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ADSORPTION AND DESORPTION CHARACTERISTICS OF CRYSTAL VIOLET IN BOTTOM ASH COLUMN

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Abstract: This study described adsorption of Crystal Violet (CV) by bottom ash in fixed-bed column mode. Equilibrium of adsorption was studied in batch mode for finding adsorption capacity of bottom ash. In fixed bed column adsorption, the effects of bed height, feed flow rate, and initial concentration were studied by assessing breakthrough curve. The slope of the breakthrough curve decreased with increasing bed height. The breakthrough time and exhaustion time were decreased with increasing influent CV concentration and flow rates. The effect of bed depth, flow rate and CV concentration on the adsorption column design parameters were analyzed. Bed depth service time (BDST) model was applied for analysis of crystal violet adsorption in the column. The adsorption capacity of bottom ash was calculated at 10% breakthrough point for different flow rates and concentrations. Desorption studies reveals that recovery of CV from bottom ash was effective by using CH₃COOH than H₂SO₄, NaOH, HCl and NaCl solutions.

Keywords: Adsorption; Crystal violet; Bottom ash; fixed bed; BDST

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INTRODUCTION

Dyes are one of the major constituents of the wastewater produced from many industries related to textile, paint and varnishes, ink, plastics, pulp and paper, cosmetics, tannery etc., and also to the industries, which produces dyes (Adak et al., 2005). Textile mill effluents are generally characterized by the parameters of BOD, COD, pH, suspended solids and color. Most of these parameters are removed satisfactorily by conventional chemical coagulation and biological treatment methods except highly polymer structured color (Selcuk, 2005).

The dyes are one important part of the pollution problem as it is estimated that 50% of their amount is not fixed on fibers and remain finally in wastewater (Harrelkas et al., 2009). Dyes concentration in effluents is usually lower than any other chemical found in these wastewaters, but due to their strong color they are visible even at very low concentrations, thus causing serious aesthetic problems in wastewater disposal (Zollinger, 2003). Environmental pollution by dyes also set a severe ecological problem which is increased by the fact that most of them and their degradation by-products are difficult to discolor and degrade using standard biological methods (Al-Momani et al., 2002). Uptake of textile effluents through food chain in aquatic organisms may cause various physiological disorders like hypertension, sporadic fever, renal damage, cramps etc. The bio-accumulation of organic and inorganic toxicants depends on availability and persistence of the contaminants in water, food and physiological properties of the toxicants (Karthikeyan et al., 2006).

Adsorption is widely used in the removal of refractory pollutants (including dye) from wastewater. The major advantages of an adsorption treatment for the control of water pollution are less investment in terms of initial development cost, simple design, easy operation, and free from or less generation of toxic substances (Crini, 2006).

Adsorption onto activated carbon 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 (Padmesh et al., 2006). Even though activated carbon showed advantages, the main drawback of the activated carbon is the cost and difficulty in regeneration (Liu et al., 2007). Therefore, in recent years, this has prompted a growing research interest in the production of activated carbons from renewable and cheaper precursors which are mainly industrial and agricultural by-products (Tan et al., 2008).

Various low-cost adsorbents from industrial by-products have been investigated to remove dyes from wastewater (Gupta et al., 2004a) and fly ash (Rachakornkij et al., 2004). Bottom ash is one of such low cost adsorbent. The bottom ash is a coarse, granular, combustible by-product of power plants, obtained after combusting coke. It is an undesired collected material, whose disposal has always been a matter of concern to the station authorities, as the dumped ash makes the land infertile (Hecht & Duvall, 1975). Already proved that bottom ash was very efficient adsorbent for removing Malachite Green (Gupta et al., 2004b), Quinoline Yellow (Gupta et al., 2005), Acid Orange 7 (Gupta et al., 2006a), 2-Aminophenol (Gupta et al., 2006b), Basic fuchsin (Gupta et al., 2008), Carmoisine A (Gupta et al., 2009), Chrysoidine Y (Mittal et al., 2010a) and Crystal Violet (Mittal et al., 2010b). But there are seldom publications about the dye adsorption behavior of bottom ash in column mode. Both batch adsorption and fixed-bed adsorption studies are required to obtain key parameters required for the design of fixed-bed adsorber (Song et al., 2011).

