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Continuous Adsorption of Methylene Blue Dye from Aqueous Solution onto Guava Leaf Powder in Fixed Bed

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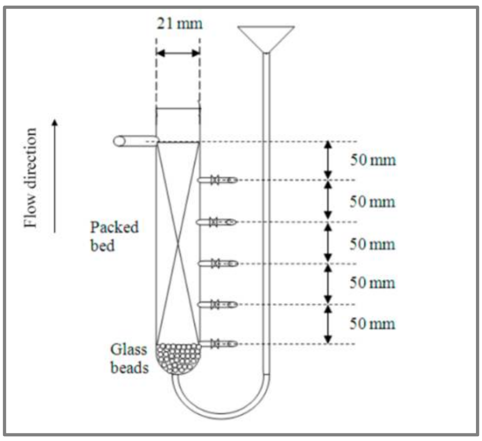
ABSTRACT

In the present study, bulk removal of methylene blue from aqueous solution using fixed bed of guava leaf powder was investigated. Fourier-transform infrared spectroscopy, surface area and particle size were employed to analyze surface morphology of guava leaf powder. Effect of solution pH (5 to 9), initial dye concentration (30 to 70 mg L^{-1}), feed flow rate (5 to 15 mL min^{-1}) and bed height (5 to 20 cm) were exerted. Thomas model and BDST predicted the breakthrough curve with high R^2 values (>96%). Methylene blue adsorption efficiency increased with increase in initial methylene blue concentration, solution pH and bed height. On the otherhand, adsorption efficiency decreases with increase in flow rate. Highest efficiency of bed was achieved at pH 7, initial concentration 70 mg L^{-1}, flow rate 10 mL min^{-1}.

Graphical Abstract



Schematic diagram of fixed bed column used in adsorption study of MB onto GLP.

Keywords: Fixed bed, Adsorption, Break through curves, Methylene Blue, Guava leaf powder.

INTRODUCTION

Synthetic dyes are widely used by the textile industries today in order to satisfy the ever-growing demands in terms of quality, variety, fastness and depth of color etc. [1]. The extensive use of dyes often poses pollution problems in the form of colored wastewater discharge into environmental water bodies. Methylene blue (MB) is one of the most synthetic dyes which used for dyeing of silk, cottons, wools, silk, leather, coloring paper and plastics. The discharge of MB from dying industries to the environment is worried for the ecosystem [2]. The MB dye cause harmful effects such as increased heart rate, vomiting, cyanosis, jaundice, quadriplegia, tissue necrosis, dermatitis, problems in respiratory tract, kidney, liver, brain, reproductive and central nervous system [3, 4]. The removal and recovery of MB dye from wastewater is important in the protection of environment and human health. The possible methods of dye removal from industrial effluents include adsorption, chemical flocculation, chemical oxidation, froth floatation, ozonation, reverse osmosis and biological techniques [5]. Owing to poor efficiency and high cost of these treatment processes, removal of color from wastewater remains to be a major challenge for many of the developing countries today [6]. Adsorption is an efficient and economically feasible process for separation and purification. It plays an important role in the removal dyes from wastewater. Activated carbon is the most common adsorbent used for color removal as it possesses a high surface area and a high adsorption capacity, but it is expensive and necessitates regeneration. The need for an alternative low-cost, easily available, adsorbent has encouraged the search for new adsorbents [7].

Some cost effective adsorbents are chitin and chitosan [8] silica [9], peat [10], natural clay [11], bagasse pith [12] and dyed cellulosic materials [13]. In the recent past some plant leaf powders had been shown to have excellent dye adsorption potential [14-19]. However, most of these works concentrate on batch adsorption kinetics and equilibrium. Batch adsorption of methylene blue using various adsorbents such as blue green algae *Oscillatoria sp*.[20], *Barleria cristata* (Koranti) leaves [21], Activated carbon from *Adenanthera pavonina L* seeds [22] and walnut shell charcoal [23] were previously experimented. The batch treatment is useful in providing information about effectiveness of dye–biosorbent system and sorption capacity parameter. The data obtained under batch conditions cannot be directly used for continuous operations. However, for industrial applications, studies on bulk removal of dye in continuous flow are required. Therefore, in the present work adsorption of methylene blue onto fixed bed of guava leaf powder has been investigated. Various parameters like height of column, initial dye concentration and pH. These results were applied to Thomas and BDST model for column adsorption.

