PACKED BED COLUMN STUDIES FOR THE REMOVAL OF DYES USING NOVEL SORBENT

A continuous fixed bed study was carried out by using tamarind seed as a sorbent for the removal of malachite green (MG) and acid blue 9 (AB9) from aqueous solution. The effect of factors such as flow rate and bed depth was studied. The data confirmed that the breakthrough curves were dependent on flow rate and bed depth. Thomas, Adams-Bohart, and Yoon-Nelson models were applied to experimental data to predict the breakthrough curves using non-linear regression and to determine the characteristic parameters of the packed bed column. Bed depth/service time analysis (BDST) model was used to express the effect of bed depth on breakthrough curves. The results showed that the Thomas model was found suitable for the normal description of breakthrough curve at the experimental conditions, while the Adams-Bohart and Yoon-Nelson models were able to explain only the initial part of dynamic behaviour of the tamarind seed column. The data were in good agreement with the BDST model. It was concluded that tamarind seed can be effectively used as a sorbent for the removal of dyes.

Keywords: tamarind seed, malachite green, acid blue 9, sorption, packed bed, breakthrough curve.

Industrialization and urbanization are the two main causes of chemical agents that trigger environmental degradation. Industrialization has played both a beneficial and harmful role in the environment. Many industries, such as dyestuffs, textile, paper and plastics, use dyes in order to colour their products, and also consume substantial volume of water. As a result, they generate a considerable amount of coloured wastewater. It was recognized that public perception of water quality was greatly influenced by the colour. Colour was the first pollutant to be recognized in wastewater [1]. The presence of very small amounts of dyes in water (less than 1 ppm for some dyes) is highly visible and undesirable [2]. Due to their good solubility, synthetic dyes are common water pollutants and they may frequently be found in trace quantities in industrial wastewater. An indication of the scale of the problem was given by the fact that 2% of produced dyes are discharged directly in aqueous effluent [3]. Dyes may significantly affect photosynthetic activity in aquatic life due to reduced light penetration and may also be toxic to some aquatic life due to the presence of aromatics, metals, chlorides, etc. in them [4-7]. Due to stringent restrictions on the organic content of industrial effluents, it is necessary to eliminate dyes from wastewater before it is discharged. Many of these dyes were also toxic and even carcinogenic and this poses a serious hazard to aquatic living organisms [8].

Dye wastewater is usually treated by physical or chemical or biological treatment processes. These include chemical coagulation/flocculation, ozonation, oxidation, ion exchange, irradiation, precipitation and sorption [9-11]. Some of these techniques have been shown to be effective, but have limitations like excess amount of chemical usage, or accumulation of concentrated sludge with obvious disposal problems, expensive plant requirements or operational costs, lack of effective colour reduction and sensitivity to a variable wastewater input. Due to the chemical stability and low biodegradability of the dyes, conventional biological wastewater treatment systems were inefficient in treating dye wastewater.
Sorption is one of the most promising options for the removal of dyes from wastewater. Activated carbon is popular among the sorbents employed for dye removal due to its effectiveness and versatility. Activated carbons are usually obtained from materials with high carbon content and possess a great sorption capacity, which is mainly determined by their porous structure. Although activated carbon, in granular or powdered form has a good capacity for the sorption of organic molecules, it suffers from a number of disadvantages. Activated carbon is quite expensive and the higher the quality the greater the cost [12]. Both chemical and thermal regeneration of spent carbon is expensive, impractical on a large scale and produces additional effluent and results in considerable loss of the sorbent.

This has led many researchers to search for cheap and efficient alternative materials such as coal, fly ash, palm-fruit bunch, rice husk, peat, activated clay, bagasse pits, cassava peel, palm tree cobs, date pits, fruit stones and nutshells, Hydrilla verticillata, Turbinaria conoides; wheat bran, tamarind seed, etc. [13-22].

The information obtained from sorption kinetics and isotherm studies is useful for the determination of the effectiveness of the sorbent. Batch mode analysis is not sufficient when designing a treatment system for continuous operation. For example, packed bed columns do not necessarily operate under equilibrium conditions because of the short contact time. The other operational problems such as uneven flow pattern in the column, recycling and regeneration cannot be effectively studied in batch experiments. For these reasons, it is necessary to analyse the sorbate and sorbent system by column mode. The objective of the present work was to analyse the effects of bed height and flow rate for the sorption of malachite green and acid blue 9 onto tamarind seed in a packed column.

