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COLUMN MODE ADSORPTION STUDIES OF ACID DYE USING A NOVEL ADSORBENT

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ABSTRACT
An activated carbon with good surface characteristics was prepared from eco-friendly and renewable source (silk cotton fibers) using microwave hydrothermal heating process. The column mode adsorption studies of an anionic dye Acid blue 113 with a molecular formula ($C_{32}H_{21}N_5Na_2O_6S_2$) were demonstrated. The Bohart-Adams, Thomas and Yoon-Nelson kinetic models were used in this study. The YN model provides excellent fit with very high r^2 (0.9611 to 0.9873) for all the range of concentration, flow rate and bed height under investigation
Keywords: Acid Blue 113, Silk cotton fiber, Adsorption, Column mode

INTRODUCTION

The pollution of aquatic environment has been amplified due to the disposal of hazardous and non-biodegradable compounds present in the effluent discharged from various industries. Developing countries in particular faces severe water pollution related issues due to the high cost involved for the wastewater treatment. Dyeing industries discharge large volume of untreated effluent into the land and water bodies. Presence of trace amount of dye molecules produces high coloration and also the dye molecules are highly resistant towards conventional treatment methods. Various treatment technologies like Membrane filtration[1], precipitation[2], nano-filtration[3], ion-exchange[4], electrochemical coagulation[5] and adsorption[6] have been widely used for the treatment of dye bearing wastewater. These technologies fail either in terms of cost effectiveness or selectivity towards all categories of pollutants. Adsorption using activated materials is one of the worth mentioning technology among other. The adsorption can be applied for the removal of dye molecules even at low temperatures and also it is suitable for all categories of dye molecules (anionic or cationic). Recently many researchers are working towards the development of low cost, non-conventional activated carbon for the wastewater treatment applications[7-12].

Therefore the use of a low cost precursor for the development of an activated carbon can minimize the effluent treatment expenses and also helps to dispose the biological waste products. In the present study, silk cotton fibers, (an eco-friendly and renewable source of carbon) is used as a precursor for the preparation of an activated carbon using microwave hydrothermal heating process. The precursor (silk cotton fiber) is available in plenty in countries like India and most parts of Asia. In the last few decades, usage of microwave for synthetic applications has grown rapidly. Microwave heating has been widely used in research and industrial purpose due to its direct interaction with matter. The major advantage of using microwave is that the treatment time can be considerably reduced, more economical and also the process is pollution free one.[13] The information obtained from adsorption kinetics and isotherm studies in a batch mode is useful for the determination of the effectiveness of the adsorbent for the selected adsorbate from its aqueous solution. The batch mode analysis is not sufficient while designing a treatment system for continuous operation. The above said factors make it necessary to analyze the adsorbate-adsorbent system by column mode.[14]

EXPERIMENTAL

The precursor, Silk cotton fiber was collected from in and around the Erode district of Tamilnadu, India. The fibers were dried in sunlight for 3 days and used without any pre treatment. All the chemicals used for the study were analytical grade reagents supplied by Aldrich-India (>99 % purity). Double distilled water was used as a solvent and also for all dilutions.

Preparation of Activated Carbon Fibers

The precursor was soaked with 0.5% (W/V) solution of $FeCl_3$ for one hour. After one hour of impregnation, the fibers were removed from the solution and carbonized in microwave oven at 600w for 05 min. The carbon was washed with plenty of water to remove any residual chemicals. The washed carbon was activated in microwave oven in N_2 atmosphere at 600w for 10 min, labeled as ASC and stored in tight lid container for further studies.

Preparation of Adsorbate

An anionic dye Acid blue 113 with a molecular formula ($C_{32}H_{21}N_5Na_2O_6S_2$) M.W: 681.65, C.I No.26360, λ_{max}= 566 nm, (E. Merck, India) was chosen as the adsorbate. A stock solution containing 1000 mg of the dye per liter was prepared by dissolving appropriate amount of dye (based on percentage purity) in double distilled water and was used to prepare the adsorbate solutions by appropriate dilution as required. The structure of Acid blue 113 is shown in fig.-1.

