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Application of mathematical models to breakthrough curves of methylene blue removal using agricultural waste of sorghum (AWS)

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***Abstract*— *In this work, the feasibility of using agricultural waste of sorghum (AWS) in the removal of methylene blue (MB) colorant was evaluated. The experiments were carried out using fixed-bed column in a continuous system and the breakthrough curves were adjusted to the mathematical models of Adams and Bohart, Yoon and Nelson, Thomas and Doses-Response by programming them in the MATLAB R2007a software. With the realization of this study, the high biosorbent adsorption capacity has been demonstrated, as well as the high operating efficiency in column filled with AWS in the elimination of methylene blue colorant.*
Keywords*— M*ethylene blue (MB), Biosorption, Fixed-bed column, Mathematical model, Agricultural waste of sorghum (AWS).

I. INTRODUCTION

The public perception of water quality is really influenced by color as it is the first pollutant to be recognized in wastewater even at concentrations less than 1 mg*g^{-1} [1, 2]. Although the amount of colorants produced worldwide is not known exactly [3], about 40000 colorants and pigments have been listed, defining 7000 different chemical structures. Methylene blue is a colorant widely used in the textile industry for sheep wool staining and for cotton and silk fibers, it is a cationic colorant and is known for its high adsorption in solid foods [4]. This colorant is not considered highly toxic, but it can have several harmful effects. It causes burns in the eyes and can cause eye diseases in humans and animals. Inhalation causes breathing difficulties and by ingestion causes burning sensation and nausea, vomiting, excessive sweating, symptoms of gastritis and mental confusion [5]. In the textile industry, considerable work has been carried out in relation to the elimination of color in waste water through chemical coagulation, oxidation and adsorption [6], other less conventional treatments such as biosorption have a large worldwide acceptance due to its high effectiveness and low implementation cost. Biosorption can be defined as the removal of organic and inorganic substances from an aqueous solution through the use of biological materials such as biomass, animal matter, agricultural by-products, forestry, crustaceans and / or waste [7]. Agricultural or agro-industrial residues are lignocellulosic materials whose disposal usually causes additional costs for the producing industry; and because of their high availability, low cost and physicochemical characteristics, they can also be considered as potential biosorbent [8]. Agricultural by-products are available in large quantities and constitute one of the most renewable sources of resources a worldwide [9, 10]. The greatest disadvantage of lignocellulosic adsorbents is their degradability, and that their use in adsorption columns is limited because the characteristics of the particles introduce hydrodynamic limitations and dirty or clog the columns [7]. The fixed-bed column system consists of a column where the biosorbent is deposited in its interior as a bed, which normally does not move; the liquid crosses the column in an ascending or descending direction.

II. MATERIALS AND METHODS

2.1. MATHEMATICAL MODELS

The design and optimization of a fixed-bed column requires knowledge of the relationship between equilibrium and mass transfer within the sorbent particles, in addition to the properties of the fluid in the column. Mathematical models, based on the principle of conservation of the mass, play a fundamental role in the

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change of scale, that is, in the passage of the laboratory on an industrial scale. These models can help to not only analyze and interpret experimental data, but also to predict the response of systems when operating conditions change. The operating time and the shape of the curve are very important characteristics to determine the response of a biosorption column.

2.2. EQUATIONS USED TO QUANTIFY THE EFFICIENCY OF THE ADSORPTION COLUMN

The operation of the adsorption column is described by the concept of breakthrough curve. The breakthrough curve, shows the behavior of a fixed-bed column from the point of view of the amount of colorant that can be retained, and usually, is expressed in terms of a normalized concentration defined as the quotient between the colorant concentrations in the liquid at the outlet and at the entrance of the column $\frac{C_i}{C_o}$, as a function of time or volume of effluent, for a fixed-bed height.

Effluent volume is calculated from equation (1):

$$V_{ef} = Q * t_{total} \ldots\ldots(1)$$

where t_{total}, total time (min) and Q, flow through the column, $(\frac{ml}{min})$.

