Research Article

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Continuous Fixed-Bed Column Studies of Textile Effluent Treatment using Multi-Walled Carbon Nanotubes Originated from *Rosmarinus officinalis Oil*

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ABSTRACT

A continuous adsorption study in a fixed-bed column was carried out using Multi-walled Carbon Nanotubes (MWNTs) derived from *Rosmarinus officinalis oil* as an adsorbent for removing the textile dye and Acid blue 40 from an aqueous solution. MWNTs were prepared from *Rosmarinus officinalis oil* as a precursor using Fe/Mo catalyst supported on silica at 650 ºC under N_2 atmosphere by spray pyrolysis process characterized by Scanning Electron Microscopy, Transmission Electron Microscopy and Raman spectroscopy. The effects of adsorbent bed height (2–6 cm), initial dye concentration (20-60 mg/L) and flow rate (10–30 mL/min) on the column performance were analyzed. The breakthrough curve was analyzed using the mathematical models of Thomas, Yoon-Nelson and bed depth service time. The Thomas model at different conditions defined the behaviors of the breakthrough curves. The bed depth service time model showed good agreement with the experimental data. The high values of correlation coefficients (R^2: 0.9875) obtained indicate the validity of the bed depth service time model for the present column system.

Keywords: Adsorption; Acid blue 40; Breakthrough curves; Fixed-bed column studies; MWNTs.

1. INTRODUCTION

Textile industries, for example, emit various synthetic dyes in the water discharged to the environment, causing environmental problems worldwide. The composition of textile wastewater varies depending on the particular textile industry. However, most dyes are not biodegradable and tend to suppress photosynthetic activities in aquatic habitats by preventing sunlight penetration. Due to the complex structures and synthetic origins of dyes, textile effluents are very difficult to treat using conventional processes because these processes are costly and cannot effectively be used to treat the wide range of dyes present in wastewater (Ahmad *et al.* 2010; Demarchi *et al.* 2013). Several conventional technologies have been developed to remove pollution from wastewaters, such as precipitation, evaporation, filtration, ion exchange, membrane processes and coagulation-flocculation. These methods have many limitations and involve complicated procedures that are economically infeasible. One of the most efficient methods for removing dye pollutants is adsorption, which has been more frequently used than other methods due to the simplicity in design, application and regeneration of adsorbents. In recent years, nanotechnology has introduced different types of nanomaterials to the water industry that can have promising outcomes. Nano-sorbents such as CNTs, polymeric materials (e.g., dendrimers) and zeolites have exceptional adsorption properties and are applied to remove heavy metals, organics, dyes and other impurities (Savage *et al.* 2005; Angulakshmi *et al.* 2012). CNTs, in particular, received special attention for their exceptional water treatment capabilities and proved to work effectively against both chemical and biological contaminants. The sorption applications of carbon nanomaterials to tackle environmental pollution problems have received considerable attention; CNTs were used as a fixed bed, continuous flow through this bed result in maximum utilization of the adsorption capacity. The CNT provides chemically inert surfaces with specific surface areas for physical adsorption. They have a relatively uniform structure, providing more adsorption sites.

For the application of CNTs as adsorbents in fixed-bed column experiments, different parameters need to be optimized, such as flow rate, bed thickness, diameters, pH of the aqueous media, initial concentration of the pollutant and the presence of other cations and anions in the media.

Therefore, this study aims to investigate the adsorption capacity of Multi-walled Carbon Nanotubes as an adsorbent derived from *Rosmarinus officinalis* oil (as a non-conventional resource) in a fixed-bed column

with regards to the textile dye AB 40. The effect of bed height, concentration and flow rate on the column performance is analyzed. The breakthrough curves are analyzed using the Thomas, Yoon-Nelson and bed depth service time (BDST) models.

2. MATERIALS AND METHODS

2.1 Chemicals (Materials)

The dye, Acid blue (CI: 62125), was supplied by Sigma Aldrich and used without purification (see Fig. 1). All other chemicals used were of analytical grade and distilled water was used to prepare all solutions.

