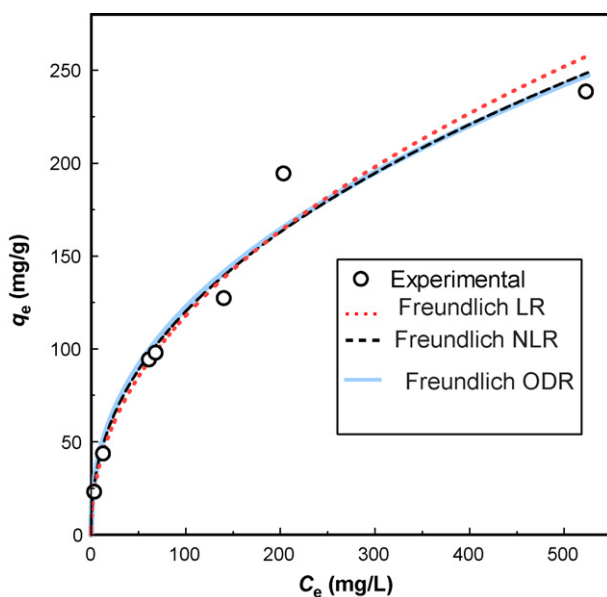


Fig. 5. Comparison of Freundlich isotherms estimated by different methods of regression for the system MB-SWH at 40 °C (pH 4.6–5.1; SWH dosage: 2 g/L; initial MB concentration: 50–1000 mg/L; agitation rate: 150 rpm).

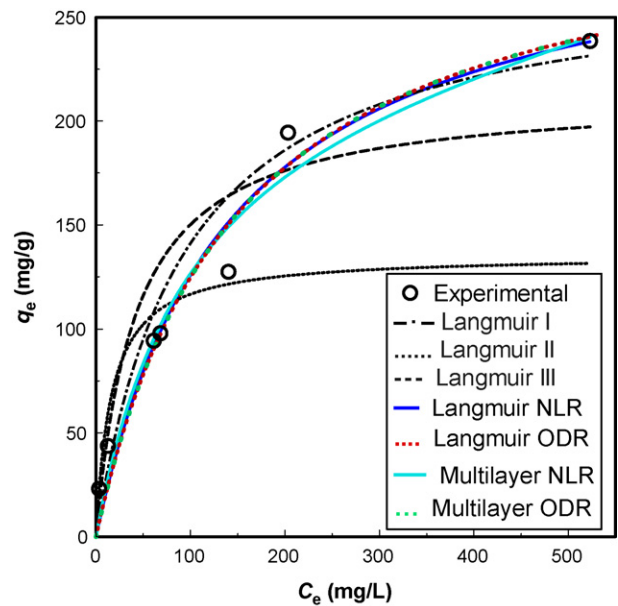


Fig. 6. Comparison of Langmuir and MLA isotherms estimated by different methods of regression for the system MB-9WH at 40 °C (pH 4.6–5.1; SWH dosage: 2 g/L; initial MB concentration: 50–1000 mg/L; agitation rate: 150 rpm).

3.1.3. Sulfonated water hyacinth (SWH)

Table 4 and Figs. 5 and 6 show the regression results of the system MB-SWH at 40 °C. Unlike the cases of NWH and WWH, similar values of Freundlich parameters were estimated by LR, NLR, and ODR. The values of K_f estimated by LR, NLR, and ODR are 13.418, 15.943, and 17.212 (mg/g)(L/g)ⁿ, respectively. The values of n are 2.119, 2.280, and 2.350 for LR, NLR, and ODR, respectively. This is seen graphically in Fig. 5 where the estimated curves are very close at the lower and middle range of C_e then the LR curve deviates at the higher end of C_e .

The results of the three linearized forms of the Langmuir isotherm in Fig. 6 show the same trend as the cases of NWH and WWH; Langmuir I gives the highest r^2 value (0.9499) among the linearized forms, while Langmuir III gives the lowest r^2 value (0.6024) but its estimated curve fits the experimental data much better than Langmuir II which has a relatively high r^2 value (0.9487). The values of K_a and q_m obtained from the three linearized forms of Langmuir isotherms are quite different from each other as shown in Table 4.

