

A discussion on linear and non-linear forms of Thomas equation for fixed-bed adsorption column modeling**Discusión sobre las formas lineal y no-lineal del modelo de Thomas para el modelado de curvas de ruptura**M.E. González-López¹, C.M. Laureano-Anzaldo¹, A.A. Pérez-Fonseca¹, M. Arellano¹, J.R. Robledo-Ortíz^{2*}¹*Departamento de Ingeniería Química, CUCEI, Universidad de Guadalajara, Guadalajara, Jalisco, México.*²*Departamento de Madera, Celulosa y Papel, CUCEI, Universidad de Guadalajara, Zapopan, Jalisco, México.*

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Abstract

The Thomas model is the most common equation to describe the dynamics of fixed-bed adsorption columns. However, its parameters validity strongly depend on the breakthrough curve region considered for the data fitting. This work aimed to provide a rigorous analysis of the linear and non-linear forms of the Thomas model based on different error functions. Data simulation was carried out to determine the accuracy of both equations at different error magnitudes. The non-linear equation proved to be more robust and less susceptible to experimental error, with less than 0.5% of deviation in q_{Th} calculation. A complete statistical analysis should be carried out to determine the fitting region if linear regression is preferred.

Keywords: fixed-bed column, Thomas model, linear regression, non-linear regression, adsorption.

Resumen

El modelo de Thomas es la ecuación más utilizada para describir la dinámica de las columnas de adsorción de lecho empacado. Sin embargo, la validez de sus parámetros depende fuertemente de la región de la curva de ruptura considerada para el ajuste de los datos. Se llevó a cabo un análisis riguroso basado en distintas funciones de error generando datos simulados para determinar la efectividad de las formas lineal y no lineal de este modelo a diferentes magnitudes de error. La ecuación no lineal demostró ser más efectiva, robusta y menos susceptible al error experimental, al mostrar menos de 0.5% de desviación en el cálculo de q_{Th} en todos los casos. En el caso que se prefiera la regresión lineal, debe realizarse un análisis estadístico completo para determinar la zona de ajuste para los datos.

Palabras clave: columna empacada, modelo de Thomas, regresión lineal, regresión no lineal, adsorción.

1 Introduction

Continuous adsorption process carried out in a fixed-bed column is desirable for industrial purposes since it has proven to be cost-effective, easy to operate, and feasible to be regenerated in-situ (Verduzco-Navarro *et al.*, 2020). This separation process performance is evaluated through the plot of the dimensionless concentration at the column exit versus time or eluted volume. This plot is usually referred to as a breakthrough curve, which provides readily available information for the direct application of adsorption columns to treat polluted streams (González-López *et al.*, 2020a).

In order to scale up the fixed-bed operation, an accurate model has to be developed to reduce time and costs often generated through the numerous experiments required to determine critical design parameters, such as rate constants or fixed-bed adsorption capacity (Kumari *et al.*, 2019). In this sense, the dynamics are often represented by conservation equations such as mass, energy, and momentum balances described by partial differential equations that result in a very complex model that requires an extensive computation capacity to be solved.

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For industrial applications, one of the primary challenges is the application of mathematical models and software rather than empirical correlations to predict the concentration distribution along the fixed-bed, which is essential in the design of separation units (Gholami *et al.*, 2016). However, it is impractical to carry out this analysis. Instead, semi-empirical correlations or less complicated mathematical relationships (based on assumptions that simplify mass transfer, energy, or momentum equations) are employed, reducing computation time without losing the accuracy in the analysis of experimental data. Those correlations allow to predict the column behavior at different conditions without carrying out further experiments (Arcos-Casarrubias *et al.*, 2018; Yoshida *et al.*, 2019).

One of the most widely reported models for predicting breakthrough curves is the Thomas model (Thomas, 1944). This model was developed from the equation of mass conservation in a flow system assuming plug flow, equilibrium described by Langmuir isotherm, and second-order reversible kinetics. Particularly, it neglects internal and external diffusion effects. The non-linear equation for this model is:

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp\left(\left(\frac{k_{Th}}{Q}\right)(q_{Th}m - C_0Qt)\right)} \quad (1)$$

where Q is the volumetric flow rate (mL/min), m is the adsorbent mass (g), and C_0 (mg/L) represents the inlet concentration, whereas k_{Th} (mL/min g) is the Thomas rate constant and q_{Th} (mg/g) represents the adsorption capacity of the fixed bed.

