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Low cost Sugarcane Bagasse Ash as an Adsorbent for Dye Removal from Dye Effluent

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***Abstract*—Sugar cane bagasse ash, an agricultural by-product, acts as an effective adsorbent for the removal of dyes from aqueous solution. Batch adsorption study was investigated for the removal of Acid Orange-II from aqueous solution. Adsorbents are very efficient in decolorized diluted solution. The effects of bed depth on breakthrough curve, effects of flow rate on breakthrough curve were investigated with the help of Thomas,Yoon-Nelson model .The removal of dyes at different flow rate (contact time),bed height by Sugarcane Bagasse Ash as an adsorbent has been studied. It is found that percent adsorption of dyes increases by decreasing flow rate from 2 lit/hr to 1 lit/hr, by increasing bed height from 15cm to 45cm.The result shows that, bagasse ash is a good adsorbent for dye effluent treatment.**

***Index Terms*—Sugarcane Bagasse Ash, dye, adsorption, effluent treatment, water pollution.**

I. Introduction

Dyes production industries and many others industries which used dyes and pigments generated wastewater, characteristically high in colour and organic content. Presently, it was estimated about 10,000 of different commercial dyes and pigments exists and over 7 x 10^5 tones are produced annually world wide [1].

Dyes are widely used in industries such as textile, rubber, paper, plastic, cosmetic etc. Among these various industries, textile ranks first in usage of dyes for coloration of fiber. The convectional wastewater treatment, which rely on aerobic biodegradation have low removal efficiency for reactive and other anionic soluble dyes. Due to low biodegradation of dyes, a convectional biological treatment process is not very effective in treating a dyes wastewater. It is usually treated with either by physical or chemical processes. However, these processes are very expensive and cannot effectively be used to treat the wide range of dyes waste [2].The adsorption process is one of the effective methods for removal dyes from the waste effluent. The process of adsorption has an edge over the other methods due to its sludge free clean operation and completely removed dyes, even from the diluted solution. Activated carbon (powdered or granular) is the most widely used adsorbents because it has excellent adsorption efficiency for the organic compound. But, commercially available activated carbon is very expensive. Furthermore, regeneration using solution produced small additional effluent while regeneration by refractory technique results in a 10-15% loss of adsorbents and its uptake capacity [3]. This had lead to further studies for cheaper substitutions. Nowadays, there is numerous number of low cost, commercially available adsorbents which had been used for the dye removal (Table 1).

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Properties of Acid orange-II

- CAS NO. - 633-96-5
- EINECS NO. - 211-199-0
- Formula -$HOC_{10}H_6N{=}NC_6H_4SO_3Na$
- Molecular weight - 350.32
- H.S. CODE - 3204.12
- Physical state - Yellow Powder
- Melting point - 164^0 C
- Solubility in water - Soluble (116 g/lit)
- FASTNESS - Light (3-4), Washing (4), Rubbing Wet (4-5), Rubbing Dry (3-4)
- NFPA RATINGS - Health: 1; Flammability: 0; Reactivity: 0
- Stability - Stable under ordinary conditions [11].

Structural formula of Acid orange – II

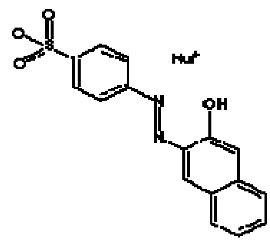


Fig 1.1 Structural formula for Acid orange-II

TABLE 1: Some Low cost materials for dyes removal from aqueous solution

Sr.No	Adsorbent(s)	Dye(s)	References
1.	Bamboo dust, coconut shell groundnut shell, rice husk	Methylene blue	[4]
2.	Silk cotton hull, coconut tree sawdust, sago waste, maize cob	Rhodamine-B, Congo red, methylene blue, methyl violet, malachite green	[2,5]
3.	Parthenium	Methylene blue,	[7]

	hysterophorus	malachite green	
4.	Rice husk	Malachite green	[12]
5.	Coir pith	Acid violet, acid brilliant blue, methylene blue, Rhodamine-B	[13,15]
6.	Orange peel	Acid violet 17	[16,20]
7.	Indian Rosewood	Malachite green	[20]
8.	Prosopic cineraria	Malachite green	[11,2]
9.	Banana and orange peels	Methyl orange, methylene blue, Rhodamine-B, congo red, methyl violet, acid black 10B	[19,17]
10	Giant duckweed	Methylene blue	[21]
11	Banana pith	Congo red, Rhodamine-B, acid violet, acid brilliant blue	[17]
12	Orange peel	Congo red, Rhodamine-B, procion orange	[10]
13	Carbonized coir pith	Acid violet, Rhodamine-B	[4]
14	Hardwood	Astrozone blue	[2]
15	Chitosan	Acid blue 25, basic blue 69	[9]
16	Mahogany sawdust, rice husk	Acid yellow 36	[14]
17	Biogas residual slurry	Congo Red, Rhodmine-B, acis violet,acid brilliant blue	[3]
18	Plum kernels	Basic Red 22, acid blue 25	[7]
19	Rice husk	Safranine,methylene blue	[18]

II. Experimental Programme

In the present study, bagasse fly ash (BFA) and wood ash have been utilized for the treatment of acid orange-II bearing aqueous solution. Experimental details of the study have been presented. This details include characterization of adsorbents, column studies etc.