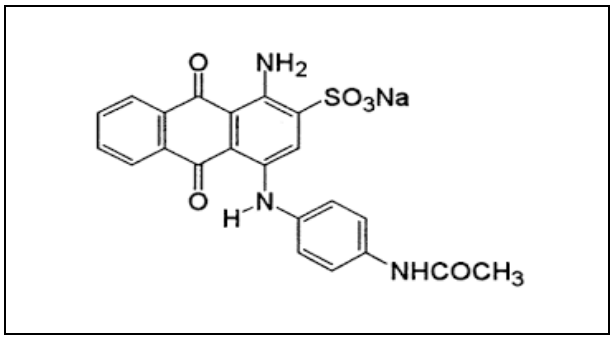

Fig. 1: Acid Blue 40

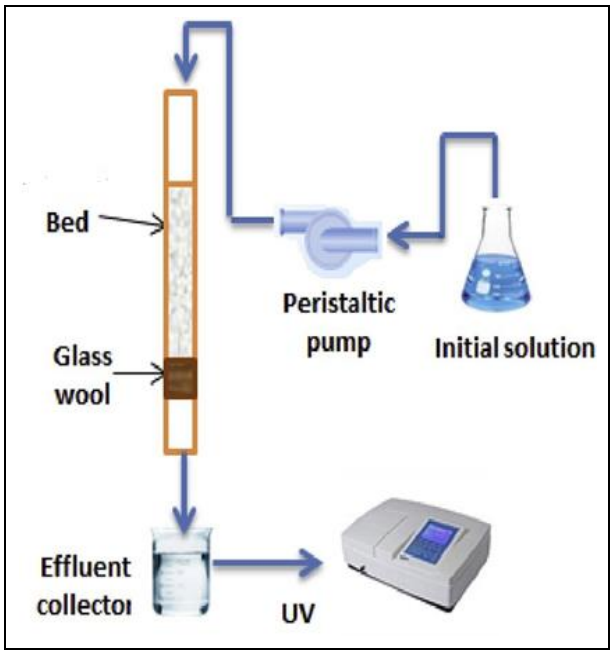

Fig. 1a: Fixed Bed Column Studies set-up

2.2 Preparation of MWNTs

MWNTs were prepared from *Rosmarinus officinalis* oil as a precursor to Fe/Mo catalyst supported on silica at 650 ºC under N_2 atmosphere by spray pyrolysis process. Fe/Mo catalyst preparation was conducted using the wet impregnation method (Angulakshmi *et al.*, 2013). $Fe(NO_3)_3.9H_2O$ and $(NH_4)Mo_7O_{24}.4H_2O$ were dissolved in methanol and mixed thoroughly with methanol suspension of silica. The solvent was then evaporated and the resultant cake was heated to 90-100 ºC for 3 hours and then removed from the furnace and was finally ground in a mortar. The fine powders were then calcined for 1 hour at 450 °C and then re-ground before loading into the reactor. The catalyst was placed on the quartz boat. The boat was placed in the heating furnace. The carrier gas nitrogen (100 mL/min) was flushed out before switching on the reaction furnace to remove air and create a nitrogen atmosphere. The temperature was raised from room temperature up to the desired growing temperature. Waiting was done for 10 minutes for stabilization of temperature. Synthesis was conducted at 650 °C in a nitrogen atmosphere, with a typical reaction time of 30 min. *Rosmarinus officinalis* oil were supplied at a rate of 0.1 g/min. The reactor was then cooled to room temperature with nitrogen gas flowing. The carbon product on the silica support was then weighed to determine the carbon yield. We define carbon yield here as the functional mass as $(m_1-m_0)/m_0$, where, m_1 and m_0 are the final mass of the catalyst support with carbon deposit and the initial mass of the catalyst support, respectively. Not all the carbon mass is in the form of MWNTs. Nevertheless, the amount of amorphous carbon detected in electron microscope images was small and our practical definition of the relative yield is believed to provide a reasonable assessment of MWNTs production in these experiments. The MWNTs were purified by 40 mg of raw material and were added to 20 mL 1N HCl to form an acidic slurry. This slurry was heated to 60 °C and stirred at 600 rpm. To this heated acidic slurry 20 mL, H_2O_2 was added to form an oxidative slurry that continued to be heated and stirred for 30 minutes. The addition of HCl, H_2O_2, subsequent heating, and stirring was repeated three more times, each time allowing the heated oxidative slurry to stir for 30 min. Phase separation occurred, followed by filtering the carbon phase and washing with 1N HCl and distilled water. The collected sample was dried at 120 °C in the air for 2 hrs. SEM, HRTEM and Raman spectroscopy characterized the sample's morphology.

2.3 Characterization Techniques

The surface morphology of the MWNTs was examined by SEM using an EVO LS 15 (Carl Zeiss SMT, Rudolf-Eber-Straße, Oberkochen, Germany). Prior to observation, the samples were lyophilized. For the magnification, the scanning electron microscope was operated at 255 magnification and 25 kV accelerated voltage to obtain high-resolution micrographs.

For HRTEM analysis, the filter was coated with carbon material and mounted onto carbon-coated copper grids (Veco, Eerbeek, Holland) using acetone vapor. Meanwhile, the CNTs were morphologically identified using a scanning transmission electron microscope

(HRTEM; Hitachi 7100, Tokyo). Then, Raman spectroscopy measurement was carried out to evaluate the purity of MWCNTs using a Raman microscope (TRIVIA, Acton).