The values of K_a and q_m estimated by NLR and ODR differ slightly, ODR giving a better fit to the experimental data as indicated by its SS_y of 534 compared to $SS_y = 1439$ of NLR. Testing the hypothesis of MLA by NLR and ODR gave the same indications given in the cases of NWH and WWH, i.e. ODR rejected the hypothesis while NLR accepts the hypothesis with high uncertainty in its results.

It is noticed in the regression results of SWH that none of the regression methods produced isotherms parameters that describe the data precisely. This may be due to experimental error (especially an influential outlier) or it may be due to the complexity of the adsorption mechanism, which makes the adsorption system unsuitable for modeling by simple isotherms.

3.1.4. Comparison of results of the different methods of regression for the system MB-NWH

In this study, several regression methods were applied to the experimental equilibrium results. However, the usual practice by researchers is to apply only one method of regression, and based on the results of this one method, the researcher proposes a model for the prediction of the adsorption behavior and also for the design calculations and sizing of equipment. The purpose of this discussion is to compare the results obtained from the different methods of regression, and to find out if there are evidence suggesting one method as the most reliable. For demonstration, the regression results of the system MB-NWH are discussed; the results of the systems MB-WWH and MB-SWH are more or less similar.

If a researcher performs a linear regression and compares the linearized Freundlich and Langmuir II (or Langmuir III) isotherms, it would be concluded by comparing the values of r^2 that the experimental results are fitted better by the Freundlich isotherm ($r^2 = 0.9587$) compared to Langmuir II or III ($r^2 = 0.9463$ and 0.7512 , respectively). The researcher will sub-

sequently conclude that the adsorption occurs as a multilayer adsorption on a heterogeneous surface. But if by coincidence the researcher uses the linearized Langmuir I formula instead of Langmuir II or III, the comparison will show that the experimental results are best fitted by Langmuir I isotherm ($r^2 = 0.9978$) and it would be concluded that the adsorption takes place as a monolayer adsorption on a homogeneous surface.

Few researchers prefer to use NLR to avoid the complications occurring from linearization [9,11,17–19,35]. In this case the researcher will find that the Langmuir MLA isotherm ($r^2 = 0.9805$) is a better fit to the experimental data than both Freundlich ($r^2 = 0.9431$) and the monolayer Langmuir isotherm ($r^2 = 0.9712$), the conclusion will be multilayer adsorption on a homogeneous surface.

ODR is not used by researchers to analyze adsorption equilibrium data in spite of the fact that unlike LR and NLR, ODR is a method that takes into consideration the presence of experimental error in both x and y . The x axis in the adsorption isotherms is C_e , which is determined experimentally by chemical analysis and is prone to several sources of error such as pipetting,

Table 4
Isotherm parameters estimated by different methods of regression for the system MB-SWH at 40 °C

Isotherm model	Regression results	Isotherm model	Regression results
Freundlich LR		Langmuir-III	
K_F (mg/g)(L/g) ⁿ	13.418 (10.576–17.025)	q_m (mg/g)	212.94 (84.7380–341.20)
n	2.119 (1.899–2.395)	K_a (L/mg)	0.0239 (0.00158–0.0462)
r^2	0.9901	R^2	0.6204
Isotherm model	Regression results	Isotherm model	Regression results
Freundlich NLR		Langmuir NLR	
K_F (mg/g)(L/g) ⁿ	15.943 (6.7343–25.1510)	q_m (mg/g)	301.86 (255.08–378.64)
n	2.280 (1.738–2.822)	K_a (L/mg)	0.00716 (0.00278–0.0115)
r^2	0.9747	r^2	0.9700
SS	1211	SS	1439
Isotherm model	Regression results	Isotherm model	Regression results
Freundlich ODR		Langmuir ODR	
K_F (mg/g)(L/g) ⁿ	17.212 (5.289–29.132)	q_m (mg/g)	308.66 (245.13–372.20)
n	2.350 (1.673–3.026)	K_a (L/mg)	0.00677 (0.00319–0.0104)
SS _{total}	1038	SS _{total}	783.5
SS _y	910.7	SS _y	534.5
Isotherm model	Regression results	Isotherm model	Regression results
Langmuir-I		MLA NLR	
q_m (mg/g)	272.71 (215.74–370.58)	Γ_m (mg/g)	235.11 (–20.477–490.70)
K_a (L/mg)	0.01072 (0.00789–0.0135)	K_1 (L/mg)	0.010621 (–0.00970–0.0309)
r^2	0.9499	K_2 (L/mg)	2.90×10^{-4} (– 9.98×10^{-4} to 0.00158)
		r^2	0.9709
		SS	1395
Isotherm model	Regression results	Isotherm model	Regression results
Langmuir-II		MLA ODR	
q_m (mg/g)	135.55 (88.64–288.06)	Γ_m (mg/g)	308.76 (146.41–471.11)
K_a (L/mg)	0.06145 (0.0485–0.0838)	K_1 (L/mg)	0.00677 (2.15 $\times 10^{-4}$ –0.00133)
r^2	0.9487	K_2 (L/mg)	3.19×10^{-8} (– 4.01×10^{-4} to 4.02×10^{-4})
		SS _{total}	783.5
		SS _y	534.2