A. Characterization of adsorbent

Physical-chemical characteristics of BFA & WA

Surface area(m^2/g)	205.96
Pore volume(cm^2/g)	0.115
Avg pore diameter(A^0)	19.38
Heating value(KJ/g)	7231.50
Bulk density(Kg/m^3)	97.35

Particle size analysis of (BFA & WA)

Sieve	%wt
>600	0.40
600-500	0.17
500-425	4.65
425-300	2.12
300-212	5.30
212-150	20.50
150-125	3.20
125-90	36.75
90-63	11.25
<63	15.65

Avg particle size = 130.52µm

Proximate analysis of (BFA & WA)

Characteristics	Value
Moisture (%)	5.10
Volatiles (%)	9.09
Ash (%)	35.58
Fixed carbon (%)	51.23

Ultimate analysis of (BFA & WA)

Element	Value
C (%)	61.560
H (%)	0.093
N (%)	3.235
S (%)	0.132

B. Column study

An acrylic column of 100 cm length and 2.54 cm internal diameter with 0.2cm wall thickness was used to contain the mixture of bagasse fly ash and wood ash as a fixed bed adsorber. A fine mesh was introduced at the bottom of the column over which a layer of ceramic beads was spread to prevent the escape of adsorbent. Acid orange –II was feed to the bed of BFA & Wood ash in up-flow mode to avoid channeling of effluent.

Here we used saline **tube** to control up-flow motion of solution from tank to column, which is carried out by difference in potential head .Also we provide four outlets at height of 15, 30, 45, 60 cm. A sample of treated effluent was collected periodically and analyzed for (Ct) by colorimeter. The flow through the tested column was continued until the acid orange- II concentration of column effluent approached 0.99, C_t / C_0, which indicate the exhaustion point (C_x). The curve of Ct / C_0 vs. volume treated between concentration at 10% breakthrough (Cb) and the exhaustion (Cx) is called the breakthrough curve.

C. Experimental set-up

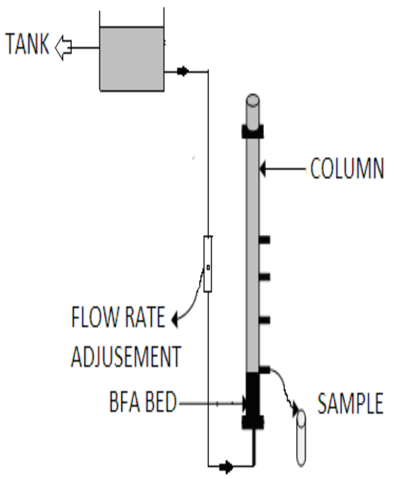


Fig. 2.1 Experimental set-up of adsorption Column

III. BREAK THROUGH CURVE MODELING

The performance of a packed bed is obtained through the concept of breakthrough curve. The time for breakthrough appearance and the shape of the breakthrough curve are important characteristics for determining the operation and dynamic response of an adsorption column. Again, successful design of an adsorption column requires prediction of the concentration–time profile from breakthrough curve for the effluent discharged from the column. In many cases, kinetics of adsorption in column has been tested for Bohart–Adams model. However, it has also been shown that BDST, Thomas and Yoon–Nelson models can sometimes provide a better description of the adsorption kinetics. So in this study, an attempt has been made to find out the best model describing the adsorption kinetics in column.

A. Thomas model

Thomas model is one of the most general and widely used models in the column performance theory. Thomas or reaction model is based on the assumption that the process follows Longmuir kinetics of adsorption–desorption with no axial dispersion. Further, it is derived with the assumption that the rate driving force obeys 2nd order reversible reaction kinetics. Thomas model also assumes a constant separation factor but is applicable to either favorable or unfavorable isotherm. The expression developed by calculates the maximum solid phase concentration of the solute on the sorbent and the adsorption rate constant for a continuous adsorption process in column. The linear zed form of the model is given as:

$$\ln\left[\left(\frac{C_0}{C_t}\right)-1\right]=\left(\frac{k_{Th}q_0m}{Q}\right)-\left(\frac{k_{Th}C_0V_{eff}}{Q}\right)$$

where *k*Th (mL/mg min) is the Thomas rate constant, *q*0 (mg/g) is the equilibrium adsorbate uptake and *m* is the amount of adsorbent in the column.

B. The Yoon–Nelson model

Yoon and Nelson have developed a relatively simple model addressing the adsorption and breakthrough of adsorbate gases with respect to activated charcoal. This 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 the linear zed model for a single component system is expressed as:

$$\ln\left[\frac{C_t}{C_0-C_t}\right]=k_{YN}t-\tau k_{YN}$$

here K_{YN} (min^{-1}) is the rate constant and is the time required for 50% adsorbate breakthrough.

C. The error analysis

In order to find out the best applicable model from the goodness of fit with the experimental values, it is necessary to study the data using error analysis. A number of error analysis methods such as the sum of the square of the error (SSE), the sum of the absolute error (SAE), have been used in the present study to find out the model which is best fit to the experimental observations.

The expressions for some error functions are as follows.

$$SSE=\sum_{i=1}^{n}(y_c-y_e)_i^2$$

$$SAE = \sum_{i=1}^{n} |y_c - y_e|_i$$

where *n* is the number of experimental data points, *yc* is the predicted (calculated) data and *ye* is the experimental data and *y* represents the ratio *Ct*/*C*0. The above statistical error expressions were applied to all the breakthrough curve model equations.

D. Application of Thomas Model

The experimental data were fitted to the Thomas model to determine the Thomas rate constant (k_{TH}) and maximum solid phase concentration (*q*0). The k_{TH} and *q*0 value were calculated by plotting ln(*C*0/*C*t -1) against *t* using values from the column experiments. From the regression coefficient (R^2) and other statistical parameters, it can be concluded that the experimental data fitted well to the Thomas model. The predicted uptake capacity and experimental uptake capacity along with k_{TH} and other statistical parameters are given in Table. The well fit of the experimental data on to the Thomas model indicate that the external and internal diffusion will not be the limiting step.