MATERIALS AND METHODS

Adsorbate: Methylene blue (C.I. No. 52015) is a heterocyclic aromatic chemical compound with molecular formula $C_{16}H_{18}N_3SCl$ and molecular weight 319.85 g mol^{-1}. The dye was purchased from Sigma Aldrich, India and structure of same is mentioned in figure 1. It has many uses in a range of different fields, such as textile, biology, chemistry, medicine, etc. The concentration of MB in each aqueous solution was measured using an UV-Visible spectrophotometer (ELICO SL 164 Double Beam UV-Visible spectrophotometer at the characteristic wavelength of methylene blue (λ_{max} = 665 nm). Methylene blue stock solution was prepared by dissolving dye 1 g of MB dye in 1 L of distilled water and subsequently diluted to the required concentration. Samples were diluted if the absorbance exceeds 0.8. Final concentration was then determined from the calibration curve.

Adsorbent: The mature guava leaves used in the present investigation were collected from the available trees near Navyug Science College, Gujarat. They were washed thrice with water to remove dust and water-soluble impurities and were dried until the leaves become crisp. The dried leaves were powdered and further washed with distilled water till the washings were free of color and turbidity. Once again guava leaf powder was dried and preserved in glass bottles for future use.

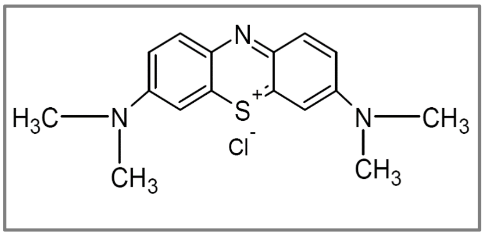


Figure 1. Structure of Methylene Blue dye.

Fixed Bed column: Continuous adsorption of MB was carried out in a glass column with internal diameter of 2 cm. The column was provided with five sampling points at 5 cm intervals. At the bottom of the column 2 cm high layer of glass beads were used to ensure uniform inlet flow to the column. Guava leaf powder was filled over this glass beads to a height of 25 cm (packed with 19.5 g of GLP). MB solution was introduced into the column in bottom to top mode using a peristaltic pump at desired flow rate. The schematic diagram of fixed bed column used in adsorption study is shown in figure 2.

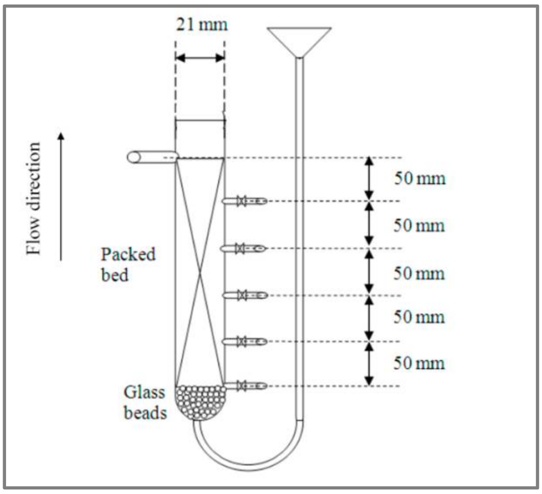


Figure 2. Schematic diagram of fixed bed column used in adsorption study of MB onto GLP.

The experimental solutions were obtained by diluting the stock solutions to required initial concentrations. The known concentration of MB solution (30 to 70 mg L^{-1}) was passed through column with controlled flow-rate (5 to 15 mL min^{-1}) and specified pH (5 to 9). The pH of the feed solution was adjusted by adding 1.0 N HCl or 1.0 N NaOH during experiment. All the chemicals used in the study were of analytical reagent grade. Samples were collected periodically from all the sample ports and analyzed for residual concentration of methylene blue.

