Chapter 5

A Statistical Approach to Model Selection for Dynamic Adsorption Columns

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Abstract

A variety of models have been used to describe and predict breakthrough curves for dynamic adsorption systems, in order to scale up laboratory and pilot plant systems. There are however limitations in the applicability of existing models. The study is aimed at providing unambiguous approaches in selecting the best performing model between Thomas, Yoon-Nelson and Bohart-Adams (B-A) models for three dynamic adsorption systems. Three approaches were implemented in this study using published experimental data of three adsorption systems. The first approach was the application of statistical analysis between actual and predicted breakthrough curves without modifying the models. The second and third approaches were application of local mean values (LMV) and global mean values (GMV) of empirical constants to predict breakthrough curves. Predictive and generalization performances of the three models were evaluated using the statistical criteria of Mean Absolute Error (MAE), Root mean Squared Error (RMSE) and Correlation Coefficient (R^2).

Keywords

Acid Mine Drainage, Adsorption, Yoon-Nelson Model, Thomas Model, B-A Model

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1. Introduction

Acid mine drainage (AMD) is currently the major pollutant on both land and water in South Africa. The main source of Acid Mine Drainage is oxidation of sulphide mineral ores, which are primarily exposed to the environment by vigorous mining activities [1]. In the 21st century, where environmental protection and rehabilitation are considered as a priority, technical feasibility and economic sustainability are key drivers in determining the most suitable proposed system or method for any application [2]. Biosorption is eco-friendly, cost effective, ease of operation, high efficiency and wide range of applications [3]. Biosorption is the process of binding contaminants (metal ions, dyes etc.) on the surface of the biological material due to the presence of characteristic functional groups e.g. carboxylic, hydroxyl, amino, carbonyl, phosphate, sulphonic etc. [4]. In water treatment by biosorption, the solid phase/substance and pollutants are respectively called adsorbent and adsorbates. The treatment of water by adsorption technology for both batch and column operations depends upon many factors such as pH, nature of adsorbent and adsorbates, temperature, particle size, dose of adsorbent, presence of other pollutants, flow rate, concentration of adsorbates and bed volume/porosity. For a dynamic adsorption system (column adsorption), the method to determine concentration-time profiles (breakthrough curves) is a significant factor since it provides the basic and foremost information for design and performance of a column adsorption system. Breakthrough curve information assist in determining rational scale of the adsorption column for practical applications. Direct experimentation and mathematical modelling are the basic approaches in predicting breakthrough curves. However, mathematical modelling though it is complex for dynamic adsorption processes it is readily realised with minimal experimental work and therefore it has attracted increasing attention in the preceding decades [5]. However, since dynamic adsorption processes operate at unsteady state conditions, the development of a model that predicts concentration-time profiles is laborious in most cases. This is due to the fact that adsorbate(s) concentration in the influent varies as it moves through the bed [6]. Fundamental equations derived to model the dynamic adsorption system with theoretical precision are differential in nature and to solve them, intricate numerical methods are required. Hence, elementary mathematical models such as Thomas, Bohart-Adams, Yoon-Nelson and Dose-Response models have been developed to anticipate the dynamic behaviour of the column [6]. Since technology has dominated the world to an extreme extent, machine learning or artificial intelligence is another alternative path in solving complex problems such as the adsorption process, which depends upon many factors and is operated under unsteady conditions. The artificial neural networks (ANN) are modelling tools that are commonly used to predict complex systems that are difficult to model using conventional modelling methods, such as mathematical modelling [7]. A linear model is

not appropriate to constitute a substantial relationship between inputs and outputs for an adsorption process, hence ANN approach is suitable for problems where interactions between variables are nonlinear [8]. From reviewed adsorption systems, a significant observation was that model parameters were observed to vary with operating conditions, hence the response of dynamic models to these variations is not well studied for dynamic adsorption systems. Moreover, the parameter that must be varied to reflect deviations in kinetic behavior is ambiguous for each considered dynamic adsorption model. Typically, refitting is the only alternative technique applied to attain a new set of model parameters when operating conditions vary. However, what if one value of each model parameter can be applied for a certain range of operation in order to mitigate refitting when conditions change? The current work reports the application of critical analyses on model parameters for Fe-sea shell, Pb-charcoal and Pb-*Agirus bisporus* adsorption systems. The critical analyses include applying mean values of model parameters based on range of operation as well as generalized model parameters based on the experimental data in order to predict breakthrough curves for each system. As previously mentioned, biosorption is among one of the complex processes and the interaction between the variables is known to be nonlinear. Thus, three-layered feed-forward backpropagation neural network models for modelling Fe-seashell, Pb-charcoal and Pb-*Agirus bisporus* adsorption systems were developed. The three layers of the networks were input, hidden and output layers. The data for the aforementioned systems was obtained from previously published data. The investigated process variables for considered dynamic adsorption systems were sorbent mass, flow rate, influent sorbate concentration, processing time and bed depth. The efficient operation of considered adsorption systems in plant scale requires optimization of all operating conditions, which involves quite a number of experiments without automation. Hence, artificial neural network models would allow the development and application of automated wastewater treatment plant at low operating costs.

2. Dynamic adsorption systems

Batch mode operation results are very significant when developing column operation; however, the latter have distinct advantages over the former since the rates of adsorption depend upon the concentration of the adsorbate(s) in the solution being treated [3, 9].

2.1 Breakthrough curve characteristics and development

The dynamic behaviour of column operation is best described in terms of concentration-time profile, which is known as breakthrough curve [6]. Typical breakthrough curves are illustrated in Fig. 1. During water purification in a column, a mass transfer zone is developed as illustrated in Fig. 1. The mass transfer zone is the area of the bed where the

adsorption process takes place. When the contaminated water starts to flow through the column, the mass transfer zone changes from 0% of the initial concentration which corresponds to the sorbate-free or clean adsorbent to 100% of the initial concentration which corresponds to the complete saturation of the bed [6].

Figure 1. Illustration of a typical breakthrough curve [6].

The breakthrough curve is generated by plotting a graph of nominal concentration, i.e. the ratio of metal (sorbate) concentration in the effluent (C_i) to the influent concentration (C_o) versus time. The nominal concentration falls on the y-axis and processing time on the x-axis. The nominal concentration changes from 0 to 1, and the s-shaped breakthrough curve is generated due to the rapid rise in the effluent concentration. The point at which rapid rise begins is known as the breakthrough point. Column capacity with respect to the influent sorbate concentration and flow rate is highly significant in attainment of breakthrough point. From Fig. 1, breakthrough point is qualitatively indicated. The rapid rise of the breakthrough curve also indicates that the available binding sites of the adsorbent are approaching saturation. Saturation point or exhaustion point indicate a time where the column is totally saturated and sorbate concentrations in the effluent and influent are balanced or equal. However, the most important part of the breakthrough curve as far as metal (sorbate) sorption is concerned comprises only the origin up to breakthrough point section [9]. The breakthrough or service time, t_r or t_b , is generally predetermined by the breakthrough point concentration, C_r or C_b , which is related to the allowable disposal limit

for a particular metal (sorbate), which in turn makes it possible to determine volume of water treated [6]. Service time of the packed column is directly reflected by the time required to attain breakthrough point, hence the longer the service time, the higher metal (sorbate) uptake or removal capability of the column. The steepness of the breakthrough curve is the measure of column efficiency to attain the saturation point; however, it is worth noting that the steepness of the breakthrough curve changes with particle size and sorbent type [9].

2.2 Modelling of dynamic adsorption systems

Experimental evaluation of adsorption performance under various conditions is usually high-priced and time-consuming, thus development of mathematical models that have the capability to predict and optimise fixed-bed adsorption is therefore essential.

The unsteady state differential mass balance in the fluid for a section dz length of the bed is therefore given by,

$$\varepsilon \frac{\partial C(t, z)}{\partial t} + u \frac{\partial C(t, z)}{\partial z} + (1 - \varepsilon) \rho_p \frac{\partial q(t, z)}{\partial t} = D_L \frac{\partial^2 C(t, z)}{\partial z^2} \quad (1)$$

Where ε is the porosity of the bed, ρ_p is the sorbent density, other models use the bulk density of the bed, ρ_b which is equal to $(1 - \varepsilon) \rho_p$ (kg/m³), u is superficial velocity for an empty bed (m/s), D_L is an axial dispersion coefficient (m²/s). The first and second terms in Eq. 1 represent accumulation of solute in the liquid and in the solid, respectively. The third term represents the amount of solute flowing in by convention to the section dz minus that flowing out of the bed. The last term denotes axial dispersion of the solute in the bed, which results in mixing of the solute and solvent [10].

The initial and boundary conditions for the fixed-bed column initially free of adsorbate and subjected to a step change in the influent sorbate concentration in the column inlet at time zero are given by,

$$\begin{aligned} &\{t = 0, \quad C(t, z) = q(t, z) = 0\} \\ &\{z = 0, \quad C(0, t = 0) = 0; C(0, t > 0) = C_o\} \\ &\left\{ z = Z, \quad \frac{\partial C}{\partial z} = 0 \right\} \end{aligned}$$

When axial dispersion is ignored, Eq. 1 reduces to;

$$\varepsilon \frac{\partial C(t, z)}{\partial t} + u \frac{\partial C(t, z)}{\partial z} + (1 - \varepsilon) \rho_p \frac{\partial q(t, z)}{\partial t} = 0 \quad (2)$$

Thus, the initial and boundary conditions are then as follows,

$$\begin{aligned} &\{t = 0, \quad C(t, z) = 0\} \\ &\left\{z = 0, \quad \frac{D_L \varepsilon}{u} \frac{\partial C}{\partial z} = C - C_o\right\} \\ &\left\{z = Z, \quad \frac{\partial C}{\partial z} = 0\right\} \end{aligned}$$

Where t is the time, C_o is the influent sorbate concentration and Z is the bed height. An appropriate rate expression relating the rate of sorbate uptake, $\partial q / \partial t$, to liquid phase concentration, C or solid phase concentration, q or both concentrations is required to complete the model that describes dynamic performance of biosorption.

