Optimization of Crystal Violet Dye Removal in Fixed Bed Column Using *Eucalyptus camaldulensis* as a Low-Cost Adsorbent

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Abstract: Adsorption through waste adsorbents is one of the developing technologies used for treating textile wastewater. The present study explores the possible outcome of *Eucalyptus camaldulensis* biomass as an adsorbent for removing crystal violet dye from aqueous solutions. *Eucalyptus camaldulensis* biomass was used as such and used in fixed bed column mode to testify its potential at different parameters. Effect of different constraints like bed height (cm), flow rate (ml min⁻¹), initial dye concentration (mg L⁻¹), and pH were studied along with breakthrough curve and exhaust time. Maximum breakthrough curve and exhaust time and utilization of mass transfer zone were observed at bed height of 20 cm. However, the promising results are obtained at higher dye concentration (50 mg L⁻¹), lower flow rate (1 ml min⁻¹), and at lower pH of 5. This study reveals promising results at acidic pH. This study reflects that adsorption capacity and breakthrough curve favor lower acidic pH. The adsorption data in batch mode follow the Langmuir isotherm and best fit to pseudo-second-order reaction kinetics. The breakthrough curve and mass transfer zone are individually testified, and the breakthrough curve obeys the assumptions of the Thomas model, and R² (0.933-0.997) values confirm the data that its best fit with the Thomas model.

Keywords: adsorbent material; breakthrough, Thomas model; *Eucalyptus camaldulensis*.

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1. Introduction

The textile industry is one of the most important industries in Asia. Many processes are associated with yarn and fabric manufacturing and are termed wet processing, including dyeing, finishing, and printing. The dyeing and finishing process consumes a lot of freshwater used in multiple washing and rinsing cycles. In a typical dyeing and finishing mill, about 150 m³ of water is consumed on average for every ton of cloths processed [1-5]. A huge amount of textile wastewater is released directly into the streams containing contaminants like color. A large number of suspended solids, fluctuating pH, high temperature, and high chemical oxygen demand concentration were generated [6,7]. Basic dyes pre-owned for reform polyesters, cation dyeable polyethylene terephthalate, paper, polyacrylonitrile, reform nylon, and use in medicines. Initially, they were pre-owned for tannin-mordant cotton, wool, and silk.
dyes are water-soluble and produce colored cations in the solution and, because of this factor, are termed cationic dyes. The leading chemical classes are oxazine, acridine, thiazine, triarylmethane, diazahemicyanine, cyanine, and hemi cyanine. Dyes are one of the most hazardous chemical compound classes found in industrial effluents, which need to be treated since their presence in water bodies reduces light penetration, precluding the photosynthesis of aqueous flora [8-15]. They are also aesthetically objectionable for drinking and other purposes. Dyes can also cause allergy, dermatitis, skin irritation and provoke cancer in humans [16-24].

Crystal violet is also termed basic violet 3, gentian violet, and methyl violet 10B. Its molecular weight is 407.98, and it belongs to a class of triarylmethane dyes [25]. The maximum wavelength of crystal violet dye is 594 nm. This dye is widely used in textile fabrics such as cotton and silk, paints, and printing ink. This dye has the ability to irritate the eye [26-30]. This dye also has the ability to cause severe injury in the cornea and conjunctiva as the product has cationic dye features, and it also causes toxicity to mammalian cells. It also affects the skin, causes irritation to it, and affects the digestive system too. If this dye goes in extreme cases, then it may cause kidney failure and permanent blindness. All the above consequences of this dye motivated me to research to remove its effects from the wastewater [31-35].

Adsorption is one of the attractive methods for treating dye wastewater due to its low cost and availability of the adsorbents [36]. Adsorption is the process of accumulating substances that are in solution on a suitable solid surface. It involves the mass transfer operation in which contaminant in the liquid phase is transferred to the solid phase. Different adsorption techniques rely on the attraction between the solid surface and the adsorbate molecules that is physical. The adsorption is referred to as physical adsorption (physisorption) due to weaker Van der Waals forces [37]. When the attraction forces are due to chemical bonding, the Adsorption process is termed chemisorption. In view of the higher strength of the bonding in chemisorption, it is difficult to remove the chemisorbed contaminant from the solid surface. Major adsorbents include activated carbon, synthetic polymeric, and silica-based adsorbent [38,39].