With the advent of computing technology, non-linear least-squares regression has drawn attention as it has become less complicated to carry out. Moreover, it has proven to be more robust and less sensitive to experimental error (Das *et al.*, 2015). In this method, model parameters are first estimated and, through a trial-error procedure, evolve towards the values that minimize a given error function, i.e., the sum of squares error, based on a selected algorithm (Tan and Hameed, 2017).

An alternative to the non-linear regression method is to linearize the model equation and determine its feasibility to describe a set of experimental data. The calculation of the model parameters becomes associated with the slope and intercept of a straight line (Rojas-Valencia *et al.*, 2020). However, the linear transformation strongly modifies error distribution and

alters the weight associated with each point, either for the worse or the better (Tran *et al.*, 2017). Although linear regression is no longer recommended for data modeling, many literature reports still select this regression method, as discussed in the following sections.

The linearized form of the Thomas model is commonly expressed as follows:

$$\ln\left(\frac{C_0}{C_t} - 1\right) = \frac{k_{Th}q_{Th}m}{Q} - k_{Th}C_0t \quad (2)$$

From this expression, both constants k_{Th} and q_{Th} could be obtained from the linear plot of $\ln\left(\frac{C_0}{C_t} - 1\right)$ versus t from the slope and intercept, respectively.

Some papers have been published discussing the use of the linearized form of equilibrium equations and compared it to its non-linear counterpart, such as isotherms (Nagy *et al.*, 2017) and kinetic expressions (Tan and Hameed, 2017). However, only a few reports have considered the analysis of linear and non-linear equations of models used for breakthrough curves modeling (Dissanayake *et al.*, 2016). Several authors have noted that the application of non-linear regression is more suitable than linear regression (Tejada-Tovar *et al.*, 2020; Villabona-Ortíz *et al.*, 2019). Some authors propose using a proper error analysis method to corroborate this asseveration validity (Unuabonah *et al.*, 2016). Even if a proper error analysis was carried out, it was not evident in any of these papers whether the values for the model constants obtained through linearization are consistent with those obtained through non-linear regression or reliable to any extent (Han *et al.*, 2007; Zhang *et al.*, 2013).

The error distortion generated through linearization could lead to misleading outcomes when the experimental error is present, i.e., a suitable model could present a large error while minimal error could be observed for an equation that does not represent the dynamics of the system. Thus, it is inaccurate to compare model equations that were subjected to different transformations (Xiao *et al.*, 2018). Regarding the latter, literature reports a balance between non-linear regression and the linearized form of the Thomas model to describe different adsorbent-adsorbate systems. It stands out that so many papers employ linear regression despite non-linear regression is more recommended for this purpose. Interestingly, it was noticed that the plot of the linear regression is not shown or remains unclear in many cases.

Table 1. Literature review on the use of the linear and non-linear form of the Thomas model.

Adsorbent	Adsorbate	Linear/non-linear	r^2	Curve fitting plot	Reference
Graphene oxide/MgO	Pb(II)	Linear	0.960-0.990	Shown	(Mohan <i>et al.</i> , 2017)
Watermelon rind	Pb(II)	Linear	0.910-0.998	Not shown	(Lakshmipathy and Sarada, 2015)
Kenaf	Cr(VI)	Linear	0.959	Shown	(Omidvar Borna <i>et al.</i> , 2016)
Coconut shell	Cu(II)	Linear	0.961-0.993	Not shown	(Acheampong <i>et al.</i> , 2013)
Zeolite	Methylene blue	Linear	0.723-0.921	Shown	(Han <i>et al.</i> , 2007)
		Non linear	0.878-0.969		
Biomass	Pb(II)	Linear	0.904-0.967	Shown	(Dissanayake <i>et al.</i> , 2016)
		Non linear	0.993-0.996		
Citrus peels	Methylene blue	Non linear	0.972-0.995	Shown	(Aichour <i>et al.</i> , 2019)
Tunisian soil	Phosphorous	Non linear	0.952-0.991	Not shown	(Beji <i>et al.</i> , 2018)
Biochar	Methylene blue	Non linear	-	Shown	(Dawood <i>et al.</i> , 2019)
Chitosan composite	Cr(VI)	Non linear	0.981-0.999	Shown	(González-López <i>et al.</i> , 2020b)