The area under the breakthrough curve, between the appropriate limits, represents the total amount of adsorbate retained (or maximum adsorption capacity of the column), q_{total} in mg, for a determinate concentration of the feed and is determined from integration using the equation (2):

$$q_{total} = \frac{Q}{1000}\int_{t=0}^{t=t_{total}} CRdt \ldots\ldots(2)$$

CR, is the concentration of adsorbate retained, mg / l

The total amount of adsorbate passing through the column, m_{total} in mg, is calculated from expression (3).

$$m_{total} = \frac{C_i * Q * t_{total}}{1000} \ldots\ldots(3)$$

Therefore, the total percentage of adsorbate retained during the operation of the column is obtained from the expression (4).

$$\%Retention = \frac{q_{total}}{m_{total}} * 100 \ldots\ldots(4)$$

Column equilibrium studies require knowledge of the biosorption capacity, q_e (mg of adsorbed adsorbate / g of sorbent), and the concentration of adsorbate that remains in solution when equilibrium is reached, C_e (mg/l) and can be determined for the expressions (5) and (6),

$$q_e = \frac{q_{total}}{m} \ldots\ldots(5)$$

$$C_e = \frac{m_{total} - q_{total}}{V_{ef}} \ldots\ldots(6)$$

where m is the mass of sorbent used in the column, (g).

2.3. KINETIC MODELS

The kinetic models of the biosorption processes allow to determine the speed at which the coloring are removed from the aqueous phase, as well as a set of variables that indicate the efficiency of the system. In this work, four models were used for kinetic studies. These models are: Adams and Bohart, Thomas, Yoon and Nelson and Dosage-Response.

2.4. ADAMS AND BOHART MODEL

This model assumes that the sorption velocity is proportional to the residual capacity of the solid and the concentration of the retained species and is used to describe the initial part of the breakthrough curve. The equation that describes this model is equation (7) [11].

$$\ln\left(\frac{C_i}{C_o}\right) = K_{AB} * C_0 * t - \frac{K_{AB} * N_0 * Z}{v} \ldots\ldots(7)$$

where K_{AB} is the kinetic constant (l/mg min), v is the linear flow rate (ml/min), Z is the bed depth of column (cm), N_0 is the saturation concentration (mg/l), t is the time (min), C_0 and C_i are, respectively, the adsorbate concentration at the entrance and at the exit of the column.

Parameters describing the characteristic operations of the columns (K_{AB} and N_0) were calculated using linear regression analysis according to Equation (7). From a linear plot of $\ln\left(\frac{C_i}{C_o}\right)$ against time (t), values of K_{AB} and N_0 were determined from the intercept and slope of the plot.

2.5. THOMAS MODEL

The Thomas model [12] is one of the most general and used to describe the behavior of the biosorption process in fixed bed columns. This model is described by equation (8):

$$\frac{C_i}{C_o} = \frac{1}{1 + e^{\left(\frac{K_{Th}}{Q}\right)*(q_o m - C_i V_{ef})}} \ldots\ldots(8)$$

where C_o and C_i are respectively the concentrations of input and output of the column, K_{Th}, Thomas's velocity constant $(\frac{ml}{mg * min^{-1}})$, q_o the maximum concentration of solute in the solid phase, $(\frac{mg}{g})$, m is the mass of adsorbent in the column (g), V_{ef} is the effective volume (ml) and Q is the volumetric flow $(\frac{ml}{min})$.

The linearization of equation (8) is:

$$\ln\left(\frac{C_o}{C_i} - 1\right) = \frac{K_{Th} * q_o * m}{Q} - \frac{K_{Th} * C_i}{Q} * V_{ef} \ldots\ldots(9)$$

Values of q and K_{Th} were determined from the intercept and slope of the linear plot of $\ln\left(\frac{C_0}{C_i}-1\right)$ against time (t).

2.6. YOON AND NELSON MODEL

Yoon and Nelson [13] developed a model aimed at the adsorption of vapors or gases in activated carbon. This model assumes that the speed at which the adsorption probability decreases for each adsorbate molecule is proportional to the adsorption probability and the probability that it does not adsorb on the adsorbent. The mathematical model proposed by Yoon and Nelson is expressed as:

$$-\frac{\partial A}{\partial t} = K_{YN} * (t-\tau) \qquad (10)$$

The linearized Yoon and Nelson model for a single component system is expressed as:

$$\ln\left(\frac{C_i}{C_0-C_i}\right) = K_{YN} * (t-\tau) \qquad (11)$$

where K_{YN} (1/min) constant speed Yoon and Nelson and τ (min) time required to retain 50% of the initial adsorbate (min). From a linear plot of $\ln\left(\frac{C_0}{C_i}-1\right)$ against sampling time (t), values of k_{YN} and τ were determined from the intercept and slope of the plot for a given height, flow, and the initial concentration.