Change in the pH values also influences the breakthrough curves values. The behavior of dyes adsorption can be optimized at different pH values, i.e., 3.0 to 11.0. The slow saturation rate and breakthrough curve shift are observed at basic pH during the adsorption of methylene blue. This indicates that the binding sites of the adsorbent; contain the opposite charges which attract each other between the adsorbate and adsorbent. The adsorbent is negatively charged, and the adsorbate has a positive charge cause the force of attraction and adsorption to occur [40-48]. Different curves can be obtained by varying the flow rate and bed height. Breakthrough curves values are taken at equal intervals of time, while saturation values are measured with the help of a double beam spectrophotometer.

The present study aims to optimize the crystal violet dye removal from an aqueous solution using Eucalyptus camaldulensis as a low-cost adsorbent in a fixed bed column. To validate the Thomas model application, the batch experiment has been carried out at different initial dye concentrations [49,50].

2. Materials and Methods

2.1. Adsorbent preparation.

Eucalyptus camaldulensis bark was collected from the premises of COMSATS Institute of Information Technology, Abbottabad. The bark was collected from the eucalyptus tree
during the autumn season. The bark was washed from the deionized water to remove the dust particles and other contaminants. After washing, the bark was sun-dried for a few days and then crushed by JM disk mill. After sieving, a particle size of 40 mesh size (420 µm) was used throughout the experimental studies. The biomass was stored in air-tight packed bags [25].

2.2. Activated carbon prepared by physical activation.

The process requires hot gases to activate the adsorbent. This process goes under two steps, i.e., Carbonization and activation. Carbonization is carried out by pyrolysis at high temperatures (300°C) in the presence of nitrogen gas. Then heating is carried out for many hours for physical activation of *Eucalyptus* bark [14].

2.3. Chemicals and reagents preparation.

2.3.1. Preparation of crystal violet dye stock solution.

A stock solution of crystal violet dye with 250 mg L⁻¹ concentration was prepared by dissolving 0.25 gm analytical grade (Merck) crystal violet dye in 250 mL of deionized water. Suitable dilutions were made for obtaining different dye concentrations using the following formula:

\[ C_1 V_1 = C_2 V_2 \]

Where, C1 concentration of the stock solution, V1 volume of stock solution need, C2 required concentration, V2 volume of the required diluted aqueous solution

2.3.2. Preparation of 0.1M HNO₃ and 0.1M NaOH solution.

In this experiment, the adsorbent is tested for dye removal efficiency on different pH. The experiments were conducted under different acidic (5 and 6) and basic pH (9 and 11), which were adjusted through acid and base solution, i.e., HNO₃ and NaOH, respectively. 0.1 Molar HNO₃ was prepared by adding 0.8 mL of HNO₃ into 100 mL of deionized water. Likewise, 0.1 Molar NaOH solution was prepared by adding 400 mg of analytical grade NaOH in 100 mL of deionized water.

2.4. Batch adsorption experiments.

Kinetics batch experiments were conducted by taking 0.05 g of *Eucalyptus camaldulensis* bark into 50 mL of deionized water in Erlenmeyer flasks. The initial pH, i.e., 6.5, was maintained using buffer solution, and pH was determined using a PHS-3BW microprocessor pH/temperature meter. After preparation, the solution was shaken in the orbital shaking incubator (wise cube WIS-20) at 220 rpm for 120 min at room temperature 30°C ± 1°C [30]. The adsorbed dye was then measured through T80+UV/VIS Spectrometer at a wavelength of 590 nm. The amount of crystal violet dye adsorbed by the adsorbent was calculated from the following equation:

\[ Q = (C_0 - C_f)M \]

Where, Q dye uptake (mg g⁻¹), C₀ initial dye concentration (mg L⁻¹), C_f Final dye concentration (mg L⁻¹), M adsorbent mass (g).
2.5. Effect of initial dye concentration.