Although it is not the intention of this study to criticize the experimental work and findings of such reports, it is critical to emphasize the importance of the data range used for curve fitting, as it affects the accuracy of the obtained parameters. For instance, Han *et al.*, (2007) carried out the analysis using linear regression within a range of C/C_0 between 0.05 and 0.95, while Tsai *et al.*, (2016) carried out the curve fitting of the breakthrough curves within a range of 0.01 and 0.99. However, it was not clear why those ranges were selected in any of these cases or whether further shortening the range leads to more feasible data fitting or not. Table 1 summarizes some literature reports using linear and non-linear forms of the Thomas model.

Thus, this work aims to discuss the validity of the linearized form of the Thomas model against its non-linear form, to describe the dynamic behavior of fixed-bed adsorption columns and compare the significance of the parameters obtained through the linearized and non-linear forms of this equation. A rigorous error analysis is also carried out to determine the optimal range of C/C_0 that should be considered to obtain the most reliable parameters through linear regression depending on the experimental error magnitude.

reactions, among others, data were mathematically simulated according to the following procedure: firstly, a breakthrough curve was generated with Thomas equation as a function of parameters of the fixed-bed adsorption, i.e., Q , C_0 , and m (which is directly related to bed length), as well as the Thomas parameters q_{Th} and k_{Th} , as listed in Table 2. Then, a simulated error (e_{sim}) similar to the typical experimental error: 2.5, 5.0, or 10.0%, was distributed to the data using a function that randomly generates an error in the curve according to a normal distribution.

Also, the simulated error range was selected to illustrate that larger deviation increases distortion compared to when a smaller experimental error is observed. Then, data were corrected to have a monotonically crescent function by generating a new value at the point when a value “ i ” is smaller than its preceding one “ $i - 1$ ”. This routine was programmed in MATLAB®, and five sets of data were generated to carry out the further analysis of the model linearity versus its non-linearity. For this purpose, linear and non-linear regressions were also carried out using MATLAB®.

2 Materials and methods

2.1 Data generation

In order to avoid uncontrolled experimental error and other errors associated with the adsorbent itself, such as adsorbate-adsorbent interactions (neglected for the assumptions inherent to Thomas equation), side

Table 2. Parameters used for the simulation of the breakthrough curves.

	Parameter	Value
Process	Mass of sorbent (m)	26.30 g
	Flow rate (Q)	4.22 mL/min
	Inlet concentration (C_0)	100 mg/L
Thomas model	k_{Th}	0.1287 mL/min g
	q_{Th}	9.55 mg/g

2.2 Statistical error (e_{sta}) calculation

Error functions represent statistics that measure the error between experimental and predicted values. In either linear or non-linear regressions, the fitted parameters are determined or evolve, according to the least-squares method to minimize the error according to the error sum of squares function (SSE) described as:

$$SSE = \sum_{i=1}^n (y_c - y_{exp})_i^2 \quad (3)$$

However, other notable error functions are used to estimate the statistical error (e_{sta}). These functions were calculated to confirm and support the validity of the model along with the correlation coefficient. Some of these error functions are the following:

2.2.1 Average relative error (ARE)

$$ARE = \frac{1}{n} \sum_{i=1}^n \left| \left(\frac{y_c - y_{exp}}{y_{exp}} \right)_i \right| \quad (4)$$

2.2.2 Average relative standard (ARS)

$$ARS = \sqrt{\frac{\sum_{i=1}^n \left(\frac{y_c - y_{exp}}{y_{exp}} \right)_i^2}{n-1}} \quad (5)$$

2.2.3 Root mean sum of squares (RMSE)

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (y_c - y_{exp})_i^2} \quad (6)$$

In all cases, y_c stands for the estimated value, y_{exp} for the real value, and n is the number of data.

