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# Modeling of Fixed Bed Column Studies for Adsorption of Azo Dye on Chitosan Impregnated with a Cationic Surfactant

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**Abstract:** Removal of diazo dye Brilliant Black BN from aqueous solution was studied by conducting adsorption in fixed bed column using chitosan beads impregnated with a cationic surfactant Cetyl Trimethyl Ammonium Bromide. Effect of flow rate, bed height and initial dye concentration were investigated. Maximum bed capacity, percentage dye removal and equilibrium dye uptake were determined and break through curves were plotted. Percentage dye removal increased with decrease in flow rate and increase in bed height. Maximum bed capacity of 6.80 mg was obtained at a flow rate of 0.8 ml/min, bed height of 8 cm and initial dye concentration of 100 ppm. Data from column studies were fitted to three well established column models, Thomas model, Adams-Bohart model and Yoon-Nelson model. The experimental data were in good agreement with theoretical results. The study revealed the applicability of chitosan in fixed bed column for removal of azo dyes.

**Key words:** Cationic surfactant, Chitosan Beads, Diazo dye, Fixed Bed Column Studies, Thomas Model, Adams-Bohart model, Yoon-Nelson Model

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## 1. INTRODUCTION

Water pollution is a major problem faced by the world today. It is one of the leading cause of death and diseases all over the world. This form of environmental degradation occurs when pollutants are directly or indirectly discharged into water bodies without adequate treatment to remove harmful compounds. The textile industry is one of the largest polluters in the world. The World Bank estimates that almost 20% of global industrial water pollution comes from the treatment and dyeing of textiles. Today there are ten thousand dyes available commercially and seven lakh tones of dye is produced annually [1]. Azo dyes represent 60 % of all dyes used in food and textile industries. Azo dyes are synthetic colors which contain azo group, -N=N- in their structure. The aromatic side group around the azo bond helps to stabilize the azo group. Aromatic azo compounds are usually stable and produce strong colors. The textile industry is the largest consumer of dye stuffs. During the coloration process a large percentage of the synthetic dye does not bind and is lost to the waste stream [2]. Approximately 10-15% dyes are released into the environment during dyeing process making the effluent highly colored and aesthetically unpleasant. Dyes can be transported easily through sewers and water bodies like rivers because they are designed to have high water solubility. They are very difficult to remove because of their complex structures. Most of the dyes undergo degradation to form products that are carcinogenic and even mutagenic. Dyes are always manufactured with the property to resist degradation by sunlight and detergents. To protect environment from dyes, removal of dyes from effluent is very important. At present there are many methods for dye removal. It can be divided into physical, chemical and biological [3]. Biological processes using fungi and bacteria is cost effective but the long growth cycle is a disadvantage. Chemical methods like coagulation, flocculation, and oxidation and rapid and highly efficient on large scale. The major drawback of chemical process is the requirement of chemicals. It was reported that adsorption is the best process for removal of contaminants from wastewater [3]. The choice of adsorbent is the most important factor in adsorption. It should be cost-effective, biodegradable and reusable. Chitosan, a linear biopolymer of glucosamine, exhibits a high adsorption capacity towards many classes of dyes especially anionic dyes because of its high amino and hydroxyl functional group content [4]. Though chitosan has been proved to be effective in adsorption, the adsorption capacity of chitosan has not been realized to a satisfying level because chitosan powder and flakes crumbles and swells and because of this, it is very difficult to pack chitosan in adsorption column [5]. To overcome these difficulties, chitosan can be modified into beads and the adsorption capacity of chitosan can be increased. Chemical modifications were proposed to improve mechanical strength and chemical stability of chitosan in acidic media.

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They may also increase its resistance to biochemical and microbiological degradation [6]. In our previous work, chitosan beads impregnated with a cationic surfactant Cetyl Tri methyl Ammonium Bromide (CTAB) has shown high adsorption capacity for the azo dye Brilliant Black BN (BBN). As batch studies cannot be applied to most of the treatment systems, fixed bed column studies were conducted to study the effect of flow rate, bed height and initial dye concentration. The modeling of fixed bed column experiment was carried out to predict the performances on the basis of the experimental data and to scale up the same with other systems without further experimental run. In the present work, adsorption data from fixed bed column studies were analyzed using Thomas model, Adams-Bohart model and Yoon-Nelson model.