Batch experiments were carried out using different initial crystal violet dye concentrations, i.e., 20, 30, 60 mgL\(^{-1}\). The adsorbent and dye mixture was shaken using 1 gL\(^{-1}\) for 2 h [10].

2.6. Column studies.

2.6.1. Fixed bed bio adsorption studies.

A continuous flow bio adsorption experiment was conducted in a glass tube having an internal diameter of 2 cm and 50 cm in length. *Eucalyptus* bark was packed into a glass column to obtain the desired bed height. The bed top was covered with a layer of glass wool to avoid the loss of bioadsorbent and to ensure a close-packed arrangement. Afterward, dye solution of the known concentration at desired pH was pumped downward with the help of a peristaltic pump with desired flow rate at room temperature. A series of experiments were conducted to study the effect of flow rate and bed height. The samples were analyzed through a UV spectrophotometer at regular intervals of time [23,25].

![Figure 1. Fixed bed column apparatus.](https://nanobioletters.com/)

2.6.2. Column study parameters.

2.6.3. Effect of Bed Height.

The breakthrough curves are generated for crystal violet adsorption onto camaldulensis biomass at different bed heights (10-15-20 cm). Breakthrough time determines the process; the larger the breakthrough time, the higher the adsorption capacity of the adsorbent in the column. This is because the dye molecule got more time in contact with the adsorbent [10].

2.6.4. Effect of solution flow rate.

In the continuous mode of the experiment, the flow rate is also an important parameter. The effect of flow rate on breakthrough curves was also evaluated using three flow rates (2.5, 5, 10 mlmin\(^{-1}\)), keeping the bed height and initial dye concentration (10 cm and 25 mgL\(^{-1}\)) constant [35].

2.6.5. Effect of initial dye concentration.

The effect of initial dye concentration was justified by taking different dye concentration of crystal violet dye that ranges from 10 to 75 mgL\(^{-1}\) having a constant bed height of 10 cm and flow rate of 1mLmin\(^{-1}\) [14].
2.6.6. Effect of pH.

pH greatly influence the adsorption capacity of the adsorbent. For this purpose, the fixed bed experiments were conducted on wide pH, i.e., 5, 6.5, 9, 11 [15].

2.7. Justification of Thomas model application.

2.7.1. Langmuir isotherm.

K_{ads} = \text{Constant rate of adsorption (Lmg}^{-1}) \text{ } In \text{ } Langmuir \text{ } isotherm, \text{ } it \text{ } is \text{ } presumed \text{ } that \text{ } there \text{ } will \text{ } be \text{ } no \text{ } interaction \text{ } between \text{ } the \text{ } adsorbed \text{ } molecules, \text{ } and \text{ } the \text{ } nature \text{ } of \text{ } the \text{ } adsorption \text{ } will \text{ } be \text{ } monolayer. \text{ } A \text{ } single-layer \text{ } of \text{ } adsorbent \text{ } molecules \text{ } saturates \text{ } the \text{ } adsorbent \text{ } surface [25]. \text{ } The \text{ } linearized \text{ } Langmuir \text{ } isotherm \text{ } equation \text{ } is \text{ } represented \text{ } as:

\[
\frac{K_{ads}}{Q_{max}} = C_e
\]

\[
Q_e = 1 + K_{ads} C_e
\]

where, \(C_e\) = Equilibrium concentration (mgL^{-1}), \(q_e\) = Amount of contaminant adsorbed /unit mass of adsorbent (mgg^{-1}), \(Q_{max}\) = Maximum adsorption capacity (mgg^{-1})

2.7.2. Pseudo-second order kinetics model.

The pseudo-second-order model is based on the assumption that the rate-limiting step may be chemisorption. It involves sharing of electrons between the adsorbent and the adsorbate. Adsorption capacity, the rate constant of pseudo-second-order, and the initial adsorption rate can be directly determined from the equation where other parameters like (temperature, pH, and particle size) are not necessary [30].

\[
\frac{1}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e T}
\]

Where, \(k_2 \text{ (g/mg.hr)}\) = pseudo 2nd order rate constant, \(q_t \text{ (mg/g)}\) =amount of adsorbate adsorbed at time t, \(q_e \text{ (mg/g)}\) =equilibrium adsorption capacity.