Keeping these in view it was considered worthwhile to use bottom ash as an adsorbent for the removal of crystal violet (CV) from aqueous solution. Crystal violet, also known as Basic Violet 3, is a well-known cationic dye being used for various purposes: a biological stain, a dermatological agent, a veterinary medicine, an additive to poultry feed to inhibit propagation of mold, intestinal parasites and fungus etc. It is also extensively used in textile dying and paper printing (Adak et al., 2005). Mass Transfer Zone (MTZ) and breakthrough characteristics were studied for CV adsorption in bottom ash column for different flow rate, bed depth and initial CV concentration. Bed Depth Service Time Model (BDST), which offers a simple approach and rapid prediction of adsorber performance, was applied for modeling adsorption of CV in bottom ash column.

MATERIALS AND METHODS

Adsorbent and adsorbate

The thermal power plant waste material, ‘Bottom ash’ (size of 300 to 600 µm) was utilized as potential adsorbent in this study. The adsorbent was obtained from Neyveli Lignite Corporation Limited, Neyveli, Tamilnadu, India. Crystal Violet (A.R Grade, C.I.42555, λ_max = 579 µm, Molecular weight = 407.99 g/mol, Molecular Formula = C_{25} H_{36}Cl N_{2}), from S.D. fine chem. Pvt Ltd, was the adsorbate used for this study. The chemical structure of Crystal violet is shown in Fig. 1.

SEM and FTIR study

Most of the characteristics of bottom ash were given in our previous work (Nidheesh et al., 2011). Scanning
bottom ash to study their surface textures. The SEM analysis was done at 1000× magnification. In addition, the surface functional groups of bottom ash were detected by Fourier Transform Infrared (FTIR) Spectroscope (FTIR-2000, Perkin Elmer) using KBr pellet method. The spectra were recorded from 4000 to 400 cm⁻¹. SEM and FTIR were carried out for bottom ash after adsorption to find their changes in respective characteristics.

**Adsorption isotherm**

The batch sorption studies were carried out by shaking a series of bottles containing different amounts of Bottom ash dosage (0.08 to 0.53) in 100 mL of 10 mg/L dye solution prepared in the laboratory. The samples were stirred at room temperature at 150 rpm for equilibrium time, and their content was then centrifuged at 3500 rpm for 5 min and the supernatant liquid was analyzed for dye concentration. An IHC-3280 Orbital shaking incubator was used for batch adsorption experiments. A UV/Vis spectrophotometer (Lambda 25) was used for measurement of dye concentration.

**Column studies**

Fixed bed column studies were conducted using columns of 2 cm diameter and 50 cm length. The column was packed with bottom ash between two supporting layers of pre equilibrated glass wool and glass beads. The schematic diagram of the column study is shown in Fig. 2. The particle size was 300–600 µm with a bed depth of 30 cm and filling weight of 45.98 g.

The packed density or bulk density of the adsorbent in the column was approximately 0.312 g cm⁻³. The dye solution was fed through the fixed-bed column in the down flow mode. Before operation, the bed was rinsed with distilled water and left overnight to ensure a closely packed arrangement of particles with no void, channels, or cracks. The effluent samples were collected at specified time intervals and measured for the dye concentration by UV/Vis spectrophotometer. The flow to the column was continued until the effluent concentration (C) approached the influent concentration (C₀).

**Design parameters of adsorption column**

When adsorbate is introduced at the top of a clean bed of adsorbent, most solute removal initially occurs at top of column in a rather narrow band at the top of column, known as adsorption zone (Benfield *et al.*, 1982). When the adsorption zone moves down and the lower edge of this zone reaches the bottom of the column, the effluent concentration starts to rise rapidly (Faust & Aly, 1987).