## 2. MATERIALS AND METHODS

### 2.1. Materials

Adsorbent: chitosan (90% de acetylated) was purchased from Marine Biotech Ltd, Kerala.

Reagents and chemicals: Acetic acid (Fisher Scientific), NaOH (Fisher Scientific), CTAB (Cetyl Tri methyl Ammonium Bromide, S.D.Fine Chem Ltd), Acetone (Qualigens) and HCl (RFCL Ltd) and Briliiant Black BN were purchased locally.

### 2.2. Preparation of Chitosan Beads Impregnated with CTAB

1% (wt/v) CTAB solution was prepared by dissolving 1 gm CTAB in 100 ml distilled water. 0.01%, 0.02%, 0.03% and 0.04% CTAB chitosan beads were prepared by dissolving required amount of CTAB solution to 2 gm chitosan. The volume was made up to 60 ml using 5% (v/v) acetic acid. The solution was stirred in a magnetic stirrer for twenty minutes. After stirring, solution was added drop wise to 500 ml of 0.5 M NaOH using syringe. Beads werewashed thoroughly with distilled water and stored in distilled under used.

### 2.3. Fixed Bed Column Studies

Chitosan beads modified with CTAB were packed in a column made of glass (Borosil). The internal diameter of the column was 1 cm and height was 60 cm. The dye solution to be treated was stored in an overhead tank. The solution was made to flow under gravity. Control valves were used at the inlet and outlet to control the flow rate. Effect of flow rate, bed height and initial dye concentration were investigated. To study the effect of inlet flow rate, column was packed with CTAB impregnated chitosan beads to a height of 6 cm (5.23 gm). Experiments were conducted, at 0.8 ml/min, 1ml/min and 1.5 ml/min and initial dye concentration was fixed at 20 ppm. To investigate the effect of be height, experiment was conducted at three different bed heights of 4 cm (3.48 gm), 6 cm (5.23 gm) and 8 cm (6.96 gm). Inlet flow rate was fixed at 0.8 ml/min with the help of control valve and inlet dye concentration was fixed at 20 ppm. To study the effect of initial dye concentration, column was packed with CTAB impregnated chitosan beads to a height of 6cm (5.23 gm) and dye solution of required concentration (20 ppm, 50 ppm and 100 ppm) was made to flow through the column at a rate of 0.8 ml/min. For all the experiments pH of dye solution was fixed at 4. Dye solution was collected after every 10 minutes and concentration of dye was determined using UV spectrophotometer.

The effluent volume was calculated using the following equation:

$$V_{eff} = Qt_{total} \qquad (1)$$

Where, $V_{eff}$ is effluent volume collected, ml; Q is volumetric flow rate, ml/min; $t_{total}$ is total flow time, min.

The maximum bed capacity for a given flow rate and feed concentration is given by the following equation:

$$q_{total} = \frac{Q\int C_{ad}\,dt}{1000} \qquad (2)$$

Where, $q_{total}$ is maximum bed capacity, mg; Q is inlet flow rate, ml/min; $C_{ad}$ is adsorbed dye concentration, ppm. The value of integral is obtained from the area under the curve of adsorbed dye concentration versus time.

The total amount of dye sent to the column is given by the following equation:

$$M_{total} = \frac{C_0 Qt_{total}}{1000} \qquad (3)$$

Where, $M_{total}$ is total amount of dye sent to the column, gm; $C_0$ is initial dye concentration, ppm; Q is volumetric flow rate, ml/min; $t_{total}$ is total flow time, min.

Total percentage of dye removal is given by the following equation:

$$\%\,\mathrm{Re}\,moval = \frac{q_{total}}{M_{total}}100$$

(4)

Where, $q_{total}$ is maximum bed capacity, mg; $M_{total}$ is total amount of dye sent to the column, mg.

Equilibrium dye uptake in the column is given by the following equation:

$$q_{eq(xp)} = \frac{q_{total}}{x}$$

(5)

Where, $q_{eq(exp)}$ is equilibrium dye uptake, mg/gm; x is amount of chitosan beads in the column, gm.