2.7.3. Thomas model.

Thomas model is mostly used to describe the fixed bed column performance and the prediction of breakthrough curve. Thomas model is associated with the batch experiments as well, as it follows the Langmuir model and pseudo-second-order to verify the assumption that there is no axial dispersion and it obeys pseudo-second-order kinetics. The regression coefficient can be estimated earlier by assuming that its conditions are favorable or unfavorable [29].

The linearized form of the Thomas model can be expressed as follows:

\[
\text{ln}(C_0^{-1}) - 1 = K_{th} C_0 t
\]

\[
Q_f = \frac{C_f}{K_{th} M}
\]

Where, \(K_{th} \text{ (mL/min mg)}\) = Thomas rate constant, \(M = \text{Mass of adsorbent (g)}, C_0 = \text{Inlet dye concentration (mgL}^{-1}), C_f = \text{Outlet concentration (mgL}^{-1}) \text{ at time t}, q_0 = \text{Adsorption capacity (mgg}^{-1}), Q = \text{flow rate in mL/min}, t = \text{Total time that represents the flow time}.\n
https://nanobioletters.com/
The linear plot of \( \ln (\text{Co}/\text{Ct}-1) \) vs. time was plotted to obtain the values of \( k \)th and \( q_0 \) by using the values of intercept and slope.

2.7.4. Breakthrough curve.

The breakthrough curve plots the concentration measured at any point in the column against time \( t \). It also shows the loading behavior of adsorbed dye onto the adsorbent. It is expressed as the ratio of outlet dye concentration to the inlet concentration and plotted against time, i.e., \( \text{Ct}/\text{Co} \) vs. \( t \), whereas the effluent volume can be calculated as [39].

\[
V_{ef} = F \cdot t
\]

Whereas, \( F = \) Total Flow (mL/min), \( T = \) Total time (min)

Breakthrough capacity \( Q_{0.5} \) (at 50%) expressed in mg of dye adsorbed per gram of bioadsorbent which can be calculated by the following equation

\[
Q_{0.5} = \frac{B \cdot T \cdot \text{flow rate} \cdot \text{inlet conc}}{M}
\]

Whereas, \( Q_{0.5} = \) Breakthrough time at 50%, \( \text{Flow rate} = \) mL/min, \( \text{Inlet concentration} = (\text{mgL}^{-1}) \), \( M = \) Mass of bioadsorbent (g)

3. Results and Discussion

3.1. Isotherm and kinetics models.

Thomas model applies to the adsorption data if the latter obey the following: (i) the adsorption data should obey Langmuir isotherms; (ii) the adsorption data should also follow the pseudo-second-order kinetics. Different initial dye concentrations (10, 30, 40, 70 mgL\(^{-1}\)) were simulated in batch experiment [36]. In the present study, data best fit Langmuir’s isotherm (\( R^2 0.96 \)) and followed the pseudo-second-order reaction at 30mgL\(^{-1}\) (\( R^2 0.996 \)).

3.2. Column Adsorption for Eucalyptus camaldulensis.

The adsorption capacity of Eucalyptus camaldulensis biomass was evaluated at different bed heights, flow rate, pH, and initial dye concentrations.

3.2.1. Effect of Bed Height.

Glass columns filled with different adsorbent doses occupying variable bed depths were prepared and subjected to flow of 1mlmin\(^{-1}\) containing 20 mgL\(^{-1}\) initial dye concentration aqueous solutions with pH 6.7 at room temperature across 10, 15, and 20 cm bed height. It was observed that mass transfer zone and breakthrough curved was obtained at 600 minutes service time at bed height of 20 cm, which was quite higher compared to bed heights 10 cm and 15 cm (Fig 2).