MODELING OF COLUMN OPERATION

Full-scale column operation can be designed based on data collected at the laboratory level. Many mathematical models have been proposed in the past for the evaluation of efficiency and applicability of the column models for large scale operations. To design a column sorption process, it is necessary to predict the breakthrough curve or concentration time profile and sorption capacity of the sorbent for the selected sorbate under the given set of operating conditions. Many models have been developed to predict the sorption breakthrough behaviour with high degree of accuracy. The Thomas model and BDST model were used in this study to analyse the behaviour of the selected adsorbent-adsorbate system.

MATERIALS AND METHODS

Tamarind seed

The tamarind seed used in this study was separated from tamarind indica fruits. It was soaked in water for overnight to remove the seed hull and then washed twice with double distilled water to remove soluble lighter materials, then dried in an oven at 70 °C for an hour. After that, it was crushed and sieved to different mesh size. The characteristics of tamarind seed was studied by FTIR and SEM in our earlier study [14].

Packed bed reactor

The experimental arrangement of the packed bed column is shown in Figure 1. Continuous-flow

![Figure 1. Experimental setup of the packed bed reactor; 1) synthetic dye effluent; 2) peristaltic pump; 3) feed inlet; 4) packed sorbent; 5) sampling port; 6) feed out; 7) treated effluent.](image-url)
sorption experiments were conducted in an acrylic column with an internal diameter of 3 and 58 cm in height. The reactor was designed with three ports along the height of the column (each 11 cm apart). These ports, as well as the two ends of the column, were connected to filter discs and fitted with 0.45 μm cellulose filter paper; an O-ring and plug stoppers were also used as fitting items. Plastic beads (1.5 mm in diameter) were placed at the column base in order to provide a uniform inlet flow of the solution into the column.

Experimental procedure

A known quantity of sorbent was packed in the column to yield the desired bed height. Dye solutions of initial concentration of 100 mg/L were pumped upward through the column at a desired flow rate using a peristaltic pump (pp60, Miclins). The temperature and pH were maintained at 37 °C and pH 7 for MG [15], and 35.5 °C and pH 3 for AB9, respectively. The size of the sorbent used in this study was 85 mesh (0.17 mm). Samples were collected from the exit of the column at different time intervals and analysed for dye concentration.

The supernatant was separated by centrifugation at 4000 rpm for 10 min. The residual concentration in the supernatant was determined. The dye concentration in raw and treated sample was determined by a UV-Vis (Elico, SL 164, Hyderabad, India) spectrophotometer. The analyses were carried out at a wavelength of 619 nm for MG and 625 nm for AB9 in a UV-Vis spectrophotometer. A calibration plot was drawn between percentage absorbance and standard dye solutions of various concentrations. From the noted absorbance value of the initial concentration of the dye, the concentration to reach 1 mg/L of the dye. The bed height was varied from 5 to 25 cm. In order to obtain different bed heights, 3.82, 6.24, 9.445, 12.234 and 14.012 g of sorbent were added to give a 5, 10, 15, 20 and 25 cm bed height, respectively. The inlet malachite green and acid blue 9 concentration (100 mg/L) and the flow rate (10 mL/min) were kept constant. The pH was adjusted according to the optimized readings. From the results, it was observed that higher removal of dye occurs at the highest bed height. This was due to the increase in the surface area of adsorbent, which provided more binding sites for the sorption [24]. It was also observed that the maximum colour removal occurred at the initial stage of the experiments. After some time of operation, the colour removal decreased and reached zero. This was due to the non-availability of sorbent sites for the sorption to occur.

Bed depth service time (BDST) model

The bed depth service time (BDST) model describes the relationship between $C/t$ and $t$ in a continuous system. The experimental data can be modelled by establishing a term called service time, which was defined as the time required for the effluent concentration to reach 1 mg/L of the dye. The bed height ($Z$) and service time ($t$) have a linear relationship which was given by BDST model [25-26], written as:

$$t = \frac{N_z Z}{C_0 v} - \frac{1}{K_s C_0} \ln\left(\frac{C_0}{C} - 1\right)$$

where $C$ is the breakthrough dye concentration (mg/L), $N_z$ is the sorption capacity of bed (mg/L), $v$ is the linear velocity (cm/min) and $K_s$ is the rate constant (L mg$^{-1}$ min$^{-1}$).