The figure shows the comparison of the experimental and predicted breakthrough curves for Dye removal using Bagasse ash according to Thomas Model.

E. Application Of The Yoon–Nelson Model

A simple theoretical model developed by Yoon–Nelson was applied to investigate the breakthrough behavior of Dye on Low cost Adsorbent. The values of K_{YN} and were estimated from the graph between ln(*Ct*/*C*0 -*C*t) versus *t* at different flow rates, Adsorbent Dosage. The values of τ was found to decrease with increase in flow rate. With increase in initial dye concentration, the K_{YN} values increased whereas the values showed a reverse trend. The values of K_{YN} and along with other statistical parameter are listed in Table. It can be seen that simulation of the whole breakthrough curve is effective with the Yoon–Nelson model at higher flow rate and at higher inlet concentration. From Table it can be seen that the theoretical uptake capacity, were very close to those predicted by the Yoon–Nelson model.

The figure shows the comparison of the experimental and predicted breakthrough curves for dye removal using Bagasse ash according to Yoon–Nelson model.

IV. Result and Discussion

A. Effect of bed depth on break through curve

Fig.**4.1, 4.2** shows the breakthrough curve for different BFA bed depth between 15 to 45 cm, at a flow rate of 1.0 and 2.0 lit/hr. The time required for the effluent to reach breakthrough concentration, t_b increased with increase in bed depth. This may be attributed to the increase in binding sites on the adsorbent. Although an increasing bed depth increases t_b , Very high bed depth is not useful for single column. The shape and gradient of the breakthrough curves were slightly different with the variable bed depth. As the bed height increases from the 15 cm to 45cm the curve changes their profile steep concave to flatter concave. The breakthrough curve of longer beds tended to be more gradual, meaning that the column was difficult to be completely exhausted . Here, breakthrough time is taken as time of operation at which the ratio of effluent to the inlet Acid orange –II concentration becomes 0.1 i.e. the effluent concentration gives the value of 10 mg/lit.

In the present study, the flow rate of outlet was unstable when the bed depth was to high due to higher flow resistance, resulting from tighter packing of the longer bed containing larger amount of BFA and wide size distribution. Since the treated effluent was not properly drawn of at the top of the packed bed higher than the 45 cm for the diameter of 2.54 cm, the optimum depth to diameter ratio of the column containing BFA should not be higher than 18 (45 cm/2.54 cm). Actually this ratio can be applied for the scale up of the column adsorber [5].

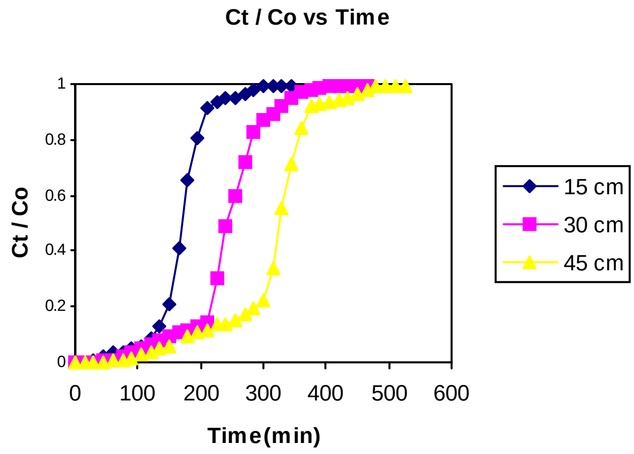


Fig. 4.1 Effect of bed height with respect to time on removal of Acid orange – II by BFA (C_0 = 100 mg/lit, flow rate = 1.0 lit/hr)

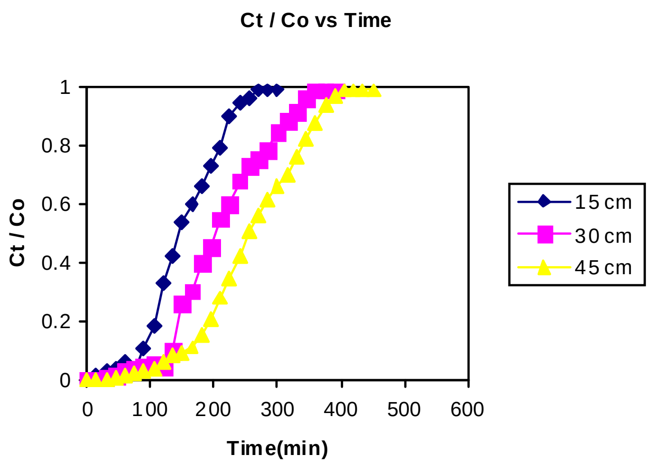


Fig. 4.2 Effect of bed height with respect to time on removal of Acid orange– II by BFA (C_0 = 100 mg/lit, flow rate = 2.0 lit/hr

B. Effect of flow rate on breakthrough curve

Fig. **4.3** shows the breakthrough profile for the adsorption of Acid orange –II removal in the continuous flow fixed column of 15 to 45 cm bed depth with BFA at room temperature. The flow rate was varied from 1.0 to 2.0 lit/hr while the inlet Acid orange –II concentration in the feed was held constant at 100 mg/lit. When the adsorption zone moves upwards and upper edge of this zone reaches the top of the column, the effluent concentration start to rise rapidly. This point is called breakthrough point, which indicate the t_b . Result shows that a decrease in the flow rate at constant bed depth increases the t_b,and therefore the V_b (volume of solution treated at breakthrough point), due to an increase in empty bed contact time (EBCT). Using a smaller flow rate, the front of the adsorption zone reaches the top of the column later, there by giving higher t_b . An increase in the flow rate appears to increase the sharpness of the breakthrough curve. These results indicates that as the flow rate increases the shape of the breakthrough curve drastically changes from S- shaped to that of downwardly concave shape. The curves exhibit a sharp leading edge and a broad trailing edge. The broadness of the trailing edge is most likely due to slow intra-particle diffusion within the pores of BFA.