3.2.2. Effect of flow rate.

The flow rate of the contaminant in any designed fixed-bed column plays an important role in determining the efficiency of the process. Higher flow rates allow the contaminant to keep in contact with the adsorbent for less time than cases where slower flow rates are applied. To assess the effect of flow rate on the adsorption process, variable flow rates of 1 mlmin\(^{-1} \), 5
mlmin⁻¹ and 10 mlmin⁻¹ aqueous solutions were conducted at column bed depth of 10 cm, 20 mgL⁻¹ initial dye concentration, pH 6.57 at room temperature [24].

It was observed that column exhaust time reached much earlier at higher flow rates than slower flow rates. Column exhausted at 180 mints contact time at a flow rate of 10 mlmin⁻¹ which is much quicker than 1 mlmin⁻¹ which exhausted at 300 min contact time (Fig 3).

3.2.3. Effect of pH.

The pH of the effluents has a significant role in affecting the rate of contaminant adsorption onto the surface of the adsorbents. Variability of adsorbent surface charges is mainly governed by changes in the pH of the wastewater. Acidic and basic conditions are equally responsible for affecting the mechanisms responsible for binding contaminants onto the surface of the adsorbent. To assess the effect of effluent pH on the adsorption process, column experiment was carried out under different initial inlet pH conditions of pH 5, 6.5, 9, and 11 at a flow rate of 1 mlmin⁻¹ and bed depth of 10 cm. It was noted that maximum adsorption was taking place under acidic conditions [36]. The breakthrough curve was obtained late in the case of pH 5 initial dye concentration compared to other tested effluent pH values (Fig. 4).
3.2.4. Effect of initial dye concentration.

Initial dye concentration is also an important parameter significantly affecting the adsorption process. Higher initial dye concentrations resulted in earlier breakthrough curves as compared to low initial dye concentration. In the current study, fixed bed columns were subjected to three different initial inlet dye concentrations of 20, 50, and 75 mgL$^{-1}$ at a constant bed depth of 10 cm and pH 6.75 (Fig 5).

Table 1. Breakthrough values at 50 percent exhaust time.

| Initial dye concentration (mgL$^{-1}$) | Bed Height (cm) | flow rate (mlmin$^{-1}$) | Vol treated (V) | BT point at 50% (mgg$^{-1}$) | Adsorption (mgmL$^{-1}$) |
|-------------------------------------|----------------|------------------------|----------------|----------------------------|------------------------|
| Bed Height                          |                |                        |                |                            |                        |
| 20                                  | 10             | 1                      | 1              | 225                        | 0.9                    |
| 20                                  | 15             | 1                      | 1              | 300                        | 1.2                    |
| 20                                  | 20             | 1                      | 1.5            | 425                        | 1.7                    |
| Flow Rate                           |                |                        |                |                            |                        |
| 20                                  | 10             | 1                      | 1              | 185                        | 0.74                   |
| 20                                  | 10             | 5                      | 1              | 105                        | 2.1                    |
| pH 5                                |                |                        |                |                            |                        |
| 22                                  | 10             | 1                      | 1              | 190                        | 0.76                   |
| pH 9                                |                |                        |                |                            |                        |
| 22                                  | 10             | 1                      | 1              | 108                        | 0.47                   |
| pH 11                               |                |                        |                |                            |                        |
| 21                                  | 10             | 1                      | 1              | 60                         | 0.252                  |
| Dye concentration                   |                |                        |                |                            |                        |
| 20                                  | 10             | 1                      | 1              | 160                        | 0.64                   |
| 50                                  | 10             | 1                      | 1              | 90                         | 0.9                    |
| 75                                  | 10             | 1                      | 1              | 105                        | 1.575                  |
3.2.5. Justification for Thomas model.