Figure 2. Schematic presentation of mass conservation of a control volume [5].

With reference to Fig. 2 and Eq. 1 (or Eq. 2), in which the former and the latter illustrates schematic presentation and mathematical presentation of mass conservation equation, respectively. The development of the mass balance differential equation is based upon the following assumptions:

- The process operates under isothermal conditions.
- No chemical reaction takes place in the column.
- The sorbent or packing material is made of porous particles that are uniform in size and spherical shape.
- The flow rate is constant and invariant with the column position.
- Each species have activity coefficient that is one.

Various mathematical models such as Bohart-Adams, Thomas, Yoon-Nelson models have been developed to predict the dynamic behaviour of the biosorption column and allow some kinetic coefficients to be estimated. Following is the description of these models.

2.2.1 Bohart – Adams (B-A) model and bed depth service time (BDST) model

Bohart-Adams model was developed by [11], when they continued with their work of analysing the typical chlorine charcoal transmission curve. They theorized that “the uptake rate of chlorine is proportional to the concentration of the chlorine existing in the bulk fluid and the residual adsorptive capacity of charcoal”. Bohart-Adams model is widely applied in the design of activated carbon adsorbers. Both models assume the rectangular isotherm at equilibrium. The sorbate-sorbent interaction for BDST model is represented by the subsequent quasi-chemical rate differential expression:

$$\frac{\partial q}{\partial t} = k_B C (q_0 - q) \quad (3)$$

As indicated on Fig. 3, the above rate expression shows that at equilibrium ($\partial q / \partial t = 0$). Consequently, Eq. 3, reduces to a rectangular or irreversible relationship between the sorbent and the bulk solution i.e. $q = q_0$.

Figure 3. Equilibrium adsorption isotherms illustrating the definition of favourable (Langmuir) and irreversible (rectangular) systems [12].

When axial dispersion is ignored, the analytical solution of equation Eq. 2 and equation Eq. 3 derived by Bohart and Adams is as follows:

$$\frac{C_t}{C_o} = \frac{\exp(\alpha)}{\exp(\alpha) + \exp(\beta) - 1} \quad (4)$$

Where,

$$\beta = \frac{K_B \rho_p q_o z}{v} \left(\frac{1 - \varepsilon}{\varepsilon} \right); \quad \alpha = K_B C_o \left(t - \frac{z}{v} \right)$$

In order to simplify the above formal solution to a well-known bed depth service time model, two simplification procedures are considered. Firstly, the two exponential terms $\exp(\alpha)$ and $\exp(\beta)$ are frequently much greater than unity, as a result the term “1” on Eq. 4 is neglected. Secondly, sorption time required for the sorbate to exit the column is much greater than the time required for the bulk solution to flow from inlet to outlet of the column, which is represented by z/v . Hence, an assumption can be made that t is much greater than z/v and ignore the z/v term in the expression of α . Finally, the above-mentioned simplifications for equation Eq. 4 yield:

$$\frac{C_o}{C_t} \exp(K_B C_o t) = \exp(K_{BA} C_o t) + \exp \left[\frac{K_B \rho_p q_o (1 - \varepsilon) z}{\varepsilon v} \right] \quad (5)$$

The expression $\rho_p q_o (1 - \varepsilon)$ is officially identical to N_o , which is known as the sorption capacity per unit volume of the bed. The product term, εv is equivalent to the superficial velocity u . When replacing $\rho_p q_o (1 - \varepsilon)$ and εv in Eq. 5 with N_o and u , respectively and setting nominal concentration (C/C_o) as subject of the formula, the well-known BDST model is obtained as shown in Eq. 6:

$$\frac{C_t}{C_o} = \frac{1}{\left[1 + \exp \left(\frac{K_B N_o z}{u} - K_B C_o t \right) \right]} \quad (6)$$

In order to derive the well-known B-A model, [5] reviewed vital equations that were based on the hypothesis that Bohart and Adams made during their work of analysing typical chlorine-charcoal transmission curve. The following Eq. 7 and 8 were based on the hypothesis;

$$\frac{\partial C}{\partial z} = - \frac{K_B q_r C}{u} \quad (7)$$

$$\frac{\partial q_r}{\partial t} = -K_B q_r C \quad (8)$$

Where q_r is the residual adsorptive capacity, additionally the initial conditions were as follows,

$$\left\{ t = 0, \quad \frac{q_r}{q_m} = 1 \right\}$$

$$\left\{ z = 0, \quad \frac{C_t}{C_o} = 1 \right\}$$

Consequently, the fundamental form of B-A model is as follows;

$$\ln \left(\frac{C_o}{C_t} - 1 \right) = \ln \left[\exp \left(K_B q_m \frac{z}{U_o} \right) - 1 \right] - K_B C_o t \quad (9a)$$

The well-known linear of B-A model is given by Eq. 9b below,

$$\ln \left(\frac{C_t}{C_o} \right) = K_{BA} C_o t - K_{BA} N_o \left(\frac{z}{U_o} \right) \quad (9b)$$

Further simplifying Eq. 9b, and setting nominal concentration as subject of the formula, the commonly applied B-A model is obtained, also noting that q_m is equivalent to N_o .

$$\frac{C_t}{C_o} = EXP \left[\left(K_B C_o t - K_B N_o \left(\frac{z}{U_o} \right) \right) \right] \quad (10)$$

Where K_B is the kinetic constant (L/mg.min), N_o is the saturation concentration or sorption capacity per unit volume of fixed bed (mg/L), z is the adsorbent bed depth (cm) and U_o is the linear velocity (cm/min). It is also worth noting that when $\exp \left(K_B q_m \frac{z}{U_o} \right)$, in Eq. 9a is much greater than 1, Eq. 10 is obtained an observation that was made by [13]. Empirical constants in both of the models are not constant when the process variable(s) is/are changed which can lead to unsatisfactory predictions of breakthrough curves at 50% breakthrough i.e., nominal concentration (C_t/C_o) of 0.5. The validity of these model is limited to the range of process parameters used according to [14]. Another main limitation of B-A model stated by [15] is that the model is best at predicting initial region of the breakthrough curve at nominal concentration of less than 0.15 but not limited to.

2.2.2 Thomas model

The Thomas model is one of the frequently applied models to estimate the adsorptive capacity of adsorbent and predict breakthrough curves. A reaction model [16] was developed based on the assumptions that axial and radial dispersion in the fixed bed column are negligible and that the pseudo second-order reaction rate principle describes the adsorption process, which reduces to a Langmuir isotherm at equilibrium. The physical properties of the adsorbent (solid-phase) and the liquid phase and column void fraction were also assumed constant. In addition isothermal and isobaric process conditions were assumed and finally negligible intra particle diffusion and external resistance during the mass transfer processes. Hence, theoretically it is suitable to estimate the adsorption process where external and internal diffusion resistances are extremely small. The model consists of seven parameters which are five process variables (influent, effluent concentrations, flow rate, adsorbent mass and processing time) and two empirical constants. The Thomas model predicts better processes that follow Langmuir isotherm, which means that the model is more suitable for monolayer adsorption and homogenous surfaces. The well-known Thomas model is given by:

$$\ln\left(\frac{C_o}{C_t} - 1\right) = \frac{K_{Th}q_o m}{Q} - K_{Th}C_o t \quad (11)$$

Another significant aspect to consider is that the Thomas model is mathematical equivalent to the BDST model (Eq. 10) since linear velocity or superficial velocity, u or u_o is determined by volumetric flow rate and cross-sectional area:

$$u = U_o = Q/A_c \quad (12)$$

Hence, substituting the above expression into Eq. 10, result in Eq. 13 below,

$$\frac{C_t}{C_o} = \frac{1}{\left[1 + EXP\left(\frac{K_B N_o z A_c}{Q} - K_B C_o t\right)\right]} \quad (13)$$

Now, when considering that,

$$\begin{aligned} N_o z A_c &= \left(\frac{\text{sorbate mass}}{\text{bed volume}}\right) (\text{bed depth})(\text{bed cross sectional area}) \\ &= \left(\frac{\text{sorbate mass}}{\text{bed volume}}\right) (\text{bed volume}) = \text{sorbate mass} \end{aligned}$$

And from Eq. 11,

$$q_o m = \left(\frac{\text{sorbate mass}}{\text{sorbent mass}} \right) (\text{sorbent mass}) = \text{sorbate mass}$$

Thus, from the above expressions the following relation can be obtained;

$$N_o z A_c = q_o m \quad (14)$$

Finally, when substituting $q_o m$ in Eq. 6 for $N_o z A_c$ and setting K_B to equal to K_{TH} , Eq. 6 then becomes:

$$\frac{C_t}{C_o} = \frac{1}{\left[EXP \left[\left(\frac{K_{TH} q_o m}{Q} - K_{TH} C_o t \right) \right] + 1 \right]} \quad (15)$$

Eq. 15 is clearly identical to Eq. 11 after linearization. As a result of BDST and Thomas models being mathematically equivalent it is therefore not recommended that both of these models are applied in the same study to predict breakthrough curves. In Eq. 15, K_{TH} is the Thomas model constant (L/mg.min), q_o is the adsorption capacity (mg/g), m is the adsorbent mass (g) and Q is the volumetric flow rate (mL/min).