2.7. DOSE-RESPONSE MODEL

This model has been commonly used in pharmacology to describe different types of processes, is currently used to describe column behavior in biosorption process [14, 15]. The general equation that represents the model is the following:

$$Y = b_0 - \frac{b_0}{1+\left(\frac{X}{b_2}\right)^{b_1}} \qquad (12)$$

where X and Y represent the dose and the response in terms of percentage of the maximum possible response, respectively. The parameter b_0 is the expected response when saturation is reached, b_1 represents the slope of the function, and b_2 indicates the concentration at which half of the maximum response occurs.

Equation (13) describes this model for the biosorption process:

$$\frac{C_i}{C_0} = 1 - \frac{1}{1+\left(\frac{V_{ef}*C_i}{q_0*m}\right)^{a}} \qquad (13)$$

This model is of relative importance since it usually describes the complete breakthrough curve with high precision; however, it is difficult to relate the empirical parameter "a" with the experimental conditions, making it practically impossible to carry out a change in the scale of the system [14].

2.8. BIOSORBENT MATERIAL

The biosorbent used was the agricultural waste of sorghum (AWS), it was obtained from a producer in the municipality of "Encrucijada" belonging to the province of Villa Clara, Cuba; collecting days after the harvest and subjected to a process of washing with distilled water. Once washed, they were dried, crushed and sieved. The particle size used ranged between 0.342 mm and 2.40 mm. Figure 1 corresponds to a sample of biosorbent material.

Fig.1: Agricultural waste of sorghum (AWS), washed, dried and crushed.

The agricultural waste of sorghum (AWS) used were characterized employment a set of physical and chemical tests such as determination of the zero charge point, acid and basic sites, analysis of the elemental composition of the biosorbent material, infrared analysis and thermogravimetric analysis. The results of the characterization of the AWS are shown in Table 1. This results presented in this table are published in the journal of the Faculty of Chemistry-Pharmacy of the Central University "Marta Abreu" of Las Villas, Cuba, Centro Azúcar [16].

Table 1. Physical-chemical characterization carried out on agricultural waste of sorghum (AWS) by means of infrared, thermogravimetric analysis, elemental composition, zero load point and acid and basic sites [17].

Physical-chemical characterization of agricultural waste of sorghum (AWS).	
Zero load point (ZLP)	pH= 7.5
Acid sites	0.75 $\frac{meq}{g}$
Basic sites	0.525 $\frac{meq}{g}$
Elementary composition of N,C,H,O y S.	0.51 % nitrogen; 47.58 % carbon; 8.72 % hydrogen; 43.19 % oxygen; insignificant sulfur concentration
Infrared Analysis	Hydroxyl (OH), Carbonyl (C = O),

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(Main functional groups detected).	aliphatic structures, structures of simple bonds carbon-carbon (Csp3-H), esters and ethers (C-O-C). Figure 2.
Thermogravimetric analysis.	Three fundamental zones are detected, one corresponding to the temperature range from 0 ° C to 200 ° C where the desorption of the retained water and the combustion of the cellulose take place, a second zone comprised in the temperature range of 200 ° C and 550 ° C where anaerobic pyrolysis of the hemicellulose takes place and a third zone in the temperature range of 500 ° C to 800 ° C where there is a constant mass loss which is associated with the loss of residual H +, where occur the decomposition of the lignin. Figure 3.

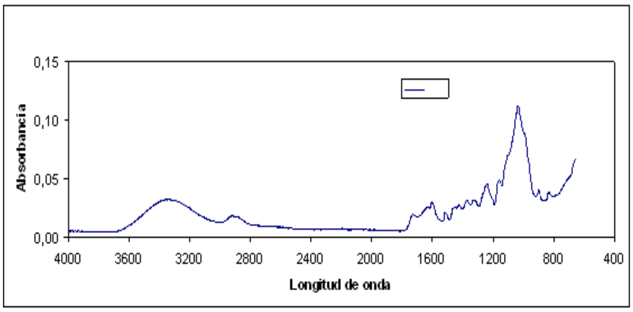

Fig.2: Analysis of samples of agricultural waste of sorghum using infrared spectrum. (AWS).