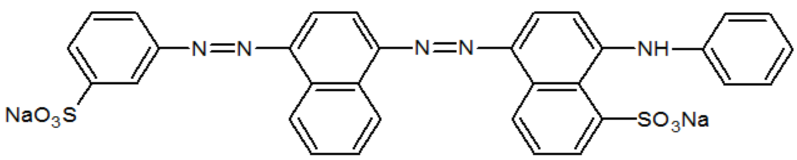


Fig. - 1: Structure of Acid blue 113

Column studies

Fixed bed column studies were carried out using a glass column of 1.2 cm inner diameter and 40 cm length. The activated carbon packed in the column with two layers of glass wool at the top and bottom as shown in the Fig.-2. The dye solution of specified concentration was charged from the bottom of the column in up flow method at fixed inflow rate using peristaltic pump. The effluent samples were collected at specified intervals and analyzed for the residual dye concentration using (Elico Make) Bio UV-Vis spectrometer by fixing the wavelength of 566 nm for Acid blue 113**.**

Modeling of column adsorption

Full-scale column operation can be designed on the basis of data collected at laboratory level. Many mathematical models have been proposed in the past for the evaluation of efficiency and applicability of the column models for large-scale operations. To design a column adsorption process it is necessary to predict the breakthrough curve or concentration-time profile and adsorption capacity of the adsorbent for the selected adsorbate under the given set of operating conditions. Many models have been developed in the past to predict the adsorption breakthrough behavior with high degree of accuracy. The Bohart-Adams (1920), Thomas (1944) and Yoon-Nelson model (1984) were used in this study to analyze the behavior of the selected adsorbent-adsorbate system.

Bohart–Adams Model[15]

Oulman[16] proposed the use of a bed depth service model for simulating granular activated carbon (GAC) adsorption beds. The model, first developed by Bohart and Adams[15], was based on surface reaction theory as given by the following equation-

$$\frac{C_0}{C} = \frac{1}{1+e^{a-bt}} \qquad (1)$$

The Bohart–Adams equation is as follows-

$$\ln\left(\frac{C_0}{C}-1\right)=\frac{KNx}{u}-KC_0t \tag{2}$$

Where, C = effluent concentration (mg/L); C_0 = influent concentration (mg/L); K = adsorption rate coefficient (L/mg/min); N = adsorption capacity coefficient (mg/L); x = bed depth (cm); u = linear velocity (cm/min); and t = time (min).

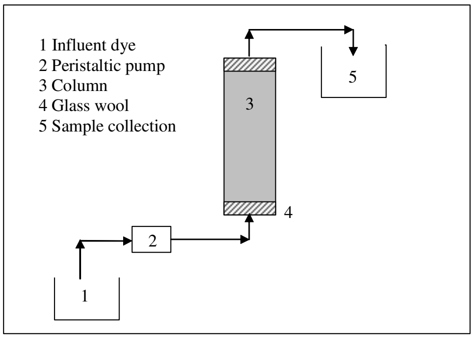


Fig.- 2: Flow chart of up flow packed bed column.

Thomas Model[17]

Successful design of a column adsorption process requires prediction of the concentration-time profile or breakthrough curve for the effluent. The Thomas model is used to calculate the adsorption rate constant and the solid phase concentration of the dye on the adsorbent from the continuous mode studies. The kinetic model suggested by Thomas is one of the widely used kinetic models for the evaluation of column performance. The Thomas model has the following form-

$$\frac{C_t}{C_0}=\frac{1}{1+\exp[k_T(q_0.m-C_0.v)]/r} \tag{3}$$

Where, C_t is effluent dye concentration (mg/L), C_0 is initial dye concentration (mg/L), k_T is Thomas rate constant, (L/min.mg), q_0 is maximum dye adsorption capacity (mg/g), m is mass of the adsorbent (g), v is effluent volume (mL) and r is flow rate (ml/min). The value of time, t = v/r.

The constants k_T and q_0 were determined from a plot of C_t/C_0 against t for a given set of conditions using non-linear regression analysis.

