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Fixed bed adsorption studies of Rhodamine-B dye using polymer bound adsorbent

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ABSTRACT

An eco-friendly adsorbent developed by coating polyaniline over an activated carbon prepared from the seeds of Prosopis Juliflora using $ZnCl_2$ as an activating agent (PPAC). The polymer bound adsorbent has good adsorption characteristics with a surface area of 1028 m^2/g. A continuous flow fixed bed study carried out by using PPAC as an adsorbent packed in a column for the removal of Rhodamine-B dye from aqueous solution. The effect of operating parameters such as flow rate, bed height and inlet dye concentration on the sorption characteristics of RB investigated at room temperature (30°C) and the natural pH of dye solution. On increasing the influent concentration from 25 to 75 mg/L, the volume of effluent treated decreases from 3800 mL to 2950 mL. The kinetic model suggested by Bohart-Adam, Thomas and Yoon-Nelson were employed to study this adsorption system. The YN model fits exceptionally well for the adsorption of RB onto PPAC with respect to all of the calculated parameters with high correlation coefficient (0.9431 to 0.9668) and low standard deviation(0.04 to 0.75).

Keywords: *Prosopis Juliflora*, Activated Carbon, Adsorption, Polyaniline & Rhodamine B

INTRODUCTION

Violation of environmental ethics by the human community leads to severe consequences. Most of the wastes generated by human activities are discharged onto the environment without any treatment. Disposal of untreated wastes not only makes haphazard appearance, produces so many diseases to human being, animals, and plants as well. Dyes are group of compounds used for colouring in textile, tannery, printing, and paint industries. Owing to their chemical structure, wastewater containing dye molecules are highly resistant to exposure to light and other chemical as well as biological treatment processes. Conventional treatment methods are inefficient to decolourize the dyeing industry effluent [1].

Application of adsorption using activated carbon for the treatment of industrial wastewater and for the recovery of organic compounds finds growing interest [2]. In general, the adsorption methods are used in the final stage in the industrial wastewater treatment [3,4]. Adsorption using activated carbon is best-suited method for the treatment of dye bearing wastewater. The high cost involved for the use of activated carbon limits its usage in the small-scale industries particularly in the developing countries. The recent research in the surface chemistry is to find an economically viable and easily available low-cost adsorbent from biologically waste products.

Plenty of agro based waste products have been evaluated for their capacity to adsorb heavy metals and dye pollutants present in the wastewater [5-14]. The information obtained from adsorption kinetics and isotherm in a batch mode is useful for the determination of the effectiveness of the adsorbent-adsorbate system. Fixed bed columns do not necessarily operate under equilibrium conditions because the contact time is not sufficiently long for the attainment of equilibrium.

The column adsorption process is an effective process for the treatment dyeing industrial wastewater; the adsorbent can be effectively used to treat the effluent for better quality. Large volume of wastewater can be continuously treated using a limited quantity of adsorbent is also an added advantage. Besides, other operational problems such as uneven flow pattern in the column, recycling of the spent adsorbent and regeneration cannot be studied in batch experiments [15.

Prosopis juliflora is a shrub or small tree in the Fabaceae family. The Mesquite tree grows to a height of up to 12 meters (39 ft) and has a trunk with a diameter of up to 1.2 meters. A mature plant can produce hundreds of thousands of seeds. Seeds remain viable for up to 10 years. *Prosopis juliflora* has become an invasive weed in several countries where it was introduced. Livestock that consume excessive amounts of seedpods are poisoned. The wood of this plant is being used as a precursor for the commercial production of activated carbon. In this work an activated carbon was prepared from *Prosopis juliflora seed* using $ZnCl_2$ as an chemical activating agent. The prepared carbon was encapsulated with polyaniline matrix (PPAC) to improve the mechanical strength and improve the abrasion resistance. The removal of Rhodamine-B (RB) dye using Polyaniline coated Prosopis Juliflora Activated Carbon (PPAC) in column adsorption process. Previously derived mathematical models used to evaluate the column performance for various operating conditions.