The point at which the effluent concentration increases rapidly is known as breakthrough point. When the effluent concentration C is approaching to 90% of C₀ (initial adsorbate concentration) then the adsorbent is considered to be essentially exhausted. As per Benfield *et al.* (1982) depth of exchange zone, time required for exchange zone to move its own height, adsorption rate, adsorption capacity etc. are the main design parameters of adsorption column.
The time required for the exchange zone to move the length of its own height up/down the column once it has become established is:

\[ t_z = \frac{(V_E - V_B)}{r} \]  

(1)

where \( V_E \) = total volume of wastewater treated to the point of exhaustion (L); \( V_B \) = total volume of wastewater treated to the point of breakthrough (L); \( r \) = wastewater flow rate (L/hr).

The time required for the exchange zone to become established and move completely out of the bed is:

\[ t_E = \frac{V_E}{r} \]  

(2)

Rate at which the exchange zone is moving up or down through the bed is:

\[ U_z = \frac{h_z}{t_z} = \frac{h}{t_z - t_f} \]  

(3)

where, \( h_z \) = height of exchange zone (cm); \( h \) = total bed depth (cm); \( t_f \) = time required for the exchange zone to initially form (h). Rearranging Eq. (3) provides an expression for the height of the exchange zone as given below.

\[ h_z = \frac{ht_z}{t_z - t_f} \]  

(4)

The value of \( t_f \) can be calculated as follows:

\[ t_f = (1 - F)t_z \]  

(5)

At breakthrough, the fraction \( F \) of adsorbent present in the adsorption zone still possessing ability to remove solute is:

\[ F = \frac{S_a}{S_{max}} = \frac{\int_{V_e}^{V_B} (C_e - C) dV}{C_a(V_E - V_B)} \]  

(6)

where, \( C_a \) = initial solute concentration (mg/L); \( S_a \) = amount of solute that has been removed by the adsorption zone from breakthrough to exhaustion; \( S_{max} \) = amount of solute removed by the adsorption zone if completely exhausted. The percentage of the total column saturated at breakthrough is

\[ \%saturation = \frac{h + (F - 1)h_z}{h} \times 100 \]  

(7)

Weber (1972) gives an equation for height of MTZ as a function of volume as:

\[ h_z = h\left(\frac{V - V_B}{V_E - V_B}\right) \]  

(8)

Desorption study

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the dye. If the adsorbed dyes can be desorbed through using neutral pH water, then the attachment of the dye of the adsorbent is by weak bonds (Ansari & Mosayebzadeh, 2010). Desorption study was carried out in batch followed by column methods. For batch study, 1N solution of H2SO4, NaOH, CH3COOH, HCl, and NaCl (50mL each) is used for saturated adsorbent and kept in shaker up to 1 h. The sorbent solution mixtures were then centrifuged at 3600 rpm for 5 minutes and the supernatant was analyzed for the dye concentration.

The chemical reagent having higher CV recovery in batch recovery was used for column study. Column saturated with 20 mL/min with CV of 25 mg/L has been selected for desorption study. The reagent was passed through the column at a flow rate of 15 mL/min slightly less than 20 mL/min. Effluent concentration was noted in an interval, in order to analyze desorption behavior of CV in bottom ash column.

RESULTS AND DISCUSSION

Adsorption isotherms

The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state (Bello et al., 2010). The simplest proposed model for characterizing adsorption is the Langmuir isotherm. The Langmuir isotherm is developed by assuming that a fixed number of adsorption sites are available, and that the adsorption is reversible. The Langmuir isotherm may be used when the adsorbent surface is homogeneous. The Langmuir isotherm is expressed as (Langmuir, 1915).

\[ q_e = \frac{X}{M} = \frac{q_{max} b C}{1 + b C} \]  

(9)

where \( b \) is constant that increases with increasing molecular size, \( q_{max} \) is amount adsorbed to form a complete monolayer on the surface (mg/g), \( X \) is weight of substance adsorbed (mg), \( M \) is weight of adsorbent (g), and \( C \) is concentration remaining in solution (mg/L). The above equation can be recast in a linear form as:

\[ \frac{1}{X/M} = \frac{1}{q_{max}} + \frac{1}{q_{max} b C} \]  

(10)

Isotherm plot for the removal of CV onto bottom ash is shown in Fig. 3.
From Fig. 3, regression values ($R^2$) indicates that the adsorption data for CV onto bottom ash fitted well with the Langmuir isotherm. The intercept and slope of straight line were used to obtain the Langmuir constants. Langmuir constants $b$ and $q_{\text{max}}$ were evaluated and have the value of 4.44 and 5.24 mg/g, respectively. The correlation coefficient ($R^2$) was obtained as 0.877.