Values in parenthesis are the 95% confidence interval of the estimate.

dilution, calibration of instruments, losses during separation of adsorbent, etc. The y axis in adsorption isotherms is q_e , which is calculated from the formula:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{15}$$

where C_0 is the initial concentration of adsorbate (mg/L), V the volume of adsorbate solution in the adsorption experiment (mL), and m is the weight of adsorbent (g). From Eq. (15), it can be seen that the error in measuring C_e affects q_e but with a different sign, i.e. a negative error in C_e leads to a positive error (with a different magnitude) in q_e . It can also be seen that q_e is prone to additional sources of error in the measurement of C_0 , V , and m . Therefore, there is no basis for assuming that the error in C_e is negligible compared to the error in q_e , and consequently the method used for regression of isotherm data should take the error in C_e into consideration.

3.1.5. Analysis of regression residuals

The residuals from different regression methods used in this study, LR, NLR, and ODR, were analyzed to identify the type and mode of their distribution, and also to detect their possible deviations from the basic assumptions in the method of least squares. The case of NWH is presented for demonstration.

The assumption of homoskedasticity is verified by plotting the residuals ($q_{e(estimated)} - q_{e(experimental)}$) versus C_e as shown in

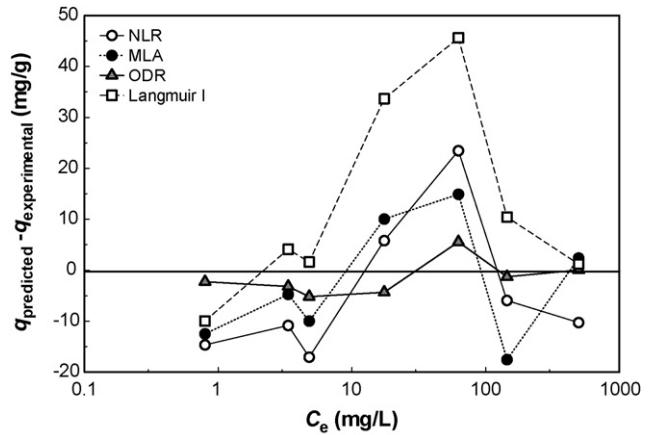


Fig. 7. Distribution of residuals from the different methods of regression for the system MB-NWH at 40 °C (residuals from ODR are taken in the orthogonal direction).

Fig. 7. It is seen in the figure that values of the residuals are not correlated with the level of C_e , indicating homoskedastic residuals.

The assumption of normality is checked by the normal probability plots [36] (NPP) in Fig. 8 and by Tukey-lambda probability plot correlation coefficient (PPCC) diagrams in Fig. 9. The NPP are constructed by plotting the residual (error) against a normal distribution. If the plotted points form a straight line then