MATERIALS AND METHODS

Preparation of adsorbent

Prosopis juliflora seed used as precursor for the preparation of activated carbon. The seeds collected in and around Erode District, Tamilnadu, India and they cut into pieces of 2 cm to 3 cm size, dried in sunlight for 5 days. The dried seeds were washed with distilled water, soaked in a boiling solution of 10% $ZnCl_2$ and kept aside at room temperature for 24 h. After 24 h the residue filtered, initially air dried for 2 days and then carbonized in muffle furnace at 400°C for 15 min. The carbonized material washed with plenty of distilled water to remove any residual $ZnCl_2$. The dried carbon powdered, sieved to a particle size of 300 to 500 μ and finally activated at 800°C in a closed container.

The poly aniline was synthesized on *Prosopis juliflora seed* activated carbon surface, which was previously soaked in monomer aniline solution (0.2 M) for 12 h at room temperature followed by slow addition of chemical oxidants 0.5 M Ammonium persulphate in 1.5 M HCl at room temperature for 4 h.

The physico chemical characteristics of the activated carbon were studied as per the standard procedures [16,17] and given in table 1. Surface area of the activated carbon sample measured at 77K using N_2 gas sorption analyzer (Nova 1000, Quanta Chrome Corporation, USA).

Table 1 – Physico-chemical properties of PPAC

S.No	Properties	Values
1	pH	7.48
2	Conductivity, mS/cm^2	0.273
3	Moisture content, %	11.4
4	Ash, %	16.4
5	Volatile matter, %	15.5
6	Matter soluble in water, %	0.44
7	Matter soluble in 0.25 M HCl, %	1.27
8	Bulk density, (g / ml)	0.46
9	Specific Gravity	0.93
10	Porosity, %	50.54
11	Surface area, m^2 / g	1028
12	Methylene Blue Value, mg/g	443

2.2 Adsorbate preparation

A cationic dye Rhodamine-B with a molecular formula ($C_{28}H_{31}N_2O_3Cl$; mol. wt. 479; C.I No. 45170, λmax 554 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 used to prepare the adsorbate solutions by appropriate dilution as required. The structure of Rhodamine-B is shown in fig. 1.

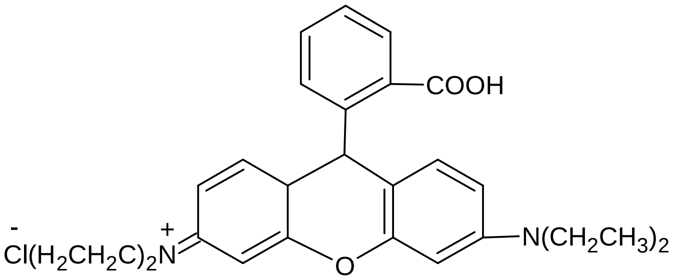

Fig 1 – Structure of Rhodamine B

2.3 Column studies

Fixed bed column studies carried out using a glass column of 1.5 cm inner diameter and 40 cm length. The column packed with the prepared adsorbent by keeping glass wool at top and bottom as shown in the fig. 2. The adsorbate fed into the column through up-flow method at specified rate using peristaltic pump. The effluent samples coming out of the column collected at specified intervals and analyzed for the residual dye concentration using (Elico Make) Bio UV-Vis spectrometer at a wavelength of 554 nm.

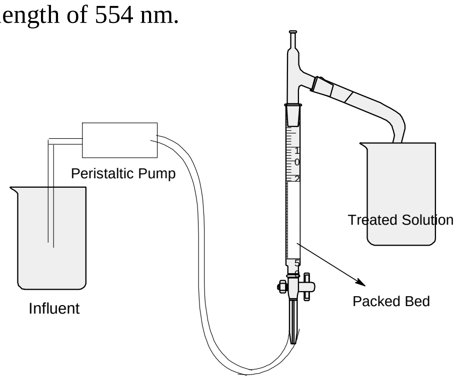

Fig. 2 – Flow chart of the packed bed column

2.4 Theoretical background

2.4.1 Bohart–Adams Model

Oulman proposed the use of a bed depth service model for simulating granular activated carbon (GAC) adsorption beds [18]. The model, first developed by Bohart and Adams [19], based on surface reaction theory as given by Eq. (1)