2.2.3 Yoon – Nelson model

In existing adsorption models, the Yoon-Nelson model is extremely concise in form assuming that “the rate of decrease in the probability of adsorption of adsorbate molecule is proportional to the probability of the adsorbate adsorption and the adsorbate breakthrough on the adsorbent” [17]. The model consists of five parameters which are three process variables (influent, effluent concentrations and processing time) and two empirical constants. The rough form of the Yoon-Nelson model makes it less valuable or convenient to obtain process variables and to predict adsorption under variety conditions [5] stated. This model does not consider the effect of each variable during adsorption process. The linearized form of Yoon-Nelson model is as follows;

$$\ln \left(\frac{C_t}{C_o - C_t} \right) = K_{YN} t - K_{YN} \tau \quad (16)$$

Where C_t and C_o are effluent and influent adsorbate concentrations (mg/L) respectively, K_{YN} is the rate constant (min^{-1}), t is the processing time (min) and τ is the time required for 50% adsorbate breakthrough (min). The mathematical form of Yoon-Nelson model that is ready to be applied to generate breakthrough curve(s) is given below.

$$\frac{C_t}{C_o} = \frac{\text{EXP}(K_{YN}t - K_{YN}\tau)}{[1 + \text{EXP}(K_{YN}t - K_{YN}\tau)]} \quad (17)$$

The conventional method to estimate empirical constants of the dynamic models is through the slopes and intercepts of the linear plots. For B-A model the linear plot is obtained by plotting $\ln(C_t/C_o)$ versus t and for BDST and Thomas models the linear plot is obtained by plotting $\ln((C_o/C_t)-1)$ versus t . Finally, linear plot for Yoon-Nelson model is given by $\ln((C_t/(C_o-C_t)))$ versus t . In this review more emphasis was placed on dynamic adsorption modelling.

3. Factors affecting dynamic adsorption systems

3.1 Adsorbent mass

In predicting concentration-time profiles using modified dynamic models, sorbent mass was varied according to Table 1 below.

Table 1. Effect of sorbent mass at constant flow rate and initial concentration.

Adsorption Systems	m	Q	C
	[g]	[mL/min]	[mg/L]
Fe-seashell	30	5	425.4
	60	5	425.4
	90	5	425.4
Pb-charcoal	1.12	15	20
	2.52	15	20
	3.501	15	20
Pb- <i>Agirus bisporus</i>	0.4	3	50
	0.8	3	50
	1.2	3	50

3.2 Flow rate

The investigated flow rates to predict breakthrough curves were varied according to Table 2 below.

Table 2. Effect of flow rate at constant sorbent mass and initial concentration.

Adsorption Systems	Q	C	m
	[mL/min]	[mg/L]	[g]
Fe-seashell	2.5	425.4	60
	5	425.4	60
	7.5	425.4	60
Pb-charcoal	10	20	2.52
	15	20	2.52
	20	20	2.52
Pb- <i>Agirus bisporus</i>	1	50	0.8
	3	50	0.8
	5	50	0.8

3.3 Initial adsorbate concentration

The considered levels of initial concentration under investigation are shown in table below.

Table 3. Effect of initial concentration at constant sorbent and flow rate.

Adsorption Systems	C	m	Q
	[mg/L]	[g]	[mL/min]
Fe-seashell	233.2	60	5
	308.4	60	5
	425.4	60	5
Pb-charcoal	10	2.52	15
	20	2.52	15
	30	2.52	15
Pb- <i>Agirus bisporus</i>	20	0.8	3
	50	0.8	3
	100	0.8	3

4. Statistical selection approach

4.1 Preliminary quantitative analysis of model performance

When theoretical and experimental breakthrough curves are plotted on the same set of axes, most researchers tend to focus solely on qualitative rather than quantitative analysis. Quantitative analyses are statistical measures of accuracy between the actual and predicted breakthrough curves. The statistical measures do not only assist in generating quantitative conclusions between the actual and predicted breakthrough curves but also assist in determining the overall performance or classification of dynamic models.

Table 4. Summary of performance evaluation metrics in comparing Yoon-Nelson, Thomas and Bohart-Adams models for Fe-seashell system before application of mean values.

Parameters	Yoon – Nelson			Thomas			B – A		
	MAE	RMSE	R ²	MAE	RMSE	R ²	MAE	RMSE	R ²
Mass [g]									
30	0.014	0.021	0.998	0.014	0.022	0.998	0.255	0.387	0.530
60	0.039	0.051	0.984	0.040	0.051	0.984	0.103	0.133	0.826
90	0.044	0.054	0.979	0.044	0.053	0.979	0.120	0.146	0.738
Flow rate [mL/min]									
2.5	0.019	0.024	0.993	0.021	0.025	0.992	0.087	0.106	0.839
5	0.039	0.051	0.984	0.040	0.051	0.984	0.093	0.120	0.880
7.5	0.109	0.170	0.868	0.109	0.170	0.868	0.133	0.207	0.551
Concentration [mg/L]									
233.22	0.106	0.109	0.908	0.108	0.111	0.906	0.063	0.064	0.959
308.4	0.042	0.050	0.981	0.042	0.050	0.981	0.103	0.123	0.901
425.4	0.036	0.046	0.987	0.037	0.047	0.987	0.325	0.415	0.666

Tables 4, 5 and 6 illustrate the actual performance evaluation metrics of the Fe-seashell, Pb-charcoal, and Pb-*Agirus bisporus* adsorption systems preliminary to the application of averaged model parameters. The coefficient of determination, R² assesses how good a model predicts output or experimental data. Lower values of RMSE and MAE and higher R² signifies a model with better output prediction. The results in Table 4 show that Thomas and Yoon-Nelson models are better at predicting experimental data in contrast to the Bohart-Adams model. The data utilized in generating tables 4, 5 and 6 was obtained from the studies that were done by [18], [19] and [20], respectively.

Table 5. Summary of performance evaluation metrics in comparing Yoon-Nelson, Thomas and Bohart-Adams models for Pb-charcoal system before application of mean values.

Parameters	Yoon – Nelson			Thomas			B – A		
	MAE	RMSE	R ²	MAE	RMSE	R ²	MAE	RMSE	R ²
Mass [g]									
1.12	0.055	0.102	0.920	0.055	0.102	0.920	0.491	0.913	0.256
2.52	0.036	0.090	0.958	0.036	0.090	0.958	0.572	1.428	0.322
3.501	0.015	0.036	0.993	0.015	0.036	0.993	0.292	0.688	0.575
Flow rate [mL/min]									
10	0.020	0.048	0.987	0.021	0.052	0.986	1.024	2.478	0.352
15	0.036	0.091	0.957	0.036	0.091	0.957	0.573	1.426	0.321
20	0.054	0.124	0.906	0.055	0.127	0.902	0.445	1.027	0.263
Concentration [mg/L]									
10	0.045	0.108	0.934	0.043	0.103	0.941	0.867	2.094	0.330
20	0.037	0.092	0.956	0.037	0.092	0.956	0.570	1.419	0.320
30	0.031	0.075	0.966	0.032	0.078	0.963	0.310	0.746	0.365

The performance of the models in Table 5 and 6 for the Pb-charcoal and Pb-*Agirius bisporus* adsorption systems is similar to that of the Fe-seashell adsorption system in Table 4. The Bohart-Adams model continued to result in low R² values and higher values of MAE and RMSE, while Yoon-Nelson and Thomas models continued to show close correlations between experimental and predicted data as indicated by higher R² values and lower values of error metrics. Tables 4, 5 and 6 show that Yoon-Nelson and Thomas models predict the experimental data similarly when model parameters are not modified to average values. The model validity assessed by employing MAE, RMSE, and R² is consistent in all three considered adsorption systems i.e., the Yoon-Nelson and Thomas models outperform the Bohart-Adams model when model parameters are not modified to average values. The Yoon-Nelson and Thomas models are both performing well, however, the Thomas model was selected as the best performing model since the model incorporates significant process variables such as flow rate, mass and initial concentration in contrast to the Yoon-Nelson model. These process variables are very substantial when optimizing dynamic adsorption systems and in scaling up procedures.

Table 6. Summary of performance evaluation metrics in comparing Yoon-Nelson, Thomas and Bohart-Adams models for Pb-Agirus bisporus system before application of mean values.

Parameters	Yoon – Nelson			Thomas			B – A		
	MAE	RMSE	R ²	MAE	RMSE	R ²	MAE	RMSE	R ²
Mass [g]									
0.4	0,031	0,052	0,987	0,031	0,051	0,987	46,31	77,32	0,341
0.8	0,014	0,027	0,997	0,013	0,026	0,997	67,96	131,4	0,295
1.2	0,005	0,011	0,999	0,005	0,011	0,999	1565	3222	0,358
Flow rate [mL/min]									
1	0.006	0.015	0.998	0.006	0.014	0.998	55.17	133.5	0.396
3	0.025	0.048	0.989	0.024	0.047	0.989	87.50	169.9	0.284
5	0.033	0.056	0.984	0.034	0.057	0.983	264.8	447.9	0.232
Concentration [mg/L]									
20	0.011	0.024	0.996	0.011	0.024	0.996	6.387	13.92	0.518
50	0.022	0.042	0.992	0.022	0.041	0.992	14.47	27.19	0.359
100	0.043	0.069	0.976	0.043	0.069	0.976	882.0	1420	0.277

The underperformance of the Bohart-Adams model was expected since the statistical analysis take into account all data points and the Bohart-Adams model is best at predicting the initial part of the breakthrough curve at the nominal concentration of less than 0.15 (Han *et al.* 2009). The observed results are a clear indication that the number of process variables that are included in the model cannot be used to classify the efficacy of the model since the Bohart-Adams model incorporates more process variables than the Thomas model yet the latter outperforms the former. The overall model validity that is preliminary to the application of averaged model parameters is Thomas > Yoon-Nelson > Bohart-Adams. The next section of the study will assess the efficacy of the models when model parameters are modified to average values.

4.2 Application of local mean values (LMV)

This section of the study focuses on the application of local mean values (LMV) of the empirical constants or model parameters to predict breakthrough curves. The local mean values were determined from raw data tables by averaging the model parameters based on the range of operating variables i.e. sorbent mass, flow rate and initial sorbate concentration.

4.2.1 Fe-seashell system

Conventionally, empirical constants of a particular dynamic model vary with operating conditions for a distinct adsorption system. Hence, for this reason, an explicit approach

was adopted to investigate how these variations in empirical constants affect model performance.

Table 7. Local mean values (LMV) applied during the prediction of breakthrough curves for Fe-seashell system.