Fixed bed adsorption models: Performance of the column operation is described by break through curves. For efficient design and operation of the continuous adsorption column, it is necessary to predict the breakthrough curve or concentration–time profile of the adsorbate for the selected adsorbent under the given set of operating condition. From such curves, the maximum sorption capacity and height of the column required for given condition can be determined.

In a fixed bed adsorption process, operating at a constant flow rate of Q (mL min^{-1}) for a period of t_{total} (min), total volume of effluent (V_{eff}, mL) processed is calculated as:

$$V_{eff} = Q \, X \, t_{total} \ldots\ldots\ldots (1)$$

Total amount of dye adsorbed in the column for a given feed concentration and flow rate over a time interval of t_{total} (min) can be calculated using the formula:

$$q_{total} = \frac{Q}{1000}\int_{t=0}^{t_{total}}\left(1-\frac{C_t}{C_o}\right)dt \qquad \ldots (2)$$

Then percentage dye removed is calculated by the expression:

$$\text{Total removal \%} = \left(\frac{q_{total}}{m_{total}}\right) * 100 \qquad \ldots (3)$$

Where, m_{total}(= Q $C_0 t_{total}$/1000) is the total amount of dye passed through the column.

Thomas model: Thomas model is one of the most general and widely used models to describe packed bed adsorption. Thomas model assumes the following: i) Langmuir isotherm, ii) no axial dispersion and iii) second order adsorption kinetics. Linear form of the model is given by the following equation [**1, 24**]

$$\ln\left(\frac{C_o}{C}-1\right) = \frac{K_{Th} q_0 X}{Q} - \frac{K_{Th} C_0}{Q} V_{eff} \qquad \ldots (4)$$

K_{Th} and q_0 determined from the slope and intercept of the plot of ln (C_0/C-1) vs. t at a given flow rate. Since Thomas model could satisfactorily predict the concentration decay curve other models were not tested in this study.

BDST models: The Bed Depth Service Time model relates the service time of a fixed-bed with the height of adsorbent in the bed, hence with its quantity, because quantity is directly proportional to the bed height. The measurement of sorbent quantity is more precise than the determination of the respective volume, especially for the case of granules. Therefore, sorbent quantity is being preferably used, instead of the bed height. The linear form of BDST model [**25**] is given by the following expression:

$$t = \frac{q_0}{C_0\, V} M - \frac{1}{k\, C_0}\ln\left(\frac{C_0}{C_t}-1\right) = aM + b \quad \ldots (5)$$

Where, t is the service time (min), q_0 the adsorption capacity (mg g^{-1}), C_0 the initial concentration of adsorbate (mg L^{-1}), V the applied flow-rate (mL min^{-1}), M the quantity of sorbent inside the column (g), k the rate constant of adsorption (L- min^{-1} mg), and C_t the respective effluent concentration of adsorbate (mg L^{-1}) at time t. A plot of t versus bed depth, Z, should yield a straight line. The adsorption capacity (q_0) and rate constant (k) can be evaluated from the slope and intercept of the linear plot [**25**].

RESULTS AND DISCUSSION

Analysis of GLP: Figure 3 depicted the FTIR spectra of GLP, in which large stretching between 3000-3500 cm^{-1} was found due to amino group, band at 3000-2800 cm^{-1} was due to the aliphatic CH stretching of methyl group and a sharp band around 1700 and 1653 cm^{-1} was due to stretching frequency of C=O and bending N-H groups respectively. Bands around 1365 and 1240 cm^{-1} were due to phenolic –OH and -SO_3H groups respectively. Also, bands near 1220 and 1145 cm^{-1} were to have tertiary amino group in GLP. Some bands near 1000 cm^{-1} were also exposed due to aliphatic and/or vinyl C-H group. Such types of materials were shown to possess good adsorption potential for cationic dyes [**26, 27**]. The particle size and surface area (by BET method) of GLP were found to be 50-65 µm and 502.7 $m^2\,g^{-1}$ respectively.