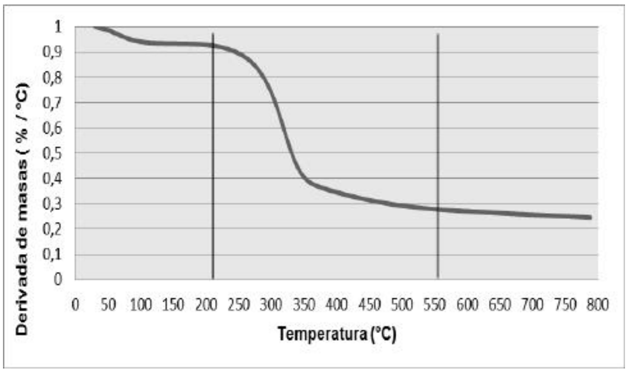

Fig.3: Thermal analysis performed in agricultural waste of sorghum (AWS) in the temperature range (0 to 800) ° C.

2.9. HYDRAULIC TEST AND SELECTION OF OPERATION PARAMETERS

Hydraulic tests are carried out before carrying out the adsorption tests. The column is filled with AWS and distilled water is pumped for the purpose of determining the most suitable flows in order to avoid particle dragging and fractionation of the bed when the column is in operation.

The flows selected for the test were (6 and 9 $\frac{ml}{min}$) allowing the bed to remain stable not fragment and no-draining when the operation stops. A standard solution of the methylene blue colorant was prepared at concentrations of 100 and 500 $\frac{mg}{l}$, the solution is adjusted to pH = 5 using HCL or 0.1 N NaOH.

For the selection of the height of the bed, the design criteria suggested in the literature [18] are taken into account, which state that the internal diameter of the column may be six times or more. The heights of the packing evaluated were 17 cm and 21 cm corresponding to the AWS masses of 3.85 g and 4.72 g respectively. The feed solution and the fixed bed column temperature were maintained at 30˚C. The operating variables of this test are shown in Table 2.

Table.2: Operational variables studied during continuous biosorption of methylene blue using AWS.

Operating conditions	**Q (ml/min)**	$\mathbf{H_b}$ **(cm)**	$\mathbf{C_o}$**(mg/l)**
Scale 1	9	21 (4.72g)	500
Scale 2	6	17 (3.85g)	100

2.10. QUANTIFICATION OF THE SAMPLES

The absorbance readings of methylene blue were quantified in a Rayleígh VIS-7236 spectrophotometer at a wavelength (λ = 575 nm) previously determined in this same equipment, for which a sweep was performed in the wavelength interval (λ) from 320 to 700 nm.

III. RESULTS AND DISCUSSION

3.1. EFFECT OF THE OPERATIONAL VARIABLES ON THE CHARACTERISTICS OF THE BREAKTHROUGH CURVES

Table 3 shows the main parameters obtained through the *breakthrough* curves for each experimental, already averaged with their respective replicas.

Table 3. Main parameters obtained employing the breakthrough curves of the biosorption operation of methylene blue (MB) with AWS at pH 5, temperature 30 ° C and colorant concentration of 100 and 500 mg / l.

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Parameters of the breakthough curves					
Operating Conditions			Parameters		
C_o (ª H_b (,Q (m)			Efficiency (%)	q_e (m/g. Veffective (m)	
100	17	6	93.49	16.89	504
100	21	6	90.68	17.82	654
100	17	9	90.00	21.44	513
100	21	9	92.87	10.12	387
500	17	6	98.24	21.72	66
500	21	6	98.78	18.85	60
500	17	9	91.48	17.81	54
500	21	9	95.73	28.33	108

Analyzing table 3 it is noted that the highest effective volume is reached when the column is operating at a concentration of 100 mg/l, a bed height corresponding to 21 cm (4.72 g) and a feeding flow of 6 ml/min for 654 ml of effective volume, under these conditions has an efficiency of 90.68% and a maximum capacity of adsorption (q_e) of 17.82 mg of (MB)/g of AWS, so we can say that C_o = 100 mg (MB)/l, Q = 6 ml/min and a H_b = 21 cm (4.72g) are the optimal parameters to operate the fixed-bed column system with agricultural waste of sorghum (AWS) in the removal of methylene blue (MB).