### 2.4. Modeling of Fixed Bed Column Studies

Data from lab scale experiments can be used as the basis for the design of full scale column operations. Many models have been proposed for the evaluation of efficiency and applicability of column models for operations at industrial level. To design a column adsorption operation, prediction of break through curve and adsorbent capacity for the required adsorbate under given set of operating conditions is necessary. In the present work, adsorption data from fixed bed column studies were analyzed using Thomas model, Adams -Bohart model and Yoon-Nelson model.

Thomas model is based on the mass transfer model which assumes that dye migrates from the solution to the film around the particle and diffuses through the liquid film to the surface of adsorbent. This is followed by intraparticle diffusion and adsorption on active site. Linear form of Thomas model for adsorption is:

$$\ln(\frac{C_o}{C_t} - 1) = \frac{K_{TH} q_e x}{Q} - K_{TH} C_o t$$

(6)

Where, $C_o$ is initial dye concentration, ppm; $C_t$ is effluent dye concentration at time t; ppm $K_{TH}$ is Thomas model constant, L/min.mg; $q_e$ is prediction adsorption capacity, mg/gm.

x is mass of adsorbent, gm; Q is inlet flow concentration, ml/min. The value of $K_{TH}$ and $q_e$ are determined from slope and intercept of a plot of ln ($C_0/C_t$ -1) versus t.

Adams-Bohart model assumes that the rate of adsorption is proportional to the residual concentration of the adsorbent and concentration of adsorbing species. This model is used for describing the initial part of the break through curve. Linear form of Adams- Bohart model is given by the following equation:

$$\ln(\frac{C_t}{C_0}) = K_{AB} C_0 t - \frac{K_{AB} N_0 Z}{U_0}$$

(7)

Where, $C_0$ is initial dye concentration, ppm; $C_t$ is concentration of effluent at time t, ppm; Z is bed depth, cm $N_0$ is maximum dye uptake capacity per unit volume of adsorbent column, mg/L; $U_0$ is linear velocity of influent dye solution, cm/min; $K_{AB}$ is Adams-Bohart rate constant, L/mg.min, The values of $K_{AB}$ and $N_0$ are determined from the slope and intercept of ln ($C_t/C_o$) versus t.

The main aim of Yoon-Nelson model is to predict the time of column run before regeneration or replacement of column becomes necessary. The model is a very simple way to represent the break through curve. The major advantage of using this model is that it requires no detailed data concerning the type of adsorbent, characteristics of adsorbate and physical properties of adsorbent bed. This model assumes 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. According to this model, the amount of dye adsorbed in a fixed bed is half of the total dye entering the adsorbent bed within time period 2τ, where τ is the time required for 50 % break through. Linear form of Yoon-Nelson model is given below:

$$\ln(\frac{C_t}{C_0 - C_t}) = K_{YN} t - K_{YN} \tau$$

(8)

Where, $C_0$ is initial dye concentration, ppm; $C_t$ is dye concentration at time t, ppm; t is flow time, min.; τ is time required for 50 % breakthrough, min; $K_{YN}$ is Yoon-Nelson rate constant, 1/min. The values of KYN and τ are determined from the slope and intercept of ln ($C_t$/ ($C_0$-$C_t$)) versus t.

## 3. RESULTS AND DISCUSSION

### 3.1. Effect of Inlet Flow Rate on Adsorption

On varying the inlet flow rate from 0.8 ml/min to 1.5 ml/min, the following trend was observed on break through curve.