This simplified design model ignores the intraparticle mass transfer resistance and external film

RESULTS AND DISCUSSION

Sorption of dyes in a packed bed reactor using tamarind seed

Continuous studies were carried in a packed bed reactor. A known quantity of the tamarind seed powder was packed in the reactor to yield the desired bed height. Dye solution of known concentration (100 mg/L) was pumped at a desired flow rate. The effect of bed height and flow rate on sorption of dyes was studied. Sorption of MG and AB9 using tamarind seed was presented in the form of breakthrough curves $(C/C_0)$ vs. $t$. The following equations were used for the calculations [23]:

$$\text{Volume of dye} = \text{Flow rate (L/min)} \times \text{Exhaustion time (min)}$$

$$\text{Dye uptake} = \frac{\text{Dye mass (mg)}}{\text{Sorbent mass (g)}}$$

$$\text{Dye mass} = \frac{\text{Concentration of the dye adsorbed (mg/L)}}{\text{Volume of dye (L)}}$$
Resistance such that the adsorbate was adsorbed onto the adsorbent surface directly. With these assumptions, the BDST model works well and provides useful modelling equations for the changes in system parameters [24]. The column service time was selected as the time when the effluent dye concentration reached 1 mg/L. Service time against bed height at a desired flow rate of 10 mL/min was plotted. The sorption capacity of the bed per unit bed volume, $N_0$, was calculated from the slope of the BDST plot (Figure 2) for MG and AB9, assuming initial concentration, $C_0$, and linear velocity, $v$, as constant during the column operation. The rate constant, $K_a$, calculated from the intercept of BDST plot, characterizes the rate of solute transfer from the fluid phase to the solid phase [24]. The computed $N_0$, $K_a$ and parameters for MG and AB9 are presented in Tables 1 and 2. The BDST model parameters can be useful to scale up the process for other flow rates without further experimental run. Comparison of experimental and Thomas model predicted breakthrough curves are shown in Figures 3 and 4 for MG and AB9, respectively.

### Table 1. BDST Model parameters for the sorption of dyes using tamarind seed

<table>
<thead>
<tr>
<th>Constant</th>
<th>Malachite green</th>
<th>Acid blue 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_0$ / mg L$^{-1}$</td>
<td>1235</td>
<td>1148</td>
</tr>
<tr>
<td>$K_a$ / L mg$^{-1}$ min$^{-1}$</td>
<td>0.0026</td>
<td>0.0115</td>
</tr>
<tr>
<td>$v$ / cm min$^{-1}$</td>
<td>2.209</td>
<td>2.318</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.994</td>
<td>0.9548</td>
</tr>
</tbody>
</table>

### Effect of flow rate

The influence of flow rate on sorption of malachite green and acid blue 9 by tamarind seed was investigated. The initial dye concentration (100 mg/L) and bed height (25 cm) were kept constant and the flow rate was varied from 10 to 20 mL/min. In contrast to bed height results, the column performed well at the lowest flow rate. Earlier breakthrough time appeared for highest flow rate, resulting in low uptake and least percentage removal. This behavior may be due to insufficient time for the solute inside the column and the diffusion limitations of the solute into the pores of the sorbent at higher flow rates [24].

![Figure 2. BDST Model for the sorption of MG and AB9 onto tamarind seed.](image)

<table>
<thead>
<tr>
<th>Bed height, cm</th>
<th>$M$ / g</th>
<th>$t_b$ / min</th>
<th>$t_e$ / min</th>
<th>$q$ / mg g$^{-1}$</th>
<th>$V_{eff}$ / L</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MG</td>
<td>AB9</td>
<td>MG</td>
<td>AB9</td>
<td>MG</td>
</tr>
<tr>
<td>5</td>
<td>3.84</td>
<td>40</td>
<td>40</td>
<td>120</td>
<td>30.93</td>
</tr>
<tr>
<td>10</td>
<td>6.24</td>
<td>60</td>
<td>50</td>
<td>220</td>
<td>34.90</td>
</tr>
<tr>
<td>15</td>
<td>9.445</td>
<td>90</td>
<td>70</td>
<td>400</td>
<td>41.92</td>
</tr>
<tr>
<td>20</td>
<td>12.234</td>
<td>120</td>
<td>110</td>
<td>560</td>
<td>45.32</td>
</tr>
<tr>
<td>25</td>
<td>14.012</td>
<td>150</td>
<td>140</td>
<td>670</td>
<td>47.34</td>
</tr>
</tbody>
</table>
Thomas model