Parameters	Thomas		Yoon-Nelson		B-A	
	$K_{TH,ave_1} \times 10^{-5}$ [L/min.mg]	q_{o,ave_1} [mg/g]	K_{YN,ave_1} [min ⁻¹]	τ_{ave_1} [min]	$K_{B,ave_1} \times 10^{-5}$ [L/min.mg]	N_{o,ave_1} [mg/L]
Mass	±4.62	±20.47	±0.020	±569.9	±1.88	±47129.19
Flow rate	±4.08	±20.8	±0.017	±710.6	±1.80	±44571.34
Concentration	±5.51	±21.9	±0.017	±878.3	±2.58	±38202.06

The local mean values of model parameters for the Fe-seashell adsorption system are tabulated in Table 7. Fig. 4 and 5 demonstrates actual and predicted breakthrough curves at different sorbent masses and flow rates, respectively, whereas Fig. 6 illustrates actual and predicted breakthrough curves at different influent sorbate concentrations. Statistical analysis results and water treatment performance parameters are tabulated in Tables 8 and 9, respectively.

4.2.1.1 Effect of sorbent mass

In predicting concentration-time profiles using modified dynamic models, sorbent mass was varied from 30 to 90 g for the Fe-seashell system. Flow rate and sorbate initial concentration were kept constant at 5 mL/min and 425.4 mg/L, respectively. The sorbent mass was observed to increase with amount of water treated at breakthrough, thus saturation points were reached much quicker at a lower sorbent mass as seen in Fig. 4. Three dynamic models were considered in predicting experimental data namely, Thomas, Yoon-Nelson and Bohart-Adams model.

From Fig. 4 it was observed that the Yoon-Nelson model resulted in practically identical predictions at different sorbent masses when mean values were applied as indicated by one black dashed line. The three predicted breakthrough curves for the Yoon-Nelson model were observed to overlay, thus resulting in identical profiles at different sorbent masses. The results observed for the Yoon-Nelson model signified that no sensitivity was observed as seen in Fig. 4. The Thomas model on the other hand showed close correlation between predicted and actual breakthrough curves at 30 and 60 g, respectively. At 90 g the Thomas model slightly over predicted the experimental data. The observed over prediction at 90 g was attributed to the value of the adsorption capacity (q_o) being further away from the

variable range mean. The sensitivity observed for the Thomas model was attributed to the number of operating parameters incorporated in the model in contrast to the Yoon-Nelson model. The Thomas model was observed to track the experimental data very well for sorbent masses of 30 and 60 g as indicated by R^2 values of 0.999 and 0.984 in Table 8, respectively. It is therefore feasible to apply mean value per variable for a Thomas model to predict breakthrough curves since the predictions were satisfactory and sensitivity was observed. The Bohart-Adams model showed sensitivity when mean values were applied as observed in Fig. 4, however the predictions were not satisfactory. The Bohart-Adams model over predicted the experimental data for all sorbent masses. The observed model validity in Fig. 4 is Thomas > Bohart-Adams > Yoon-Nelson.

Figure 4. Actual and predicted breakthrough curves for removal of Fe using seashells at different sorbent masses during application of variable range mean values. (TH – Thomas, YN – Yoon-Nelson and BA – Bohart-Adams).

4.2.1.2 Effect of flow rate

The flow rates to predict concentration-time profiles for the Fe-seashell adsorption system were varied from 2.5 to 7.5 mL/min, while the sorbent mass and initial concentration were kept constant at 60 g and 425.4 mg/L, respectively. From Fig. 5, it was observed that flow rate was increasing with a decrease in the amount of water treated at breakthrough. Higher flow rates reduce residence time, thus increasing the saturation rate of the bed.

Figure 5. Actual and predicted breakthrough curves for removal of Fe using seashells at different flow rates during application of variable range mean. (TH – Thomas, YN – Yoon-Nelson and BA – Bohart-Adams).

Comparable nature of the curves was observed for the Yoon-Nelson model in Fig. 5. The observed results for the Yoon-Nelson model were analogous to those that were seen in Fig. 4. The Yoon-Nelson model resulted in profiles that had identical profiles when variable range mean values were applied. The Thomas model was seen closer to experimental breakthrough curves when compared to the Yoon-Nelson and Bohart-Adams models. The Thomas model was in line with the experimental data at breakthrough point ($C_t/C_0 = 0.05$) for the flow rates of 5 and 7.5 mL/min. At 2.5 mL/min the Thomas model was seen over predicting the experimental data. The observed over prediction at 2.5 mL/min was attributed to the value of the kinetic constant (K_{TH}) being lower than the variable range mean. The standard deviation was lower for K_{TH} and higher for q_0 for the results in Fig. 4, contrasting with the standard deviation results for the profiles in Fig. 5, thus the shift of the breakthrough curve is highly influenced by the kinetic constant (K_{TH}) for the Thomas model. The Thomas model was observed to track the experimental data very well for the flow rate of 5 mL/min as indicated by R^2 value of 0.985 tabulated in Table 8. Process parameters such as flow rate, sorbent mass and initial concentration of sorbate play a pivotal role in ensuring higher predictive capabilities for the Thomas model. The Bohart-Adams model on the other hand was observed to overpredict the experimental data for all flow rates studied when variable range mean values were applied as seen in Fig. 5. The profiles in Fig. 5 for the Bohart-Adams model were significantly worse than those observed in Fig. 4. It is worth emphasizing that the Bohart-Adams model profiles were unexpected since the model incorporated most operating variables that are significant for a dynamic

adsorption system. The exclusion of significant process parameters such as flow rate and sorbent mass in the Yoon-Nelson model makes it virtually impossible for the model to be applied in real life situations where process parameter(s) may vary. Thus, it is not feasible to apply Bohart-Adams and Yoon-Nelson models in practical applications when considering fixing the model parameters.

4.2.1.3 Effect of initial concentration

The levels of initial sorbate concentration under investigation were 233.22, 308.4 and 425.4 mg/L, while sorbent mass and flow rate were kept constant at 60 g and 5 mL/min for the Fe-seashell system. Figure 6 show that the initial sorbate concentration is decreasing with an increase in the amount of water treated at the breakthrough point. The saturation point was reached much quicker at a higher initial sorbate concentration as seen in figure 6.

Figure 6. Actual and predicted breakthrough curves for removal of Fe using seashells at different initial concentrations during application of variable range mean (TH – Thomas, YN – Yoon-Nelson and BA – Bohart-Adams).

When variable mean values for model parameters were applied, Yoon-Nelson model resulted in comparable concentration-time profiles at different sorbate concentrations as seen in Fig. 6. The nature of the profiles observed for the Yoon-Nelson model was similar for all cases studied as seen in Fig. 4, 5 and 6. The Yoon-Nelson model in its current form will always require experimental work when process parameter(s) vary which may take time to complete and may delay the adsorption process. Thus, practical application of this

is very limited. On the contrary, the Thomas and Bohart-Adams models were seen over predicting and under predicting the experimental data at breakthrough point, with the former being the most dominant as seen in Fig. 6. From the profiles for sorbate concentrations of 308.4 and 425.4 mg/L, the models were seen overpredicting the experimental data when considering the breakthrough section in Fig. 6. At 233.22 mg/L, the models resulted in profiles that were under predicting the experimental data at breakthrough. The overall performance of the Thomas model was consistent for all cases studied, however the standard deviation values of the model parameters that were used to predict profiles in Fig. 6 were above 1. The Thomas model, nonetheless, continued to outperform the Yoon-Nelson and Bohart-Adams models. The Bohart-Adams model in Fig. 6 continued to result in profiles that were deviating from the ideal s-shape, similar to those that were seen in Fig. 4 and 5. The exclusion of intra-particle diffusion in the Bohart-Adams model has a greater impact on the performance of this model, though some authors argue that the Bohart-Adams model is best in predicting the initial part of breakthrough curve before 50 % breakthrough point, supporting the nature of the curves observed on Fig. 6. It is worth noting that although the ideal shape of the breakthrough curve is s-shaped, the breakthrough point is the most prominent part of the curve as it determines the amount of water treated before saturation is attained. Consequently, the aforementioned fact support the nature of the profiles observed for the Bohart-Adams model.

Table 8. Summary of performance evaluation metrics in comparing Yoon-Nelson, Thomas and Bohart-Adams models for the Fe-seashell system during application of local mean values (LMV) of empirical constants.

Parameters	Yoon – Nelson			Thomas			B – A		
	MAE	RMSE	R ²	MAE	RMSE	R ²	MAE	RMSE	R ²
Mass [g]									
30	0.186	0.283	0.528	0.011	0.017	0.999	3.191	4.843	0.317
60	0.037	0.047	0.987	0.040	0.051	0.984	0.054	0.070	0.732
90	0.214	0.260	0.702	0.066	0.080	0.948	0.007	0.009	0.809
Flow rate [mL/min]									
2.5	0.277	0.338	0.492	0.044	0.054	0.962	0.002	0.003	0.878
5	0.101	0.131	0.813	0.038	0.049	0.985	0.081	0.104	0.747
7.5	0.157	0.245	0.343	0.096	0.150	0.896	1.056	1.646	0.340
Concentration [mg/L]									
233.22	0.297	0.304	0.567	0.112	0.115	0.904	0.052	0.053	0.983
308.4	0.057	0.069	0.961	0.047	0.057	0.976	0.128	0.154	0.822
425.4	0.054	0.069	0.547	0.071	0.091	0.947	0.327	0.417	0.633

The results in Table 8 show that the Thomas model is better at predicting the experimental data in contrast to the other two models. The Yoon-Nelson and Bohart-Adams models

resulted in low R^2 values and higher values of MAE and RMSE, while the Thomas model showed close correlations between experimental and predicted data as indicated by higher R^2 values and lower values of error metrics. Application of variable range mean values changed the overall model validity from Thomas > Yoon-Nelson > Bohart-Adams to Thomas > Bohart-Adams > Yoon-Nelson. Thomas model was the best performing model for this approach, followed by the Bohart-Adams model.