**Effect of bed-depth**

Fixed-bed column studies were conducted using column packed with bottom ash for three different heights such as 10, 20 and 30 cm. The column was fed with Crystal violet solution in the down flow mode with a flow rate of 15 mL/min and the initial dye concentration of 25 mg/L. The breakthrough curves (at different masses or bed-depths) are shown in Fig. 4. From the Fig. 4, it was observed that the breakthrough and exhaustion time increases with bed depth.

The higher bed column resulted in a decrease in the effluent concentration at the same service time. The slope of the breakthrough curve decreased with increasing bed height, which resulted in a broadened mass transfer zone (Han et al., 2009).

A higher CV uptake was also observed at a higher bed height due to the increase in the specific surface of the adsorbent which provided more fixation binding sites for the dye to adsorb. The increase in the adsorbent mass in a higher bed provided a greater service area which would lead to an increase in the volume of the solution treated (Tan et al., 2008).

**Effect of initial dye concentration**

To evaluate the effect of the influent CV concentration on its reduction in the column, the concentration of CV was increased from 10 to 25 mg/L under the same operating condition. Fig. 5 depicts three breakthrough curves of CV removal by bottom ash at different initial dye concentration, for the 10 cm bed-depth, and flow rate of 20 mL/min. It is illustrated that the breakthrough time decreased with increasing influent CV concentration. At lower influent CV concentration, breakthrough curve was dispersed and breakthrough occurred slowly. As influent concentration increased, sharper breakthrough curves were obtained. These results demonstrate that the change of concentration gradient affects the saturation rate and breakthrough time. This can be explained by the fact that more adsorption sites were being covered as the CV concentration increases (Han et al., 2009).

**Effect of flow rate**

Columns were run at different flow rates such as 10, 15 and 20 mL/min with a fixed adsorbent bed of 10 cm at an initial CV concentration of 25 mg/L to study the effect of flow rate in the performance of bottom ash bed. The breakthrough curves at various flow rates are shown in Fig. 6. From the Fig. 6, it can be seen that the breakthrough generally occurs faster with a higher flow rate. Breakthrough times ($C/C_0 = 0.1$) were found to be 11, 6 and 3.5 h for the flow rate of 10, 15 and 20 mL/min, respectively. Similarly the exhaustion times were increased with decrease in flow rate. This is due to the fact that at a low rate of influent; CV had more time to be in contact with adsorbent, which resulted in a greater removal of CV molecules in column (Han et al., 2009). At a higher flow rate, the adsorption capacity was lower due to insufficient residence time of the solute in the column and diffusion of the solute into the pores of the adsorbent, and therefore, the solute left the column before equilibrium occurred (Tan et al., 2008).

**Effect of bed depth, flow rate and initial CV concentration on MTZ Development**

Development of MTZ with time for different depth, initial CV concentration and flow rate is shown in Fig. 7. Figure revealed that the mass transfer rate increases...
with bed depth, initial CV concentration and flow rate. Column design parameters for different depths, initial CV concentration and flow rate are given in Table 1. From Table 1, it was found that all the design parameters excluding percentage of bed saturation increases with bed depth. Then, it was clear that the adsorption capacity of bottom ash decreases with increase in bed depth. It was also found that $t_E$ and $t_z$ decreases with increase in CV concentration and flow rate. But $h_z$ and $U_z$ increases with increase in CV concentration and flow rate.