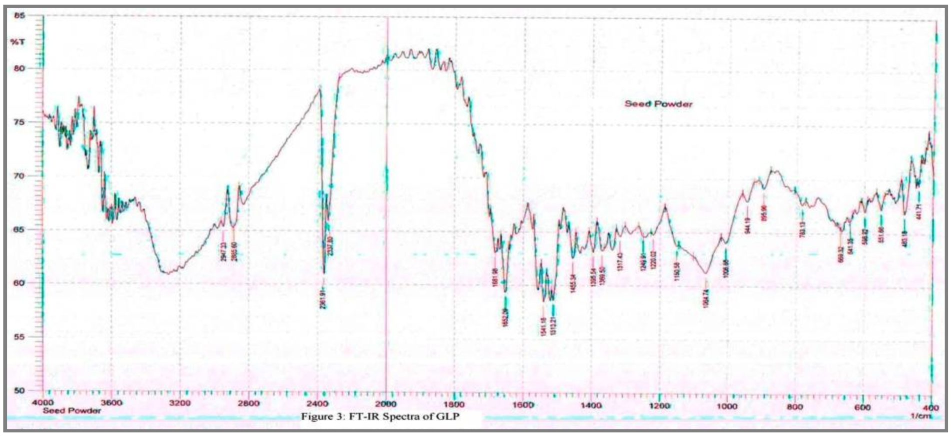


Figure 3. FT-IR spectra of GLP.

Effect of Flow rate: Adsorption breakthrough curves i.e. plot of effluent concentration (C_o) versus time for adsorption of MBD onto GLP at different flow-rates of 5, 10 and 15 mL min^{-1} at constant bed height of 10 cm, pH 7 and initial dye concentration of 50 mg mL^{-1} are shown in figure 4. Breakthrough generally occurs faster at higher flow rate. Thus, breakthrough curve shifted towards lower time scale with flow-rates from 5 to 15 mL min^{-1}. However, difference between 10 mLmin^{-1}and 15 mL min^{-1} was not very less. Thomas model parameters are shown in table 1. R^2 values greater than

Table 1. Thomas isotherm parameters for MB adsorption onto GLP column

Flow rate (mL min^{-1})	pH	Concentration (ppm)	Height (cm)	K_{Th}	q_o	% R (at C/C_o)=0.5	R^2
5	7	50	10	0.0244	23.37	89.41	0.9911
10	7	50	10	0.0301	22.33	86.64	0.9773
15	7	50	10	0.0242	18.98	80.62	0.9649
10	7	30	10	0.0494	9.11	95.81	0.9682
10	7	70	10	0.0221	31.58	83.97	0.9763
10	5	50	10	0.0242	12.04	79.06	0.9855
10	9	50	10	0.0286	20.69	88.35	0.9893
10	7	50	5	0.0389	28.58	85.19	0.9938
10	7	50	15	0.0271	14.82	87.90	0.9676
10	7	50	20	0.0225	14.67	88.82	0.9912