As the flow rate through the bed increases, the depth of the adsorption zone increases and the time of the contact of the solution with adsorption zone decreases. In designing a column, the length of the adsorption zone represents the minimum bed depth needed to produced a low effluent Acid orange –II concentration this results suggest that low flow rate or longer contact time may required for Acid orange-II adsorption by column field BFA and Wood ash[5].

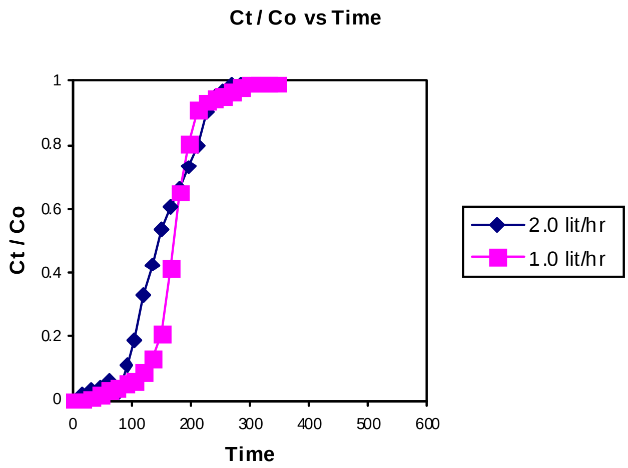
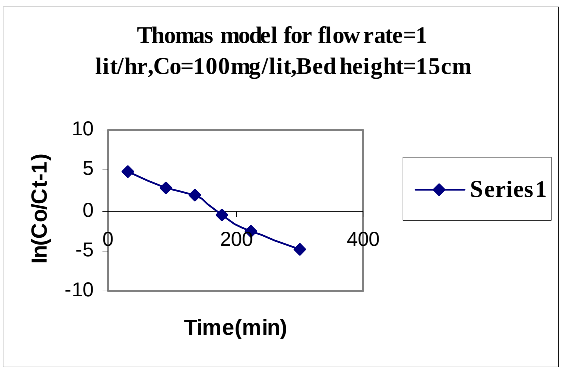


Fig. 4.3 Effect of flow rate with respect to time on removal of Acid orange– II by BFA (C_0 = 100 mg/lit, bed height =15 cm)

C. *Modeling*

1) *Thomas Model*

Plots for Comparison of the Experimental and Predicted breakthrough curves using Thomas model



For the above fig. we can draw the straight line passing through max.points we get following Straight line equation

y = -0.036x+8

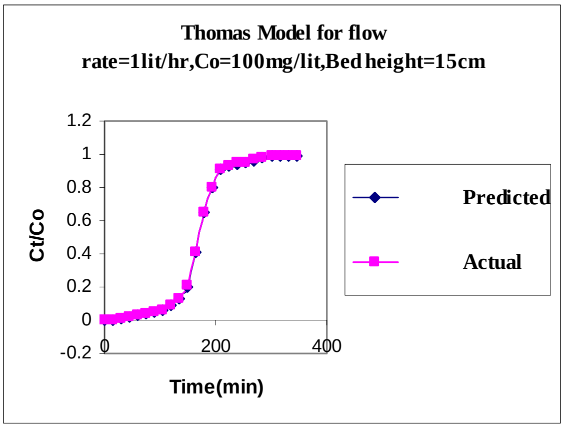
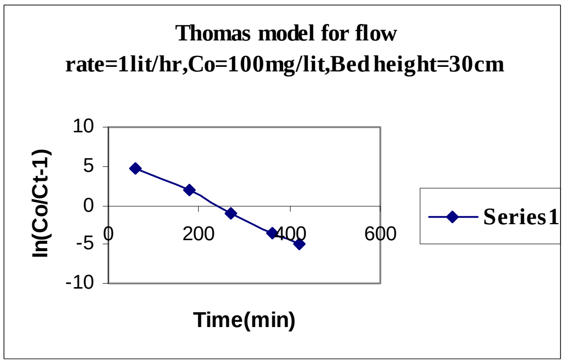