Thomas model calculates the sorption rate constant and the solid phase concentration of the dye on the adsorbent from the continuous mode study. It estimates the adsorptive capacity of the adsorbent and predicts breakthrough curves, assuming the second-order reversible reaction kinetics and the Langmuir isotherm. Normally process follows the Langmuir, where there is no axial dispersion theoretically. It is suitable to estimate the adsorption process where external and internal diffusion resistances are extremely small. The isotherm follows the Langmuir assumptions ($R^2=0.9634$). The results show that data favors pseudo-second-order, which reflects the chemisorption nature [40].

3.2.6. Thomas model for Bed Height.

The graph was plotted among the values of natural log (ln) vs. time. The $Kth$ rate constants and $qo$ were obtained from the slope. The regression coefficients support the breakthrough values in the fixed bed column (figure 8). Different bed heights were utilized to study the column behavior, and it was found that all bed heights follow the Thomas model coefficient [41].

3.2.7. Thomas model for flow rate.

The values in different flow rates support the Thomas model. The rate constants and adsorption capacity of the bed are given in Table 2. Little fluctuations were observed in the adsorption data that is probably because of the color of the adsorbent. Good regression
coefficients were obtained at a lower flow rate than those at higher flow rates (figure 9). However, the breakthrough curve confirms the Thomas model and fulfills its assumptions [42,45].

![Thomas model for Bed Height](image1)

**Figure 8.** Thomas model for Bed Height.

![Thomas Model for flow rate](image2)

**Figure 9.** Thomas Model for flow rate.

3.2.8. Thomas model and initial dye concentration/

The difference in concentration effect, the rate constants, and behavior of the breakthrough curve were observed (figure 10). The regression value obtained good at a high concentration of 50 mgL⁻¹ the data support the Thomas rate constants while the adsorption rates and breakthrough curves also favor the Thomas values.
3.2.9. Thomas model and pH.

pH plays an important role in the column adsorption parameter. The regression values were fit at lower pH, and it supports the breakthrough curve obtained at lower pH compared to higher ones (figure 11). The kth and qo values were best fitted at acidic pH [45,48].

Table 2. Calculations of the Thomas Model.

| Parameters     | Inlet concentration (mgL⁻¹) | Bed height (cm) | Flow rate (mlmin⁻¹) | pH    | Kth mLmin⁻¹ | Qo Mgg⁻¹ | R²       |
|----------------|----------------------------|-----------------|---------------------|-------|-------------|---------|---------|
| Bed Depth      | 20                         | 10              | 1                   | 6.57  | 1.35        | 0.1804  | 0.9783  |
|                | 20                         | 15              | 1                   | 6.57  | 2.23        | 0.181   | 0.9824  |
|                | 20                         | 20              | 1                   | 6.57  | 3.35        | 0.336   | 0.9663  |
| Flow Rate      | 20                         | 10              | 1                   | 6.57  | 2.25        | 0.28    | 0.972   |
|                | 20                         | 10              | 5                   | 6.57  | 3           | 0.262   | 0.9348  |
| pH             | 22                         | 10              | 1                   | 5     | 1.01        | 0.4     | 0.9988  |
|                | 21                         | 10              | 1                   | 9     | 1.15        | 0.34    | 0.9462  |
| Dye Conc.      | 20                         | 10              | 1                   | 6.57  | 1.35        | 0.18    | 0.9783  |
|                | 50                         | 10              | 1                   | 6.57  | 2           | 0.67    | 0.9989  |
|                | 75                         | 10              | 1                   | 6.57  | 1.62        | 2.27    | 0.9958  |
3.3. Effect of different bed depths on breakthrough curve.