Successful design of a column sorption process required the prediction of the concentration time profile or breakthrough curve for the dye. Various mathematical models can be used to describe packed bed sorption. Among these, the Thomas model was simple and widely used by several investigators [27-30]. The column sorption data obtained at different bed heights, flow rates and dye concentrations were fitted using the Thomas model. The linearized form of the Thomas model can be expressed as follows [27]:

$$\ln \left( \frac{C_o}{C} - 1 \right) = \frac{k_{th} Q_i M}{F} - \frac{k_{th} C_i V}{F}$$  \hspace{1cm} (3)$$

where $k_{th}$ is the Thomas model constant (L mg$^{-1}$ min$^{-1}$), $Q_i$ is the maximum solid phase concentration of solute (mg/g) and $V$ is the throughput volume (L).

The model constants, $k_{th}$ and $Q_i$, can be determined from the plot of $\ln((C/C_o)-1)$ vs. time. Comparison of experimental and Thomas model predicted breakthrough curves are shown in Figures 5 and 6 for MG and AB9, respectively. In general, good fits were obtained in all cases with correlation coefficient ranging from 0.93 to 0.96. Table 3 summarizes the Thomas model parameters obtained at different flow rates for the sorption of MG and AB9, respectively. With the increase in flow rate, the bed capacity $Q_i$ decreases and Thomas constant $k_{th}$ increases. Similar results were observed by Aksu and Gonen [27] for the sorption of phenol. In most cases, a negligible difference between the experimental and predicted values of the bed capacity was observed. However, there were some deviations in the predicted values from the experimental values at higher flow rates.
The Adams–Bohart model

The Adams–Bohart model was used for the description of the initial part of the breakthrough curve. The model was expressed as [27]:

\[
\frac{C}{C_0} = \exp(K_{AB}C_0 t - K_{AB}N_0 \frac{Z}{F})
\]  

(4)

where \(K_{AB}\) is the kinetic constant (L mg\(^{-1}\) min\(^{-1}\)), \(F\) is the linear velocity calculated by dividing the flow rate by the column section area (cm/min), \(Z\) is the bed depth of column and \(N_0\) is the saturation concentration (mg/L). From this equation, values describing the characteristic operational parameters of the column can be determined from a plot of \(C/C_0\) vs. \(t\) at a given bed height and flow rate using the non-linear regressive method.

The Adams–Bohart sorption model was applied to experimental data for the description of the initial part of the breakthrough curve. This approach focuses
on the estimation of characteristic parameters, such as maximum sorption capacity ($N_0$) and kinetic constant ($K_{AB}$) from Adams-Bohart model. After applying Eq. (4) to the experimental data, the parameters were obtained for the relative concentration region up to 0.5, i.e., up to 50% breakthrough, for all breakthrough curves using MATLAB software. For all breakthrough curves, respective values of $N_0$ and $K_{AB}$ were calculated and presented in Table 4. The predicted curves were compared with the corresponding experimental curves and are shown in Figures 7 and 8. It is clear from the figures that there was a good agreement between the experimental and predicted curves, suggesting that the Adams-Bohart model was valid for the relative concentration region up to 0.5 and beyond which large discrepancies were found between the experimental and predicted curves. Although the Adams-Bohart model provides a simple and comprehensive approach to running and evaluating sorption-column tests, its validity was limited to the range of conditions used.

**The Yoon-Nelson model**

The Yoon-Nelson equation for the single component was expressed as [27]:

$$\frac{C_t}{C_0 - C_t} = \exp(K_{YN}t - \tau K_{YN})$$  \hspace{1cm} (5)

where $K_{YN}$ is the rate constant (min$^{-1}$) and $\tau$ is the time required for 50% adsorbate breakthrough (min). The approach involves a plot of $C_t/(C_0 - C_t)$ versus sampling time ($t$) according to Eq. (5). The parameters of $K_{YN}$ and $\tau$ were obtained using the MATLAB software.