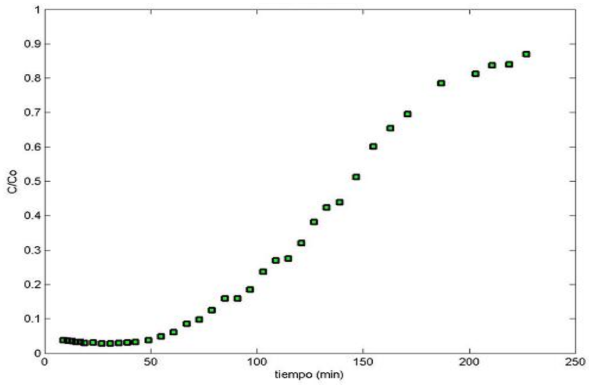

Fig.4. Breakthrough curve of the biosorption operation of methylene blue with agricultural waste of sorghum at a concentration of 100 mg/l of methylene blue, flow of 6 ml /min and height of the AWS bed of 21 cm (4, 72g).

2.2. BREAKTHROUGH CURVES: ADJUSTMENT OF MODELS AND DETERMINATION OF THE MAIN PARAMETERS OF EACH EQUATION

2.2.I. ADAMS AND BOHART MODEL FOR FIXED-BED COLUMN

From the equation 7 we obtain the parameters of the model and adjustment of Adams and Bohart, which are shown in table 4 for each of the combinations of concentration, flow of feeding and height of the bed studied. Figures 5 and 6 show the adjustment of the linearized model and its breakthrough curve for the optimal conditions of the experimental design. It is appreciated that the Adams and Bohart model does not present a good fit for any of the experimental design conditions. At high concentrations of methylene blue colorant (500 mg/l) the linear correlation coefficient has very low values. The capacity of volumetric sorption does not decrease in almost all cases when increasing the packing height except at the conditions of C_o = 500 (mg (MB)/l), Q = 6 ml/min and H_b = 21 cm. These results are similar to the other authors like [19].

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Table 4. Parameters of the models of Adams and Bohart, Thomas, Yoon and Nelson and Dosage-Response for the experimental data of the biosorption process of methylene blue using AWS.

Operating Conditions			Admos and Bohart			Thomas		Yoon and Nelson	Dosage-Response		
$Co(\frac{mg}{l})$	$H\ (cm)$	$Q(\frac{ml}{min})$	$K_{ab}(\frac{l}{mg*min})$	$N_o(\frac{mg}{l})$	$q_e(\frac{mg}{g})$	$K_{Th}(\frac{ml}{mg*min^{-1}})$	$q_e(\frac{mg}{g})$	$K_{YN}(\frac{1}{min})$	$\tau(min)$	a	$q_e(\frac{mg}{g})$
100	17	6	0.000276	2490.17	8.71	0.36	18.75	0.036	120.37	1.51	26.71
100	21	6	0.000190	2203.64	7.71	0.28	18.97	0.027	149.27	1.75	20.23
100	17	9	0.000245	1699.59	5.94	0.35	23.39	0.035	100.06	1.81	21.12
100	21	9	0.000620	1391.80	4.87	0.83	10.85	0.082	56.90	2.18	12.30
500	17	6	0.000143	3374.81	11.80	0.24	25.16	0.118	32.29	3.17	21.13
500	21	6	0.000113	5261.29	18.40	0.19	21.49	0.095	33.80	2.89	17.07
500	17	9	0.000106	3484.84	12.18	0.24	19.69	0.120	16.85	2.48	16.74
500	21	9	0.000105	3443.28	12.04	0.25	30.61	0.124	32.11	3.71	25.41

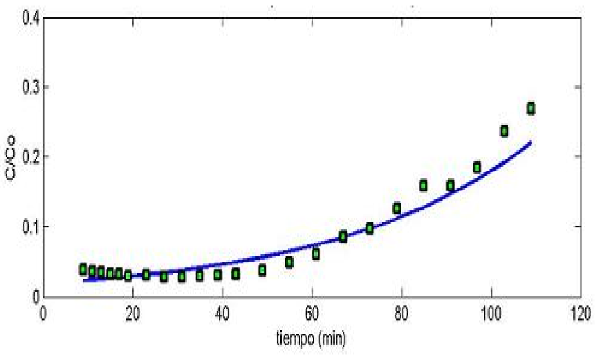

Fig.5. Breakthrough curve of the Adams and Bohart model for the biosorption process of methylene blue with AWS at $C_o = 100\frac{mg(MB)}{l}, Q = 6\frac{ml}{min}$ *and a* $H_b = 21\ cm\ (4.72\ g)$.