### Analysis of CV adsorption in column by BDST model

BDST is a simple model for predicting the relationship between bed depth, and service time, $t_1$ in terms of process concentrations and adsorption parameters (Han et al., 2009). This model is used only for the description of the initial part of the breakthrough curve, i.e. up to the breakpoint or 10–50% of the saturation points (Chen et al., 2006). The objective of fixed-bed operations is to reduce the concentration in the effluent so that it does not exceed a specific breakthrough concentration (Faki et al., 2008).

This BDST model was focused on the estimation of characteristic parameters such as the maximum adsorption capacity and kinetic constant (Suksabye et al., 2008). The BDST model is based on the assumption that the rate of adsorption is controlled by the surface reaction between adsorbate and the unused capacity of the adsorbent (Goel et al., 2005). The original BDST theory was developed for the removal of chlorine gas by charcoal column. Adams–Bohart model (Bohart & Adams, 1920) is presented as:

\[
\ln \left( \frac{C_o}{C_B} - 1 \right) = \ln \left( e^{K_v t} - 1 \right) - K_v C_o t
\]

where $C_o$ is the initial concentration of solute (mg/L), $C_B$ the desired concentration of solute at breakthrough
Table 1 Column design parameters

<table>
<thead>
<tr>
<th>Concentration (mg/L)</th>
<th>Flow (mL/min)</th>
<th>Bed depth (cm)</th>
<th>t_E (hr)</th>
<th>t_z (h)</th>
<th>h_z (cm)</th>
<th>U_z (cm/h)</th>
<th>Bed Saturation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>20</td>
<td>10</td>
<td>89</td>
<td>76</td>
<td>9.337</td>
<td>0.123</td>
<td>90.82</td>
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<tr>
<td>20</td>
<td>30</td>
<td>10</td>
<td>67</td>
<td>60</td>
<td>9.836</td>
<td>0.164</td>
<td>91.56</td>
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<td>40</td>
<td>10</td>
<td>27</td>
<td>23.5</td>
<td>9.53</td>
<td>0.41</td>
<td>92.13</td>
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<tr>
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<td>20</td>
<td>20</td>
<td>92</td>
<td>73</td>
<td>17.273</td>
<td>0.237</td>
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<td>20</td>
<td>30</td>
<td>30</td>
<td>39</td>
<td>29</td>
<td>24.10</td>
<td>0.83</td>
<td>91.97</td>
</tr>
<tr>
<td>30</td>
<td>40</td>
<td>10</td>
<td>30.5</td>
<td>24</td>
<td>8.54</td>
<td>0.36</td>
<td>91.46</td>
</tr>
<tr>
<td>10</td>
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<td>20</td>
<td>34</td>
<td>28.5</td>
<td>18.33</td>
<td>0.64</td>
<td>90.8</td>
</tr>
<tr>
<td>15</td>
<td>30</td>
<td>10</td>
<td>94</td>
<td>67</td>
<td>7.67</td>
<td>0.114</td>
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<td>30</td>
<td>115</td>
<td>75</td>
<td>13.95</td>
<td>0.186</td>
<td>92.15</td>
</tr>
</tbody>
</table>

Concentration (mg/L), \( k_a \) the adsorption rate constant (L/mg/h), \( N_o \) the adsorption capacity (mg/L), \( H \) the bed depth of column (cm), \( u \) the linear flow velocity of feed to bed (cm/hr), \( t \) is the service time of column under above conditions (hrs). Since \( e^{k_AN_o/u} \) always greater than 1, Eq. (11) reduced to:

\[
t = \frac{HN_o}{uC_o} \ln \left( \frac{C_o}{C_b} - 1 \right)
\]

This is in the form of

\[
t = aH - b
\]

That is, a plot of service time \( t \) against \( H \) should generate a straight line with slope \( a \) equal to \( \frac{N_o}{C_o u} \) and intercept \( b \) of \( \frac{-1}{k_a C_b} \ln \left( \frac{C_b}{C_o} \right) \). From the slope and intercept, both \( N_o \) and \( k_a \) are calculated.