Fig-4.4 Thomas Model for Flow rate 1Lit/hr, Co=100mg/lit, Bed height=15cm



For the above fig. we can draw the straight line passing through max.points we get following Straight line equation

y = -0.027x+6

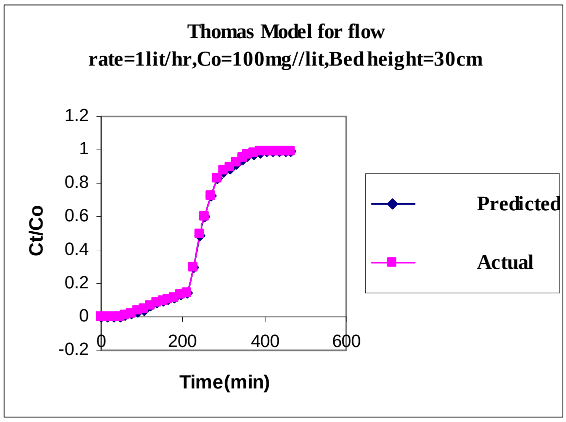
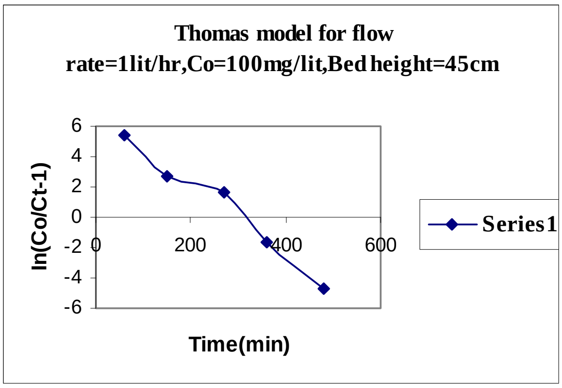


Fig-4.5 Thomas Model for Flow rate 1Lit/hr, Co=100mg/lit, Bed height=30cm



For the above fig. we can draw the straight line passing through max.points we get following Straight line equation

y = -0.023x+7

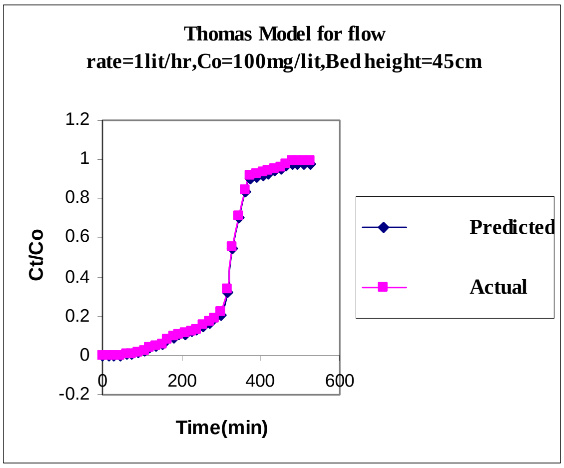
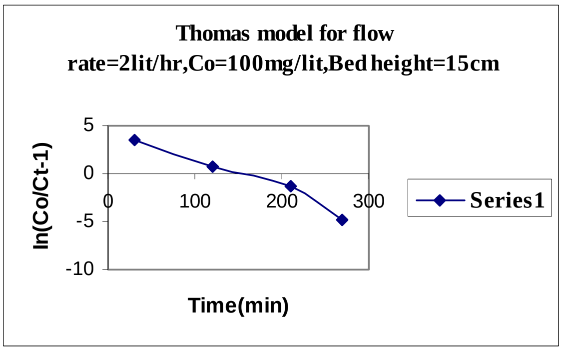


Fig-4.6 Thomas Model for Flow rate 1Lit/hr, Co=100mg/lit, Bed height=45cm



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y = -0.034x+6

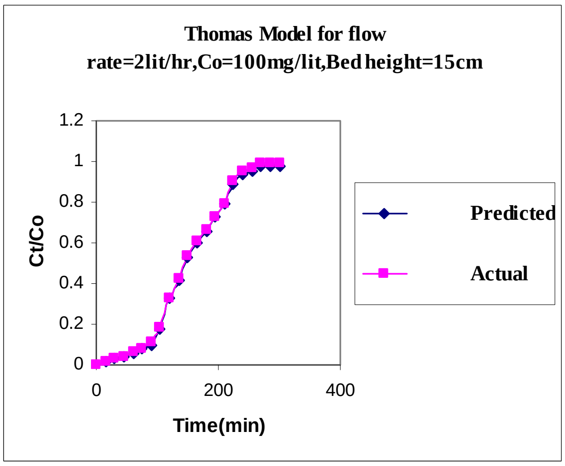
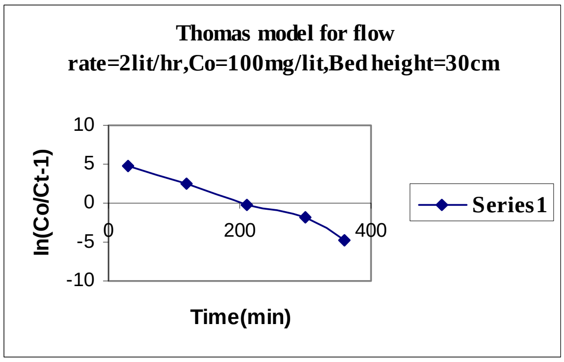


Fig-4.7 Thomas Model for Flow rate 2Lit/hr, Co=100mg/lit,Bed height=15cm



For the above fig. we can draw the straight line passing through max.points we get following Straight line equation