3 Results and discussion

Five simulations ($n = 5$) were carried out at different error magnitudes ($e_{sim} = 2.5, 5.0$, and 10.0%), and the resulting breakthrough curves (mean values) are presented in Figure 1. The simulated data represents a breakthrough curve described by the Thomas equation, and an increase in the simulated error is noticeable in the breakthrough curves. The error magnitude is typical according to the range of the data in the breakthrough curve; values close to zero have a low error magnitude, which increases when C/C_0 starts to increase.

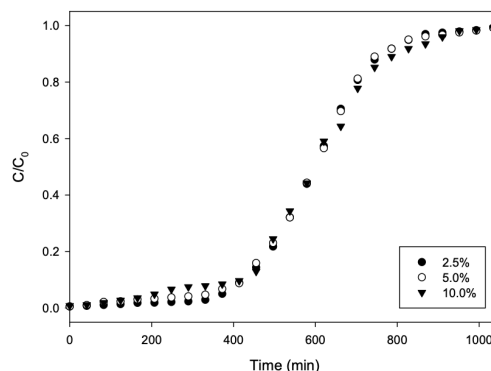


Fig. 1. Simulated mean values for Thomas non-linear equation at different error magnitude.

Then, as values approximate to the asymptote at $C/C_0 = 1.0$, the error magnitude starts to decrease. This behavior could be considered typical for these plots, and thus the programed routine is considered valid for further analysis.

Then, linear fitting was carried out according to Equation 2. Since the logarithmic function is not defined at $C/C_0 = 0$, these values were removed after linearization. Figure 2 presents the scatter plot of the five simulations on their non-linear and linear form. As discussed above, in the non-linear plot, the Thomas model general trend is observed even at the highest magnitude of the simulated error ($e_{sim} = 10.0\%$).

In linearized data, a portion of the curve exists so that the linearity is consistent within the five sets of data. This region is located in the middle of the curve between breakthrough and exhaustion points, which are two critical points of the breakthrough curve. However, in values closer to the function limits, the error increases drastically, indicating that linearization provides more significant weight to points near the limit of the logarithmic function, and this effect becomes more critical when the used simulated error increases (Figure 3). As pointed out by other authors, the problem with linear transformations is the distortion of the error. Through the linear least-squares method, scatter points are assumed around a line that follows Gaussian distribution, and the error distribution is the same within each point of the curve. In contrast, in non-linear equations, the error is uniformly distributed throughout the points at the whole range of data (Ganguly et al., 2020).

The above behavior was observed in this analysis, indicating that the range of data used for the curve fitting must be thoughtfully selected based on error functions.