The critical bed depth \( (H_o) \) is the theoretical depth of adsorbent sufficient to ensure that the outlet solute concentration does not exceed the breakthrough concentration \( (C_b) \) value at time \( t = 0 \). \( H_0 \) can be calculated as (Sarin et al., 2006).

\[
H_o = \frac{u}{N_o k_a} \ln \left( \frac{C_o}{C_b} - 1 \right)
\]

Figure 8a shows the applied BDST curve for different concentration at a flow rate of 20 mL/min. Figure reveals that the BDST model fit very well for the experiment data. The parameters of fixed-bed column system for various flow rates and concentration are given in Table 2.

Adsorption capacity of bottom ash is calculated by dividing \( N_o \) by mass of adsorbent. As per model predicted values, the adsorption capacity of bottom ash increases with decrease in flow rate. But exception is there in case of 15 mL/min. This may be due to experimental error. The adsorption capacity is also increases with decrease in concentration, for a constant flow rate. The adsorption rate constant is directly proportional to flow rate. That is adsorption rate constant is increases with decrease in flow rate and concentration. The critical bed depth is decreases with decrease in flow rate and concentration.

At 50% of breakthrough, the logarithmic term in Eq. (12) reduces to zero, and the final term in the BDST equation become zero, giving the relationship as (Suksabye et al., 2008).

\[
t_{0.5} = \frac{N_o H}{C_b u}
\]

If the curve of \( t_{0.5} \) versus \( H \) is a straight line passing through the origin, it can be explained that the adsorption data follow the BDST model (Netpradith et al., 2004; Zulfadhly et al., 2001). Figure 8b shows that the applied BDST curve for different experiment values at 50% breakthrough. But it is not passing through origin, even \( R^2 \) values is very high.

Table 2 Experimental constants of BDST model

<table>
<thead>
<tr>
<th>Concentration (mg/L)</th>
<th>Flow Rate (mL/min)</th>
<th>u (cm/h)</th>
<th>( N_o ) (mg/cm³)</th>
<th>( k_a ) (L/mg/h)</th>
<th>( R^2 )</th>
<th>( H_0 ) (cm)</th>
<th>q (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>20</td>
<td>381.97</td>
<td>7.83</td>
<td>0.031</td>
<td>0.998</td>
<td>3.46</td>
<td>170.29</td>
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<tr>
<td>15</td>
<td>20</td>
<td>381.97</td>
<td>5.73</td>
<td>0.062</td>
<td>0.987</td>
<td>2.36</td>
<td>124.62</td>
</tr>
<tr>
<td>20</td>
<td>10</td>
<td>190.98</td>
<td>11.22</td>
<td>8.37×10⁻³</td>
<td>0.978</td>
<td>4.47</td>
<td>244.01</td>
</tr>
<tr>
<td>25</td>
<td>15</td>
<td>286.47</td>
<td>2.32</td>
<td>0.035×10⁻³</td>
<td>0.982</td>
<td>7.75</td>
<td>50.46</td>
</tr>
</tbody>
</table>
This indicates that the transport of crystal violet from the aqueous solution onto bottom ash is quite complex and involves more than one rate-limiting step (Sharma & Foster, 1995; Zulfadhly et al., 2001).

**SEM and FTIR pattern**

In order to confirm CV adsorption in bottom ash column, SEM analysis was carried out for raw and CV adsorbed bottom ash. The SEM photographs of adsorbents before and after adsorption are shown in Figs 9a and 9b, respectively. From these pictures, it is clear that there was significant difference in the appearance of the adsorbent surfaces. The white clumps on the adsorbent surface represent the adsorbate (Ghosh & Liji Philip, 2005).