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

The Bohart–Adams equation is as follows:

$$\ln\left(\frac{C_0}{C} - 1\right) = \frac{KNx}{u} - KC_0 t \quad \text{....(2)}$$

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

2.4.2 Thomas Model [20]

The solid phase concentration of the dye on the adsorbent from the continuous mode studies expressed by the Thomas model. The kinetic model suggested by Thomas model is one of the widely used kinetic models for the evaluation of column performance. The Thomas model has the following form

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp\left[k_T\left(q_{0(T)}.m - C_0.v\right)\right]/r} \qquad \ldots(3)$$

Where, C_t is effluent dye concentration (mg/L) at time t, C_0 is initial dye concentration (mg/L), k_T is Thomas rate constant, (L/min.mg), $q_{0(T)}$ 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.

2.4.3 Yoon-Nelson Model [21]

Yoon and Nelson have proposed a less complicated model to represent the breakthrough of gases onto activated charcoal. The model 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 breakthrough on the adsorbent. The linear form of Yoon-Nelson model is

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

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 [22]. For a given bed

$$q_{0YN} = \frac{q_{(total)}}{m} = \frac{\frac{1}{2}C_0[(r/1000)\times 2\tau]}{m} = \frac{C_0.r.\tau}{1000m} \qquad \ldots(5)$$

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

2.4.4 Error analysis [23]

The adsorption capacity obtained by the three kinetic models compared with the experimental adsorption capacity using the following error analysis method.

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

Where, $q_{0(exp)}$ is experimental adsorption capacity, $q_{0(cal)}$ is the adsorption capacity calculated using Thomas and Yoon-Nelson kinetic models and N is the number of experimental points run.

RESULTS AND DISCUSSION

3.1 Effect of initial dye concentration

Results obtained for the adsorption of RB onto a column prepared from PPAC at various operating conditions presented in fig. 3. On increasing the influent concentration from 25 to 75 mg/L, the volume of effluent treated decreases from 3800 mL to 2950 mL. The numbers of solute molecules compete for the vacant sites of adsorbent increases on increasing the influent concentration, which results in quicker exhaustion of the column. The concentration gradient solid liquid interface is more at higher concentration that drives the solute molecules to enter into the adsorption sites. Though, the volume of influent treated decreases with respect to influent concentration but the amount of dye removed from the solution is high at higher concentration.

Table 2 – Results of various column adsorption models for the adsorption of RB onto PPAC Column.

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		38.78	70.41	90.31	75.51	59.18	59.18	50.00
Breakthrough Volume, mL		3800	3450	2950	3700	2900	4350	4900
Bohart – Adams Model Results	K x 10^{-3}, L/mg/min	3.55	1.6	1.08	0.72	2.2	1.64	1.53
	N, mg/L	21.52	39.93	50.60	42.28	34.22	32.11	27.26
	$Q_{0(ba)}$, mg/g	28.20	47.51	51.47	53.94	34.22	32.11	23.03
	r^2	0.9681	0.9629	0.9668	0.9445	0.9437	0.9663	0.9431
	Sd	2.07	4.49	7.62	4.23	4.90	5.31	5.29
Thomas Model Results	k_T x 10^{-4}, mL/min/mg	8.4	6.4	6.6	2.3	6.6	5.0	5.2
	$q_{0\ (T)}$, mg/g	51.61	91.76	130.05	102.67	87.46	75.92	62.59
	r^2	0.8585	0.9324	0.9577	0.9124	0.9659	0.8594	0.8721
	Sd	2.52	4.19	7.79	5.33	5.55	3.28	2.47
Yoon Nelson Model Results	$k_{(YN)}$, L/min	0.09	0.08	0.11	0.04	0.11	0.08	0.08
	τ,	429.89	399.33	337.34	845.60	228.11	481.59	545.12
	$q_{0(YN)}$, mg/g	37.06	68.85	87.24	72.90	58.99	55.36	46.99
	r^2	0.96	0.9629	0.9668	0.9445	0.9437	0.9663	0.9431
	Sd	0.34	0.31	0.60	0.51	0.04	0.75	0.59