Table 9. Summary of water treatment performance parameters in comparing Yoon-Nelson, Thomas and Bohart-Adams models for the Fe-seashell system during application of variable range mean (VRM) of empirical constants.

Parameters	Experimental		Yoon – Nelson		Thomas		B – A	
	V_b [L]	q_b [mg]	V_b [L]	q_b [mg]	V_b [L]	q_b [mg]	V_b [L]	q_b [mg]
Mass [g]								
30	0.745	301.1	2.1	848.7	0.695	280.9	0.485	196.0
60	1.84	743.6	2.1	848.7	2.14	864.8	2.845	1150
90	3.125	1263	2.1	848.7	3.585	1449	5.205	2103
Flow rate [mL/min]								
2.5	2.2	889.1	1.353	546.6	2.51	1014	3.485	1408
5	1.825	737.5	2.705	1093	2.085	842.6	2.51	1014
7.5	1.425	575.9	4.058	1640	1.665	672.9	1.538	621.3
Concentration [mg/L]								
233.22	4.85	1075	3.525	781.0	4.49	994.8	4.48	992.6
308.4	3.025	886.3	3.525	1033	3.395	994.7	3.39	993.2
425.4	1.85	747.6	3.525	1425	2.46	994.2	2.46	994.2

To further classify the dynamic models, performance parameters such as the volume of water treated at breakthrough point (V_b) and total mass of metal removed at breakthrough point (q_b) were also evaluated and compared to experimental performance parameters. These performance or design parameters are very significant when assessing the efficacy of dynamic models at the breakthrough point section. Table 9 show experimental and predicted performance parameters after the application of variable range mean. The results in Table 9 show that the Thomas model tracks the experimental data very well, in contrast to the Yoon-Nelson and Bohart-Adams models. The observed model validity in Table 9 is Thomas > Bohart-Adams > Yoon-Nelson.

4.2.2 Pb-Charcoal System

An unambiguous approach of utilizing mean values per variable (or variable range mean) was also applied in the Pb-charcoal system to predict concentration-time profiles. Mean values of model parameters and statistical analysis results for the Pb-charcoal system are tabulated in Tables 10 and 11, respectively.

Table 10. Local mean values (LMV) applied during the prediction of breakthrough curves for Pb-charcoal system.

Parameters	Thomas		Yoon-Nelson		B-A	
	$K_{TH,ave_1} \times 10^{-5}$ [L/min.mg]	q_{o,ave_1} [mg/g]	K_{YN,ave_1} [min ⁻¹]	τ_{ave_1} [min]	$K_{B,ave_1} \times 10^{-5}$ [L/min.mg]	N_{o,ave_1} [mg/L]
Mass	±71.3	±64.7	±0.0143	±479.9	±36.5	±11795.2
Flow rate	±77.7	±55.9	±0.0155	±497.8	±47.2	±8554.7
Concentration	±92.4	±54.6	±0.0145	±501.5	±60.7	±8593.2

Table 11. Summary of performance evaluation metrics in comparing Yoon-Nelson, Thomas and Bohart-Adams models for Pb-charcoal system during application of Local mean values (LMV) of empirical constants.

Parameters	Yoon – Nelson			Thomas			B – A		
	MAE	RMSE	R ²	MAE	RMSE	R ²	MAE	RMSE	R ²
Mass [g]									
1.12	0.152	0.282	0.578	0.020	0.038	0.988	7.555	14.06	0.161
2.52	0.024	0.059	0.982	0.053	0.131	0.908	0.061	0.153	0.376
3.501	0.068	0.160	0.866	0.055	0.130	0.850	0.003	0.006	0.646
Flow rate [mL/min]									
10	0.055	0.134	0.908	0.047	0.114	0.909	0.021	0.051	0.516
15	0.033	0.082	0.965	0.019	0.047	0.989	0.756	1.882	0.288
20	0.117	0.271	0.627	0.052	0.120	0.920	4.984	11.50	0.146
Concentration [mg/L]									
10	0.026	0.063	0.980	0.045	0.108	0.601	0.003	0.008	0.607
20	0.035	0.086	0.961	0.015	0.036	0.994	1.349	3.360	0.216
30	0.087	0.211	0.768	0.024	0.058	0.983	469.1	1130.6	0.087

Local mean values approach proved to be very pertinent for dynamic models under evaluation, particularly for the Thomas model. The results in Table 11 show that the Bohart-Adams model yield low regression values and higher values of MAE and RMSE. The Thomas model on the other hand show a close relation between experimental and theoretical breakthrough curves as indicated by higher regression values and lower values of MAE and RMSE. The Yoon-Nelson model did not mimic changes in operating conditions when mean values were applied, consequently, model validity assessed by employing two error metrics and coefficient of determination was observed to be Thomas

> Bohart-Adams > Yoon-Nelson. The Thomas model continued to outperform the Yoon-Nelson and Bohart-Adams models.

Table 12. Summary of water treatment performance parameters in comparing Yoon-Nelson, Thomas and Bohart-Adams models for the Pb-charcoal system during application of variable range mean (VRM) of empirical constants.

Parameters	Experimental		Yoon – Nelson		Thomas		B – A	
	V _b [L]	q _b [mg]	V _b [L]	q _b [mg]	V _b [L]	q _b [mg]	V _b [L]	q _b [mg]
Mass [g]								
1.12	0.975	18.53	4.11	78.09	0.54	10.26	0	0
2.52	4.62	87.78	4.11	78.09	5.07	96.33	8.79	167.0
3.501	6.75	128.3	4.11	78.09	8.235	156.5	14.78	280.7
Flow rate [mL/min]								
10	4.5	85.5	3.09	58.71	5.15	97.85	7.67	145.7
15	4.62	87.8	4.635	88.07	4.2	79.8	6.075	115.4
20	3	57	6.18	117.4	3.26	61.94	4.5	85.5
Concentration [mg/L]								
10	6.375	60.56	4.485	42.61	9	85.5	14.39	136.7
20	4,5	85,5	4.485	85.22	4.5	85.5	7.2	136.8
30	2,85	81,2	4.485	127.8	3	85.5	4.8	136.8

Table 12 show experimental and predicted performance parameters after the application of variable range mean values for the Pb-charcoal system. The results observed show that the Thomas model tracks the experimental data very well, in contrast to the Yoon-Nelson and Bohart-Adams models. The observed model validity in Table 12 is Thomas > Bohart-Adams > Yoon-Nelson.

4.2.3 Pb-Agirus bisporus system

The approach of applying local mean values (LMV) of model parameters was also adopted in the Pb-*Agirus bisporus* system. Mean values of model parameters are tabulated in Table 13. The statistical analysis and water treatment parameters results for the aforementioned system are tabulated in Tables 14 and 15, respectively.

Table 13. Local mean values (LMV) applied during the prediction of breakthrough curves for Pb-Agirus bisporus system.

Parameters	Thomas		Yoon-Nelson		B-A	
	$K_{TH,ave_1} \times 10^{-5}$ [L/min.mg]	q_{o,ave_1} [mg/g]	K_{YN,ave_1} [min ⁻¹]	τ_{ave_1} [min]	$K_{B,ave_1} \times 10^{-5}$ [L/min.mg]	N_{o,ave_1} [mg/L]
Mass	±62,5	±63,3	±0,032	±330	±55,6	±6829,30
Flow rate	±62,1	±63,6	±0,031	±533,2	±56,3	±6814,39
Concentration	±62,6	±63,2	±0,030	±429,8	±55,8	±6787,03

Table 14. Summary of performance evaluation metrics in comparing Yoon-Nelson, Thomas and Bohart-Adams models for Pb-Agirus bisporus system during application of Local mean values (LMV) of empirical constants.

Parameters	Yoon – Nelson			Thomas			B – A		
	MAE	RMSE	R ²	MAE	RMSE	R ²	MAE	RMSE	R ²
Mass [g]									
0.4	0.067	0.112	0.524	0.048	0.080	0.962	15.32	25.58	0.441
0.8	0.022	0.042	0.992	0.012	0.024	0.997	134.7	260.4	0.267
1.2	0.129	0.266	0.681	0.034	0.070	0.974	15537	31984	0.280
Flow rate [mL/min]									
1	0.172	0.416	0.232	0.039	0.094	0.947	1769	4283	0.290
3	0.098	0.189	0.445	0.022	0.042	0.992	199.2	386.8	0.253
5	0.001	0.002	0.293	0.021	0.036	0.992	26.99	45.65	0.323
Concentration [mg/L]									
20	0.171	0.373	0.375	0.020	0.044	0.980	0.783	1.707	0.653
50	0.088	0.165	0.839	0.022	0.041	0.992	169.8	319.2	0.274
100	0.007	0.012	0.437	0.092	0.147	0.899	2447	3940	0.253

The results in Table 14 show that the Thomas model is better at predicting the experimental data in contrast to the other two models. The Yoon-Nelson and Bohart-Adams models resulted in low R² values and higher values of MAE and RMSE, while the Thomas model showed close correlations between experimental and predicted data as indicated by higher R² values and lower values of error metrics. Model validity assessed by employing two error metrics and coefficient of determination was observed to be Thomas > Bohart-Adams > Yoon-Nelson. The Thomas model continued to outperform the Yoon-Nelson and Bohart-Adams models.

Table 15. Summary of water treatment performance parameters for the Yoon-Nelson, Thomas and Bohart-Adams models for the Pb-Agirus bisporus system during application of Local mean values (LMV) of empirical constants.