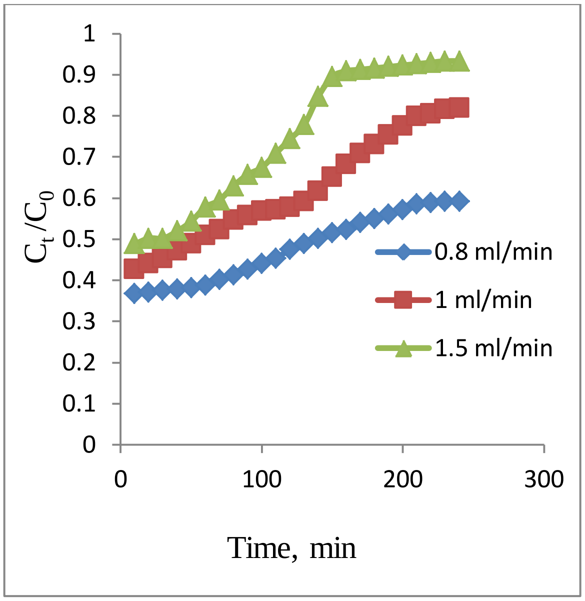

**Fig 1:** Effect of inlet flow rate on break through curve

The above plot shows that faster break through occurred at higher flow rate. At lower flow rate, there was sufficient time for the dye solution to get adsorbed on adsorbent. Higher dye removal occurred at lower flow rates for both dyes. The break through curve became steeper and shifted to origin at higher flow rate. At higher flow rate, it will take more time for the bed to get saturated. The parameters obtained from effect of inlet flow rate are listed in the table below.

TABLE 1

Effect of inlet flow rate on adsorption

| Flow Rate (ml/min) | $q_{total}$ (mg) | $q_{eq(exp)}$ (mg/gm) | $M_{total}$ (mg) | % Dye Removal | $V_{eff}$ (ml) |
|---|---|---|---|---|---|
| 0.8 | 1.92 | 0.36 | 3.84 | 50.00 | 192 |
| 1 | 1.75 | 0.32 | 4.8 | 36.40 | 240 |
| 1.5 | 1.73 | 0.26 | 7.2 | 24.00 | 360 |

The above table shows that the total adsorption capacity of the bed, $q_{total}$ decreased with increase in flow rate. At higher flow rate, residence time of solute in the bed was less. The solute left the column before equilibrium was reached. The percentage dye removal also decreased with increase in flow rate. Higher adsorption was observed at lower flow rate.

### 3.2. Effect of Bed Height on Adsorption

The effect of bed height on adsorption by varying the bed height from 4 cm to 6 cm is shown in the following figure.

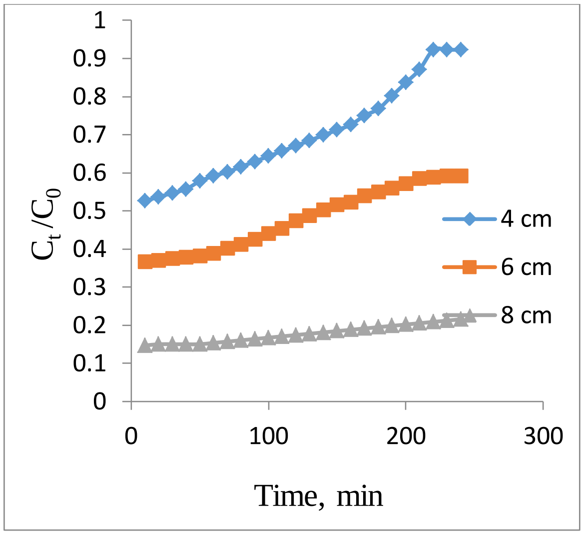

**Fig 2**: Effect of bed height on breakthrough curve

As the bed height increased, dye solution had more time to contact with the adsorbent. This resulted in higher dye removal. This resulted in lower dye concentration in the effluent. From the above figure, it can be observed that the slope of the breakthrough curve decreased with increase in bed height, which resulted in a higher mass transfer zone. The break through curve was steeper at lower bed height. The column parameters obtained from effect of bed height is listed in the table below.

TABLE 2

Effect of bed height on adsorption

| Bed Height (cm) | $q_{total}$ (mg) | $q_{eq(exp)}$ (mg/gm) | $M_{total}$ (gm) | % Dye Removal | $V_{eff}$ (ml) |
|---|---|---|---|---|---|
| 4 | 1.11 | 0.31 | 3.84 | 28.95 | 192 |
| 6 | 1.92 | 0.36 | 3.84 | 50.00 | 192 |
| 8 | 3.02 | 0.43 | 8.84 | 78.82 | 192 |

The total adsorption capacity of the bed increased with increase in bed height. At higher bed depth, more sites were available for adsorption and this resulted in higher dye removal.

### 3.3. Effect of initial Dye Concentration on Adsorption

Effect of initial dye concentration was studied by conducting the experiment at 20 ppm, 50 ppm and 100 ppm. The following trend was observed with increase in dye concentration.