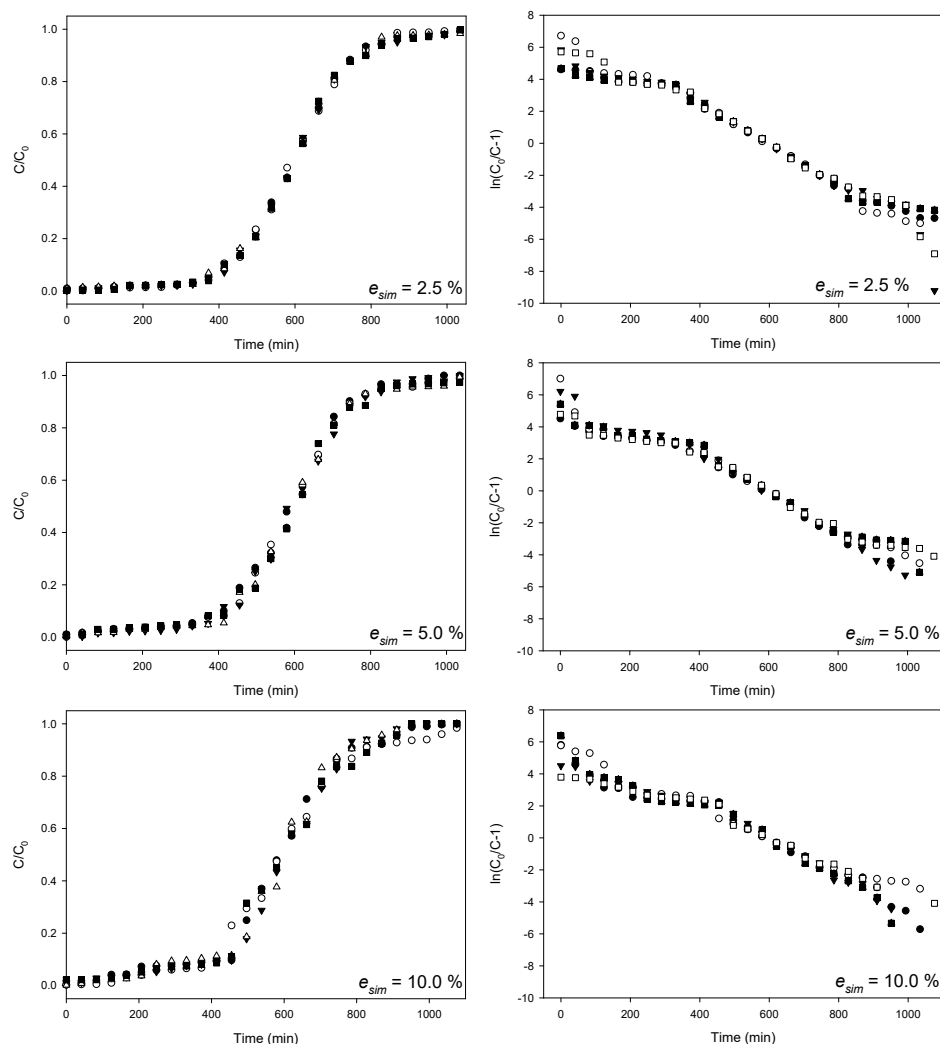


Fig. 2. Data simulation and linearization at different error values (e_{sim}).

Hence, five intervals were analyzed in terms of the error in predicting the model parameters generated by linear and non-linear regression (using the complete range of data). The results for the predicted parameters q_{Th} and k_{Th} are presented in Table 3. The difference between $q_{Th,calc}$ and $q_{Th,real}$ was defined as Δq (%), and it was calculated as follows:

$$\Delta q(\%) = \left| \frac{q_{Th,real} - q_{Th,calc}}{q_{Th,real}} \right| \times 100 \quad (7)$$

The values of q_{Th} and k_{Th} are not consistent with the non-linear regression when the complete range of data is selected (0 - 1.00), indicating that linearization leads to error distortion as it has been reported for

adsorption isotherms and kinetic models (Lin and Wang, 2009). However, by shortening the data range, parameters start to resemble those obtained by non-linear regression at all error magnitudes analyzed (Figure 4).

Error functions were estimated to analyze the optimal range for data fitting. The statistical error (e_{sta}) is minimized using the non-linear regression. In the case of the linear regression, shortening the range minimizes e_{sta} up to a minimum obtained when the linearized curve was fitted between 0.05 - 0.95 when the simulated error was equal or below 5.0%, and further decreasing this range increases the error because the number of available data becomes smaller after this point.

Table 3. Error analysis of Thomas linear and non-linear model as a function of the C/C_0 range.

