CHAPTER – VIII
REMOVAL OF DYEST BY FIXED BED COLUMN

8.0 Introduction

Reactive dyes are the most common dyes used due to their advantages, such as bright colors, excellent color fastness and ease of application [1-4]. They exhibit a wide range of different chemical structures, primarily based on substituted aromatic and heterocyclic groups. A large number of reactive dyes are azo compounds that are linked by an azo bridge [5]. Many reactive dyes are toxic to some organisms and may cause direct destruction of creatures in water [6]. In addition, since reactive dyes are highly soluble in water, their removal from effluent is difficult by conventional physico-chemical and biological treatment methods [7, 8].

Batch experiments are usually done to measure the effectiveness of adsorption for removing specific adsorbates as well as to determine the maximum adsorption capacity. The continuous adsorption in fixed-bed column is often desired from industrial point of view. It is simple to operate and can be scaled-up from a laboratory process [9]. A continuous packed bed adsorber does not run under equilibrium conditions and the effect of flow condition (hydrodynamics) at any cross section in the column affects the flow behavior downstream. The flow behavior and mass transfer aspects become peculiar beyond a particular length to diameter ratio of the column [10]. In order to design and operate fixed-bed adsorption process successfully, the break through curves under specific operating conditions must be predictable. The shape of this curve is influenced by the individual transport process in the column and in the adsorbent [11]. Breakthrough determines bed height, operating life span of the bed and regeneration times [12]. Adsorption in fixed-bed columns using activated carbon has been widely used in industrial processes for the removal of contaminants.
from aqueous textile industrial effluents. since it does not require the addition of
chemical compounds in the separation process [13].

Activated carbon adsorption has been found to be superior for wastewater
treatment compared to other physical and chemical techniques, such as flocculation,
coagulation, precipitation and ozonation as they possess inherent limitations such as
high cost, formation of hazardous by-products and intensive energy requirements
[14]. However, commercially available activated carbons are still considered
expensive [15].

Hence, there is a growing interest in using low cost and easily available
materials for the adsorption of dyes. A wide variety of materials [16-21] are employed
as low-cost alternatives to activated carbons. Several models have been developed to
analyse data and predict results for a variety of adsorption systems [21-25]. In the
present study two models víz., Adams-Bohart and BDST model [23] have been
successfully used in describing the adsorption of dyes [24], in column. The purpose of
this study is to investigate the removal of MG, RB and CV by CELC, MLLC, PPLC
respectively to investigate the adsorption behaviour of CELC, MLLC and PPLC in
column studies. Column adsorption equilibrium, column adsorption kinetics, effect of
dose, effect of flow rate of solution and effect of pH were studied.

8.1 Materials and methods

The preparation of IPACs was made according to the literature method [26].
The various experimental conditions were given in Table 8.1. A stock solution of
MG, RB and CV (500 mg L⁻¹) was prepared and suitably diluted to the various
required initial concentrations. Column adsorption experiments were carried out in a
glass column with an inner diameter of 10 mm and various column heights at room
temperature (30 ± 1 °C). The adsorbents with known weight of fixed particle size (150-250 micron) were placed into the column in the form of slurry and packed uniformly. The column was safe-guarded with glass wool. The influent/feed solution of dyes (MG, RB and CV) of known initial concentration, at specified pH was fed from the glass bottle container (5 L capacity). The initial pH of the solutions were adjusted by adding 1 M HCl or 1 M NaOH solution. Initial pH values of dye solutions were noted with digital pen pH meter (Hanna instruments, Portugal). Auto flow meter (McClins, India) was used to adjust the required flow rate (mL min.\(^{-1}\)). The effluent from the column was collected at desired intervals of time to study effect of contact time. The concentrations of the dye solutions before and after adsorption were estimated by measuring OD at corresponding \(\lambda_{\text{max}}\) value of dyes with the help of Systronics spectrophotometer (Model: 105, India) and then interpolated into the standard curve.

**Table 8.1 Various experimental conditions for the removal of MG, CB and CV on CELC, MLLC and PPLC in column adsorption studies at 30 ± 1 °C**

<table>
<thead>
<tr>
<th>S.No</th>
<th>Process parameter varied</th>
<th>Initial dye concentration (ppm)</th>
<th>Contact time (min.)</th>
<th>Bed height (cm)</th>
<th>Flow rate (mL min.(^{-1}))</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Initial dye concentration</td>
<td>MG 125-175 RB 40-70 CV 60-120</td>
<td>MG-130 RB-200 CV-130</td>
<td>0.5</td>
<td>5.0</td>
<td>*Solution pH</td>
</tr>
<tr>
<td>II</td>
<td>Contact time</td>
<td>Optimum # MG-150 RB-50 CV-80</td>
<td>MG 5-130 RB 10-200 CV 5-130</td>
<td>0.5</td>
<td>5.0</td>
<td>*Solution pH</td>
</tr>
<tr>
<td>III</td>
<td>Bed height</td>
<td>Optimum # MG-130 RB-200 CV-130</td>
<td></td>
<td>0.3-0.7</td>
<td>5.0</td>
<td>*Solution pH</td>
</tr>
<tr>
<td>IV</td>
<td>Flow rate</td>
<td>Optimum # MG-130 RB-200 CV-130</td>
<td></td>
<td>Optimum # 0.5</td>
<td>5.0-7.0</td>
<td>*Solution pH</td>
</tr>
<tr>
<td>V</td>
<td>pH</td>
<td>Optimum # MG-130 RB-200 CV-130</td>
<td></td>
<td>0.5</td>
<td>5.0</td>
<td>*Solution pH</td>
</tr>
</tbody>
</table>