Yoon-Nelson Model[18]

Yoon and Nelson have proposed a less complicated model to represent the breakthrough of gases onto activated charcoal. The model was proposed based on the assumption that the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of adsorbate adsorption on the adsorbent. The linear form of Yoon-Nelson model is-

$$\ln\left(\frac{C_t}{C_0-C_t}\right)=k_{YN}.t-\tau.k_{YN} \tag{4}$$

Where, k_{YN} is Yoon-Nelson rate constant, τ is the time required for 50% of adsorbate breakthrough and t is the sampling time. A plot of $\ln\left(\frac{C_t}{C_0-C_t}\right)$ versus t gives a straight line with a slope of k_{YN} and intercept of $-\tau.k_{YN}$. Based on Yoon-Nelson model, the amount of dye being adsorbed in a fixed bed is half of the total dye entering the adsorption bed within 2τ period. For a given bed-

$$q_{0YN}=\frac{q_{(total)}}{X}=\frac{\frac{1}{2}C_0[(Q/1000)\times 2\tau]}{X}=\frac{C_0.Q.\tau}{1000X} \tag{5}$$

From this equation, the adsorption capacity, q_{0YN} varies as a function of inlet dye concentration C_0, Flow rate Q, weight of adsorbent X and 50% breakthrough time.

Error analysis

The adsorption capacity obtained by the Thomas Model and Yoon-Nelson Model was compared with the experimental adsorption capacity using the following Error analysis method.

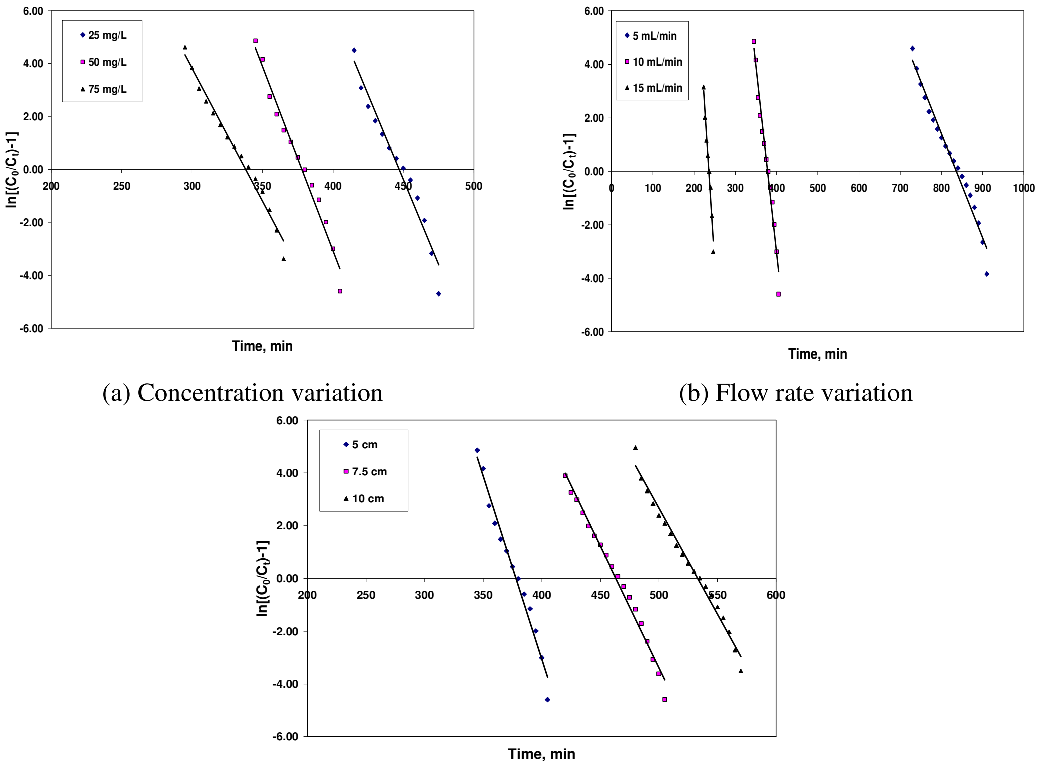
$$Sd = \sqrt{\sum \frac{(q_{0(\exp)} - q_{0(cal)})^2}{N}} \quad (6)$$

Where, $q_{0(exp)}$ is experimental adsorption capacity, $q_{0(cal)}$ is the adsorption capacity calculated using Theoretical kinetic models and N is the Number of experimental points run.

RESULTS AND DISCUSSION

Adsorbent characteristics

The carbon ASC prepared using microwave heating was found to have excellent porosity and high surface area. The carbon ASC has a BET surface area of 1041.08 m^2/g and a total pore volume of 0.4944 cm^3/g. The carbon ASC truly has the adsorption capacity towards large organic molecules and metal ions.