Simulated Error %	Equation	C/C_0 range	k_{Th} (mL/min g)	q_{Th} (mg/g)	$\Delta q(\%)$	Statistical Error				r^2
						SSE	ARE	ARS	RMSE	
2.5	Non-linear	0 - 1.00	0.1285	9.564	0.15	0.00135	0.22701	0.46589	0.00721	0.9997
		0 - 1.00	0.103	9.349	2.11	0.03065	0.31203	0.56963	0.03434	0.9797
		0.01 - 0.99	0.107	9.414	1.42	0.01965	0.28017	0.53978	0.0275	0.98
	Linear	0.05 - 0.95	0.129	9.55	-	0.00139	0.22807	0.48702	0.00733	0.9995
		0.10 - 0.90	0.13	9.578	0.29	0.00144	0.2325	0.49174	0.00746	0.9995
		0.20 - 0.80	0.129	9.588	0.4	0.00147	0.23039	0.4895	0.00752	0.9995
5	Non-linear	0 - 1.00	0.124	9.543	0.07	0.00194	0.22523	0.48399	0.00863	0.9988
		0 - 1.00	0.096	9.145	4.24	0.05919	0.28933	0.54854	0.04772	0.9977
		0.01 - 0.99	0.096	9.167	4.01	0.05644	0.28563	0.54503	0.04659	0.9725
	Linear	0.05 - 0.95	0.126	9.512	0.4	0.00561	0.27277	0.53262	0.01497	0.9971
		0.10 - 0.90	0.129	9.519	0.32	0.00603	0.28422	0.54368	0.01523	0.996
		0.20 - 0.80	0.123	9.597	0.49	0.00593	0.26819	0.52813	0.0151	0.9928
10	Non-linear	0 - 1.00	0.1093	9.591	0.42	0.01256	0.24076	0.50039	0.02198	0.9969
		0 - 1.00	0.09	9.156	4.13	0.05821	0.23521	0.49459	0.04731	0.9804
		0.01 - 0.99	0.09	9.176	3.91	0.05567	0.23425	0.49358	0.04627	0.9775
	Linear	0.05 - 0.95	0.097	9.474	0.79	0.02091	0.24426	0.50401	0.02835	0.9928
		0.10 - 0.90	0.118	9.619	0.72	0.01494	0.30268	0.56106	0.02397	0.9928
		0.20 - 0.80	0.112	9.572	0.23	0.01272	0.28208	0.54163	0.0221	0.9909

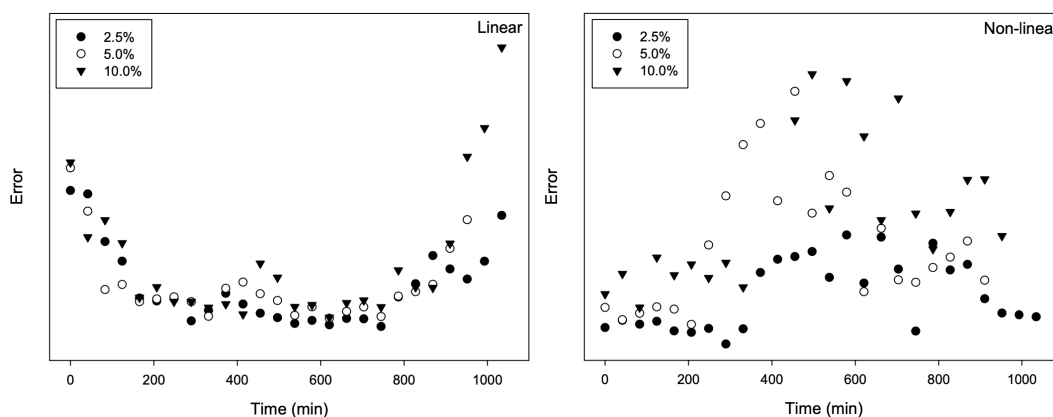


Fig. 3. Error distribution in linear and non-linear fitting.

Linear regression becomes more questionable at the simulated error of 10.0% since the range should be shortened even up to 0.20 - 0.80, and the number of data used for curve fitting could not be enough to feasibly represent the experimental behavior. Thus, the aforementioned shows a serious deficiency of the linearized equation in predicting the operation parameters due to the logarithm function nature.

Figure 5 presents the breakthrough curve fitted to the non-linear and the linear Thomas model. The

curves with the parameters obtained through the linearized equation present a larger deviation, which is clearly observable nearby the breakthrough and exhaustion points. When the experimental error is small (such as presented in this work, $e_{sim} = 2.5, 5.0\%$), the discrimination between linear and non-linear forms represents a minor effect. However, as experimental error becomes larger ($e_{sim} = 10.0\%$), error in the calculation of operation parameters could lead to incorrect conclusions.