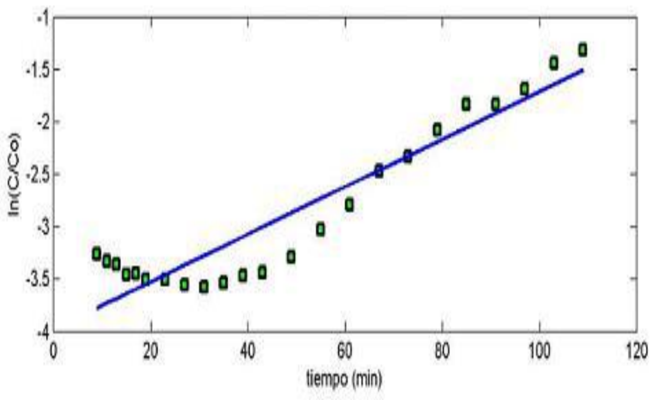

Fig.6: Linearized Adams and Bohart model for the biosorption process of methylene blue with AWS at $C_o = 100\frac{mg(MB)}{L}, Q = 6\frac{mL}{min}$ *y una* $H_b = 21\ cm\ (4.72\ g)$.

2.2.2. THOMAS MODEL FOR FIXED-BED COLUMN

From the equation 9 the parameters of the Thomas model and of adjustment are obtained that are shown in table 4. In the figure 7 and 8 the adjustment of the

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linearized model and its breakthrough curve for the optimal conditions of the experimental design is observed. The Thomas model in a general way represents very accurately the process of biosorption of methylene blue using agricultural waste of sorghum, this can be evidenced by analyzing the values corresponding to R2 for this model. Analyzing the maximum adsorption capacities qe (mg/g) of this model with those obtained experimentally, a great similarity between both datas set is observed. These results correspond to those of other researchers such as [20].

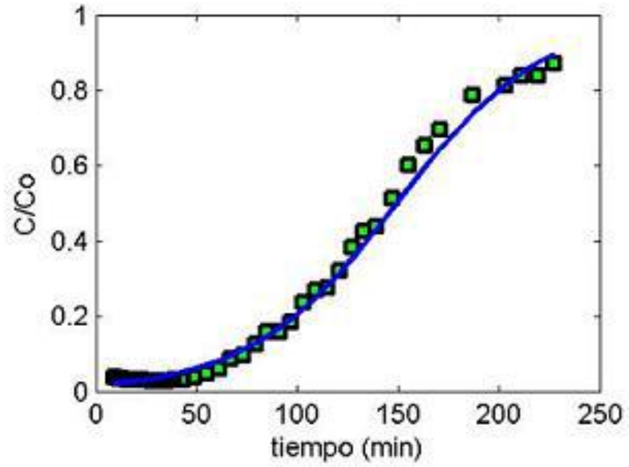

Fig.7. Breakthrough curve of the Thomas model for the biosorption process of methylene blue with AWS at $C_o = 100\,\frac{mg(MB)}{l}, Q = 6\,\frac{ml}{min}$ *y una* $H_b = 21\ cm\ (4.72\ g)$.

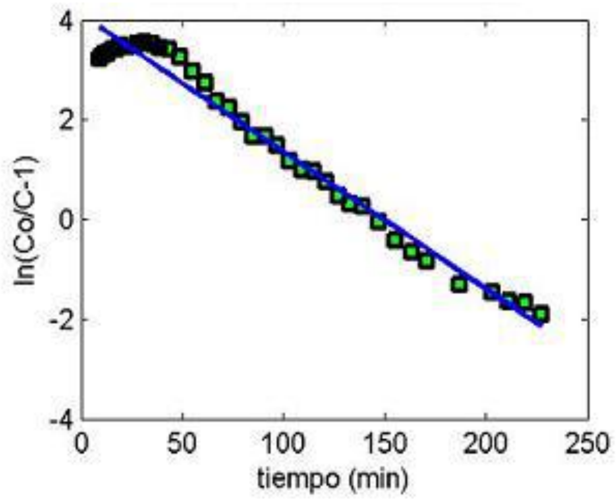

Fig.8. Linearized Thomas model for the biosorption process of methylene blue with AWS at $C_o = 100\,\frac{mg(MB)}{l}, Q = 6\,\frac{ml}{min}$ *y una* $H_b = 21\ cm\ (4.72\ g)$.