(a) Concentration variation (b) Flow rate variation

(c) Bed height variation

Fig.- 3: Bohart-Adams plot for the adsorption of AB113 onto ASC Column

Column adsorption studies

The efficiency of any column adsorption process was evaluated using the breakthrough curves obtained at various operating parameters. The time required for breakthrough appearance and the shape of breakthrough curve are important characteristics for determining the operation and dynamic response of an adsorption column[19].

Effect of initial Dye concentration

The effect of influent dye concentration on the performance of a column prepared using ASC fiber was evaluated by varying the initial dye concentration from 25 to 75 mg/L for a flow rate of 5 mL/min and a bed height of 10 cm. The breakthrough curve reaches a saturation at 4750, 4050 and 3700 mL of throughput volume for an initial dye concentration of 25, 50 and 75 mg/L respectively. The throughput volume decreases while increasing the initial dye concentration from 25 to 75 mg/L and also the rate of breakthrough is high and the breakthrough curves were sharp while increasing the initial dye concentration. The quicker saturation at higher concentrations is due to the fast exhaustion of the adsorption sites available on the surface of ASC. This can be explained by the fact that a lower concentration gradient caused a slower transport due to decrease in diffusion coefficient or mass transfer coefficient[20].

Estimation of breakthrough curves and determination of kinetic constants

The dynamic behavior of the AB113 onto ASC column was predicted with the Bohart-Adams, Thomas, and Yoon‑Nelson models. The breakthrough curves showed the superposition of experimental results (points) and the theoretical calculated points (lines). Sum of Square error coefficients (SSE) showed the fit between experimental data and nonlinear forms of Adams‑Bohart, Thomas and Yoon‑Nelson equations.

Bohart-Adams Model

The Bohart- Adams model plot for the adsorption of AB113 onto ASC column was shown in figure- 3 and the results were presented in Table- 1. The initial part of the breakthrough was well explained by applying the Bohart-Adams model to the experimental data. The amount of dye adsorbed mg/g was evaluated through the factor N (adsorption capacity coefficient in mg/L). This parameter was converted to adsorption capacity of the adsorbent packed in the column by considering the volume of dye solution treated with respect to the amount of adsorbent used.

The adsorption rate coefficient K decreases from 5.1 $x10^{-3}$ to 1.3 $x10^{-3}$ L/mg/min on increasing the influent concentration from 25 to 75 mg/L as given in Table- 1. Adsorption rate coefficient is an indication of volume of influent treated by unit amount of adsorbent at unit time. On increasing the concentration more solute molecules form greater concentration gradient which ultimately reduces the adsorption rate coefficient. When the flow rate increased from 5 to 15 mL/min the adsorption rate coefficient increases from $0.8x10^{-3}$ to $4.8x10^{-3}$ L/mg/min and it decreases from $2.8x10^{-3}$ to $1.6x10^{-3}$ L/mg/min while increasing the bed height from 5 to 10cm.

More availability of solute molecules on the adsorbent surface results in higher uptake of dye molecules by unit mass of adsorbent. Hence, the adsorption capacity coefficient (N) increases while increasing the influent concentration from 25 to 75 mg/L. The derivative adsorption capacity of the adsorbent (q_{BA}) calculated from N is also increased with respect to concentration. The experimental and calculated adsorption capacity has moderate difference as evident from the high standard deviation (Sd = 1.26 to 5.62) values. The regression coefficient values are comparatively good ($0.9611 < r^2 < 0.9873$), supports the applicability of Bohart-Adam model for the adsorption of AB113 onto ASC column.

Thomas Model

Thomas model[17] is used for the determination of adsorption capacity of an adsorbent which is essential for the design of column for an effective wastewater treatment. It also assumes plug flow behavior in the bed, and uses Langmuir kinetics of sorption‑desorption and no axial dispersion is derived with the sorption that the rate driving force obeys second-order reversible reaction kinetics[21]. This model is suitable- for adsorption processes where the external and internal diffusion limitations are absent.