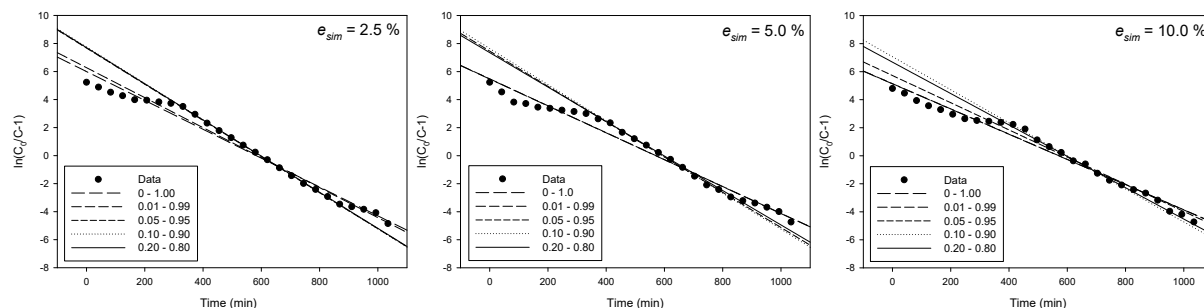


Fig. 4. Linear curve fitting plots at different error and ranges of C/C_0 .

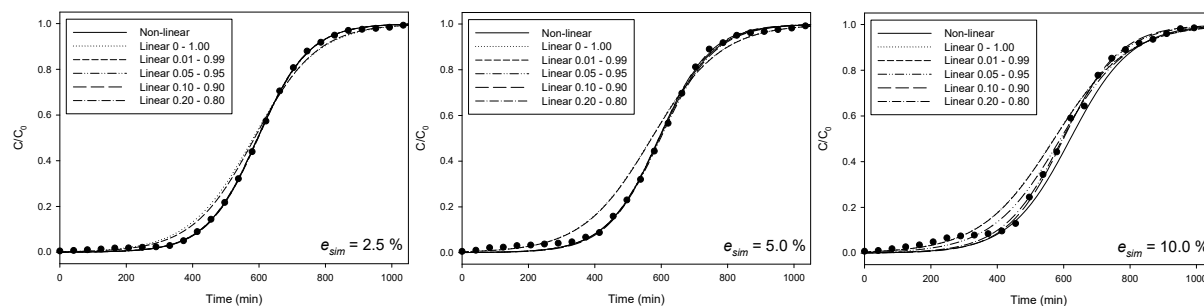


Fig. 5. Breakthrough curve fitted to Thomas model at different error magnitude.

Hence, non-linear regression is more effective and robust (less susceptible to experimental error) to calculate the Thomas model parameters. If linear regression is preferred, the linearization must be carried out using a proper range of data to obtain valid parameters of the fixed-bed operation that would be consistent with those obtained by non-linear regression.

Conclusions

Through a rigorous analysis of Thomas model linear and non-linear forms, it was observed that the range of data used for the linear curve fitting strongly affects the validity of the estimated parameters. The difference between real and estimated parameter q_{Th} was significantly high when the entire data range was used. However, if the data range is shortened between C/C_0 values of 0.05 and 0.95, the difference between the calculated and estimated parameters diminishes even at large error magnitudes. According

to several error functions, linearization of values that are close to zero (logarithmic function limit) and one (asymptotic value) leads to a critical distortion in error distribution due to the logarithmic nature function. These findings support the hypothesis that the non-linear method should be performed instead of using the Thomas model linearized equation. Moreover, if linear regression is performed, the range of data should be thoughtfully selected within C/C_0 values between 0.05 and 0.95 or depending on the magnitude of the experimental error. Herein, it was demonstrated that Thomas non-linear form must be preferred over the linearized equation to describe the dynamic behavior of fixed-bed adsorption columns.

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Nomenclature

C	Concentration
C_0	Inlet concentration
e_{sim}	Simulated error
e_{sta}	Statistical error
k_{Th}	Thomas rate constant
m	Adsorbent mass
Q	Flow rate
q_{Th}	Thomas capacity constant
$q_{Th,calc}$	Calculated Thomas capacity constant
$q_{Th,real}$	Thomas capacity constant (fixed value)
Δq	Deviation in Thomas capacity constant
y_c	Calculated value
y_{exp}	Experimental value

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