Parameters	Experimental		Yoon – Nelson		Thomas		B – A	
	V _b [L]	q _b [mg]	V _b [L]	q _b [mg]	V _b [L]	q _b [mg]	V _b [L]	q _b [mg]
Mass [g]								
0.4	0,348	16,5	0,711	33,8	0,225	10,7	0,162	7,7
0.8	0,735	34,9	0,711	33,8	0,732	34,8	0,642	30
1.2	1,041	49	0,711	33,8	1,239	59	0,546	26
Flow rate [mL/min]								
1	0,94	44,7	0,439	20,9	0,924	44	0,857	41
3	0,72	34,2	1,317	63	0,735	34,9	0,645	31
5	0,7	33,3	2,195	104	0,545	25,9	0,430	20,4
Concentration [mg/L]								
20	1,8	34	0,999	19,0	1,824	34,7	1,596	30,3
50	0,735	34,9	0,999	47	0,729	34,6	0,639	30,4
100	0,39	37,1	0,999	95	0,366	34,8	0,318	30,2

Table 15 show experimental and predicted performance parameters after the application of Local mean values (LMV) for the Pb-Agirus bisporus system. The results observed show that the Thomas model tracks the experimental data very well, in contrast to the Yoon-Nelson and Bohart-Adams models. The Yoon-Nelson model did not mimic changes in operating conditions when mean values were applied as indicated by constant values of V_b when sorbent mass and initial concentration were varied, furthermore, the change was only observed at varying flow rates but at constant breakthrough time (t_b). The observed model validity in Table 15 is Thomas > Bohart-Adams > Yoon-Nelson.

4.3 Application of global mean values (GMV)

The mean values used in this section of the study were determined based on the entire experimental domain in order to generalize the conditions, as a result, a single value of the mean for each model parameter was obtained in order to predict breakthrough curves. The averaged model parameters are tabulated in tables 16, 19 and 22 for the three considered systems, respectively. The idea behind the chosen approach was investigating the possibility of fixing model parameter(s) to predict dynamic performance of an adsorption column under varying operating conditions.

4.3.1 Fe-seashell system

How the existing dynamic models respond to changes in operating conditions is not well studied for dynamic adsorption systems, moreover, the parameter that must be varied to

reflect deviations in kinetic behaviour is ambiguous for a particular dynamic model. Typically, refitting is the only alternative technique used to obtain new set of model parameters when operating conditions vary. A generalization approach was applied on the Fe-seashell adsorption system to predict breakthrough curves. The approach evaluated model performance under generalized conditions and the metric performance of each model was evaluated and tabulated in Table 17. The water treatment performance parameters are tabulated in Table 18.

Table 16. Global mean values (GMV) of empirical constants applied during the prediction of breakthrough curves for Fe-seashell system.

Thomas		Yoon-Nelson		B-A	
$K_{TH,ave_2} \times 10^{-5}$ [L/min.mg]	q_{o,ave_2} [mg/g]	K_{YN,ave_2} [min ⁻¹]	τ_{ave_2} [min]	$K_{B,ave_2} \times 10^{-5}$ [L/min.mg]	N_{o,ave_2} [mg/L]
± 4.74	± 21.06	± 0.018	± 719.58	± 2.09	± 43300.87

Fig. 7 and 8 illustrate actual and predicted breakthrough curves at different sorbent masses and flow rates for all models under scrutiny, respectively. Fig. 9 on the other hand demonstrate the actual and predicted breakthrough curves at different influent sorbate concentrations. Generalizing empirical constants for the Yoon-Nelson model resulted in comparable predictions despite changing operating conditions, as can be seen in Fig. 7, 8 and 9. The behaviour of the Yoon-Nelson model can be seen from its mathematical form prior to fixing the empirical constants. When predicting dynamic performance of an adsorption column, the Yoon-Nelson model reduces to the form that does not contain any significant operating variable, hence the model failed to predict experimental data when the empirical constants were fixed.

4.3.1.1 Effect of sorbent mass

The first operating variable used to investigate the dynamic performance of an adsorption column was sorbent mass which was varied from 30 to 90 g. Furthermore, in predicting concentration-time profiles using generalized dynamic models for varying sorbent mass, the flow rate and initial sorbate concentration were kept constant at 5 mL/min and 425.4 mg/L, respectively. The generalized Thomas model predictions were observed to be sensitive to generalized mean values as shown in Fig. 7. Close correlation between predicted and actual breakthrough curves was observed for the generalized Thomas model.

Figure 7. Actual and predicted breakthrough curves for removal of Fe using seashells at different sorbents masses during application of generalized empirical constants (TH – Thomas, YN – Yoon-Nelson and BA – Bohart-Adams).

Likewise, the generalized Bohart-Adams model predictions showed sensitivity when generalized mean values were applied, however, poor correlation between actual and predicted breakthrough curves was observed in Fig. 7 for the generalized Bohart-Adams model. The generalized Bohart-Adams model overpredicted the actual data at sorbent masses of 60 and 90 g, respectively. The generalized Thomas model on the other hand was closely correlated with experimental data at a sorbent mass of 30 g as shown by R^2 value of 0.998, conversely, the generalized Thomas model overpredicted for 60 and 90 g at breakthrough point but R^2 values remained above 0.9. The R^2 values observed for the generalized Bohart-Adams model were increasing from 0.2 to 0.7 when the sorbent mass was varied from 30 to 90 g.

4.3.1.2 Effect of flow rate

The general approach continued to reveal that Yoon-Nelson model does not depend on operating conditions when empirical constants were generalized as seen in Fig. 8. As a result, for the Yoon-Nelson model refitting will always be a requirement whenever operating conditions vary. The predictions obtained using the generalized Thomas and Bohart-Adams models continued to show sensitivity, however with maximal deviations

from actual breakthrough curves for the Bohart-Adams model in contrast to the Thomas model.

Figure 8. Actual and predicted breakthrough curves for removal of Fe using seashells at different flow rates during application of generalized empirical constants (TH – Thomas, YN – Yoon-Nelson and BA – Bohart-Adams).

All predictions of the generalized Bohart-Adams model were non-ideal for a dynamic sorption system, despite the observed sensitivity. Fig. 8 also showed that the generalized Thomas and Bohart-Adams models were over predicting the experimental data most significantly for the flow rate of 7.5 mL/min. The observed over prediction of the models was attributed to individual model parameters deviating from the generalized mean values. The observed R^2 values of the Thomas model were above 0.9 at the flow rates of 2.5 and 5 mL/min, however at 7.5 mL/min the R^2 obtained was 0.87. The observed R^2 values for the Bohart-Adams model decreased from 0.8 to 0.3 when the flow rate was varied from 2.5 to 7.5 mL/min.

4.3.1.3 Effect of initial concentration

The concentration-time profiles demonstrating the effects of influent concentration on dynamic performance of an adsorption column under generalized conditions for the Fe-seashell system are shown in Fig. 9. The profiles represented the efficacy of the generalized Thomas, Bohart-Adams and Yoon-Nelson models. The levels of initial sorbate

concentration under investigation were 233.22, 308.4 and 425.4 mg/L, while the sorbent mass and flow rate were fixed at 60 g and 5 mL/min, respectively.

Figure 9. Actual and predicted breakthrough curves for removal of Fe using seashells at different initial concentrations during application of generalized empirical constants (TH – Thomas, YN – Yoon-Nelson and BA – Bohart-Adams).

From Fig. 9, it was observed that the generalized Thomas model outperformed the other two models in predicting concentration-time profiles. The generalized Thomas model was observed to under predict for the concentration of 233.2 mg/L, as a result, the breakthrough time was seen at 817 min versus 970 min which corresponded to 4.085 L versus 4.85 L of water treated at breakthrough ($C_t/C_o = 0.05$).

From Fig. 9, it is observed that the generalized Thomas model was closely correlated with experimental data at a sorbate concentrations of 308.4 and 425.2 mg/L. The individual model parameters for the Thomas model were close to the generalized mean values, thus explaining the observed superior performance at 308.4 and 425.2 mg/L. The R^2 value was observed to be above 0.9 for a sorbate concentrations of 308.4 and 425.2 mg/L as tabulated in Table 17. At 233.2 mg/L the R^2 obtained was 0.87 for the generalized Thomas model. The Bohart-Adams model on the other hand over predicted the experimental data for all concentrations studied, furthermore, the R^2 value decreased from 0.9 to 0.7 when the concentration was increased from 233.2 to 425.2 mg/L.

Table 17. Summary of performance evaluation metrics in comparing Yoon-Nelson, Thomas and Bohart-Adams models for Fe-seashell system during application of the Global means of the empirical constants.

Parameters	Yoon – Nelson			Thomas			B – A		
	MAE	RMSE	R ²	MAE	RMSE	R ²	MAE	RMSE	R ²
Mass [g]									
30	0.162	0.245	0.313	0.013	0.019	0.998	6.291	9.549	0.289
60	0.106	0.136	0.788	0.050	0.064	0.974	0.104	0.134	0.695
90	0.086	0.105	0.939	0.080	0.097	0.916	0.016	0.019	0.776
Flow rate [mL/min]									
2.5	0.275	0.335	0.500	0.059	0.072	0.930	0.002	0.003	0.837
5	0.106	0.136	0.788	0.050	0.064	0.974	0.104	0.134	0.695
7.5	0.156	0.243	0.325	0.107	0.166	0.876	1.688	2.630	0.299
Concentration [mg/L]									
233.22	0.387	0.396	0.366	0.130	0.133	0.875	0.017	0.017	0.988
308.4	0.099	0.118	0.927	0.034	0.040	0.989	0.041	0.049	0.884
425.4	0.105	0.133	0.799	0.047	0.060	0.978	0.102	0.130	0.708

The statistical analysis results in Table 17 show that the Bohart-Adams model yield low regression values and higher values of MAE and RMSE. The Thomas model on the other hand show a close relation between experimental and theoretical breakthrough curves as indicated by higher regression values and lower values of MAE and RMSE. The Yoon-Nelson model did not mimic changes in operating conditions when mean values were applied, thus, model validity assessed by employing two error metrics and coefficient of determination was observed to be Thomas > Bohart-Adams > Yoon-Nelson.

Table 18 show experimental and predicted performance parameters after the application of *Global means* for the Fe-seashell system. The results observed show that the Thomas model tracks the experimental data closely with slight deviations, in contrast to the Yoon-Nelson and Bohart-Adams models. The observed model validity in Table 18 is Thomas > Bohart-Adams > Yoon-Nelson. Thomas model was the best performing model for this approach, followed by the Bohart-Adams model.