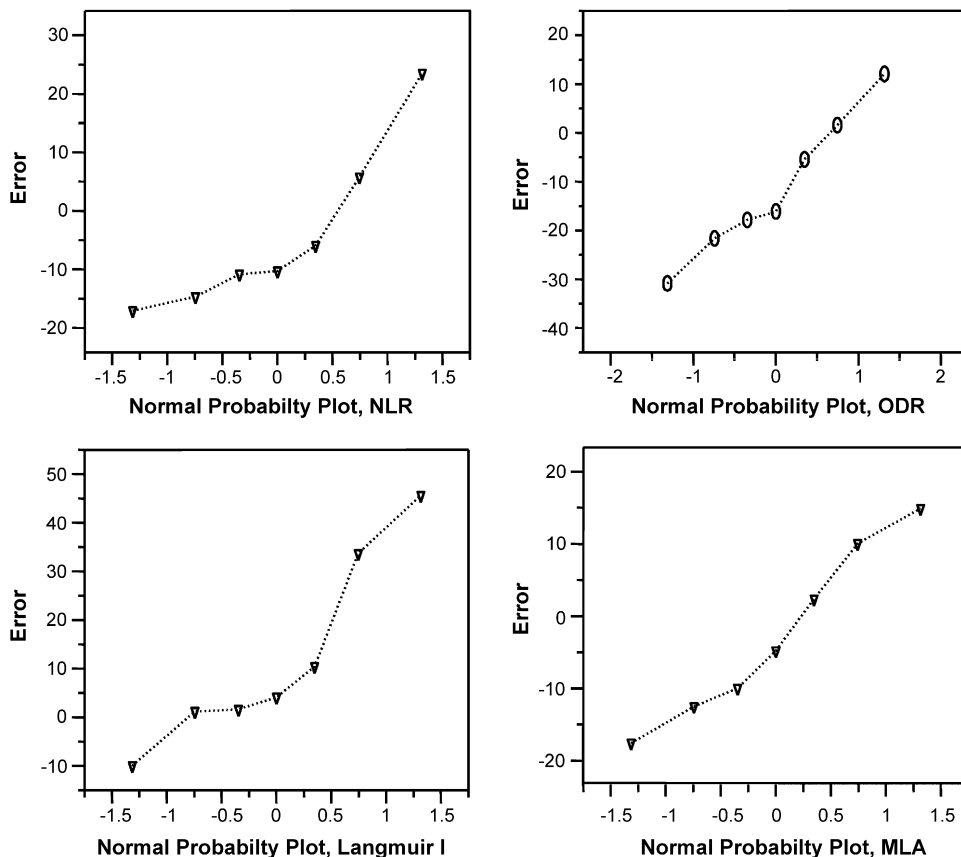


Fig. 8. Normal probability plots of residuals from the different methods of regression for the system MB-NWH at 40 °C.