The effect of bed depth on adsorption of crystal violet dye onto *Eucalyptus camaldulensis* as an adsorbent was testified by changing the bed depth from 10 cm to 20 cm by keeping flow rate (1 ml min\(^{-1}\)), initial dye concentration (25 mg L\(^{-1}\)) constant [16, 20, 25]. The column was packed, having various bed heights of 10 cm, 15 cm, and 20 cm having 5 g, 9 g, and 13 g of mass, respectively. The breakthrough curve was obtained by plotting Cf/Co against time. It can be presumed that the breakthrough curve was obtained later and increased the effluent volume and exhaustion time by increasing the bed height. With increasing bed depth, the volume of treated effluents increases due to more available binding sites [29, 32]. The increase in the adsorbent bed leads to more adsorption of the adsorbate as more availability of surface area. By decreasing the bed depth, the diffusion process also decreases in MTZ, reducing the diffusion of dye ions. With less availability of the adsorbent, the ions of dyes got minimum chances to be in contact with the adsorbent results in low adsorption [27, 38].

3.4. Effect of flow rate on breakthrough curve.

The effect of flow rate on the adsorption of crystal violet *Eucalyptus camaldulensis* biomass was explored by changing the flow rate (1-5-10 ml min\(^{-1}\)) while keeping bed depth as 10 cm and inlet dye concentration of 20 mg L\(^{-1}\) constant across fix bed column. It was recorded that at a higher flow rate, the breakthrough was obtained earlier and led to the saturation point in advance [39, 40]. But when the flow rate was reduced, the breakthrough time and saturation time appeared later. At a lower flow rate, the dye molecules get more time to be in contact with the adsorbent and hence lead to higher adsorption; thus, column exhausts consume more time compared to the former case. The changes in the breakthrough curves and slopes can be determined by the factor MTZ. The adsorption capacity is minor at lower contact time due to the high flow rate [38]. The diffusion rate is slower, and the dye molecule left the column earlier, previous to the establishment of equilibrium time; this result is verified from the other available literature.

3.5. Effect of initial dye concentration.

The execution of the inlet crystal violet dye concentration from 10-75 mg L\(^{-1}\) was carried out under the same constant experimental conditions like bed height, pH, flow rate, and temperature. As far as concentration was increasing, the breakthrough curve slightly decreased [25]. At lower concentrations, the breakthrough curve appears late due to the low diffusion of dye ions. Our adsorbent was found not effective at very low and diluted dye contaminant concentrations. The column was exhausted in no time recorded as 50 minutes. However, the breakthrough curve was attained faster by increasing the initial dye concentration. The breakthrough curve was attained later at lower dye concentration due to the slower transport of dye ions and decreased mass transfer coefficient. Different literature shows similar results regarding adsorption behavior in a column. The highest adsorption capacity obtained was (1.575 mg g\(^{-1}\)) using 75 mg L\(^{-1}\) concentration at bed height of 10 cm with the flow rate of 1 ml min\(^{-1}\) [29]. The adsorption capacities obtained are listed in Table 1.
3.6. Effect of pH.

The most important parameter that influences the adsorption capacity of any adsorbent is pH. The initial pH of the bio-adsorption medium is affiliated to the sorption tool onto the adsorbent surface from water and sends back the nature of the physiochemical communication of the species in the solution and the available adsorption sites of the adsorbent being used [39]. The consequences of pH onto the breakthrough curve and time were noticed at various pH levels ranging from pH 5 to 11 by keeping other experimental conditions constant. Values on adsorption of crystal violet dye onto the Eucalyptus camaldulensis by using a plot of linearized concentration (Ct/Co) versus time (t). As pH started to fall from the basic conditions, i.e., pH 11, the breakthrough curve was attained with less adsorption capacity, and values of Ct/Co reached 0.99 in a short time. As the pH of the aqueous dye solution was lowered to acidic conditions at pH 5, the breakthrough curve time increased and showed more adsorption of the dye; the efficiency of the adsorbent was high under acidic pH conditions of the aqueous dye solution [41] the results show that by decreasing the pH. The adsorption capacity increases, so it can be assumed that removing crystal violet dye from the aqueous solution at lower pH was more efficient.