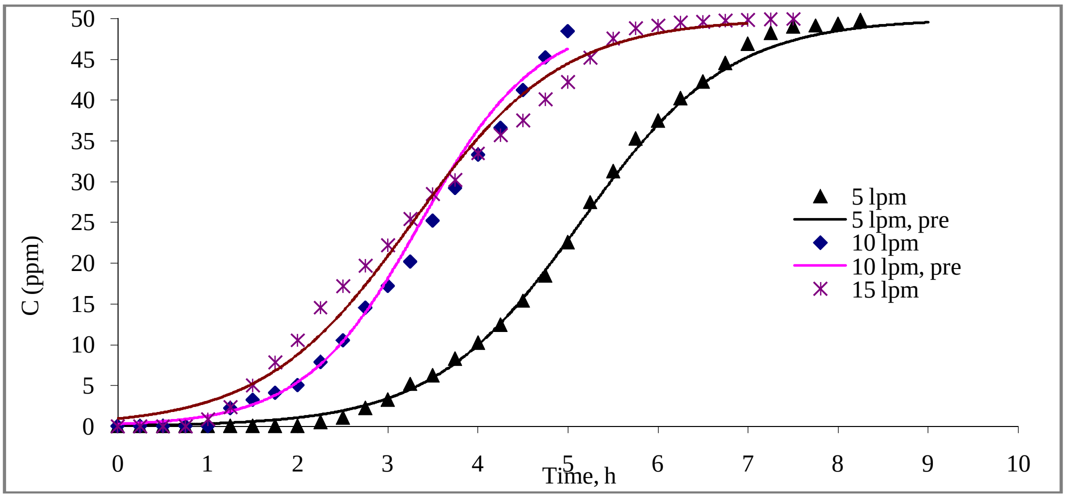


Figure 4. Break through curve for adsorption of methylene blue onto guava leaf powder: Effect of flow rate. [Q = 5, 10 and 15 mg L^{-1} pH = 7, Co = 50 mg L^{-1}, Z = 10 cm]

0.96 indicated that Thomas model predicted concentration decay curves satisfactorily. Percentage removal was higher at lower flow rates. At 5 mg L^{-1}, 10 mg L^{-1} and 15 mg L^{-1} percentage, color removal was found to be 89.41%, 86.64% and 80.62% respectively. Percentage color removal appeared to be strongly dependent on flow rate as the contact time between the adsorbate and adsorbent gets affected with change in flow rate, and in turn it affects the mass transfer parameters and column capacity [28].

Influence of influent MBD concentration: The effect of influent MBD concentration on the shape of the breakthrough curves is shown in figure 5, in which experiments were conducted at pH 7, bed height of 10 cm, flow rate of 10 mL min^{-1} and different influent concentrations of MBD (30, 50 and 70 mg L^{-1}). It is illustrated that the increase in the initial dye concentration at a constant flow rate increases the slope of breakthrough curve and decrease the throughput (output) until breakthrough. This may be caused by high initial concentration saturating the adsorbent more quickly, thereby decreasing the breakthrough time [5, 27].

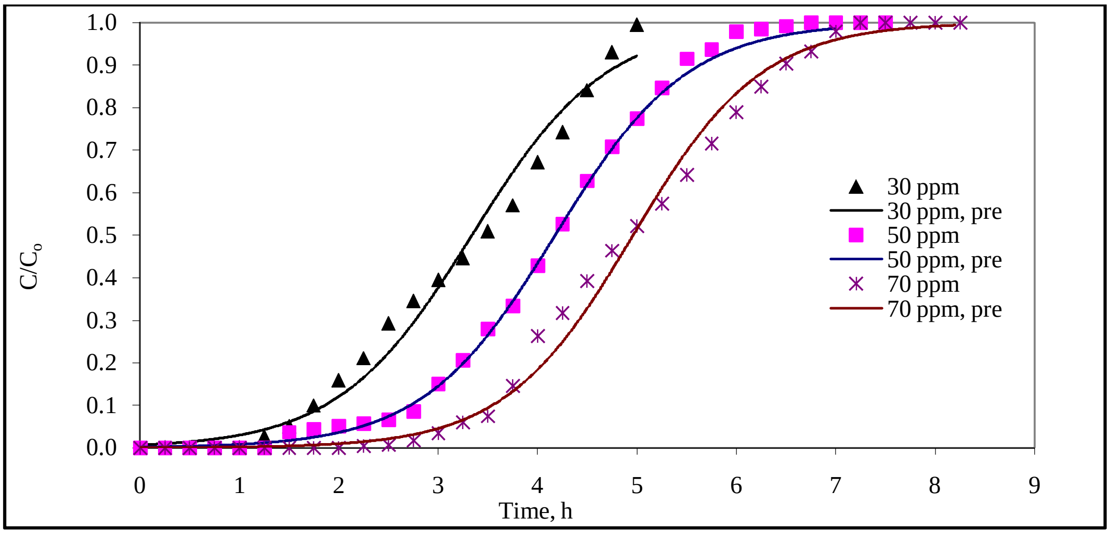


Figure 5. Break through curve for adsorption of methylene blue onto guava leaf powder: Effect of dye inlet concentration. [Q = 10 mL min^{-1}, pH =7, Z = 10 cm; Co = 30, 50 and 70 mg L^{-1}]