Table 18. Summary of water treatment performance parameters in comparing Yoon-Nelson, Thomas and Bohart-Adams models for the Fe-seashell system during application of Global means of the empirical constants.

Parameters	Experimental		Yoon – Nelson		Thomas		B – A	
	V _b [L]	q _b [mg]	V _b [L]	q _b [mg]	V _b [L]	q _b [mg]	V _b [L]	q _b [mg]
Mass [g]								
30	0.745	301.1	2.78	1123	0.755	305.1	0.48	194.0
60	1.84	743.6	2.78	1123	2.24	905.3	2.65	1071
90	3.125	1263	2.78	1123	3.725	1505	4.815	1946
Flow rate [mL/min]								
2.5	2.2	889.1	1.39	561.7	2.605	1053	3.49	1410
5	1.825	737.5	2.78	1123	2.97	1200	2.65	1071
7.5	1.425	575.9	4.17	1685	1.875	757.7	1.808	730.5
Concentration [mg/L]								
233.22	4.85	1075	2.78	615.9	4.085	905.1	4.83	1070
308.4	3.025	886.3	2.78	814.5	3.09	905.3	3.65	1069
425.4	1.85	747.6	2.78	1123	2.24	905.3	2.65	1071

4.3.2 Pb-charcoal system

The generalization approach was also applied on the Pb-charcoal system and similar trends were observed for all models under consideration. The generalized model parameters for all considered models are tabulated in Table 19. The approach evaluated model performance under generalized conditions and statistical analysis results were tabulated in Table 20.

Table 19. Global means of the empirical constants values applied during the prediction of breakthrough curves for Pb-charcoal system.

Thomas		Yoon-Nelson		B-A	
K _{TH,ave2} × 10 ⁻⁵ [L/min.mg]	q _{o,ave2} [mg/g]	K _{YN,ave2} [min ⁻¹]	τ _{ave2} [min]	K _{B,ave2} × 10 ⁻⁵ [L/min.mg]	N _{o,ave2} [mg/L]
±80.478	±58.405	±0.0147	±493.024	±48.133	±9647.679

The predictions of the Yoon-Nelson model, refitting is warranted in order to obtain a new set of model parameters when operating conditions change. The Thomas model predictions showed sensitivity when generalized mean values were applied, furthermore, refitting when operating conditions change can be mitigated since the effects of varying operating conditions was evident when the Thomas model parameters were generalized.

Table 20. Summary of performance evaluation metrics in comparing Yoon-Nelson, Thomas and Bohart-Adams models for Pb-charcoal system during application of the Global means of the empirical constants.

Parameters	Yoon – Nelson			Thomas			B – A		
	MAE	RMSE	R ²	MAE	RMSE	R ²	MAE	RMSE	R ²
Mass [g]									
1.12	0.158	0.293	0.550	0.006	0.011	0.999	53.90	100.3	0.116
2.52	0.030	0.075	0.971	0.030	0.074	0.972	0.325	0.811	0.282
3.501	0.063	0.147	0.887	0.035	0.083	0.956	0.012	0.029	0.526
Flow rate [mL/min]									
10	0.057	0.137	0.902	0.058	0.141	0.846	0.005	0.013	0.508
15	0.030	0.076	0.970	0.030	0.075	0.972	0.325	0.810	0.282
20	0.114	0.262	0.643	0.061	0.141	0.893	2.767	6.384	0.142
Concentration [mg/L]									
10	0.030	0.072	0.973	0.033	0.080	0.611	0.002	0.006	0.694
20	0.030	0.077	0.970	0.030	0.076	0.971	0.323	0.805	0.280
30	0.085	0.204	0.785	0.009	0.021	0.998	34.28	82.62	0.113

Table 21. Summary of water treatment performance parameters in comparing Yoon-Nelson, Thomas and Bohart-Adams models for the Pb-charcoal system during application of Global means of the empirical constants.

Parameters	Experimental		Yoon – Nelson		Thomas		B – A	
	V _b [L]	q _b [mg]	V _b [L]	q _b [mg]	V _b [L]	q _b [mg]	V _b [L]	q _b [mg]
Mass [g]								
1.12	0.975	18.53	7.395	140.5	0.54	10.26	0.225	4.275
2.52	4.62	87.78	7.395	140.5	4.62	87.78	7.56	143.6
3.501	6.75	128.3	7.395	140.5	7.485	142.2	12.45	236.6
Flow rate [mL/min]								
10	4.5	85.5	4.93	93.67	5.53	105.1	5.04	95.76
15	4.62	87.8	7.395	140.5	4.62	87.78	13.67	259.6
20	3	57	9.86	187.3	3.72	70.68	6	114
Concentration [mg/L]								
10	6.375	60.56	7.395	70.25	9.24	87.78	15.12	143.6
20	4,5	85,5	7.395	140.5	4.62	87,78	7.56	143.6
30	2,85	81,2	7.395	210.8	3.09	88,1	5.04	143.6

The observed error metrics are significantly higher for the generalized Bohart-Adams model when compared to those of the generalized Thomas model as seen in Table 20. Overall, the generalized Thomas model outperformed the generalized Bohart-Adams and Yoon-Nelson models in predicting the breakthrough curves as shown by higher R² values

lower values of MAE and RMSE in Table 20. The observed model validity in Table 20 under generalized conditions for the Pb-charcoal is Thomas > Bohart-Adams > Yoon-Nelson.

Table 21 show experimental and predicted performance parameters after the application of *Global means* of model parameters for the Pb-charcoal system. The results observed show that the Thomas model tracks the experimental data very well, in contrast to the Yoon-Nelson and Bohart-Adams models. The observed model validity in Table 21 is Thomas > Bohart-Adams > Yoon-Nelson.

4.3.3 Pb-Agirus bisporus system

The generalization approach was lastly applied to the Pb-*Agirus bisporus* system and similar trends were observed for all models under consideration. The generalized model parameters for are tabulated in Table 22. The statistical analysis and water treatment performance parameters results are tabulated in Tables 23 and 24, respectively.

Table 22. *Global means of the empirical values applied during the prediction of breakthrough curves for Pb-Agirus bisporus system.*

Thomas		Yoon-Nelson		B-A	
$K_{TH,ave_2} \times 10^{-5}$ [L/min.mg]	q_{o,ave_2} [mg/g]	K_{YN,ave_2} [min ⁻¹]	τ_{ave_2} [min]	$K_{B,ave_2} \times 10^{-5}$ [L/min.mg]	N_{o,ave_2} [mg/L]
±62,4	±63,4	±0,030	±431	±55,9	±6810,24

The concentration-time profiles demonstrating the efficacy of the considered generalized dynamic adsorption models in predicting experimental data at different sorbent masses, flow rates and initial sorbate concentrations are presented as follows.

The generalized Thomas model proved to be superior at predicting experimental data, in contrast to the generalized Bohart-Adams and Yoon-Nelson models as displayed by the mean absolute error (MAE) and root mean squared (RMSE) presented in Table 23. The generalized Bohart-Adams model was seen failing to mimic the experimental data in most cases from all cases studied, as a result, the error metrics were significantly higher when compared to those of the generalized Thomas model as seen in Table 23. The observed model validity in Table 23 under generalized conditions for the Pb-*Agirus bisporus* system is Thomas > Bohart-Adams > Yoon-Nelson. Table 24 show experimental and predicted performance parameters after the application of generalized mean values of model parameters for the Pb-*Agirus bisporus* system. The results observed show that the generalized Thomas model tracks the experimental data very well, in contrast to the

generalized Yoon-Nelson and Bohart-Adams models. The observed model validity in Table 24 is Thomas > Bohart-Adams > Yoon-Nelson.

Table 23. Summary of performance evaluation metrics in comparing Yoon-Nelson, Thomas and Bohart-Adams models for Pb-Agirus bisporus system during application of Global means of the empirical constants.

Parameters	Yoon – Nelson			Thomas			B – A		
	MAE	RMSE	R ²	MAE	RMSE	R ²	MAE	RMSE	R ²
Mass [g]									
0.4	0.006	0.010	0.410	0.048	0.080	0.962	15.93	26.60	0.439
0.8	0.089	0.171	0.818	0.012	0.023	0.997	143.5	277.4	0.265
1.2	0.049	0.101	0.953	0.034	0.070	0.974	16949	34889	0.278
Flow rate [mL/min]									
1	0.170	0.410	0.168	0.041	0.100	0.940	1680	4066	0.292
3	0.084	0.164	0.839	0.023	0.045	0.990	190.6	370.1	0.255
5	0.024	0.041	0.319	0.022	0.037	0.992	26.13	44.21	0.325
Concentration [mg/L]									
20	0.172	0.374	0.375	0.021	0.045	0.978	0.762	1.662	0.625
50	0.090	0.169	0.831	0.020	0.038	0.993	166.3	312.6	0.274
100	0.006	0.011	0.427	0.090	0.145	0.902	2404	3871	0.253

Table 24. Summary of water treatment performance parameters in comparing Yoon-Nelson, Thomas and Bohart-Adams models for the Pb-Agirus bisporus system during application of Global means of the empirical constants.