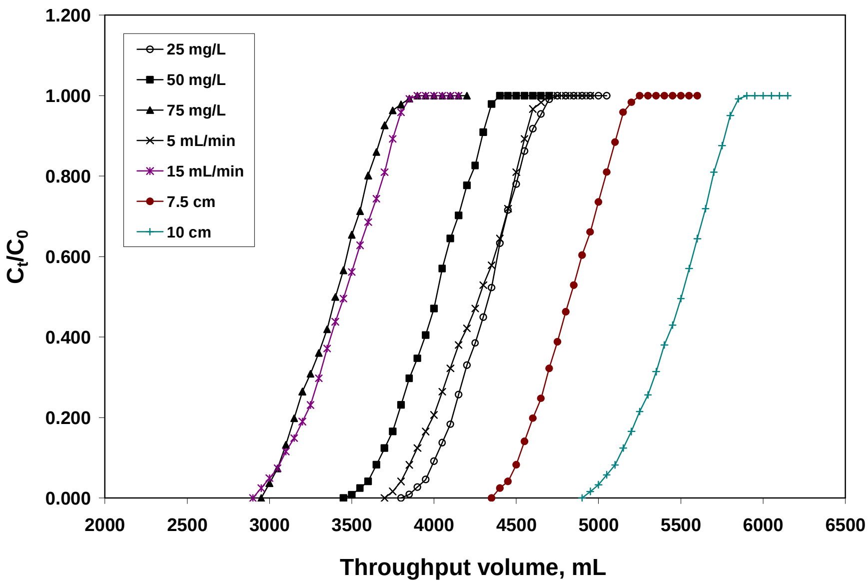

Figure 3 – Breakthrough curve for the adsorption of RB onto PPAC

The results obtained at various flow rate indicated that the influent flow rate also influences the quantities of dye removed. On increasing the flow rate from 5 to 15 mL/min at 50 mg/L of Initial dye concentration and 5 cm bed height the volume of dye solution treated decreases from 3700 to 2900 mL. At higher flow rates the contact time between the solute and the surface of adsorbent decreases which minimizing the possibilities adsorbate-adsorbent interaction and results in reduced uptake of solute by the column. In-order to set an effective column for the solute adsorption it is essential to give maximum contact time between the solute and sorbent. In this study 5mL/min of flow rate gives maximum efficiency with 75.51 mg/g of solute removal.

The breakthrough curve reaches saturation at higher volume on increasing the bed height from 5cm to 10cm. It was clearly observed that the system efficiency in terms of volume of dye solution treated increases with increase of bed height. Even a bed height of more than 10cm can be tried to improve the efficiency but the size of adsorbent particles must be increased to avoid clogging. For this selected adsorbent-adsorbate system, 10cm bed height gives maximum efficiency without any operational difficulties.

3.2 Bohart-Adam Model

Many researches have applied the Bohart-Adam model equation directly to evaluate the adsorption system. In this work, the amount of dye-adsorbed mg/g evaluated through the factor N (adsorption capacity coefficient in mg/L). This parameter 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 Bohart-Adam model plot for the adsorption of RB onto PPAC is shown in fig. 4.

The adsorption rate coefficient K decreases from 3.55 x10^{-3} to 1.08x10^{-3} L/mg/min on increasing the influent concentration from 25 to 75 mg/L as given in table 2. 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 decreases from 7.2 x 10^{-3} to 2.2 x 10^{-3} L/mg/min owing to the poor dwell time for the solute while increasing the bed depth from 5 to 10cm.