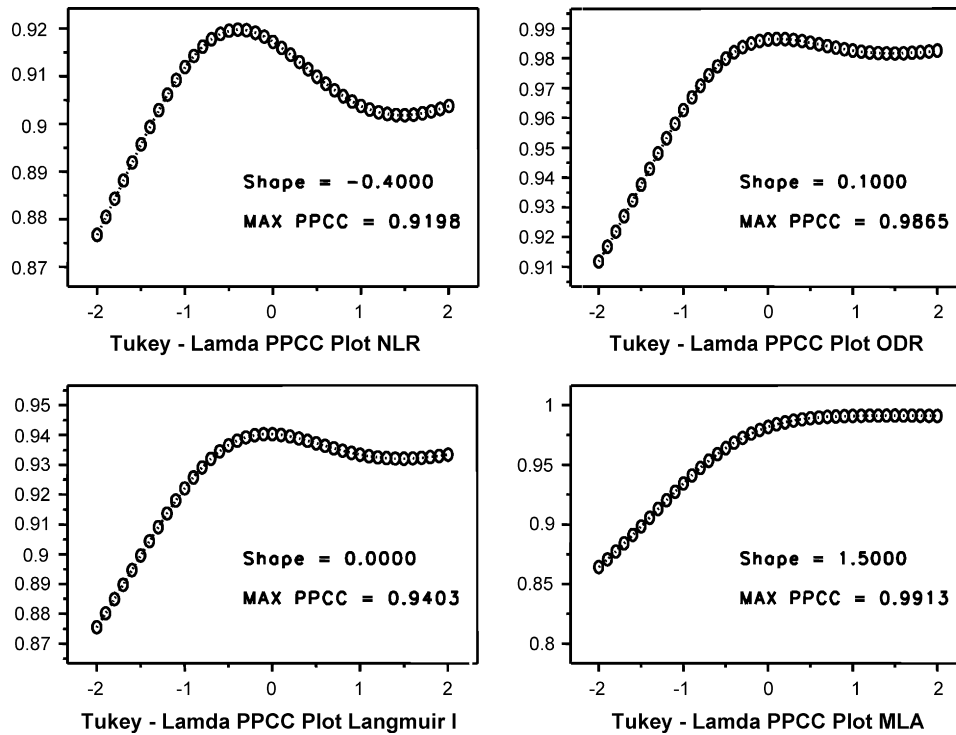


Fig. 9. Tukey-lambda probability plots correlation coefficient plots of residuals from the different methods of regression for the system MB-NWH at 40 °C.

the residual distribution is actually normal. Departures from the straight line indicate departures from the normal distribution. By examining Fig. 8, it can be seen that the NPP of the residuals from NLR, Langmuir I, and MLA are not linear, while the NPP of the residuals from ODR show a strongly linear pattern with only a minor deviation from linearity. The fact that the points in the upper and lower extremes of the ODR

plot do not deviate significantly from the straight-line pattern indicates that there are no significant outliers. This is further confirmed from the PPCC plot of ODR in Fig. 9. The high value of the maximum PPCC (0.9865) indicates little deviation from linearity, while the value of the shape parameter $\lambda = 0.10$ is close to the theoretical ideal normal distribution of 0.14.

Table 5
Statistics of errors in estimation of q_m by different methods of regression

Error variance	Statistic	NLR	ODR	Langmuir I	Langmuir II	Langmuir III
2	q1	-0.34	-0.06	-0.19	-7.38	-2.88
	min	-0.67	-0.62	-0.58	-24.30	-8.55
	median	0.50	-0.02	0.14	5.14	1.64
	max	1.16	0.81	0.65	22.46	6.39
	q3	0.90	0.22	0.27	8.74	1.65
5	q1	-0.25	-0.25	-0.95	-24.30	-8.55
	min	-1.67	-0.57	-1.24	-25.44	-8.59
	median	0.75	-0.11	-0.58	0.79	1.50
	max	2.95	0.78	2.14	35.90	9.30
	q3	0.91	0.43	0.75	16.51	8.99
10	q1	1.32	-0.79	-0.69	-49.61	-5.12
	min	-0.06	-1.90	-2.176	-83.78	-92.32
	median	2.89	-0.46	1.456	-10.17	2.84
	max	5.70	2.26	3.423	120	19.91
	q3	3.33	0.36	1.951	34.23	16.72
20	q1	2.53	0.22	0.84	-72.48	-5.93
	min	-0.87	-5.18	-8.57	-86.48	-19.05
	median	3.60	0.73	4.21	133.24	12.67
	max	6.96	4.40	15.21	285.21	52.16
	q3	4.50	1.04	7.23	255.60	37.44

q1: first quartile, q3: third quartile, min: largest positive error, and max: largest negative error.

Although the maximum PPCC values of the three other regression methods are all above the critical value 0.8970 for a data set of seven observations [37], all of them showed clear deviations of their residuals from normality. NLR has a NPP that is skewed to the right, and its shape parameter λ equals 0.40 which indicates a very long-tailed distribution. Langmuir I has a NPP which shows skewness in the center of the data range and a value of $\lambda = 0.00$ typical for a logistic distribution. MLA has the highest value of PPCC of its residuals (0.9913) but the shape of its NPP shows a linear pattern in the center of the data range and tails in the upper and lower extremes, a typical short tailed distribution. Also, its value of $\lambda = 1.5$ is close to the theoretical uniform distribution ($\lambda = 1.0$).

3.2. Regression analysis of simulated isotherm data

A typical isotherm data set consists of 5–10 points, with no replication. In this study, an ideal Langmuir-type equilibrium data set was generated using Eq. (2) with values of $q_m = 250.00$ mg/g and $K_a = 0.0500$ L/mg. The values of q_e were

computed for C_e values of 5, 10, 25, 50, 125, 250, and 450 mg/L. Regression analysis was applied to the simulated data by NLR, ODR, and linearized Langmuir I, II, and III methods. All the regression methods performed equally good and estimated the values $q_m = 250.00$ mg/g and $K_a = 0.0500$ L/mg, with absolutely no error.