3.7. Application of Thomas model on Bed Height breakthrough curves.

The column data were fitted well with the Thomas model to determine the Thomas rate constant (kth), maximum solid-phase concentration (qe), and regression coefficient ($R^2$). The $R^2$ was in the range of (0.993-0.997), which indicates that the correlation of Ct/Co and t according to Thomas equation is significant [42,44]. The results indicate that there is no significant change in the values of qo, but kth values differ concerning bed height. At a higher Kth value, the adsorption capacity was low and vice versa (Table 1). However, moderate adsorption was noticed at 20 cm of bed height. Because the adsorbent is first pre-washed with deionized water, and later on, the adsorbate was passed through, reflecting little fluctuations in the values of qo. However, regression values favored the application of the Thomas model.

3.8. Application of Thomas model on flow rate breakthrough curves.

The adsorption capacity was low at a higher value of Kth. At a higher flow rate, the adsorption capacity was low and, resultantly, the higher Kth value. Similarly, at a lower flow rate, the adsorption capacity was found comparatively high and lower Kth. It is because of the driving force of the concentration difference between the dye on the adsorbent and in the aqueous solution (Thomas 1944). The regression values for different flow rates follow the Thomas model.

3.9. Application of Thomas model on the initial dye concentration breakthrough curves.

The coefficient of determination ($R^2$) for initial dye concentration indicated that at a higher initial dye concentration, the adsorption capacity was higher with a lower kth value. Similarly, the adsorption capacity was observed high at lower initial dye concentration, but Kth values were also observed high. However, overall performance is affected by the adsorbent color that needs to be removed completely for obtaining high adsorption capacity [25]. The regression values of different initial dye concentrations follow the Thomas model (Table 2).
3.10. Impact of pH on breakthrough curves and Thomas model application.

The role of pH plays a very important in the adsorption phenomenon. Breakthrough curves data follow the Thomas model and its assumptions. At lower pH, the adsorption capacity was observed high compared to the other pH values, whereas Kth was lower. Similarly, at a high pH value, the Kth and the adsorption capacity have been observed low [30]. The adsorption capacity was also high at pH 9 as compared to pH 11. A lower Kth value resulted from a high adsorption value compared to pH 11, which reflected a high kth value and lower sorption capacity (Table 2). Overall, when pH moved towards acidic, the sorption capacity increased, and breakthrough time appeared later than basic pH.

4. Conclusions

Dyes are the primary pollutant and have a negative impact on human and aquatic life. Many treatments were introduced to treat textile wastewater, but they were restricted due to high operational costs. Adsorption is one of the most favorable upcoming methods of wastewater treatment. Surplus biomasses that are abundant can be explored as operative bioadsorbent. The breakthrough time and mass transfer zone phenomenon were observed at different bed heights, flow rates, initial dye concentrations, and pH. It was noticed that breakthrough time was increased up to 600 min at 20 cm. The result reveals that the exhaust time will be higher at high bed heights and vice versa. Similarly, at lower flow rates and lower initial dye concentrations, the exhaust time gets long and vice versa. The significant results were obtained at lower pH 5. The breakthrough curve and acceptable adsorption capacity were noticed at acidic pH. The acidic pH was suitable for the adsorption of different dye concentration solutions. The adsorption capacity was significantly high, and mass transfer and breakthrough curves later favored the Thomas model. The column exhaust time ranged from 390 to 600 min. The dye removal and exhaust time increased with increased bed height. The high initial dye concentration and high flow rate caused exhaustion in a shorter time because it fasters the mass transfer zone. Thomas's model fits well with the column adsorption data. However, the overall adsorption capacity was found to be less during experimentation. The color compounds resist the adsorption, and this phenomenon is reduced by adjusting pH at an acidic medium. The R2 values range from (0.93-0.997), and the breakthrough values obtained from the data favor the Thomas model. It is concluded that *Eucalyptus camaldulensis*, which is abundant biomass in northern areas and Punjab province, can be applied in textile wastewater treatment operations.

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Conflicts of Interest

The authors declare no conflict of interest.

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