III.2.3. YOON AND NELSON MODEL FOR FIXED-BED COLUMN

The equation of the Yoon and Nelson model is mathematically analogous to the equation that represents the Thomas model (equation 9). From the equation 11 the parameters of the model and of adjustment are obtained that are shown in table 4. Figures 9 and 10 show the adjustment of the linearized Yoon and Nelson model and its breakthrough curve for the optimal conditions of the experimental design. This model, being mathematically equal to that of Thomas, has given rise to the same adjustment results, therefore, it reproduces acceptably the breakthrough curves. However, the values of the time required to retain 50 % of the initial colorant, t, are very similar to those obtained experimentally, which coincides with other researchers during studies of different biosorbent-colorant systems in fixed-bed column [21].

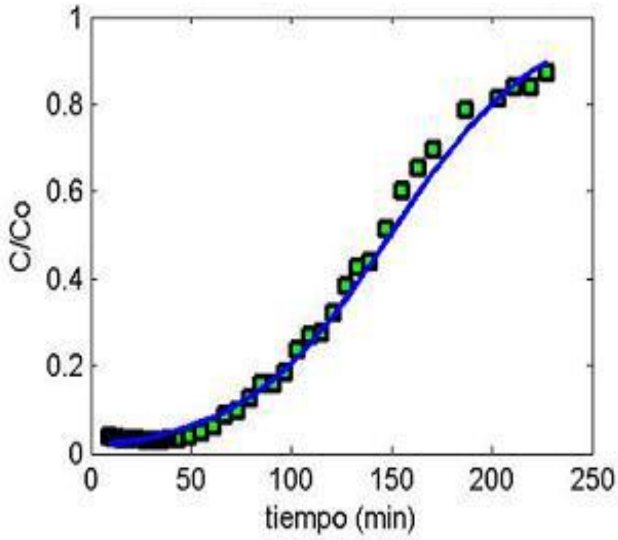

Fig.9. Breakthrough curve of the Yoon and Nelson model for the biosorption process of methylene blue with AWS at $C_o = 100\,\frac{mg(MB)}{l}, Q = 6\,\frac{ml}{min}$ *y una* $H_b = 21\ cm\ (4.72\ g)$.

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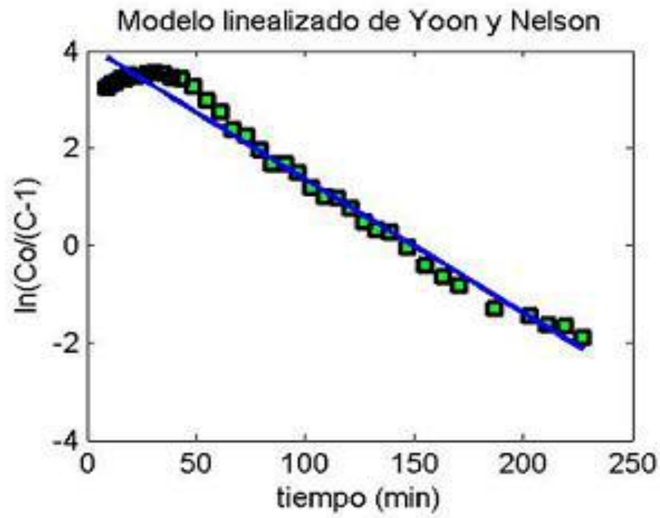

Fig.10. Linearized Yoon and Nelson model for the biosorption process of methylene blue with AWS at $C_o = 100\ \frac{mg(MB)}{l}, Q = 6\ \frac{ml}{min}$ *y una* $H_b = 21\ cm(4.72\ g)$.

2.2.4. DOSE-RESPONSE MODEL FOR FIXED-BED COLUMN

From the equation 13 and by means of non-lineal regression, the parameters of the Dose-Response model are obtained, which are shown in table 4. Figures 11 and 12 show the adjustment of the linearized model of Dose-Response and its breakthrough curve for the optimal conditions of the experimental design. The results show that this model reproduces in an acceptable way some of the breakthrough curves for the biosorption process studied, however, in some cases, it is difficult to relate the adjustment parameters with the operating conditions, so it is of little use to model the behavior of the column. On the other hand, the values of maximum adsorption capacity (qe) correspond quite well with the experimental values. These results are similar to those obtained by other researchers [22, 23, 15].