y = -0.023x+6

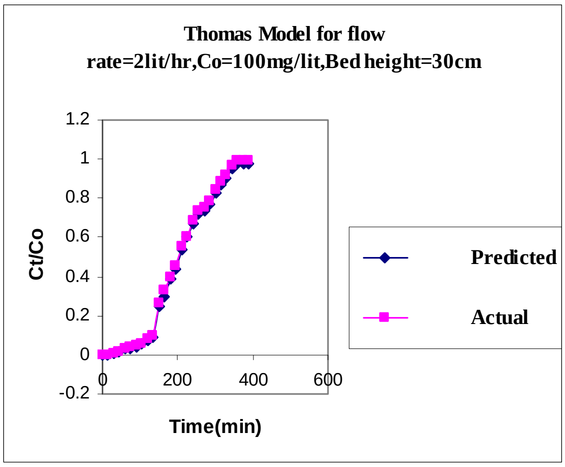
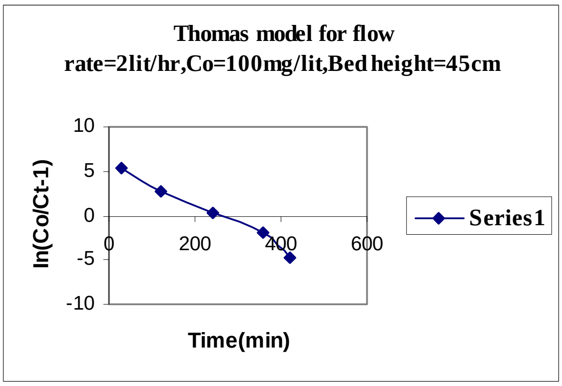


Fig-4.8 Thomas Model for Flow rate 2Lit/hr, Co=100mg/lit, Bed height=30cm



For the above fig. we can draw the straight line passing through max.points we get following Straight line equation

y=-0.022x+7

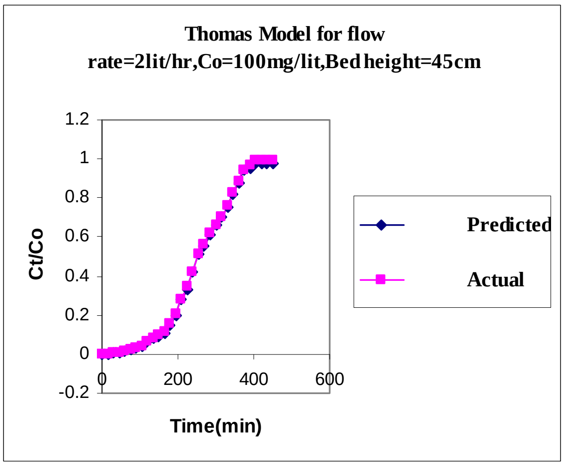


Fig-4.9 Thomas Model for Flow rate 2Lit/hr, Co=100mg/lit, Bed height=45cm

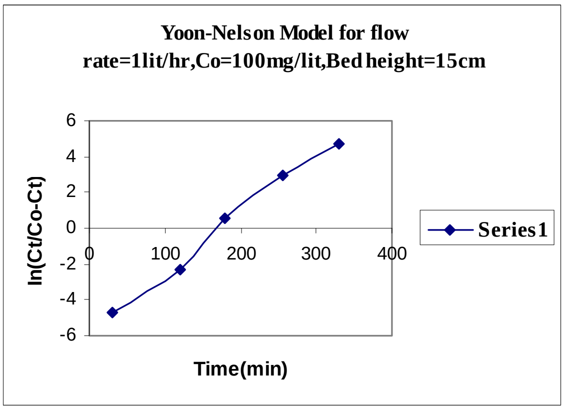
Thomas model for effect of Bed depth on break through curve

These fig.**4.4 to 4.9** shows the breakthrough curve for different BFA bed depth between 15cm to 45cm at a flow rate of 1.0 lit/hr & 2.0 lit/hr.The time required for effluent to reach breakthrough conc. tb, increases with increase in bed depth. The predicted value (Ct/Co) from model also match with the actual value (Ct/Co)

Thomas model for effect of Flow rate on break through curve

These fig. **4.4 to 4.9** shows the breakthrough curve for flow rate of 1 lit/hr & 2 lit/hr.An increase in flow rate appears to increase the sharpness of the breakthrough curve.Thease result indicates that as the flow rate increases the shape of the breakthrough curve drastically changes from S shaped to that of downwardly concave shape. The curves exhibit a sharp leading edge and broad tailing edge. The predicted value (Ct/Co) from model also match with the actual value (Ct/Co)

2) Yoon-Nelson model



For the above fig. we can draw the straight line passing through max.points we get following Straight line equation

y = 0.03x-8

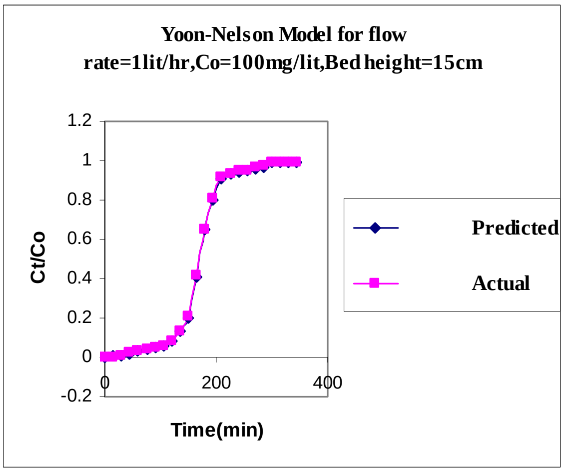
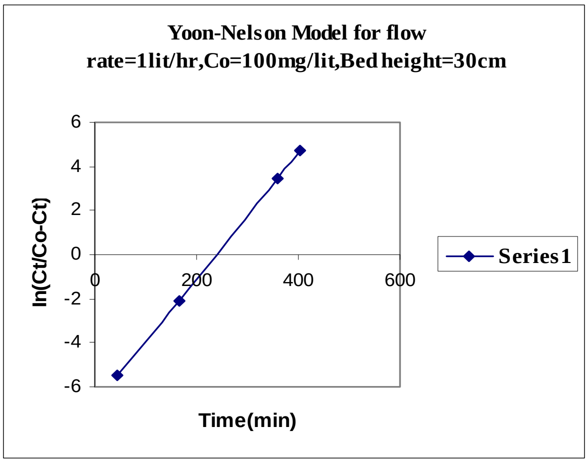