Effect of pH: To study the effect of pH experiments were conducted, at constant bed height of 10 cm, flow-rate of 10 mg min^{-1} and initial dye concentration of 50 mg L^{-1}, by adjusting solution pH to 5, 7 and 9. Figure 6 demonstrated the breakthrough time increased with increasing pH. From table 2 it can be seen that percentage dye removal increased with increase in solution pH. Adsorption capacities were 12.04, 18.98 and 20.69 mg g^{-1} at solution pH 5, 7 and 9 respectively. It is known that ionic dyes release colored anions or cations while the dye dissolve in a solution. The amount of dyes adsorbed on the adsorbent surface was mainly influenced by the surface charges, which is in turn affected by the pH of solution. Low adsorption of MBD at acidic pH was probably due to the presence of excess proton (H^+) ions which complete with the cationic dye for adsorption on negatively charged surface of the adsorbent [29, 30]. The dye adsorption may also derive support from the ion exchange reaction. All amino groups of the GLP are captions and thereby the dye anion is pulled inside strongly by electrostatic attraction [31].

Table 2. BDST model parameters for MB adsorption onto GLP column

Ct/Co	q_o (mg mL^{-1})	K (mL mg^{-1} min^{-1})	r^2
0.2	6.975	0.02844	0.9982
0.3	7.0875	0.1458	0.9885
0.4	8.1375	0.00676	0.9959

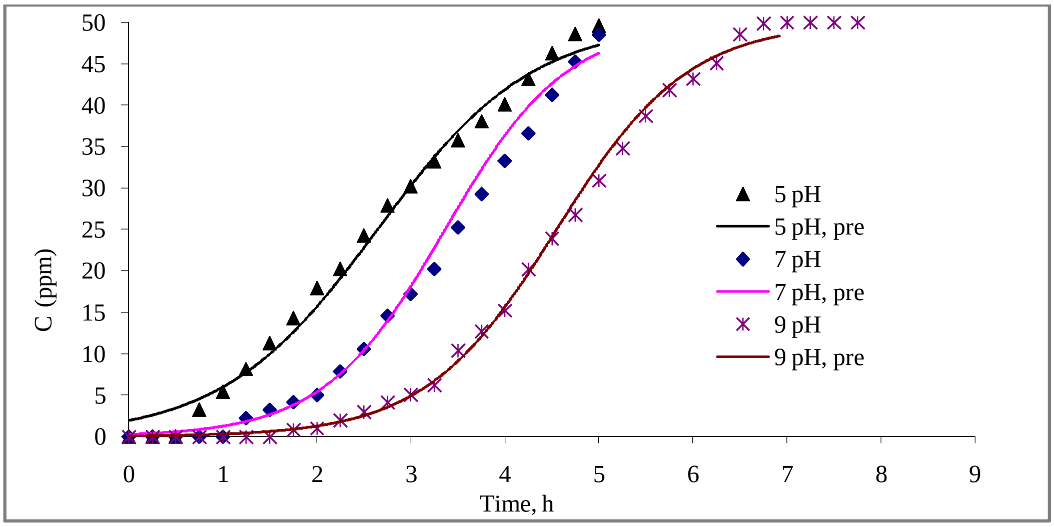


Figure 6. Break through curve for adsorption of methylene blue onto guava leaf powder: Effect of solution pH. [Q = 15 mL min^{-1}; pH =3, 5 and 7; Co = 50 ppm; Z = 10 cm]

Effect of bed height: The column height variation was studied by introducing 50 mg mL^{-1} MB solution at a rate of 10 mL min^{-1}and pH 7. Samples were collected from ports located in the column at distances of 5, 10, 15 and 20 cm (top of the column) from its bottom and breakthrough curves was prepared and shown in figure 7. From table 2 it can be seen that there was small increase in percentage color removal as bed height increases. Initially, the feed solution contacts with the fresh