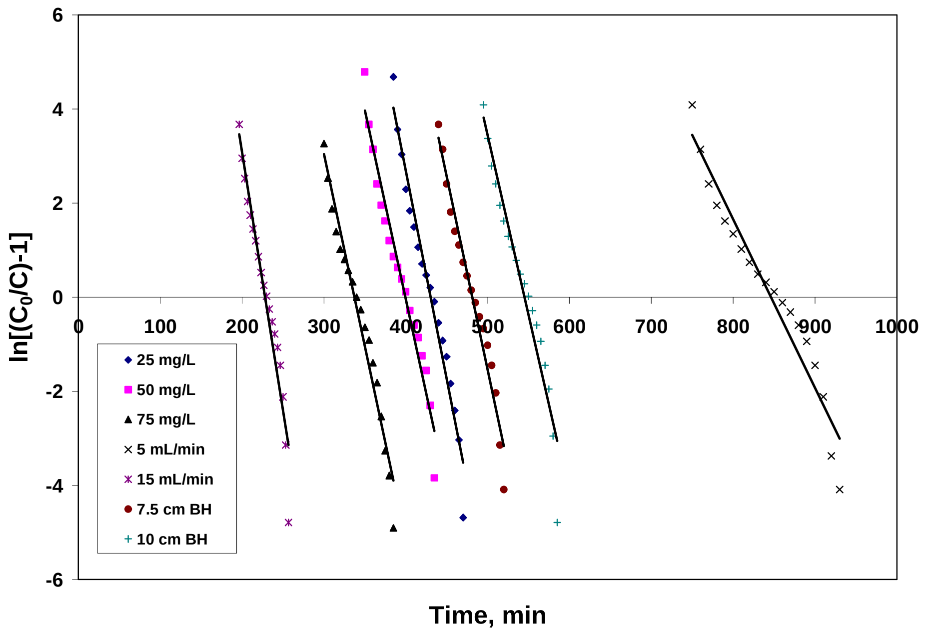

Figure 4 – Bohart Adam model plot for the adsorption of RB onto PPAC

The adsorption capacity coefficient (N) and its derivative adsorption capacity of the adsorbent (q_{BA}) increases while increasing the influent concentration from 25 to 75 mg/L. More availability of solute molecules on the adsorbent surface results in higher uptake of dye molecules by unit mass of adsorbent. The experimental and calculated adsorption capacity has moderate difference as evident from the high standard deviation values. The regression coefficient values are comparatively good enough to support the applicability of Bohart-Adam model for the adsorption of RB onto PPAC column.

3.3 Thomas Model

The mathematical model suggested by Thomas was applied for the adsorption of RB onto a column prepared using PPAC. The Thomas model parameters were calculated from the slope and intercept of the plot. The adsorption data at various initial dye concentration, flow rate and bed depth applied to Thomas model to determine the kinetic coefficients for the selected adsorbent-adsorbate system. The fitness of the data to the Thomas model was analyzed using non-linear regression method (fig.5). The regression coefficients indicated that the model provides nominal fits to the experimental data with r^2 ranging from 0.8585 to 9577.

The adsorption capacity $q_{0(T)}$ increases from 51.61 to 130.05 mg/g on increasing the influent concentration from 25 to 75 mg/L. The adsorption capacity shows a decrease trend while increasing the flow rate and bed depth. Though, the bed depth increase enhances the quantity of treated effluent, but the amount of solute per unit quantity of adsorbent decreases. The experimental adsorption capacity (q_{exp}) and the calculated value do not coincide very much, which may due the poor fit of the Thomas model. The high standard deviation also substantiates the poor fitness of Thomas model.