In order to test the sensitivity of the different regression methods to experimental errors, a random number generator was used to generate independent random errors in both q_e and C_e . The levels of error variance studied were 2, 5, 10, and 20. The units of error variance are the same as the units of q_e and C_e . The same numerical values of variance were used for both q_e and C_e . After adding the random errors to q_e and C_e , the values of q_m and K_a were estimated by different methods of regression. The errors in the estimated values were calculated as

$$\%Error = \left[\frac{\text{estimated value} - \text{true value}}{\text{true value}} \right] \times 100$$

For each level of error variance, this procedure was repeated 20 times, and the distributions of %errors in estimates were statistically analyzed.

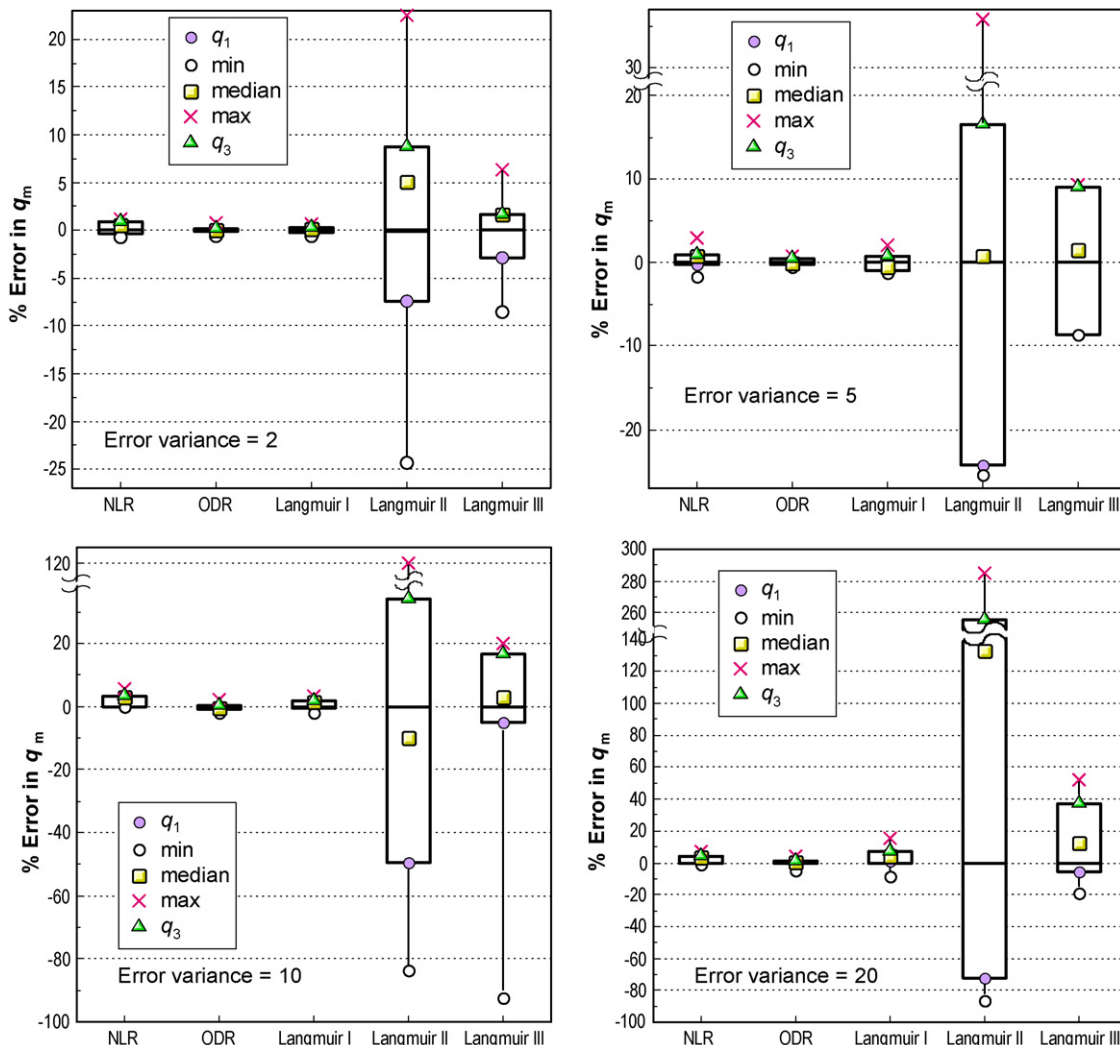


Fig. 10. Box plots for the error in estimation of q_m by different methods of regression of a simulated adsorption equilibrium data set at different levels of error variance.