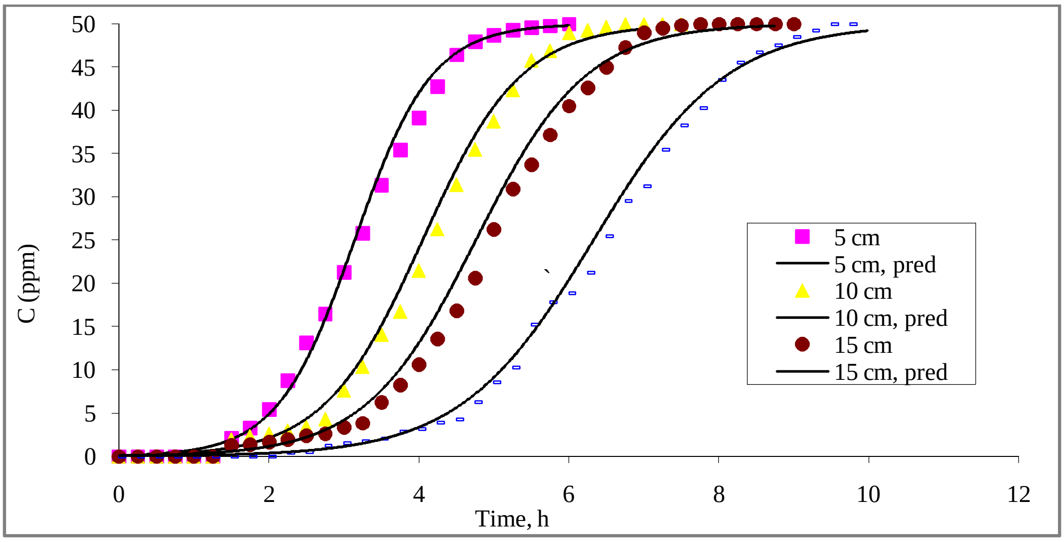


Figure 7. Break through curve for adsorption of methylene blue onto guava leaf powder: Effect of bed height. [Q = 10 mL min^{-1}; pH =7; Co = 50 ppm; Z = 5, 10, 15 and 20 cm]

adsorbent at the bottom of the column. Methylene blue dye was adsorbed progressively on the sorbent as it flowed upward. As more fluid was fed to the column, the bottom portion of the adsorbent becomes saturated with methylene blue dye; thus, the adsorption zone moves upwards. Therefore, the concentration of solute in the lower portions of the packed bed is usually higher than that in the top portions [32].

BDST model: The lines of t–Z at values of different C_t/C_0(0.2, 0.3 and 0.4) were drawn and its related values of q_o (mgmL^{-1}) and k (mL mg^{-1} min^{-1}) were evaluated and mentioned in table 2. Also, its correlation coefficient values were also depicted in table 2. From table 2, as the value of C_t/C_0 increased, the rate constant of K decreased while the adsorption capacity of the bed per unit bed volume, q_o, increased. From the values of R^2 (>0.98), it indicated the validity of BDST model for the present system. The BDST model can be utilized to plan out the process for other flow rates and concentration without further experiments.

APPLICATION

The results indicate that for Guava leaf powder the maximum adsorption capacity value (q_o) of methylene dye solution was obtained as 53.05 mg g^{-1} using flow-rate of 10 mL min^{-1}, pH 7, initial MB concentration of 70 mg mL^{-1} and packed bed-height of 5 cm.

CONCLUSION

From the present study following conclusions can be drawn:

1. The feasibility for removal of methylene blue dye using column with natural material, Guava Leaf powder was investigated in this study.
2. Increasing column height, decreasing influent flow rate and decreasing MB influent and MB concentration, all the results in increase in the breakthrough time.
3. Thomas model and BDST models were applied to data obtained from experimental studies performed on fixed column to predict the breakthrough curves and to determine the column kinetic parameters.
4. The maximum adsorption capacity value (q_o) was obtained as 53.05 mg g^{-1} using flow-rate of 10 mL min^{-1}, pH 7, initial MB concentration of 70 mg L^{-1} and packed bed-height of 5 cm.

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