Removal of basic dye from industrial wastewater by adsorption

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For proper understanding, the process of removal of solute dye by adsorption and to reveal the manner in which this adsorption process can be adopted for removal of the solute material from the solution, the study of isotherm, kinetics and thermodynamic parameters is of paramount importance. The growth of adsorption with time is function of the initial concentration, temperature and pH of the system. The kinetics of adsorption was found to be of first order with intra-particle diffusion at the rate-controlling step. The values of different thermodynamic properties such as \( \Delta G^o \), \( \Delta H^o \) and \( \Delta S^o \) indicate that the process is spontaneous, feasible and exothermic in nature. The adsorption process satisfies Langmuir isotherm.

A safe potable drinking water for every human is necessary. India is highly populated country and safe drinking and domestic water demand is high. Major cities of India are dependent on the fresh water stream (rivers, estuaries, lakes etc.) for daily uses. Dye and dye intermediate industries are the largest sector of chemical industries in India. Mostly, the dyes are the raw material for the textile, paints, pulp and paper, printing inks and carpet industries. Textile industry is the largest consumer of the dyestuff consuming more than 80 percent of the total production. A huge amount of water is used by these industries for the washing and cleaning purposes and they discharge highly coloured effluent containing different dyes. The high concentration of dyes in wastewater is highly objectionable for domestic use due to their high COD and toxicity upsets the biological process. Some of the dyes found are carcinogenic also. Unless properly collected, treated and disposed of such type of wastewater create serious water pollution problems. The present investigation is concerned with the removal of dyes from the aqueous solution. The dye used for this purpose is methyl violet and adsorbents are bagasse and wood charcoal. Methyl violet (Basic violet-3) is a class of triphenylmethane colour having molecular formula \( C_{25}H_{30}ClN_3 \). Most bleach paper industries are used, as tinter, which causes the paper, appear visually brighter. It is also used for colouring the cotton and silk fabrics.

Adsorption of dyes onto solid/water interface has been found to be an efficient and economically cheap process and an effective method to control the extent of water pollution due to the metallic species. The most commonly used adsorbent for colour removal is activated carbon but it is relatively expensive. The objective of the present investigation has to evaluate the efficiency of removal of methyl violet dye using bagasse and wood charcoal. Bagasse is agricultural/industrial waste/by-product and produced in large amount by the sugarcane mills and wood charcoal is produced by the timber industries. These are easily available, cheap and biodegradable and possess economic advantages.

Experimental Procedure

The adsorbent bagasse was collected from the Kashi Sahakari Mill situated at Orai, Bhadohi and wood charcoal from the local industry situated at Ramnagar, Varanasi, India. The bagasse was crushed and boiled with dil. HCl and washed with double distilled water to remove water soluble impurities and dried at 50°C while the wood charcoal was washed with doubly distilled water to remove water soluble impurities and dried at 40°C in an electric oven for 8 h. The adsorbent was characterized for bulk density, moisture content, combustible matter, ash content as per standard methods. XRD indicates the existence of aluminium oxide, manganese oxide, ammonium phosphate, Ca-P, calcite for bagasse and iron oxide, aluminium oxide, titanium oxide, calcite, ammonium phosphate for wood charcoal. The surface area was

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analysed by BET method using low temperature N$_2$ gas adsorption technique. The characteristics of adsorbents are presented in the Table 1. The dye-methyl violet used in present study was supplied by Qualigens Fine Chemicals Division of Glaxo India Limited, Bombay, India. Accurately weighed quantity of the dye was dissolved in double distilled water to prepare stock solution. Experimental solutions of the desired concentration were obtained by successive dilution. Batch adsorption studies were carried out by shaking 1.0 g of adsorbents with 50 mL of aqueous solution of methyl violet dye of desired concentration in 250 mL borosil conical flask at different temperatures, pH and at a constant agitation speed of 200 rpm in shaking thermostat. The amount of adsorption was determined at different time intervals till the equilibrium attains. The suspension solution was centrifuged and supernatant liquid was analysed using the UV-VIS spectrophotometer, type 118, systronic make, at corresponding A$_{max}$ to find out residual dye concentration. The pH of system was adjusted using HCl and NaOH and experiment was carried out at different initial concentrations of the dye ranging from 80 to 140 mg L$^{-1}$ for bagasse and 20 to 50 mg L$^{-1}$ for wood charcoal.