The column mode adsorption data for the adsorption of AB113 onto ASC column at various initial dye concentrations, flow rate and bed depth applied to Thomas model to determine the kinetic coefficients for

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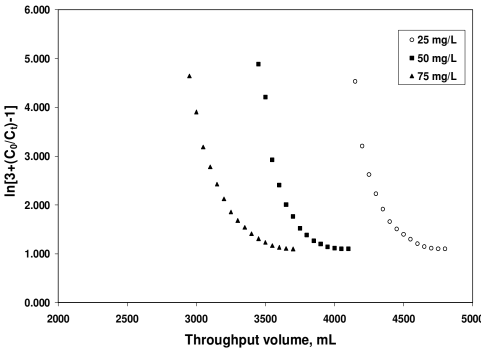
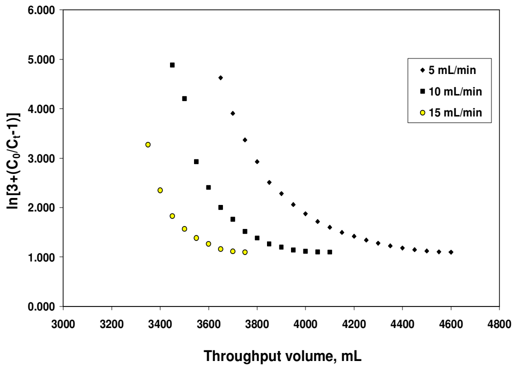
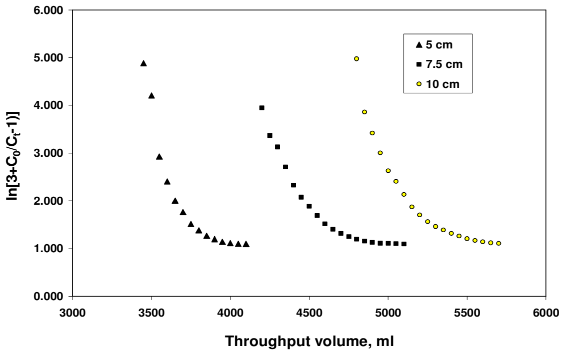
the selected adsorbent-adsorbate system was shown in the fig. 4 and the results of the plot were given in Table- 1. The fitness of the data to the Thomas model was analyzed using non-linear regression method.



(a) Concentration variation



(b) Flow rate variation



(c) Bed height variation

Fig.- 4: Thomas plot for the adsorption of AB113 onto ASC Column

From results of Thomas model (Table-1), it was seen that values of Sd range from 0.09 to 0.88. The Thomas model agreed very well with the experimental data as the Sd values were very low. The correlation coefficient of Thomas model varies from 0.7254 to 0.9116. It can be observed from the Table-1 that the Thomas constant varies from 1.0 x 10^{-3} to 1.6 x 10^{-3} L/min/mg on increasing the initial dye concentration from 25 to 75 mg/L. The reason was that the driving force for adsorption is the concentration difference between the solute on the adsorbent and the solute in the solution. Thus, the high driving force due to the higher dye concentration resulted in better column performance. The Thomas model rate constant showed an increasing trend while increasing the flow rate as well as the bed height.

The adsorption capacity calculated using Thomas model decreases from 94.59 mg/g to 77.79 mg/g on increasing the flow rate from 5 to 15 mL/min and it decreases from 83.75 to 57.95 mg/g on increasing the bed height from 5 to 10 cm. The calculated adsorption capacity values were in good agreement with the experimental adsorption capacity.

Yoon–Nelson model

This model is based on the assumption 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. The values of $k_{(YN)}$ and τ were determined by a plot of $\ln(C_t/(C_0-C_t))$ against t using nonlinear regression analysis as shown in the figure- 5 and the results were given Table- 1.

The time required for 50% adsorbent breakthrough (τ) decreases from 446.69 to 337.97 min on increasing the initial dye concentration from 25 to 75 mg/L and it decreases from 836.82 to 235.90 min on increasing flow rate from 5 to 15 mL/min. As the adsorbent get saturated quickly at higher concentration as well as at higher flow rate which leads to decrease of τ. Bed depth increase gives more and more adsorption sites there by increase the value of τ from 378.04 to 532.91 min which in-terms increases the quantity of treated dye effluent. The YN model fits exceptionally well for the adsorption of AB113 onto ASC column with respect to all of the calculated parameters.