Table 6
 Statistics of errors in estimation of K_a by different methods of regression

Error variance	Statistic	NLR	ODR	Langmuir I	Langmuir II	Langmuir III
2	q1	-6.26	-1.59	-3.90	-16.46	-10.10
	min	-8.59	-4.23	-10.77	-42.97	-24.41
	median	-5.89	0.63	-2.35	-16.37	-3.35
	max	6.93	1.78	16.17	200.92	81.60
	q3	3.86	0.82	5.34	33.77	19.71
5	q1	-7.79	-4.82	-14.06	-44.50	-27.80
	min	-21.40	-7.40	-23.55	-47.16	-34.57
	median	-7.05	-0.57	-0.39	-8.85	-10.11
	max	15.23	3.13	16.17	200.86	81.63
	q3	-4.74	0.65	6.56	177.39	59.24
10	q1	-21.06	-2.63	-33.22	-57.41	-43.76
	min	-39.62	-7.88	-37.58	-92.42	-124.76
	median	-13.86	-0.70	-17.76	132.16	-37.60
	max	-1.42	19.24	10.66	845.26	47.92
	q3	-8.96	6.22	2.01	661.74	0.74
20	q1	-28.67	-10.78	-49.80	-89.88	-58.65
	min	-33.44	-32.26	-62.92	-124.76	-70.84
	median	-25.42	-8.68	-35.03	-53.01	-23.54
	max	2.11	35.80	17.20	1273.29	1484.42
	q3	-13.28	2.34	-25.04	391.10	84.26

q1: first quartile, q3: third quartile, min: largest positive error, max: largest negative error.