### Results and Discussion

**Effect of initial dye concentration and contact time**

The amount of dye adsorbed by adsorbent bagasse from 3.600 to 4.701 mg g$^{-1}$ and percentage decreases from 90.00 to 67.50 on increasing concentration range from 80 to 140 mg L$^{-1}$, with time and attains equilibrium in 60 min while WC adsorbed from 0.938 to 1.389 mg g$^{-1}$ and percentage decreases from 93.80 to 55.48 on increasing concentration from 20 to 50 mg L$^{-1}$ and attains equilibrium in 130 min at the temperature 30°C and pH 7.2 (Figs 1 & 2) and Table 2. The result indicates that the amount adsorbed per unit mass of adsorbent is too high in the case of bagasse than on the WC and thus the bagasse establishes the supremacy over the WC. The amount of dye adsorbed increases with the increasing initial dye concentration$^{6,7}$. This is because at lower concentration, the ratio of the initial number of moles of dye to the available surface area is low and subsequently the fractional adsorption becomes independent of initial dye concentration. However, at higher concentration the available sites for adsorption become fewer and hence percentage removal of dye is dependent upon the initial concentration$^8$. The variation curves of adsorption versus time are smooth and continuous, indicating the formation of monolayer coverage on the surface of adsorbent$^{10}$ and equilibrium time is independent of initial concentration of dye.

**Effect of temperature**

The percentage removal of dye decreases from 74.16 to 68.00 and 66.60 to 62.90 with rise in...
Table 2—Amount and percent of methyl violet adsorbed at the different concentrations and temperatures at pH 7.2

<table>
<thead>
<tr>
<th>Bagasse Temp:30°C</th>
<th>WC Temp:30°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc. mgL⁻¹</td>
<td>Ads mgg⁻¹ %</td>
</tr>
<tr>
<td>80</td>
<td>3.600</td>
</tr>
<tr>
<td>100</td>
<td>4.056</td>
</tr>
<tr>
<td>120</td>
<td>4.310</td>
</tr>
<tr>
<td>140</td>
<td>4.701</td>
</tr>
</tbody>
</table>

Table 3—Thermodynamic parameters for the methyl violet

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>-ΔG° k cal mol⁻¹</th>
<th>-ΔH° k cal mol⁻¹</th>
<th>-ΔS° cal K⁻¹mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.7493</td>
<td>2.0893</td>
<td>4.5733</td>
</tr>
<tr>
<td>30</td>
<td>0.5636</td>
<td>1.7801</td>
<td>4.0148</td>
</tr>
<tr>
<td>40</td>
<td>0.5235</td>
<td>1.7730</td>
<td>3.9738</td>
</tr>
<tr>
<td>50</td>
<td>0.4837</td>
<td></td>
<td></td>
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<td>0.4099</td>
<td>1.3442</td>
<td>3.2194</td>
</tr>
<tr>
<td>30</td>
<td>0.3687</td>
<td>0.8622</td>
<td>1.6287</td>
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<td>50</td>
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<td></td>
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The rate constant, $k_{ad}$, were determined using the first order rate equation proposed by Lagergren:

$$\log (q_e - q) = \log q_e - \frac{k_{ad}}{2.303} \cdot t$$

where $q_e$ and $q$ are the amounts of the dye adsorbed at equilibrium and at any time $t$ respectively. The straight line plots of $\log (q_e - q)$ versus $t$ for adsorption of methyl violet on both the adsorbents suggest the first order kinetics (Figs 3 & 4). The values of rate constants for removal of dye for a particular system were calculated at different temperatures ranging from 20 to 50°C from the slopes of these plots and shown in the Table 4.

Intraparticle rate constant study

In batch mode, the adsorption studies were performed by agitating the adsorbate solution with the
adsorbent in adsorption cell. In the process of transport of adsorbate species from aqueous solution to the solid surface of adsorbent there is a possibility of diffusion of adsorbate species into the pores of adsorbent due to the rapid stirring. This was determined by the respective plots of amount of dye adsorbed against the square root of time \( t \) \( t^{\frac{1}{2}} \). The double nature of these plots may be due to varying extent of adsorption in initial and final stages. The initial curved portion of the plots is due to the boundary layer diffusion effect, while the final linear portion is due to the intraparticle diffusion effects. However, the prevailing linear portion of these plots indicates the possibility of intraparticle diffusion as the rate-controlling steps. The slope of the linear portion of these plots has been defined as a rate parameter \( k_{id} \). The values of \( k_{id} \) were calculated from the respective slopes of these plots at different temperatures and recorded in Table 4.