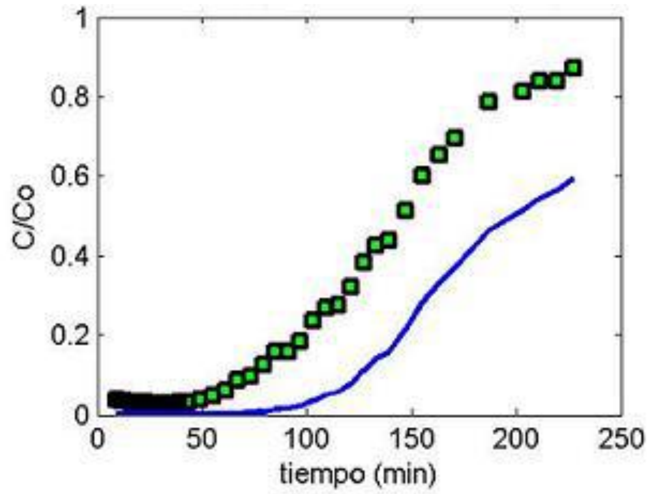

Fig.11. Breakthrough curve of the Dose-Response model to the biosorption process of methylene blue with AWS at $C_o = 100\ \frac{mg(MB)}{l}, Q = 6\ \frac{ml}{min}$ *y una* $H_b = 21\ cm\ (4.72\ g)$.

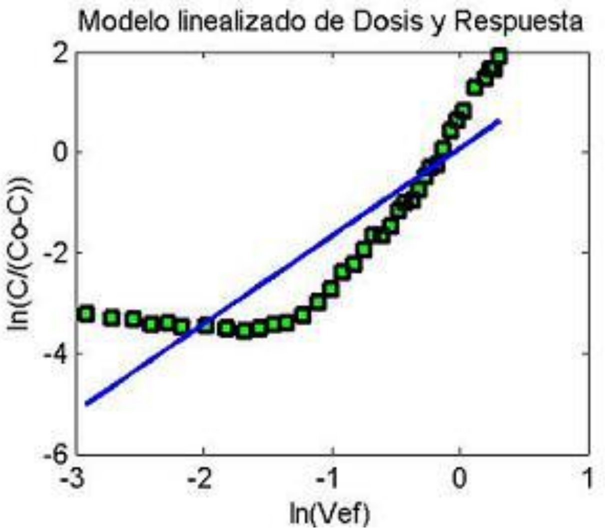

Fig.12. Linearized Dose-Response model for the biosorption process of methylene blue with AWS at $C_o = 100\ \frac{mg(MB)}{l}, Q = 6\ \frac{ml}{min}$ *y una* $H_b = 21\ cm\ (4.72\ g)$.

3.3. COMPARISON OF THE RESULTS

The results obtained in the process of biosorption of methylene blue (MB) using agricultural waste of sorghum (AWS) are compared with those of other researchers of the subject such as [24, 25, 26, 27] among others, they are shown in Table 5

Table 5. Comparison of the biosorption capacity of agricultural waste of sorghum (AWS) with different biomass.

Biosorbent Material	T (ºC)	g_e (mg/g)	Reference
Seaweed (*Caulerpa racemosa*)	18	5.25	[24]
Orange Shell	30	13.90	[25]
Banana Shell	30	15.90	[25]
Tripoli	25	16.60	[26]
Agricultural waste of Sorghum (AWS)	30	18.97	This Studio.
Madhuca Seed	30	40.00	[27]
Waste of Tea	25	85.16	[28]
Stems Anana	30	119.05	[29]
Activated Carbon	-	435	[30]

IV. CONCLUSION

The experiments were carried out to laboratory scale using fixed-bed column with agricultural waste of sorghum (AWS) and results showed that the biosorption is adequately alternative to remove methylene blue from aqueous solutions. Obtained data indicated that to remove methylene blue, the best operation conditions were obtained for a bed height of Hb=21cm, initial concentration of 100 mg/l and a flow of 6 ml/min. The characteristics of the breakthrough curves of the biosorption process of methylene blue with AWS allow to evaluate that the column operates with a high efficiency, since removals of methylene blue of up to 90.68% are achieved. Under these conditions the Thomas model best represents the experimental data of the biosorption curves of methylene blue with RAS a biosorption capacity of 18.97 (mg(MB))/(g(AWS)), comparable with that of other lignocellulosic biosorbents.

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