2.4 Column Setup

The trials were carried out on a 37 cm-long glass column having an interior diameter of 2.54 cm. At the bottom of the column, a fixed amount of glass wool was inserted to act as a support material for MWNTs. Glass wool was placed at the top of the adsorbent bed to prevent the bed from being pulled with the outflow. All the experiments were conducted at room temperature and the direction of flow was from bottom to top. The pH of the inlet AB 40 solution was set to 6 and the pH of the dye solution was adjusted with HCl (0.1–5 mol/L). Effluent samples were obtained at various time intervals. The residual concentration of AB 40 dye in the output was measured using a GENESYS 10 S UV–Vis Spectrophotometer (Thermo Scientific, Madison, Wisconsin, USA) at 587 nm.

2.5 Column Experiments

The effects of the bed height of the adsorbent, initial dye concentration and flow rate on the column performance were analyzed.

2.6 Effect of the Bed Height

The effect of varying the bed height (2, 4 and 6 cm) on the column parameters was studied. A flow rate of 10 mL/ min and an initial influent concentration of 20 mg/L were kept constant.

2.7 Effect of Initial Influent Concentration

Initial AB 40 concentrations of 20, 40, and 60 mg/L were examined. A flow rate of 10 mL/ min and a bed height of 2 cm were kept constant.

2.8 Effect of Flow Rate

Flow rates of 10, 20, and 30 mL/ min were used to analyze the effect on the column performance. An initial influent concentration of 20 mg/L and a bed height of 2 cm were kept constant.

2.9 Modeling of the Breakthrough Curves

The dye adsorption capacity of MWNTs was firm in a batch reactor. The dye solutions of required concentration were prepared by diluting the appropriate volume of a stock solution. The solution was further diluted to the required concentrations (10-100 mg/L) before use. The pH of the solutions was adjusted by adding 0.1M HCl or 0.1M NaOH. All the experiments were performed for a predetermined time at room temperature. The dye concentration was determined in the liquid phase using a UV spectrometer (Elico make). The percentage of adsorption was calculated using the relationship:

$$R_{\%} = \frac{(C_0 - C_t)}{C_0} \times 100 \qquad (1)$$

Where, C_0 and C_t are initial (inlet) and final concentrations of arsenic, respectively at time t. Then the amount of arsenic adsorption per unit mass of adsorbent at time t (q_t) was calculated using the relationship:

$$q_t = \frac{C_0 - C_t}{W} \times V \qquad (2)$$

where, V is the volume of solution (L) and W is the mass of the adsorbent (g).

The breakthrough curves were analyzed with the mathematical models of Yoon- Nelson Model, Thomas and BDST.

2.10 Bed Depth Service Time (BDST) Model

The BDST is a model for predicting the relationship between depths, X and service time, t. This model states that the bed height and service time of a column bear a linear relationship. This model was derived based on the assumption that forces like intra particle diffusion and external mass transfer resistance are negligible and that the adsorbate is adsorbed onto the adsorbent surface directly. This model is used only for the description of the initial part of the breakthrough curve, i.e., up to the breakpoint or 10–50 % of the saturation points (Gupta *et al.* 2005). This BDST model was focused on the estimation of characteristic parameters such as the maximum adsorption capacity and kinetic constant.

$$\ln\left(\frac{C_0}{C_B} - 1\right) = ln\left(\exp\left[\frac{KXN_0}{V}\right] - 1\right) - KC_0t \qquad (3)$$

A linear relationship between bed depth and service time is given by Eq. (3) (Goel *et al*. 2005).

The straight line represent as:

$$t = aX - b \qquad (4)$$

where, 'a' is the slope of BDST line $a = \left(\frac{N_0}{VC_o} - 1\right)$ and the intercept of this equation represened as Eq. (4).

$$b = \frac{1}{KC_0} ln\left(\frac{C_0}{C_B} - 1\right) \qquad (5)$$

Thus, N_0 and k can be evaluated from (a) slope and (b) the intercept of the plot of t versus X,

respectively. The critical bed depth (X_0) is the theoretical depth of adsorbent sufficient to ensure that the outlet solute concentration does not exceed the breakthrough concentration (C_B) value at time t = 0. X_0 can be calculated as Eq. (4).

$$C_0 = \frac{V}{KN_0} ln\left(\frac{C_0}{C_B} - 1\right) \quad (6)$$

The BDST model can be extended for the predication of a slope of the model at other flow rates. When the flow rate is changed from Q to a new value, Q_0, the new value of slope (a^1) is obtained by Eq. (5). However, the intercept remains unchanged because it depends on the inlet solute concentration, C_0.

$$a^1 = \frac{aQ}{Q^1} \quad (7)$$

2.11 Thomas Model

Various mathematical models can be used to describe fixed bed adsorption. Among them, Thomas model (Thomas *et al.* 1948) is simple to use in the design of a fixed-bed adsorption column. Hence, the break through data obtained from the column studies was examined using the kinetic model developed Thomas. The expression of the Thomas model for an adsorption column is as follows:

$$C_o/C_t = 1/\{1 + \exp[k/Q(N_oM - C_oV)]\} \quad (8)$$

where,

C_t effluent dye concentration, mg/L

C_0 initial dye concentration, mg/L

K Thomas rate constant L /min. mg

N_0 maximum dye adsorption capacity, mg/g

M mass of the carbon, g

V throughput volume of the dye solution, mL

Q flow rate, mL/min

Eq. 6 can be converted to the simple format as follows:

$$C_t/C_0 = 1/[\exp(b\text{-}aV)] \quad (9)$$

where,

$$a = KC_0/Q \quad (10)$$

$$b = K N_0M/Q \quad (11)$$

Therefore, if Q, M and C_0 are constants, C_t/C_0 is the function of V. Once a & b are determined, the value of K & N_o can be calculated from equations 10 and 11.