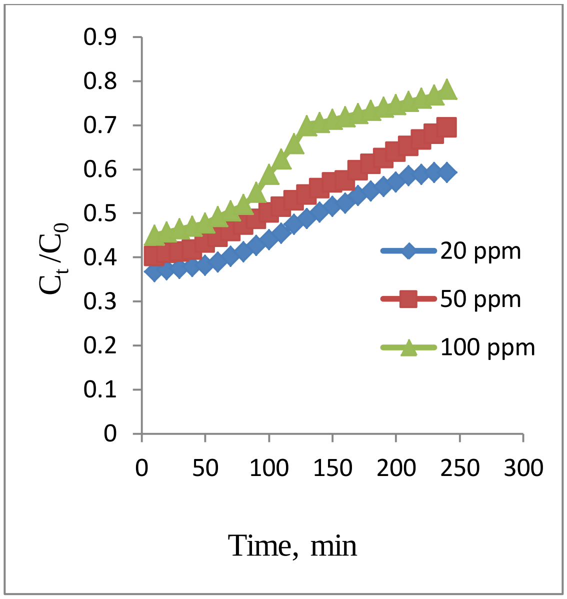

**Fig 3**: Effect of initial dye concentration on break through curve

It can be seen that, at lower dye concentration, the break through curves are dispersed. With increase in dye concentration, break through curves became sharper. The above graph demonstrates that, change in concentration gradient affects saturation rate and reduces break through time. This can be explained by the fact that, more adsorption sites will be covered with increase in dye concentration. The larger the concentration of dye, steeper is the break through curve. With increase in dye concentration, the driving force for mass transfer will increase. This resulted in a decreased adsorption zone. The column parameters obtained from effect of initial dye concentration are given in the table below.

TABLE 3

Effect of initial dye concentration on adsorption

| Conc of dye (ppm) | $q_{total}$ (mg) | $q_{eq(exp)}$ (mg/gm) | $M_{total}$ (mg) | % Dye Removal | $V_{eff}$ (ml) |
|---|---|---|---|---|---|
| 20 | 1.92 | 0.36 | 3.84 | 50 | 192 |
| 50 | 4.26 | 0.81 | 9.60 | 44.40 | 192 |
| 100 | 6.80 | 1.24 | 19.20 | 35.50 | 192 |

The above table indicates that with increase in initial dye concentration, the adsorption capacity of the bed increased. But percentage dye removal decreased with increase in concentration.

## 3.4. Modelling of Fixed Bed Column

Fixed bed adsorption data were analyzed using Thomas model, Adams- Bohart model and Yoon –Nelson Model.

### 3.4.1. Thomas model

To determine maximum adsorption capacity $q_{e(max)}$ and kinetic coefficient $K_{TH}$, experimental data were fitted to equation (6). The corresponding model parameters determined from the linear plot (figure not shown) are summarized in the following table.

TABLE 4

Thomas Model Parameters Using Linear Regression Analysis under Various Operating Conditions for BBN

| Q (ml/min | H (cm) | Co (ppm) | $q_{e(max)}$ (mg/gm) | $K_{TH}$ L/min..mg | $q_{eq(exp)}$ (mg/gm) |
|---|---|---|---|---|---|
| 0.8 | 6 | 20 | 0.43 | $2.35 \times 10^{-4}$ | 0.36 |
| 1 | 6 | 20 | 0.23 | $4.1 \times 10^{-4}$ | 0.32 |
| 1.5 | 6 | 20 | 0.16 | $6.9 \times 10^{-4}$ | 0.26 |
| 0.8 | 4 | 20 | 0.12 | $4.95 \times 10^{-4}$ | 0.31 |
| 0.8 | 8 | 20 | 1.89 | $1.1 \times 10^{-4}$ | 0.43 |
| 0.8 | 6 | 50 | 0.73 | $1.1 \times 10^{-4}$ | 0.81 |
| 0.8 | 6 | 100 | 0.74 | $7.3 \times 10^{-5}$ | 1.24 |

The above table indicates that the experimental adsorption capacities and the adsorption capacities determined using Thomas model are almost same. So, the experimental data are in good agreement with the theoretical results. It can be observed that with increase in flow rate, the maximum adsorption capacity decreased and coefficient $K_{TH}$ decreased. This is because the residence time of solute in the bed was less. The value of $q_{e(max)}$ increased with increase in bed height and corresponding $K_{TH}$ values decreased. This is because, at higher bed heights, more reactive sites were available. As concentration of dye increased, $q_{e(max)}$ increased and $K_{TH}$ decreased. This is because, with increase in concentration, the driving force for adsorption increased.