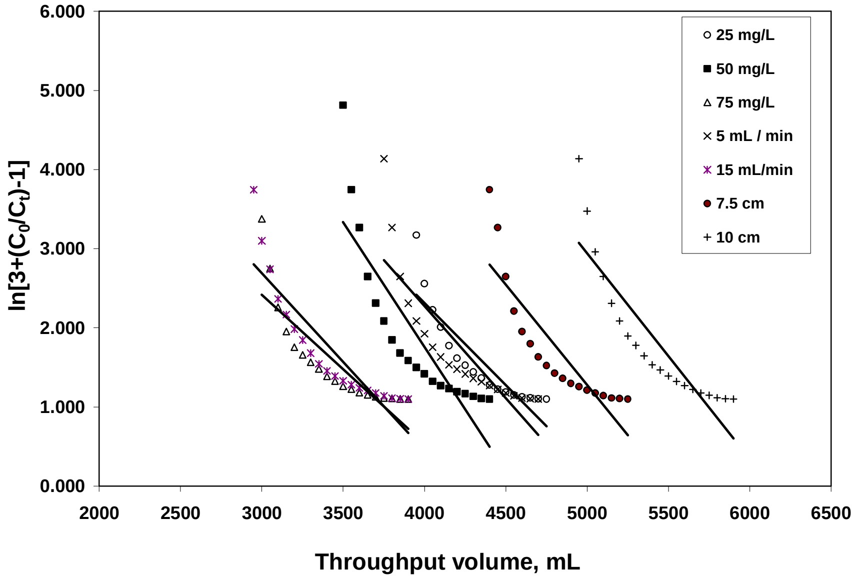

Figure 5 – Thomas model plot for the adsorption of RB onto PPAC

3.4 Yoon-Nelson Model

The Yoon-Nelson model rate constant (k_{YN}) and τ were determined from the slope and intercept of the YN model plot as shown in fig. 6 and the results presented in table 2. Out of the three models tested for the adsorption of RB onto PPAC column, the YN model provides excellent fit with very high r^2 and low Sd. For all the range of concentration under investigation, the calculated adsorption capacity and the experimental adsorption capacity were very close, which substantiates the fitness of YN model.

The time required for 50% adsorbent breakthrough (τ) decreases on increasing the concentration. As the adsorbent get saturated quickly at higher concentration which leads to decrease of τ. The increase in flow rate decrease the value of τ from 845 to 228.11 correspondingly the value of dye solution treated decreases. Bed depth increase gives more and more adsorption sites there by increase the value of τ which in-terms increases quantity of treated dye effluent. The YN model fits exceptionally well for the adsorption of RB onto PPAC with respect to all of the calculated parameters.

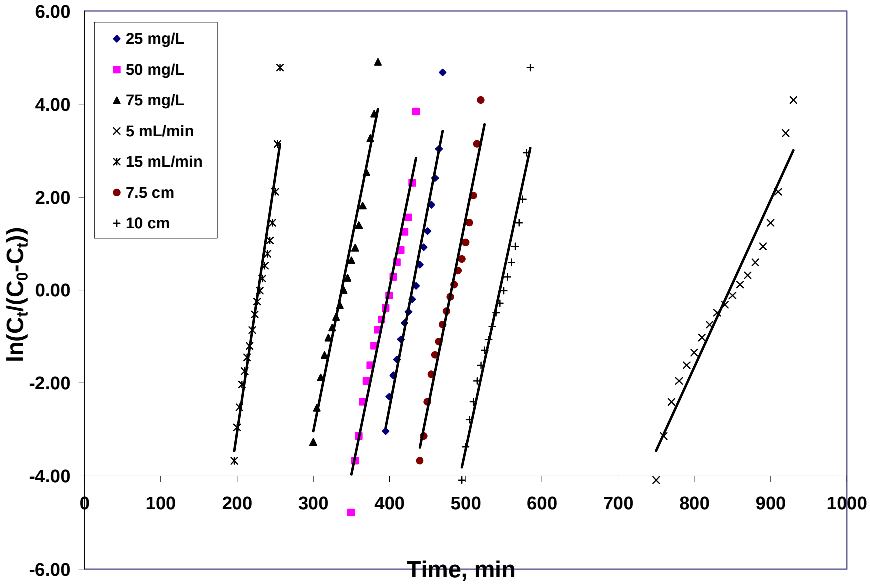

Figure 6 – Yoon-Nelson model plot for the adsorption of RB onto PPAC

CONCLUSION

An activated carbon with good adsorption characteristics was prepared successfully prepared and the same employed for the adsorption of removal of RB from aqueous solution using packed bed column. The sorption of RB by PPAC carbon predominantly depends on the initial dye concentration, flow rate and the height of packed column. The influent concentration increase causes quick exhaustion of the column and at the same time, more solute molecules removed per unit mass of the adsorbent. The three kinetic models describe the adsorption of RB onto PPAC column well with good results. The Yoon-Nelson model gives an excellent fitness to the adsorption data and the parameters derived from this model has good correlation with the experimental results. Activated carbon prepared from *Prosopis Juliflora* seeds could be a promising adsorbent for the colour removal of textile industrial effluents.

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