2.12 Yoon-Nelson Model

This model was developed by Yoon and Nelson (1984) to describe the adsorption breakthrough curves. The Yoon-Nelson model was derived 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. It is a simple model that requires no detailed data concerning the type of the adsorbent and the physical properties of the adsorption bed (Chowdhury *et al.* 2013). The linearised model for a single component system is expressed as:

$$\ln\left(\frac{C_t}{C_o - C_t}\right) = K_{YN}t - \mathcal{T}K_{YN} \quad (12)$$

where,

K_{YN} is the rate constant (min^{-1})

$\boldsymbol{\mathcal{T}}$ is the time required for 50 % adsorbate breakthrough (min) and

t is the breakthrough time (min).

The values of K_{YN} and $\boldsymbol{\mathcal{T}}$ can be calculated from a plot of $\ln\left(\frac{C_t}{C_o - C_t}\right)$ vs. t at different inlet concentrations, flow rates and bed heights. If the theoretical model accurately characterizes the experimental data, this plot will result in a straight line with a slope of K_{YN} and intercept of $\boldsymbol{\mathcal{T}}$ K_{YN} (Yoon and Nelson, 1984).

2.13 Error Analysis

All the adsorption experiments were performed in duplicate and the results are presented as means of the replicates along with standard deviation (represented as error bars in the breakthrough curves). The linear regression coefficients R^2 were determined to test the adequacy and accuracy of thelinearized forms of the model equations of the rupture curves.

3. RESULTS AND DISCUSSION

3.1 SEM

Fig. 2 shows the morphologies of as-grown Carbon nanostructures over Fe-Co bimetallic catalyst, impregnated in silica at 650°C, under the flow of nitrogen by CVD assisted spray pyrolysis method. The SEM

image clearly reveals that MWNTs grew nicely on the surface of the silica particles.

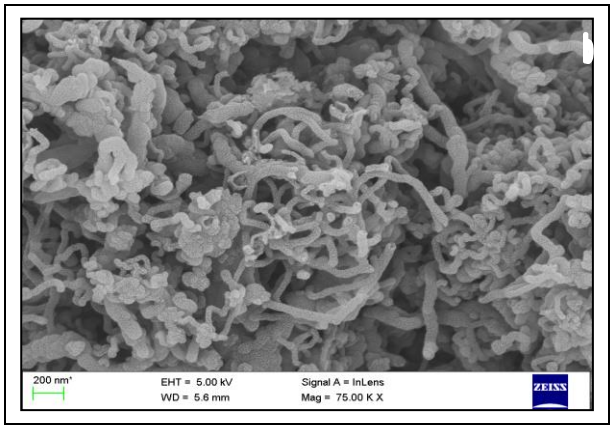

Fig. 2: SEM micrographs of MWNTs grown on Fe-Co supported silica at 650 °C

3.2 HRTEM

Fig. 3a and 3b show the high-resolution TEM images of MWNTs, grown over Fe-Co bimetallic catalyst impregnated on silica support at 650 °C with a flow rate of *Rosmarinus officinalis oil* at 0.5 mL per minute. That the inner diameters of the nanotubes were in the range of 4-6 nm and the outer diameters of the grown nanotubes were found in the range of 16-18 nm. The wall and inner core clearly visible.