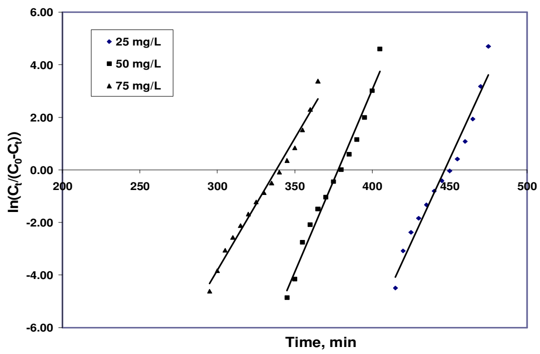
Table- 1: Column results for the Adsorption of AB113 on to ASC fiber

Concentration, mg/L		25	50	75	50	50	50	50
Flow Rate, mL/min		10	10	10	5	15	10	10
Bed height, cm		5	5	5	5	5	7.5	10
$q_{0\ (exp)}$, mg/g		47.50	81.00	111.00	92.00	75.00	67.33	57.50
Bohart – Adams Model Results	K, L/mg/min	0.0051	0.0028	0.0013	0.0008	0.0048	0.0018	0.0016
	N, mg/L	21.17	37.80	50.70	41.84	35.38	30.88	26.65
	Q_{ba}, mg/g	35.56	52.17	59.82	57.74	68.65	28.41	17.85
	r^2	0.9611	0.9783	0.984	0.9751	0.9819	0.9873	0.9848
	Sd	1.26	3.30	5.62	3.28	0.05	5.41	6.01
Thomas Model Results	k_T, L/min/mg	0.0016	0.0010	0.0014	0.0003	0.0014	0.0006	0.0007
	$q_{0\ (T))}$, mg/g	49.49	83.75	115.47	94.59	77.79	71.08	57.95
	r^2	0.7774	0.8638	0.8486	0.8658	0.7254	0.8658	0.9116
	Sd	0.39	0.54	0.88	0.51	0.55	0.73	0.09
Yoon Nelson Model Results	$k_{(YN)}$, L/min	0.13	0.14	0.24	0.04	0.24	0.09	0.08
	τ, min	446.69	378.04	337.97	836.82	235.90	463.19	532.91
	$q_{0(YN))}$, mg/g	44.67	75.61	101.39	83.68	70.77	61.76	53.29
	r^2	0.9611	0.9783	0.984	0.9751	0.9819	0.9873	0.9848
	Sd	0.52	1.30	2.53	1.80	0.47	1.13	0.94

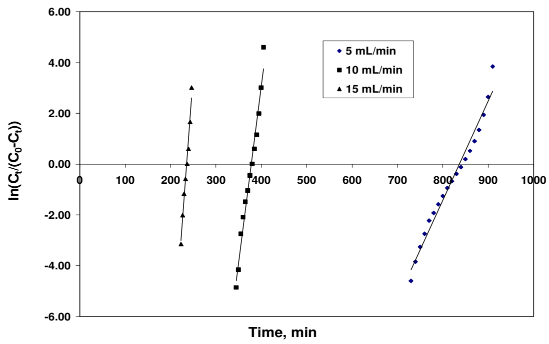
Out of the three mathematical models tested for the adsorption of AB113 onto ASC column, the YN model provides excellent fit with very high r^2 (0.9611 to 0.9873). For all the range of concentration, flow rate and bed height under investigation, the calculated adsorption capacity and the experimental adsorption capacity were very close, which substantiates the fitness of YN model.

CONCLUSIONS

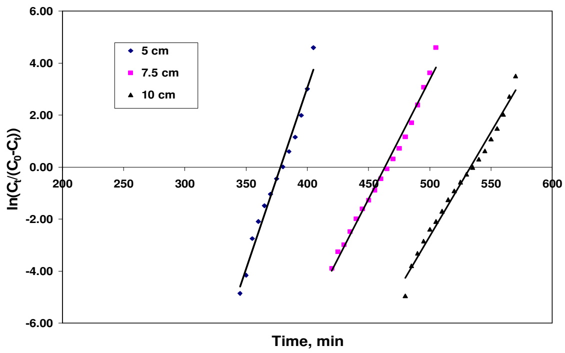
The prepared adsorbent is an effective adsorbent for the removal of dyes from wastewater. The removal efficiency of dye from waste water strongly depends on influent concentration, flow rate and bed height. The adsorption capacity increases with increase in influent concentration, decreases with increase in flow rate and bed height. Out of the three mathematical models tested for the adsorption of AB113 onto ASC column, the YN model provides excellent fit with very high r^2 (0.9611 to 0.9873). For all the range of concentration, flow rate and bed height under investigation, the calculated adsorption capacity and the experimental adsorption capacity were very close.



(a) Concentration variation



(b) Flow rate variation



(c) Bed height variation

Fig. - 5: Yoon-Nelson model for the adsorption of AB113 onto ASC Column

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