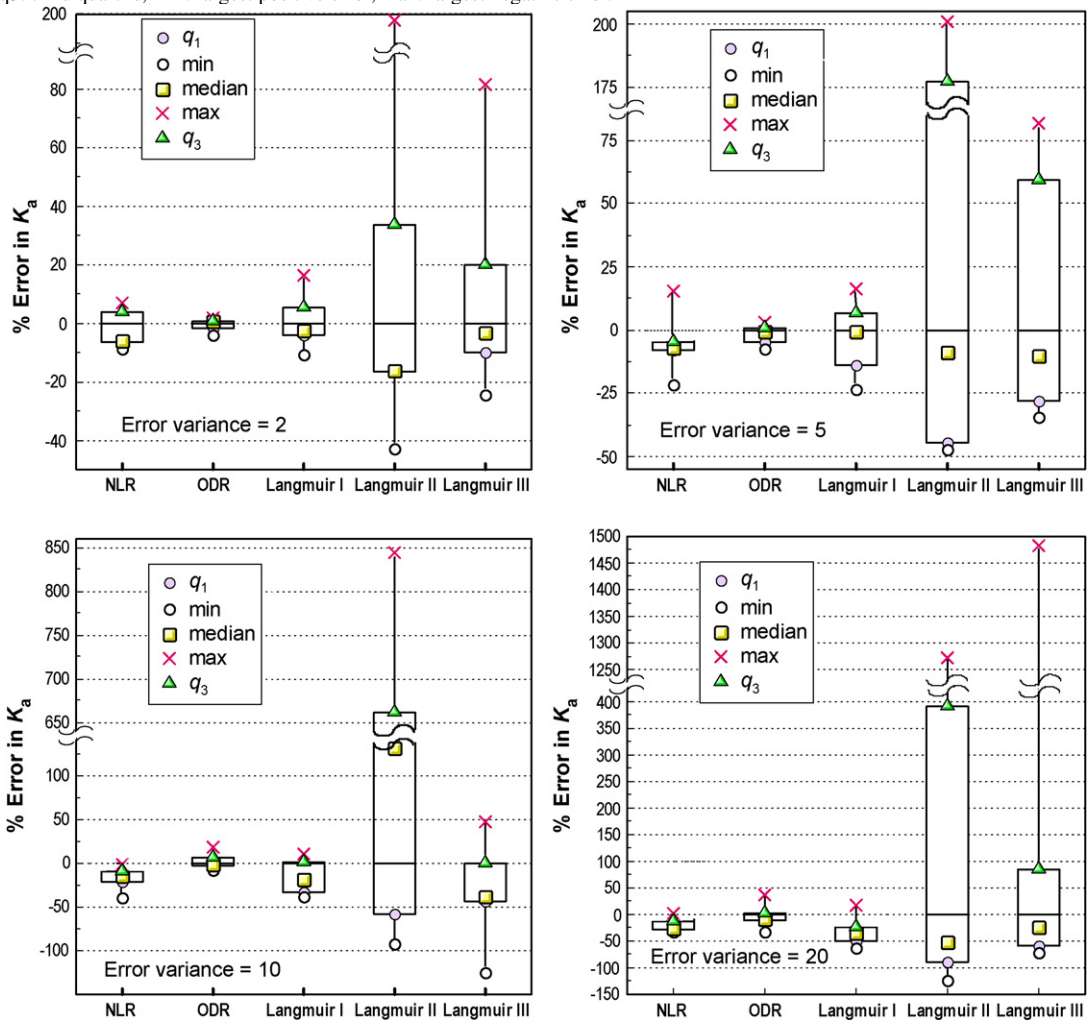


Fig. 11. Box plots for the error in estimation of K_a by different methods of regression of a simulated adsorption equilibrium data set at different levels of error variance.

The %errors in estimating q_m at different levels of random error are shown in Table 5 and their box plots are in Fig. 10. It is obvious that ODR is superior at all levels of error variance studied (2–20), with the median of the %error in q_m estimates always close to zero (–0.02–0.73%), and the values of *min* and *max* (the minimum and maximum %errors in estimated values) almost identical with opposite signs which means that estimate is unbiased. The LR of linearized Langmuir I gives better estimates of q_m than NLR when the error variance is 2, while at higher levels of error variance (5 and 10) Langmuir I and NLR gave estimates of q_m that are almost equally precise, finally at the highest level of error variance studied, 20, NLR gives more precise estimates than Langmuir I as indicated by the values of q_1 and q_3 (the 25% and 75% quartiles of the estimate distribution). It is noticed that q_m estimates of both NLR and Langmuir I become more biased towards positive errors as the error variance is increased. The estimated values of q_m by LR of Langmuir II and III show large errors even at low levels of error variance. Langmuir II gave the worst estimates with errors in predicting q_m up to 285%.

The errors in estimating K_a are presented in Table 6 and their box plots in Fig. 11. It is noticed that LR of Langmuir II and III predict values of K_a that deviate significantly from the true value even with the smallest value of error variance. This confirms that LR of Langmuir II and III are unreliable methods for estimating the parameters of Langmuir isotherm. NLR gives better estimates of K_a at all levels of error variance, while ODR, as usual, gives the most accurate estimates of K_a with the median of the %error persistently close to zero unless in case of error variance = 20.

These results show that different estimated values of isotherm parameters are estimated from linear, nonlinear, and orthogonal distance regression. The differences in estimated values increase with increasing the experimental error. It was found that Langmuir I linearization method produced estimates that are much more accurate than Langmuir II and III.

4. Conclusions

Based on the results of this study, it is not recommended to use Langmuir II and III methods in the estimation of Langmuir isotherm parameters. Nonlinear regression gives more accurate estimates than LR by Langmuir I method, especially when the experimental error is large. The results of this study also show that orthogonal distance regression gives the most accurate estimates of the isotherm parameters among the different methods compared. A further point to consider is that the challenge for fitting an equilibrium adsorption equation to data is not only the regression method, but also the choice of the correct model [11]. In cases where simple models fail to fit the data adequately, more complex models could be tested [38,39]. The results of the present study demonstrate the ODR is more robust than NLR, and therefore, it is expected that ODR would be a better alternative for fitting equilibrium data to complex isotherm models.

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