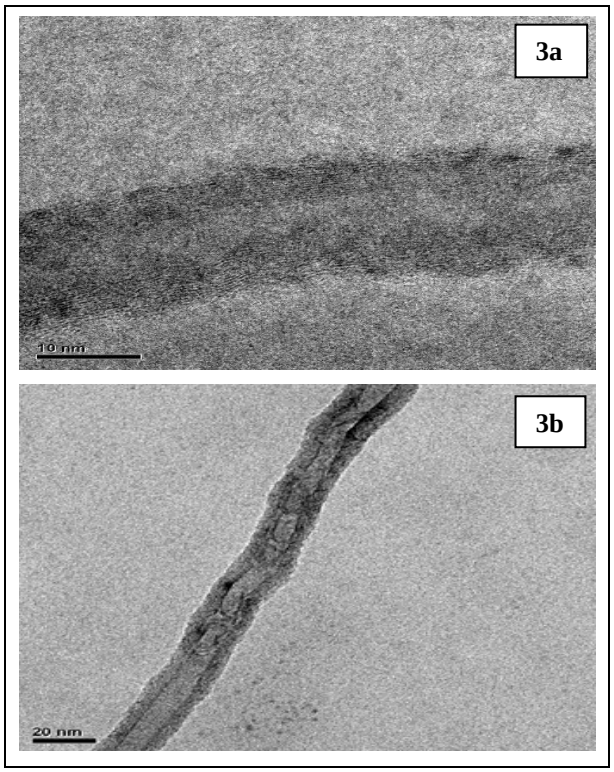

Fig. 3a & 3b: HRTEM image of MWNTs grown on Fe-Co supported silica at 650 °C

3.3 Raman spectroscopy

The results of Raman spectroscopy analysis in Fig. 4 represent the MWNTs grown on the catalyst surface at 650 °C, indicating two characteristic peaks at 1354 cm^{-1} and 1582 cm^{-1} which correspond to D and G bands, respectively. The G bands are associated with stretching vibration within the basal plane of graphite crystal, normalized to an equivalent intensity. The D bands are associated with the disorder or defective planar graphite structure. The D peaks at 1354 cm^{-1} may be attributed to the defects in the curved graphene sheets. Therefore, the Raman spectrum provides definite proof that the MWNTs have graphitic structure.

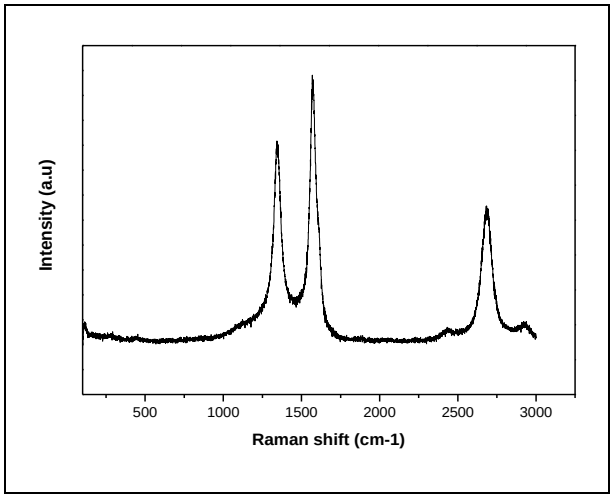

Fig. 4: Raman spectra of MWNTs grown on Fe-Co supported silica at 650 °C

3.4 Column performance at various operating conditions

The most important parameters for a breakthrough curve study are the bed height, flow rate and initial inlet concentration. The effects of these parameters on the shape of the breakthrough curve and column performance were investigated.

The inflow and outflow rate were maintained constant for a particular experiment. Frequent checks were made at an interval of 10 min to correct any change in flow rates. All the experiments in fixed bed studies were conducted in duplicate. The maximum deviations in the experiments were within 5%. Each lot of 50 mL were separately collected and analyzed for dye concentration by spectra photometric method. Percolation of dye solutions were stopped as soon as the dye concentration in the effluent exceed 0.2 mg/L (breakpoint) which is the permissible limit for discharge purpose.

If an adsorbate-adsorbent system obeys BDST model, a linear trace is expected for a plot of time vs. ln $[C_o/C_t - 1]$, where C_o and C_t are initial effluent dye

concentration and concentration of effluent at time, t, respectively.

If an adsorbate-adsorbent system obeys Thomas model, a linear trace is expected for a plot of Volume of effluent vs ln [C_o/C_t – 1], where C_o and C_t are initial effluent dye concentration and concentration of effluent at time, t, respectively.

3.5 Applicability of BDST Model

If an adsorbate – adsorbent system obeys BDST model, a linear trace is expected for a plot of ln [C_0/C_t - 1] vs. Time, where, C_0 and C_t are the initial effluent dye concentration and concentration of effluent at time t, respectively. The column experiments were conducted with a view to examine the influence of initial dye concentration on the chosen dye adsorbed by MWNTs.

Fig. 5a represents the relation between C_t/C_0 and volume of the effluent, which gives a typical S-shaped curve confirming the applicability of the BDST model for Acid Blue. Fig. 5b represents the relationship between ln[(C_0/C_t) -1] and time for various initial dye concentrations. The Fig. 5c represents the relation between ln[(C_0/C_t) -1] and time for different bed heights. Fig. 5d represent the relationship between ln[(C_0/C_t) -1] and time for different flow rates.

3.6 Applicability of Thomas Model

If a adsorbate – adsorbent system obeys Thomas model, a linear trace is expected for a plot of Volume of the effluent Vs ln[C_0/C_t -1], where, C_0 and C_t are the initial effluent dye concentration and concentration of effluent at time, t, respectively. The experiments were conducted with a view to examine the Initial dye concentration, influence of bed height and influence of flow rate on the individual dye adsorption on the chosen adsorbate adsorption. The figures 6a, 6b and 6c confirm applicability of Thomas model; the relevant data are given in Table 1.