Fig-4.10 Yoon-Nelson Model for Flow rate 1Lit/hr, Co=100mg/lit, Bed height=15cm



For the above fig. we can draw the straight line passing through max.points we get following Straight line equation

y = 0.028x-12

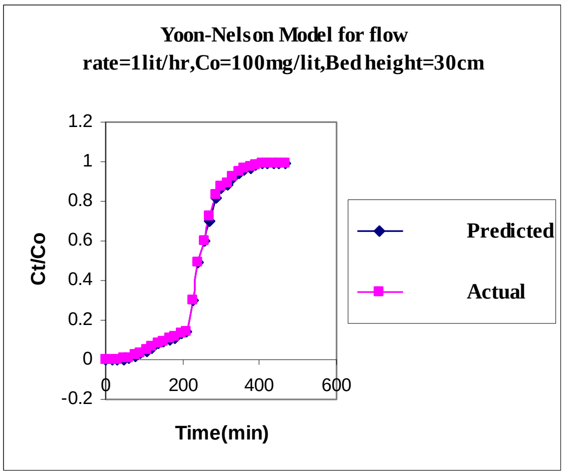
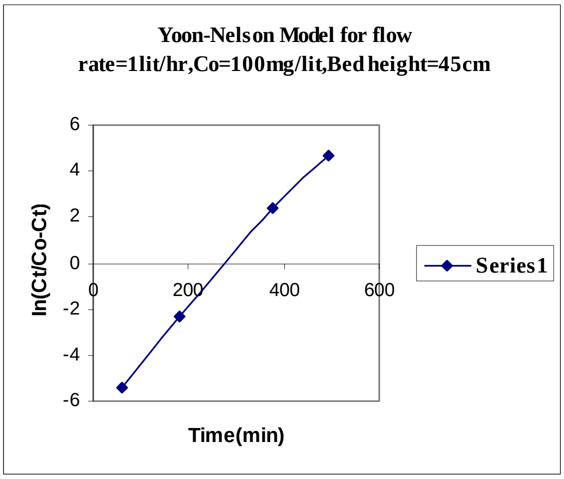


Fig-4.11 Yoon-Nelson Model for Flow rate 1Lit/hr, Co=100mg/lit, Bed height=30cm



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y = 0.023x-10

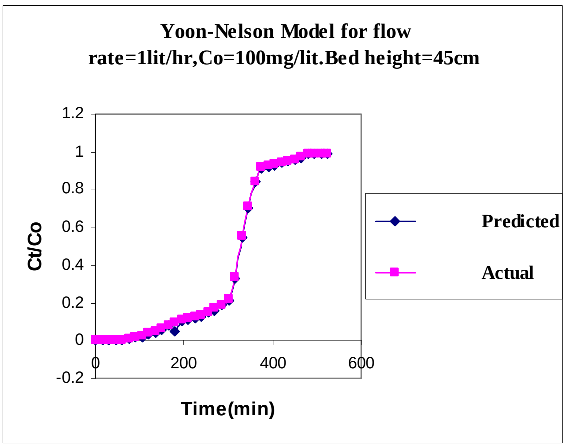
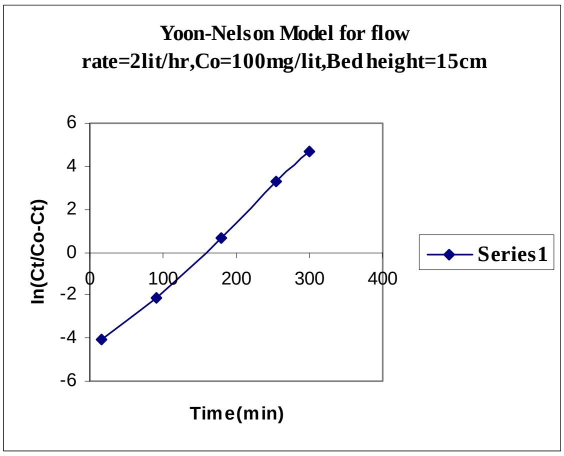


Fig-4.12 Yoon-Nelson Model for Flow rate 1Lit/hr, Co=100mg/lit, Bed height=45cm



For the above fig. we can draw the straight line passing through max.points we get following Straight line equation

y = 0.03x-5

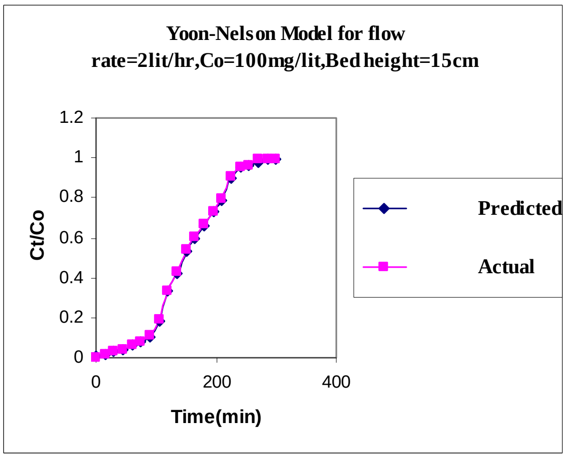
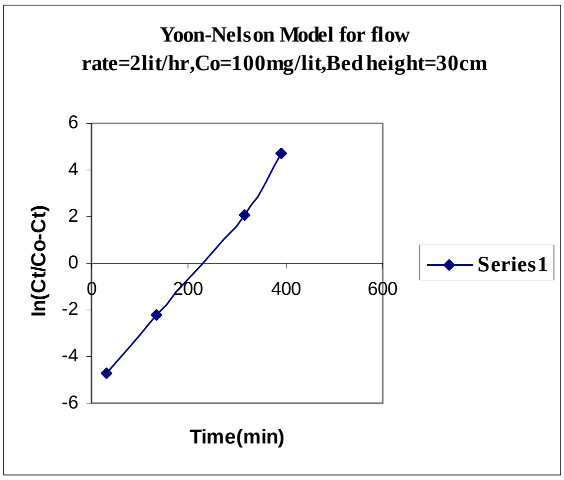