Parameters	Experimental		Yoon – Nelson		Thomas		B – A	
	V _b [L]	q _b [mg]	V _b [L]	q _b [mg]	V _b [L]	q _b [mg]	V _b [L]	q _b [mg]
Mass [g]								
0.4	0,348	16,5	1,008	48	0,225	10,7	0,162	7,7
0.8	0,735	34,9	1,008	48	0,732	34,8	0,642	30
1.2	1,041	49	1,008	48	2,139	102	0,546	26
Flow rate [mL/min]								
1	0,94	44,7	0,336	16,0	0,92	44	0,856	41
3	0,72	34,2	1,008	48	0,732	35	0,642	30
5	0,7	33,3	1,68	80	0,545	25,9	0,430	20,4
Concentration [mg/L]								
20	1,8	34	1,008	19,2	1,83	34,8	1,605	30
50	0,735	34,9	1,008	48	0,732	34,8	0,642	30
100	0,39	37,1	1,008	95,8	0,366	34,8	0,321	30

Conclusions and recommendations

Numerous mathematical models have been developed to predict dynamic adsorption performance but evaluation and efficiency of these models for large-scale operations have not been studied. In the current study, three models were evaluated to analyse the behaviour of sorbent-sorbate systems under different conditions. The considered models were namely, Yoon-Nelson, Thomas and Bohart-Adams model. The shape of the breakthrough curves contained data about the mass transfer properties of each adsorptive-adsorbent system such as breakthrough point, saturation point, maximum loading of adsorptive material, serviceable sorption capacity, among other properties. These properties were evaluated by applying modified dynamic adsorption models and fitting to experimental data by simulations. The study was aimed at providing unambiguous approaches in selecting the best performing model for dynamic adsorption systems. Predictive and generalization performances of the models were evaluated using the statistical criteria of MAE, RMSE and R^2 . Thomas and Yoon-Nelson models predicted experimental data satisfactory prior to application of mean values for all adsorption systems. Based on the findings, the present study revealed that statistical measures are of significance when evaluating model performance in dynamic adsorption systems. The observed model validity prior to application of mean values was Thomas > Yoon-Nelson > Bohart-Adams. The regression results for Yoon-Nelson and Thomas models showed close relation between experimental and theoretical breakthrough curves as the regression values were close to 1, in contrast with the Bohart-Adams model that yielded low regression values. All predictions for the Yoon-Nelson model were insensitive to the application of mean values, i.e., all predicted breakthrough curves were similar despite changing operating conditions. The trends observed for the Yoon-Nelson model when mean values were applied does not support the novelty of the chosen approach. The Thomas model on the other hand was capable of predicting successfully when empirical constants were fixed for each variable range and for the entire experimental domain. The sensitivity observed for the Thomas model can be attributed to the number of operating parameters incorporated in the model in contrast to the Yoon-Nelson model. All predicted breakthrough curves deviated from the ideal s-shape form for the Bohart-Adams model when mean values were applied, which contributed to high values of error metrics (MAE and RMSE) and low R^2 values. The Local mean values (LMV) approach proved to be very pertinent for dynamic models under evaluation, particularly for the Thomas model. The Global mean approach (GMV) revealed that Yoon-Nelson model does not depend on operating conditions when empirical constants are generalized. Refitting when operating conditions change can be mitigated for the generalized Thomas model since the effects of varying operating conditions was evident when model parameters were generalized. Model validity assessed by MAE and

RMSE and R^2 was observed to be Thomas > Bohart-Adams > Yoon-Nelson when Local mean values (LMV) and Global mean values (GMV) were applied. Thomas model was the best performing model in all three approaches considered. The kinetic constant, K_{TH} , for the Thomas model is the most important parameter and is responsible for steepening or smoothing of the breakthrough curve. The application of mean values revealed that even slight deviations in model parameters can result in a significant shift in the concentration-time profile. Hence, in order for the application of mean values to be more accurate, most especially the local means, operating variables must not be dispersed significantly, for instance, investigating the sorbent mass at 2, 3 and 4 g is better than 2, 4 and 6 g when considering applying the local mean values of model parameters. The Bohart-Adams model was developed to predict the initial part of the breakthrough curve, however, the model failed to outperform the Thomas model in predicting the breakthrough point performance parameters. The under performance of the Bohart-Adams model, revealed that the number of operating variables incorporated in the model cannot be used to classify the overall efficacy of the model. A trade off, however, exists when considering practical applications of the model i.e. a model with more process variables is preferred over the one with no operating variables. The nature of the Thomas model predictions after application of mean values were reflective of a horizontal translation i.e. $t \pm \alpha$, where α is a shifting time constant. It is worth emphasizing that, though a significant shape of a breakthrough curve is s-shaped, the most vital section of the curve is before breakthrough point as it determines the amount of water treated, thus correcting the breakthrough section is more significant for the Thomas model. The results of the neural network model for all operating parameters under study, were closely correlated, with the actual results as indicated by the R^2 values of above 0.98 and low values of MAE and RMSE. Overall, the neural network model outperformed the generalized Thomas model in predicting the breakthrough curves for all considered adsorption systems within the range of the experimental data. Artificial neural networks (ANN) are very powerful in predicting complex non-linear problems as indicated by close correlation between actual and predicted breakthrough curves. However, since the ANN methodology uses standardized equations which do not have any methodological background, the calculated model can only be applied within experimental range and cannot be used for extrapolation. In addition, ANN requires large number of experimental data prior to training in order to obtain a highly reliable model, but this limitation escalates further as there is no method available to determine minimum number of experiments required for ANN training.

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References

- [1] Kefeni, K. K., Msagati, T. A. and Mamba, B. B. 2017. Acid mine drainage: prevention, treatment options, and resource recovery: a review. *Journal of Cleaner Production*, 151: 475-493. <https://doi.org/10.1016/j.jclepro.2017.03.082>
- [2] Nleya, Y., Simate, G. S. and Ndlovu, S. 2016. Sustainability assessment of the recovery and utilisation of acid from acid mine drainage. *Journal of Cleaner Production*, 113: 17-27. <https://doi.org/10.1016/j.jclepro.2015.11.005>
- [3] Ali, I. 2014. Water treatment by adsorption columns: evaluation at ground level. *Separation & Purification Reviews*, 43 (3): 175-205. <https://doi.org/10.1080/15422119.2012.748671>
- [4] Podstawczyk, D., Witek-Krowiak, A., Dawiec, A. and Bhatnagar, A. 2015. Biosorption of copper (II) ions by flax meal: Empirical modeling and process optimization by response surface methodology (RSM) and artificial neural network (ANN) simulation. *Ecological Engineering*, 83: 364-379. <https://doi.org/10.1016/j.ecoleng.2015.07.004>
- [5] Xu, Z., Cai, J.-g. and Pan, B.-c. 2013. Mathematically modeling fixed-bed adsorption in aqueous systems. *Journal of Zhejiang University SCIENCE A*, 14 (3): 155-176. <https://doi.org/10.1631/jzus.A1300029>
- [6] Calero, M., Hernáinz, F., Blázquez, G., Tenorio, G. and Martín-Lara, M. 2009. Study of Cr (III) biosorption in a fixed-bed column. *Journal of hazardous materials*, 171 (1-3): 886-893. <https://doi.org/10.1016/j.jhazmat.2009.06.082>
- [7] Turan, N. G., Mesci, B. and Ozgonenel, O. 2011a. Artificial neural network (ANN) approach for modeling Zn (II) adsorption from leachate using a new biosorbent. *Chemical Engineering Journal*, 173 (1): 98-105. <https://doi.org/10.1016/j.cej.2011.07.042>
- [8] Oguz, E. and Ersoy, M. 2010b. Removal of Cu 2+ from aqueous solution by adsorption in a fixed bed column and Neural Network Modelling. *Chemical Engineering Journal*, 164 (1): 56-62. <https://doi.org/10.1016/j.cej.2010.08.016>
- [9] Kumar, D., Pandey, L. K. and Gaur, J. 2016. Metal sorption by algal biomass: From batch to continuous system. *Algal research*, 18: 95-109. <https://doi.org/10.1016/j.algal.2016.05.026>

- [10] Geankoplis, C. J. 2003. Transport processes and separation process principles:(includes unit operations). Prentice Hall Professional Technical Reference.
- [11] Bohart, G. and Adams, E. 1920. Some aspects of the behavior of charcoal with respect to chlorine. *Journal of the American Chemical Society*, 42 (3): 523-544.
<https://doi.org/10.1021/ja01448a018>
- [12] Chu, K. H. 2010. Fixed bed sorption: setting the record straight on the Bohart–Adams and Thomas models. *Journal of hazardous materials*, 177 (1-3): 1006-1012.
<https://doi.org/10.1016/j.jhazmat.2010.01.019>
- [13] Hutchins, R. 1973. New method simplifies design of activated-carbon systems. *Chemical Engineering*, 80 (19): 133-138.
- [14] Ahmad, A. and Hameed, B. 2010. Fixed-bed adsorption of reactive azo dye onto granular activated carbon prepared from waste. *Journal of hazardous materials*, 175 (1): 298-303. <https://doi.org/10.1016/j.jhazmat.2009.10.003>
- [15] Han, R., Wang, Y., Zhao, X., Wang, Y., Xie, F., Cheng, J. and Tang, M. 2009. Adsorption of methylene blue by phoenix tree leaf powder in a fixed-bed column: experiments and prediction of breakthrough curves. *Desalination*, 245 (1-3): 284-297.
<https://doi.org/10.1016/j.desal.2008.07.013>
- [16] Thomas, H. C. 1944. Heterogeneous ion exchange in a flowing system. *Journal of the American Chemical Society*, 66 (10): 1664-1666.
<https://doi.org/10.1021/ja01238a017>
- [17] Yoon, Y. H. and Nelson, J. H. 1984. Application of gas adsorption kinetics I. A theoretical model for respirator cartridge service life. *The American Industrial Hygiene Association Journal*, 45 (8): 509-516.
<https://doi.org/10.1080/15298668491400197>
- [18] Masukume, M., Onyango, M. S. and Maree, J. P. 2014. Sea shell derived adsorbent and its potential for treating acid mine drainage. *International Journal of Mineral Processing*, 133: 52-59. <https://doi.org/10.1016/j.minpro.2014.09.005>
- [19] Biswas, S. and Mishra, U. 2015. Continuous fixed-bed column study and adsorption modeling: Removal of lead ion from aqueous solution by charcoal originated from chemical carbonization of rubber wood sawdust. *Journal of Chemistry*, 2015.
<https://doi.org/10.1155/2015/907379>
- [20] Long, R. A. 2010. Continuous fixed-bed column study and adsorption modeling: Removal of lead ion from aqueous solution by Agirus Bisporus. *Journal of Biomedical Materials Research Part A*, 103 (3): 949-958.