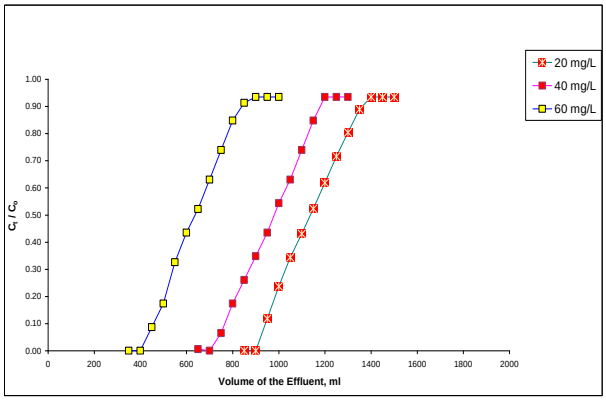

Fig. 5a: Effect of Initial dye concentration on Break through Curve for Acid Blue

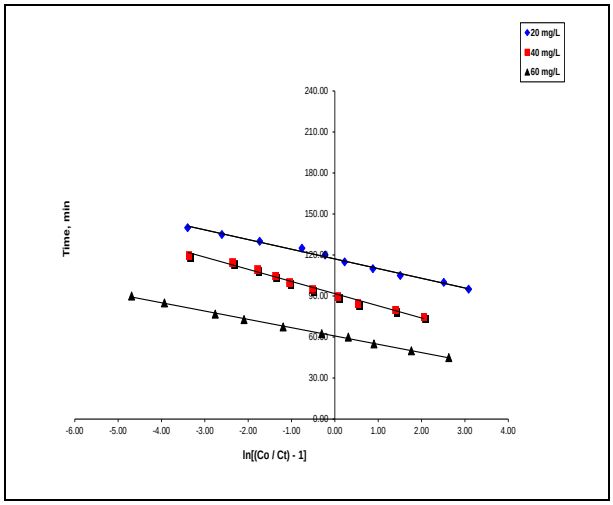

Fig. 5b: Effect of Initial Dye Concentration on BDST Model for Acid Blue

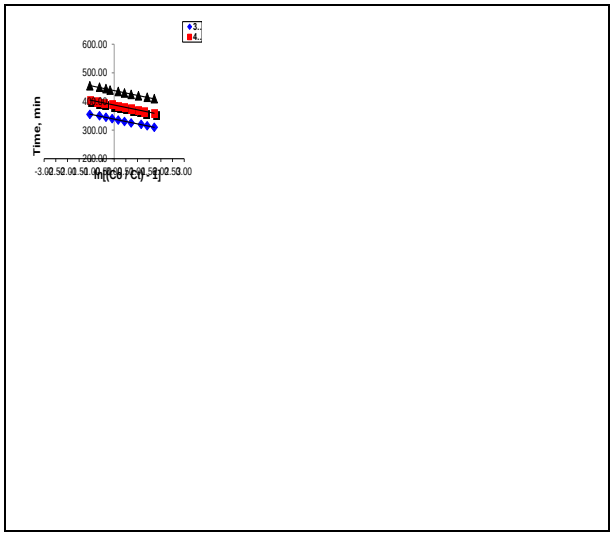

Fig. 5c: Effect of Bed Height on BDST Model for Acid Blue

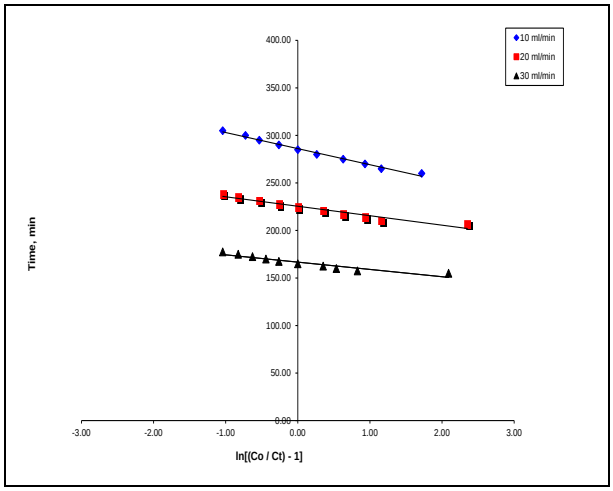

Fig. 5d: Effect of Flow Rate on BDST Model for Acid Blue

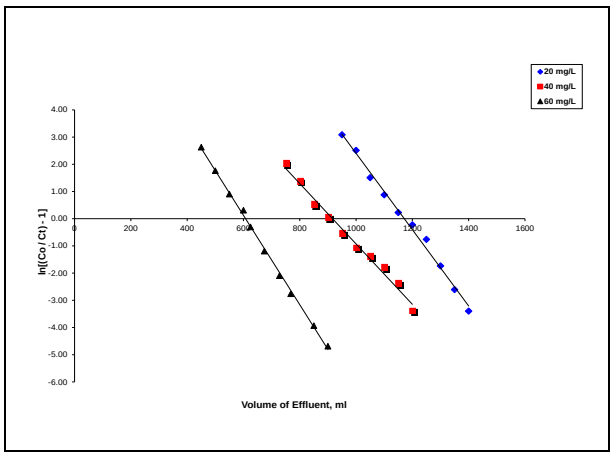

Fig. 6a: Effect of Initial Dye Concentration on Thomas Model for Acid Blue

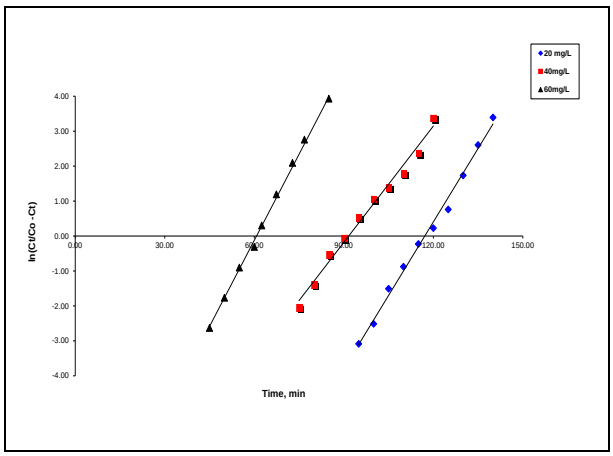

Fig. 7a: Effect of Initial Dye Concentration on Yoon & Nelson Model for Acid Blue