A simple theoretical model developed by Yoon-Nelson was applied to investigate the breakthrough behaviour of dyes onto tamarind seed. The values of $K_{YN}$ and $\tau$ were listed in Table 5. From Table 5, it was inferred that as the flow rate increases, the rate constant $K_{YN}$ increases and the 50% breakthrough time $\tau$ decreases. Figures 9 and 10 show the comparison of the experimental and predicted values obtained from Yoon-Nelson model. It is clear from the figures that there was a good agreement between the experimental and predicted values, suggesting that the Yoon-Nelson model was valid for the relative concentration region up to 0.5, beyond which large discrepancies were found between the experimental and predicted values.

### Table 4. Adam-Bohart model parameters for the sorption of dyes onto tamarind seed at different bed heights (velocity: 2.209 cm/min, $C_o$: 100 mg/L)

<table>
<thead>
<tr>
<th>Flow rate, mL/min</th>
<th>$K_{AB} \times 10^4$ L mg$^{-1}$ min$^{-1}$</th>
<th>$N_0$ / mg L$^{-1}$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MG</td>
<td>AB9</td>
<td>MG</td>
</tr>
<tr>
<td>5</td>
<td>5.5</td>
<td>6.14</td>
<td>1650</td>
</tr>
<tr>
<td>10</td>
<td>2.6</td>
<td>2.82</td>
<td>1783</td>
</tr>
<tr>
<td>15</td>
<td>2.29</td>
<td>1.32</td>
<td>2298</td>
</tr>
<tr>
<td>20</td>
<td>2.02</td>
<td>1.11</td>
<td>2026</td>
</tr>
<tr>
<td>25</td>
<td>1.09</td>
<td>0.99</td>
<td>1617</td>
</tr>
</tbody>
</table>

*Figure 7. Breakthrough curves for sorption of MG onto tamarind seed at different bed heights - Adam-Bohart model.*
Figure 8. Breakthrough curves for sorption of AB9 onto tamarind seed at different bed heights - Adam-Bohart model.

Table 5. Yoon-Nelson model parameters for sorption of MG onto tamarind seed at different flow rates (velocity: 2.209 cm/min, \( C_0 \): 100 mg/L)

<table>
<thead>
<tr>
<th>Flow rate, mL/min</th>
<th>( K_{YN} ) ( / \text{min}^{-1} )</th>
<th>( t ) ( / \text{min} )</th>
<th>( R^2 )</th>
<th>( \tau_{exp} ) ( / \text{min} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MG</td>
<td>AB9</td>
<td>MG</td>
<td>AB9</td>
</tr>
<tr>
<td>10</td>
<td>0.01274</td>
<td>0.0133</td>
<td>392.8</td>
<td>361.7</td>
</tr>
<tr>
<td>15</td>
<td>0.0149</td>
<td>0.0182</td>
<td>283.3</td>
<td>287.5</td>
</tr>
<tr>
<td>20</td>
<td>0.0265</td>
<td>0.0295</td>
<td>166.5</td>
<td>176.2</td>
</tr>
</tbody>
</table>

Figure 9. Breakthrough curves for sorption of MG onto tamarind seed at different bed heights - Yoon-Nelson model.
CONCLUSION

In this study, the effect of bed height on malachite green and acid blue 9 dye removal was studied in a packed bed reactor using tamarind seed as sorbent. The bed height was varied from 5 to 25 cm. It was observed that the maximum removal of dyes occurs at highest bed height. The effect of flow rate was studied by varying the flow rate from 10 to 20 mL/min. In contrast to bed height results, the column performed well at the lowest flow rate. Earlier breakthrough time appeared for highest flow rate, resulting in low uptake and least percentage removal. The continuous experimental data were fitted with models such as the Bed Depth Service time (BDST), Thomas, Adam-Bohart and Yoon-Nelson model. The constants were determined using MATLAB software. The predicted values were determined and compared with experimental values. High $R^2$ values show the validity of BDST and Thomas model for this system. For the initial part of the experiments, the Adam-Bohart and Yoon-Nelson models fit the data well, but after that stage they deviate from the experimental data.

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REFERENCES

Proučavanje uklanjanje boja novim sorbentom u koloni sa pakovanim slojem


Ključne reči: sema indijske ureme, malahitno zeleno, kiselo plavo 9, sorpcija, pakovani sloj, kriva probaja.