**Adsorption isotherm**

The Langmuir adsorption isotherm is based on monolayer coverage at the surface of adsorbent. The saturation of monolayer can be represented by the following equation. The plots of \( C_c/q_c \) versus \( C_c \) show the linear nature (Figs 7 & 8) for methyl violet giving the validity of the equation,

\[
\frac{C_c}{q_c} = \frac{1}{Q_0 b} + \frac{C_c}{Q_0} \quad \cdots \quad (6)
\]

The values of Langmuir constants \( Q_0 \) and \( b \) have been determined from the slopes and intercepts of the respective plots in each system at different temperatures and recorded in Table 4. From the results it is clear that the value of adsorption capacity

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**Fig. 3**—Lagergren rate constant plot for the adsorption of methyl violet dye on bagasse

**Fig. 4**—Lagergren rate constant plot for the adsorption of methyl violet dye on wood charcoal

**Fig. 5**—Weber-Morris intra-particle diffusion plot for the adsorption of methyl violet dye on bagasse

**Fig. 6**—Weber-Morris intra-particle diffusion plot for the adsorption of methyl violet dye on wood charcoal
Table 4—Rate constants $k_{ad}$, intraparticle diffusion rate $k_{ip}$, and Langmuir constants methyl violet at different temperatures

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>$k_{ad}(10^3)$</th>
<th>$k_{ip}$</th>
<th>$Q^b$</th>
<th>$b$</th>
<th>$k_{ad}(10^3)$</th>
<th>$k_{ip}$</th>
<th>$Q^b$</th>
<th>$b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>3.174</td>
<td>13.75</td>
<td>5.3153</td>
<td>0.3833</td>
<td>1.280</td>
<td>4.85</td>
<td>1.5957</td>
<td>0.5222</td>
</tr>
<tr>
<td>30</td>
<td>3.031</td>
<td>13.50</td>
<td>5.1282</td>
<td>0.2437</td>
<td>1.263</td>
<td>4.44</td>
<td>1.5625</td>
<td>0.3560</td>
</tr>
<tr>
<td>40</td>
<td>2.836</td>
<td>13.26</td>
<td>5.0847</td>
<td>0.1573</td>
<td>1.153</td>
<td>4.31</td>
<td>1.5200</td>
<td>0.2438</td>
</tr>
<tr>
<td>50</td>
<td>2.731</td>
<td>13.17</td>
<td>5.0000</td>
<td>0.1111</td>
<td>1.093</td>
<td>4.09</td>
<td>1.5150</td>
<td>0.1796</td>
</tr>
</tbody>
</table>

Fig. 7—Langmuir isotherm plot for the adsorption of methyl violet dye on bagasse

Fig. 8—Langmuir isotherm plot for the adsorption of methyl violet dye on wood charcoal

$Q^b$ of bagasse is higher than the WC, which suggests the supremacy of the adsorbent and also it decreases on increasing the temperature further, it confirms the exothermic nature of the processes involved in the system.

Effect of pH

The percent dye adsorbed increases from 65.33 to 78.60 and 54.00 to 77.60 with the increase of pH from 3.0 to 10.0 at the temperature of 30°C and attains equilibrium in 60 and 130 min for the adsorbents bagasse and WC respectively. No further adsorption has been observed up to the 11.2 pH value. This indicates the adsorbents have high uptake capacity of methyl violet from the aqueous solution at higher pH values. The adsorbents contain various oxides and these oxides are hydroxylated on the adsorbent surface in alkaline medium. At higher pH the association of dye cations with negatively charged oxide surfaces\(^6\) takes places as,

\[
(SOH)_2 + 2 OH^- + Dy^+ \rightarrow \text{S(OH)}_2 \cdot \text{Dye} \cdot \text{S(OH)}_2
\]

Above mechanism clearly shows that the adsorption decreases with pH of solution. The positive charge densities on the surface increases and adsorption decreases while at high pH adsorption increases.

Conclusions

From the above studies it is inferred that,

(i) Adsorbent bagasse has better adsorption capacity than the WC.

(ii) Removal of methyl violet by both the adsorbents happens to be attractive since the adsorbents are cheaper and easily available.

(iii) The rate of adsorption has been found to follow first order kinetics.

(iv) Investigation of adsorption isotherm was found to be in good agreement with Langmuir isotherm, which indicates monolayer adsorption.

(v) Thermodynamic parameters indicate that the process is spontaneous and exothermic in nature.

(vi) Intraparticle diffusion is the rate-controlling step.

Acknowledgements

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Nomenclature

$Ad$ = Adsorption $mg L^{-1}$

$b$ = Energy of adsorption $1 mg L^{-1}$

$C_e$ = Equilibrium concentration $mg L^{-1}$
$\Delta G^o$ = Standard Gibbs free energy change k cal mole$^{-1}$
$\Delta H^o$ = Standard enthalpy change k cal mole$^{-1}$
$\Delta S^o$ = Standard entropy change cal K$^{-1}$ mole$^{-1}$
$k_{ad}$ = Rate constant min$^{-1}$
$k_{id}$ = Intraparticle diffusion rate constant mgg$^{-1}$ min$^{-2}$
$q_e$ = Amount adsorbed at equilibrium mgg$^{-1}$
$Q_{ad}$ = Adsorption capacity mgg$^{-1}$
$T$ = Temperature °C
WC = Wood charcoal

References
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11 Lagergren S & Bil K, Svenska Vetenskapakad Hand, 24 (1898)