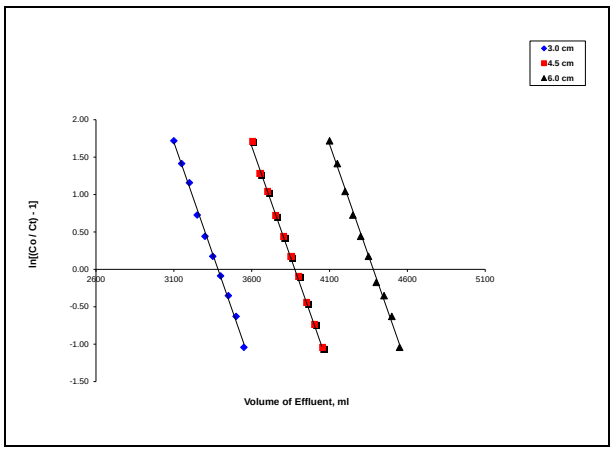

Fig. 6b: Effect of Bed Height on Thomas Model for Acid Blue

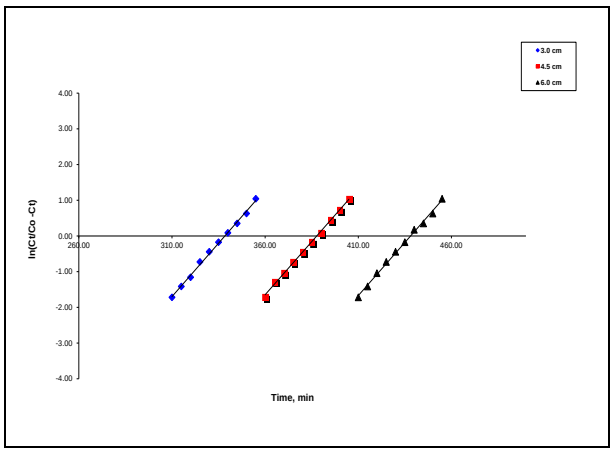

Fig. 7b: Effect of Bed Height on Yoon & Nelson Model for Acid Blue

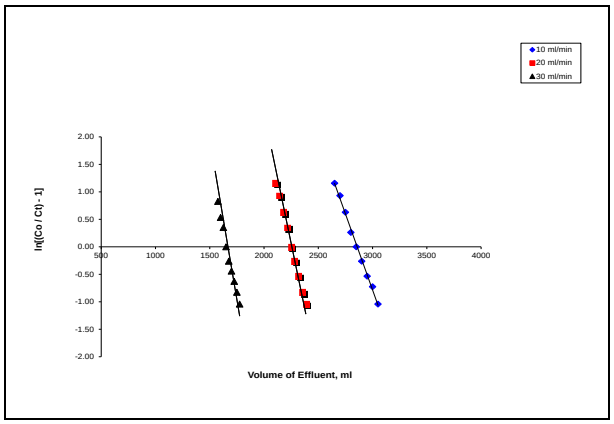

Fig. 6c: Effect of Flow Rate on Thomas Model for Acid Blue

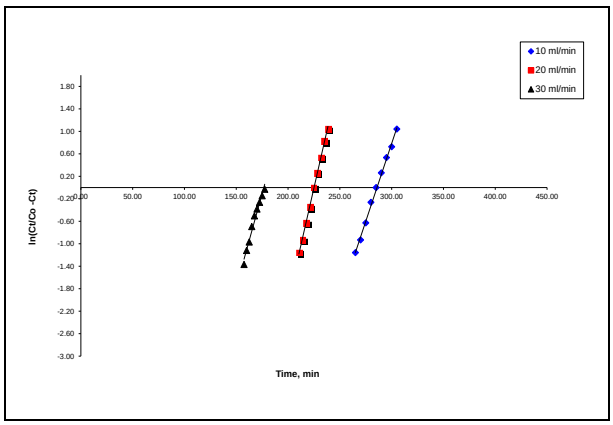

Fig. 7c: Effect of Flow Rate on Yoon & Nelson Model for Acid Blue

3.7 Applicability of Yoon-Nelson Model

If an adsorbent – adsorbate obeys Yoon-Nelson model, a linear trace is expected. For a plot of Time vs. $\ln[C_0/C_t - C_t]$, where, C_0 and C_t are initial effluent dye concentration and concentration of effluent at time, t, respectively.

The experiments were conducted with a view to examine the initial dye concentration, influence of bed height and influence of flow rate on the individual dye adsorption. Fig. 7a, 7b and 7c confirm the applicability of Yoon- Nelson model; the relevant data are given in the Table 1. The values of adsorptive capacity (N_0) obtained from each model indicates that initial dye concentration has same significant of the adsorptive capacity. Hence increase in initial dye concentration increases the adsorption capacity. It is evident from the result that the capacity per gram is higher only for lower bed height values hence, splitting into many beds will be better.

Table 1: Influence of Initial Dye Concentration on BDST, Thomas and Yoon- Nelson Models Parameters

Parameters	Values	BDST MODEL		THOMAS MODEL		YOON-NELSON MODEL	
		K, L/mg.min	No, mg/g	K_{TH} L/mg.min	No, mg/g	K_{YN}, L/min	$\mathcal{T}$, mg/g
Dye Con, mg/L	20	3.027	592.45	7.4×10^{-4}	561.72	0.147	369.8
	40	4.575	598.35	2.7×10^{-4}	514.49	0.111	588.5
	60	7.638	515.98	2.1×10^{-4}	510.62	0.124	635.3
Bed Height	3	2.205	532.00	1.35×10^{-4}	521.33	0.054	339.72
	4.5	2.174	524.43	1.32×10^{-4}	524.43	0.053	389.07
	6	2.187	527.59	1.33×10^{-4}	520.69	0.053	439.42
Flow Rate	10	2.127	527.09	1.28×10^{-4}	518.06	0.051	287.58
	20	3.524	542.74	4.05×10^{-4}	521.37	0.081	226.94
	30	5.545	562.88	9.24×10^{-4}	515.69	0.072	176.70

The adsorptive capacity of MWNTs obtained from fixed bed experiment for each model where higher than that of the value obtained by batch-mode contact experiments. It is evident from results that the rate of flow has considerable influence on dye removal when the flow rate is low, the breakthrough volume is high the slow flow rate is more effective compared with fast flow rate.