# Fixed as optimum condition at which maximum removal was observed.
*Solution pH = 7.2 (MG) and 7.3 (RB, CV)
8.2 Results and Discussion

8.2.1 Effect of initial concentration

The effect of initial concentration of dyes (MG, RB and CV) on the fixed bed column is shown in the breakthrough curves (Figs. 8.1-8.3). A decreased inlet concentration gave an extended breakthrough curves and the treated volume was also higher. The lower concentration gradient caused a slower transport due to decreased diffusion co-efficient [27]. At higher initial concentration of dyes (MG, RB and CV) the adsorbent material was saturated quickly leading to earlier breakthrough and exhaustion time. The driving force for adsorption is the concentration difference between the dye on the adsorbent and the dye in the solution [28]. Thus high driving force due to high dye concentration resulted in better column performance. Similar kind of results were already reported the adsorption dyes [28], metal ions [29] and phenols [30].

![Breakthrough curves for the removal of MG on CELC at various initial concentration](image-url)

**Figure 8.1** Breakthrough curves for the removal of MG on CELC at various initial concentration
Figure 8.2  Breakthrough curves for the removal of RB on MLLC at various initial concentration

Figure 8.3  Breakthrough curves for the removal of CV on PPLC at various initial concentration
8.2.2  Column adsorption kinetics

The experimental data of adsorption kinetics indicated that the adsorption process was very fast at the beginning and then slowed down as equilibrium approached. The column adsorption kinetics was specified by determining the mass transfer co-efficient according to Adams-Bohart equation [21, 22]:

\[
\ln \left( \frac{C_t}{C_i} \right) = k \cdot \frac{t}{C_i} - k \cdot \frac{q}{Z} \cdot (Z/u)
\] .......... (8.1)

Where, \( C_n \), is the concentration of dye in the effluent (mg L\(^{-1}\)) at time \( t \) (min.), \( C_i \) is the initial or inlet dye concentration (mg L\(^{-1}\)), \( q \) is the amount of dye solution uptaken by adsorbent (mg L\(^{-1}\)) \( Z \) is the height of column (m), \( u \), is the linear flow rate of solution (mL min\(^{-1}\)) and \( k \) is the mass transfer co-efficient (mg\(^{-1}\) min\(^{-1}\)). A straight line was attained for this system by plotting \( \ln \left( \frac{C_t}{C_i} \right) \) against \( t \), which gives the value of \( k \) from the slope of the line (Table 8.2). The mass transfer co-efficient \( k \) shows that CELC has greater adsorption capacity for MG than other dye.

<table>
<thead>
<tr>
<th>Table 8.2</th>
<th>Adam’s Bohart parameter at different initial concentration</th>
</tr>
</thead>
</table>

Bed height = 5 mm  
Flow rate = 5 mL min\(^{-1}\)

<table>
<thead>
<tr>
<th></th>
<th>MG– CELC</th>
<th>RB – MLLC</th>
<th>CV – PPLC</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_i ) (ppm)</td>
<td>( 10^2 \cdot k ) (mg L(^{-1}))</td>
<td>( r )</td>
<td>( C_i ) (ppm)</td>
</tr>
<tr>
<td>175</td>
<td>7.231</td>
<td>0.990</td>
<td>60</td>
</tr>
<tr>
<td>150</td>
<td>5.615</td>
<td>0.992</td>
<td>50</td>
</tr>
<tr>
<td>125</td>
<td>2.914</td>
<td>0.986</td>
<td>40</td>
</tr>
</tbody>
</table>

The values of \( k \) increased with increase in initial dye concentration. This showed that the overall system kinetics was dominated by external mass transfer in the initial part of adsorption in the column [31].

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8.2.3 Effect of bed height

The adsorption experiments were carried out by changing the bed height from 0.3 - 0.7 cm with increasing the dose of adsorbent. The change in the breakthrough points explain the effect of adsorbent does on the column study. As shown in breakthrough curves (Figs. 8.4 -8.6), both breakthrough point and exhaustion time increased with increasing bed height, which resulted in a broadened mass transfer zone. Higher uptake was observed at highest bed height due to the increase in the surface area of adsorbent which provided more binding for the adsorption [27, 29]. Even though the breakthrough curves become steeper as the bed height decreased, a higher removal percentage was observed at the highest bed height.