### 3.4.2. Adams-Bohart model

The values of adsorption capacity of the adsorbent, $N_0$ and kinetic constant of the model, $K_{AB}$ determined by linear regression analysis are listed in table 5. The results show that the adsorption capacity $N_0$ decreased with increase in flow rate. The values of corresponding coefficients $K_{AB}$ increased. The decrease in adsorption capacity is because of the lower residence time of solute in the column. As the bed height increased, the adsorption capacity increased. The values of $K_{AB}$ decreased. The adsorption capacity increased with increase in dye concentration.

TABLE 5

Adams-Bohart Model Parameters Using Linear Regression Analysis under Various Operating Conditions for BBN

| Flow Rate (ml/min) | Bed Height (cm) | Dye Conc (ppm) | $N_0$ (mg/gm) | $K_{AB}$ (L/min.mg) | $R^2$ |
|---|---|---|---|---|---|
| 0.8 | 6 | 20 | 1.49 | $1.2\times10^{-4}$ | 0.92 |
| 1 | 6 | 20 | 1.23 | $1.5\times10^{-4}$ | 0.98 |
| 1.5 | 6 | 20 | 1.19 | $1.65\times10^{-4}$ | 0.98 |
| 0.8 | 4 | 20 | 1.40 | $1.25\times10^{-4}$ | 0.98 |
| 0.8 | 8 | 20 | 2.78 | $9\times10^{-5}$ | 0.99 |
| 0.8 | 6 | 50 | 3.23 | $5\times10^{-5}$ | 0.99 |
| 0.8 | 6 | 100 | 5.03 | $2.8\times10^{-5}$ | 0.92 |

### 3.4.3. Yoon-Nelson model

Time required for 50 % break through was determined using Yoon-Nelson method. The values of $\tau$ and $K_{YN}$ determined by fitting the experimental data to equation (8) are summarized in table 6.

TABLE 6

Yoon-Nelson Model Parameters Using Linear Regression Analysis under Various Operating Conditions for BBN

| Flow Rate (ml/min) | Bed Height (cm) | Dye Conc (ppm) | $\tau$ (min) | $K_{YN}$ ($min^{-1}$) | $R^2$ |
|---|---|---|---|---|---|
| 0.8 | 6 | 20 | 143.77 | 0.0047 | 0.98 |
| 1 | 6 | 20 | 60.52 | 0.0082 | 0.97 |
| 1.5 | 6 | 20 | 31.23 | 0.0143 | 0.95 |
| 0.8 | 4 | 20 | 29.00 | 0.0099 | 0.98 |
| 0.8 | 8 | 20 | 823.68 | 0.0022 | 0.99 |
| 0.8 | 6 | 50 | 380.00 | 0.0025 | 0.99 |
| 0.8 | 6 | 100 | 295.53 | 0.0028 | 0.95 |

The above results show that as flow rate increased, the time required for 50 % break through decreased. This was due to the lesser residence time of solute in the column. For both dyes, the Yoon-Nelson rate constant increased with increase in flow rate. The time required for 50 % break through increased with increase in bed height. At higher bed depth, more adsorption sites were available and break through time decreased. With increase in initial dye concentration, the time required for 50 % break through decreased. At higher dye concentration, the driving force for adsorption increased. This resulted in longer time for the bed to get saturated.

## 4. CONCLUSION

In the present work, removal of hazardous diazo dye Brilliant Black BN in fixed bed column was investigated. CTAB impregnated chitosan beads were used as adsorbent. Fixed bed column studies were conducted in a column of internal diameter 1 cm and length 60 cm. Effect of inlet flow rate, bed height and initial dye concentration on break through curve was studied. It was observed that adsorption was higher at lower flow rate, higher bed depth and lower initial dye concentration. Fixed bed column was modeled using Thomas model, Adams-Bohart model and Yoon-Nelson model. The experimental data were in good agreement with theoretical results. The study revealed that chitosan beads packed in column can be used as effective adsorbent for removal of azo dyes.

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