The adsorption capacity calculated based on BDST model has good agreement with the observed R^2 value; whereas, adsorption capacity calculated by Thomas and Yoon-Nelson model shows poor correlation co-efficient. In general, the BDST model describes adsorption capacity behavior of Acid Blue onto chosen adsorbent column more responsibility than Thomas and Yoon-Nelson model out of the three models tested. The chosen adsorbent-adsorbate system fits exceptionally well with BDST model with good coefficient of determination.

4. CONCLUSION

In the present study, MWNTs were prepared from *Rosmarinus officinalis* oil as a precursor on to Fe/Mo catalyst supported on silica at 650 ºC under N_2 atmosphere by spray pyrolysis process and characterized by Scanning Electron microscopy, Transmission Electron microscopy and Raman spectroscopy.

On the basis of the experimental results of the column experiments, the following conclusions can be drawn. First, MWNTs can be used as an adsorbent to removal AB 40 from solution. Furthermore, the adsorption was dependent on the bed depth, the influent AB 40 concentration and the flow rate. When the bed height decreased, the removal percentage decreased and the total weight of AB 40 adsorbed by MWNTs in the column also decreased. On the other hand, the maximum capacity of column was found to be about 343.59 mg AB 40 per gram of MWNTs adsorbents for the flow rate of 10 mL/ min, initial concentration of 60 mg/L and 6 cm bed height. Lastly, the behavior of the breakthrough curves can be defined by the Thomas model; this may mean that the internal and external diffusions are not the controlling steps in the adsorption process of the column. The BDST model showed good agreement with the experimental data and the high values of correlation coefficients (R^2 0.9646) obtained indicate the validity of the BDST model for the present column system.

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DECLARATION OF CONFLICTING INTERESTS

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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