![Graph showing breakthrough curves for various bed heights](image)

**Figure 8.4** Breakthrough curves for the removal of MG on CELC at various bed height
Figure 8.5  Breakthrough curves for the removal of RB on MLLC at various bed height

Figure 8.6  Breakthrough curves for the removal of CV on PPLC at various bed height
Bed Depth Service Time (BDST) is a simple model, which states that bed height (Z) and service time (t) at of a column bears a linear relationship. The ‘Bed Depth Service Time model’ developed By Bohart and Adams [32] is as follows

\[
\ln\left(\frac{C_i}{C_t}\right) = -kNxt + \ln\left(\frac{C_i}{C_t}\right) \quad \ldots \ldots \quad (8.2)
\]

Where \(C_i\) is the effluent concentration (mg L\(^{-1}\)), \(C_t\) is the influent concentration (mg L\(^{-1}\)), \(k\) is the adsorption rate Co-efficient (L mg\(^{-1}\) min\(^{-1}\)), \(x\) is the bed depth (cm), \(u\) is the linear velocity (mL min\(^{-1}\)) and \(t\) is time (min.) and \(N\) is the adsorption capacity co-efficient (mg L\(^{-1}\)). This model ignores the intra-particle mass transfer resistance and external mas transfer resistance such that the adsorbate is adsorbed onto adsorbent surface directly. The observed linearity in the plots indicates the validity of the BDST model for the present system. The estimated values of adsorption rate co-efficient \((k)\) are given in Table 8.3. Similar type of values were already reported in literature [27–32].

<table>
<thead>
<tr>
<th>Table 8.3</th>
<th>Adsorption rate co-efficient obtained from BDST Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>CELC – MG</td>
<td>MLLC– RB</td>
</tr>
<tr>
<td>Bed height (mm)</td>
<td>(10^2 k) (L mg(^{-1}) min(^{-1}))</td>
</tr>
<tr>
<td>3.0</td>
<td>7.232</td>
</tr>
<tr>
<td>5.0</td>
<td>7.631</td>
</tr>
<tr>
<td>7.0</td>
<td>6.942</td>
</tr>
</tbody>
</table>

**8.2.4 Effect of flow rate**

Solution flow rate is an important parameter, which also influences the overall performance and design of the adsorbent column, 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. These results show an inverse relationship between the adsorbate flow rate and initial breakthrough time as well as bed exhaustion time. The increase in flow rate decreases the volume treated until breakthrough and therefore the service time of the bed (Figs. 8.7-8.9). The breakthrough curve becomes flatter at higher flow rate [33]. This is due to decreased contact time between the dye and the adsorbent at higher flow rates. When the flow rate is low, the equilibrium corresponding to batch experimental data could be reached and the shape of the curve is more like an ideal breakthrough curve or the critical value of the effluent (outlet) concentration is moved to theoretical one, close to 80-90% of inlet concentration.

![Breakthrough curves for the removal of MG on CELC at various flow rate](image)

Figure 8.7  Breakthrough curves for the removal of MG on CELC at various flow rate
Figure 8.8  Breakthrough curves for the removal of RB on MLLC at various flow rate

Figure 8.9  Breakthrough curves for the removal of CV on PPLC at various flow rate
8.2.5 Effect of pH

pH of the medium shows significant effect on adsorption process. Similar to batch adsorption experiments the amount of dye adsorbed were significantly affected in acidic medium. In acidic medium the adsorbent surface gets positive charge and resists the adsorption of cationic dyes [34, 35]. Therefore, in acidic medium break through point occurs very quickly.

8.2.6 Desorption studies

The exhausted column was regenerated by means of chemical regeneration method. The column regeneration was carried out with different eluents like HCl, HNO₃, H₂SO₄, CH₃COOH and NaOH. Among these eluents, nitric acid (0.5 M) was found to be the best one with maximum regeneration capacity [36]. The regenerated adsorbents were analysed for particle size degradation with the help of mechanical sieves (Jayanth, India) and the extent of degradation was found to be in the range of 1.8-4.3 %.

The regenerated columns were reused for further removal of dyes, but their adsorption capacity was found to be slightly lower (15-20 %) than that of the original adsorbents. It may be due to the incomplete desorption of the dyes loaded on adsorbents and incomplete regeneration, after the first column run. However, the regenerated column could be reused for the removal of dyes in wastewater containing low dye concentration.

Thus, the mini-column (pilot scale plant) technique provides useful information about the extent of removal of dyes from wastewater. The data will be helpful in designing the cost effective wastewater treatment plant.
8.3 Conclusions

The experimental results indicate that the amount of dye adsorbed increased with increasing the initial concentration, contact time, pH and bed height. In the packed column, the available active sites of adsorbent are minimum. So, the amount of dye adsorbed was found to be less when compared with that of batch adsorption experiments. The column adsorption kinetics obey Adams and Bohart model. The adsorption was greater at the beginning and slows down as the contact time increases. The breakthrough curves calculated from the adsorption of dyes by these adsorbents indicate that the dye removal is strongly dependent on the kinetics of adsorption of dyes. Fixed bed studies with various bed heights obey BDST model. The present study concludes that CELC, MLLC and PPLC could be employed as alternative to CAC for the removal of cationic dyes in water and waste water by column adsorption kinetics.
8.4 References