Fig-4.13 Yoon-Nelson Model for Flow rate 2Lit/hr, Co=100mg/lit, Bed height=15cm



For the above fig. we can draw the straight line passing through max.points we get following Straight line equation

y = 0.026x-6

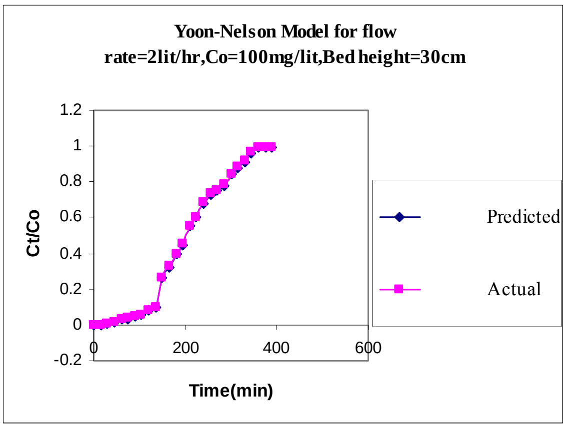
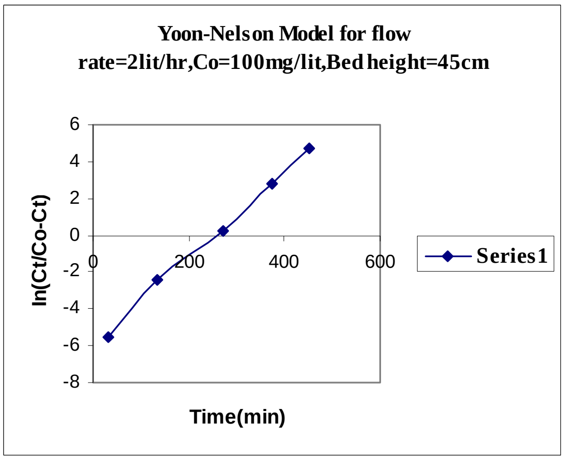


Fig-4.14 Yoon-Nelson Model for Flow rate 2Lit/hr, Co=100mg/lit, Bed height=30cm



For the above fig. we can draw the straight line passing through max.points we get following Straight line equation

y = 0.024x-8.2

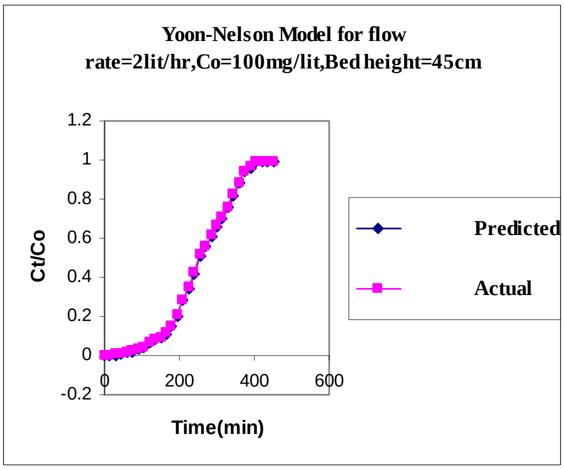


Fig-4.15 Yoon-Nelson Model for Flow rate 2Lit/hr, Co=100mg/lit, Bed height=45cm

Yoon-Nelson model for effect of Bed depth on break through curve

These fig. **4.10 to 4.15** shows the breakthrough curve for different BFA bed depth between 15cm to 45cm at a flow rate of 1.0 lit/hr & 2.0 lit/hr.The time required for effluent to reach breakthrough conc. tb, increases with increase in bed depth. The predicted value (Ct/Co) from model also match with the actual value (Ct/Co)

Yoon-Nelson model for effect of Flow rate on break through curve

These fig.**4.10 to 4.15** shows the breakthrough curve for flow rate of 1 lit/hr & 2 lit/hr.An increase in flow rate appears to increase the sharpness of the breakthrough curve.Thease result indicates that as the flow rate increases the shape of the breakthrough curve drastically changes from S shaped to that of downwardly concave shape. The curves exhibit a sharp leading edge and broad tailing edge. The predicted value (Ct/Co) from model also match with the actual value (Ct/Co)

V. Conclusion

The removal of acid orange-II from aqueous solution by using sugarcane bagasse has been investigated for different variables viz flow rate, adsorbent dosage.

It is found that percent adsorption of dyes increases by decreasing flow rate from 2 lit/hr to 1 lit/hr,by increasing bed height from 15cm to 45cm.The result shows that, bagasse ash is a good adsorbent for removal of acid orange –II from dye effluent. The effects of bed depth on breakthrough curve, effects of flow rate on breakthrough curve were investigated with the help of Thomas, Yoon-Nelson model. For Break through curve the predicted value (Ct/Co) from model also match with the actual value or experimental value (Ct/Co)

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