FTIR technique is an interesting application for studying the interaction between an adsorbate and the active groups on the surface of adsorbent (Monash & Pugazhenthi, 2009). FTIR spectroscopy was, therefore, carried out to identify the major functional groups presented in bottom ash. The FTIR spectrum of bottom ash, before and after CV adsorption, is shown in Fig. 10. From Fig. 10, it was found that bottom ash (before adsorption) have peaks at 786, 953, 1098, 1649, 3446 cm⁻¹ etc. The peak at 2926 cm⁻¹ is an indicator of the stretching vibration of the C–H group. The absorption bands at 1649, 1505 and 1407 cm⁻¹ indicates the presence of COO, N–H and C–O groups on the biosorbent surface (Kumar & Ahmad, 2011). Other functional groups corresponding to each peaks is given in our previous work (Nidheesh et al., 2011). In the case of bottom ash after adsorption, the percentage transmittance of peaks corresponding to 3446 cm⁻¹ is increased in the bottom ash after adsorption. But the peaks at 929, 1128, 1638 and 1796 cm⁻¹ are decreased in the bottom ash after adsorption.
Adsorption mechanism

There were many factors that may influence the adsorption behavior, such as dye structure and size, adsorbent surface properties, stearic effect and hydrogen bonding, Vander Waals forces etc. CV is a cationic dye having amine groups in its structure. In an aqueous solution, it dissociates as (Kumar & Ahmad, 2011):

\[
\text{CH}_3\text{N}^+\text{(CH}_3\text{)}_2\rightarrow\text{CH}_3\text{N}^+\text{(CH}_3\text{)}_2\text{Cl}+\text{H}_2\text{O}
\]

where R is used for rest of the dye molecule.

The complexation between CV and bottom ash can take place through the weak and strong forces. The weak interactions occur due to the Vander Waals forces while the strong interactions occur due to (i) hydrogen bonding interaction between the nitrogen containing amine groups of CV and bottom surface (ii) hydrophobic–hydrophobic interactions between the hydrophobic parts of CV and bottom ash (iii) electrostatic interaction between the cationic dye (due to the presence of \(+N\) \((\text{CH}_3)_2\) group) and negatively charged bottom ash surface in basic medium (Kumar & Ahmad, 2011).

On the surface of the bottom ash the functional oxidized groups are present as \(\text{SiO}_2\) and \(\text{Al}_2\text{O}_3\). The central ion of silicates (\(\text{Si}^{4+}\)) has a very strong affinity for electrons; therefore, the oxygen atoms that are bound to the silicon ions have a low basicity, making the silica surface act as a weak acid. The oxygen atoms on the silica surface are free to react with water, forming surface silanol (\(\text{SiOH}\)) groups. The acidity of the silanol (\(\text{SiOH}\)) groups determines the dependence of the charge of the silica surface on pH. At low pH, a positively charged silica surface results, and at high pH values negatively charged surface prevails (Mohan & Gandhimathi, 2009).

In this study, the adsorption experiments were carried out in the alkaline pH (around 8.07 at 27.7°C). From the point of zero charge of the bottom ash \(pH_{PZC} = 6.2\) (Nidheesh et al., 2011), it was found that the silica, alumina and iron content of the bottom ash were negatively charged above 6.2 pH value. The negative charge at an active site on the surface of the bottom ash \(\text{Eqs. 17 and 18}\) which allows \(N^+\) \(R\) (CV in aqueous solution) to be complexed at the surface \(\text{Eqs 19 and 20}\).

\[
\equiv \text{SiOH} + \text{OH}^- \rightarrow \equiv \text{SiO}^- + \text{H}_2\text{O} \quad (17)
\]
\[
\equiv \text{AlOH} + \text{OH}^- \rightarrow \equiv \text{AlO}^- + \text{H}_2\text{O} \quad (18)
\]
\[
(\equiv \text{SiO}^-) + N^+\text{R} \rightarrow (\equiv \text{Si}–\text{O})\text{N}^-\text{R} \quad (19)
\]
\[
(\equiv \text{AlO}^-) + N^+\text{R} \rightarrow (\equiv \text{Al}–\text{O})\text{N}^-\text{R} \quad (20)
\]

Desorption study

Desorption study was done both in batch and continuous mode. Column desorption study was carried out followed by batch study. The regeneration was examined (in batch mode) using 50 mL of the selected Solvents. The results are summarized in Table 3. As the data show in Table 3, maximum desorption percentage using different desorbing solutions was found to be about 47% by \(\text{CH}_3\text{COOH}\). Based on the batch desorption study results, \(\text{CH}_3\text{COOH}\) was used to recover CV from the saturated column packed with bottom ash.

The column with a bed depth of 30 cm and flow rate 20 mL/min saturated with 25 mg/L of CV was selected for desorption study. Desorption was carried out by 1N \(\text{CH}_3\text{COOH}\) solution through the exhausted bottom ash bed in the downward direction at a flow rate of 15 mL/min, slightly less that the sorption flow rate 20 mL/min.

The concentration of CV was measured at different time interval as shown in Fig. 12. It was observed that desorption cycle took 780 min, after which further desorption was negligible. The maximum concentration of CV (338.6 mg/L) was obtained at a contact time of 20 min, which is 13.54 times higher than influent CV concentration. The eluting solution was low in volume and high in concentration, which could help in easy handling and recovery and reuse of CV.

The overall mechanism of removal of CV by bottom ash is shown as in Fig. 11. The dotted line represents the bonding between bottom ash and CV.

Desorption study for regeneration of bottom ash

<table>
<thead>
<tr>
<th>Solution</th>
<th>Dye recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_2\text{SO}_4)</td>
<td>4</td>
</tr>
<tr>
<td>(\text{NaOH})</td>
<td>15</td>
</tr>
<tr>
<td>(\text{CH}_3\text{COOH})</td>
<td>47</td>
</tr>
<tr>
<td>(\text{HCl})</td>
<td>8</td>
</tr>
</tbody>
</table>
Recycling of regenerated column

To check the adsorption efficiency of the regenerated bottom ash column, it was reloaded with the dye solution of 25 mg/L at a rate of 20 mL/min. The breakthrough curve obtained was compared with that of raw bottom ash (10 cm depth; 25 mg/L CV concentration; flow rate of 20 mL/min) and is shown in Fig. 13. For raw bottom ash the breakthrough time was 4 h and exhaustion time was 27 h. But it was decreased for regenerated bottom ash. For regenerated bottom ash, breakthrough time was 2.5 h and exhaustion time was 18 h. The calculated data may prove helpful in designing a bottom ash fixed-bed for the treatment of CV of known concentration.

Desorption mechanism

CH₃COOH found to be more efficient to recover the CV from bottom ash as compared to other reagents. Addition of CH₃COOH will reduce the pH of solution. When the pH reaches less than 6.2, the surface of bottom ash predominate with positive charges. Then the bond between CV and bottom ash will break. But the regeneration capacity of CH₃COOH is very less as compared with recover of CV from Ricinus communis Pericarp carbon (Madhavakrishnan et al., 2009). Madhavakrishnan et al. (2009) reported that the percent desorption increased with increasing CH₃COOH concentration in the aqueous medium and attained a maximum desorption of 90% at 0.8 N CH₃COOH solution. Inefficient desorption in acetic acid indicates that CV was strongly attached onto bottom ash through chemisorptions. Similar results were observed for the adsorption of CV by treated ginger waste (Kumar & Ahmad, 2011). But addition of H₂SO₄ and HCl is ineffective to recover CV. This may be due to reaction of H₂SO₄ and HCl with CV and formation of colorless complex compounds. Miertschin (2007) reported that CV reacts with NaOH and the reaction mixture color becomes less and less intense, ultimately becoming colorless when all of the crystal violet has been consumed.

CONCLUSIONS

CV adsorption onto bottom ash was investigated. Adsorption capacity of bottom ash was found to be 5.24 mg/g from batch isotherm study. Removal efficiency of dyes from wastewater strongly depends on flow rate, initial CV concentration and bed depth. The slope of the breakthrough curve decreased with increasing bed height. The breakthrough time and exhaustion time were decreased with increasing influent CV concentration and flow rates. Different column design parameters were analyzed with respect to above three parameters. Experimental data fit well for BSDT model. BDST results show that the adsorption capacity of bottom ash inversely proportional to flow rate and concentration. Desorption studies reveals that recovery of CV from bottom ash was effective by using CH₃COOH solution.

REFERENCES