Colour Removal from Dye Wastewater Using Sugar Cane Dust as an Adsorbent

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ABSTRACT: Decolouration of dilute solutions of basic dye stuff was carried out using sugar cane dust as an adsorbent. It was found that low adsorbate concentration, small particle size of the adsorbent, a temperature of 25°C and a pH value of 7.5 for the medium all favour the removal of dye from aqueous solutions. The percentage of dye adsorbed by sugar cane dust decreased from 96.48% to 83.32% and from 90.78% to 78.02% for Malachite Green and Methylene Blue, respectively, when the concentration of the dye was increased from 6 mg/l to 12 mg/l. Similarly, the adsorption of Crystal Violet and of Rhodamine B also decreased with increasing dye concentration in the solutions. The amount of dye (Malachite Green and Rhodamine B) adsorbed decreased from 3.04 mg/g to 2.57 mg/g and from 2.53 mg/g to 2.17 mg/g when the temperature of the solution was increased from 25°C to 45°C, indicating that the process was exothermic. The values of the adsorption capacity (Qo) of Malachite Green and Rhodamine B on the adsorbent varied from 4.87 to 4.08 and from 4.26 to 3.82, respectively, as the temperature increased from 25°C to 45°C. The equilibrium data obey the requirements of the Langmuir adsorption model, demonstrating the formation of a monolayer of dye molecules on the outer surface of the adsorbent. The variation in the extent of removal with pH has been explained on the basis of surface ionisation and complexation. Various thermodynamic parameters (ΔG°, ΔH° and ΔS°) have also been determined in order to explain the results.

INTRODUCTION

The natural environmental resources of air, water, soil, plant and animal life constitute the natural capital on which man depends to satisfy his needs to achieve his aspirations for development. Pollution is the contamination of the natural ingredients of the environment. Water pollution is defined as the contamination of water and the alteration of the physical, chemical and biological properties of water. This includes the discharge of any sewage or trade effluent or any other liquid, gaseous or solid substances into water likely to create a nuisance by way of its physical appearance, odour or taste. Such discharge may render water harmful and injurious to public health as far as domestic, commercial, industrial and agricultural life is concerned. The discharge of dye effluents often imparts colour to the receiving waters for miles downstream from the source. This colour is objectionable aesthetically and it also reduces light penetration into the water thereby decreasing the efficiency of photosynthesis in aquatic plants and hence having an adverse impact on their growth (Bhattacharya and Sarma 1997). In addition, some dyes might be toxic to various organisms.
A number of low-cost materials (natural clay, bagasse pith and maize cob) have been used as adsorbents for dyestuffs (Astrazon Blue, Maxilon Red and Telon Blue) in aqueous solutions (Nassar and El-Geundi 1991), the adsorption capacity for each dye/adsorbent system having been determined. The ability of wood to adsorb Telon Blue (Acid Blue 25) has also been investigated with the effects of contact time, particle size and adsorption capacity being studied (Poots et al. 1976). The initial rate of removal of Disperse Blue 7 from textile effluent depends on the surface mass-transfer coefficient and the effects of certain variables, viz. agitation, initial dye concentration, particle size and solution temperature, on the dimensionless mass-transfer term have been studied (McKay and Sweeney 1980). Buffing dust generated from the leather industry can be considered as a source for obtaining activated carbon for the removal of dyes from wastewater (Sekaran et al. 1995) and 12 different adsorbents from waste materials have been used to treat wastewater with a complex composition from a chemical plant. The effectiveness of each adsorbent was measured in terms of its adsorption capacity towards the individual constituents of the effluent (Bousher et al. 1997). The ability of chitosan for removing reactive dyes such as vinyl sulphone and chlorotriazine from aqueous solutions has been examined, including both equilibrium and dynamic studies (Juang et al. 1997).

The present report deals with investigations of adsorption studies on sugar cane dust (bagasse) using different dyes (Methylene Blue, Crystal Violet, Malachite Green and Rhodamine B) at different temperatures and pH values. The adsorption dynamics and thermodynamic parameters for such systems have been evaluated.

**MATERIALS AND METHODS**

The dyes studied (Methylene Blue, Crystal Violet, Malachite Green and Rhodamine B) were supplied by Sandoz India Ltd., Bombay. Sugar cane dust (bagasse) was provided by the Balrampur sugar mill, Balrampur, India, the depithing operation having been performed in the sugar mill. The product was sieved into different particle size ranges. Batch adsorption experiments were carried out by shaking 0.5 g of the adsorbent with 200 ml of an aqueous solution of dye at a desired concentration at different temperatures and pH values in glass bottles (Corning) in a water thermostat whose temperature was maintained to within ± 1°C. Samples were drawn out of the adsorber at different time intervals using a syringe. The dye concentration was measured colorimetrically using a Shimadzu 160A spectrophotometer in the visible range of the spectrum at the maximum absorbance wavelength as listed in Table 1. The effect of different parameters on the adsorption of various dyes using the adsorbent was investigated, the experiments being conducted in duplicate to test their reproducibility. The duration of each batch experiment was maintained at 30 min while the pH value was kept constant at 7.5 by the use of the required amount of a 0.1 N potassium carbonate solution during the adsorption experiments.

**TABLE 1. Maximum Adsorption Wavelength \( \lambda_{\text{max}} \) for Dyestuffs Studied**

| Dyestuff       | \( \lambda_{\text{max}} \) (\( \mu \text{m} \)) |
|----------------|-----------------------------------------------|
| Methylene Blue | 664                                           |
| Malachite Green| 616                                           |
| Crystal Violet | 592                                           |
| Rhodamine B    | 555                                           |
SEM micrographs (see Figure 1) of the adsorbent (sugar cane dust) at different magnifications showed similar structural features associated with a strong, rough surface. Both micrographs clearly reveal the porous structure of the specimen surface which would provide a large surface area for adsorption.
RESULTS AND DISCUSSION

Effect of contact time and concentration

A series of contact experiments was undertaken at varying initial dye concentrations, viz. 6, 8 and 12 mg/l. Figures 2 and 3 show that a rapid increase of dye adsorption occurred in all cases at low concentrations which may be attributed to surface mass transfer (McKay and Sweeney 1980). Figures 2 and 3 also show that the amount of dye adsorbed from aqueous solution increased with time, with equilibrium being achieved within 14 min at 30 ± 1°C and a pH value of 7.5. The plots of adsorption versus time depicted in both figures are smooth and continuous, indicating monolayer coverage of the dye on the surface of the adsorbent. However, the percentage of the dye adsorbed by the adsorbent decreased with increasing dye concentration in the 6–12 mg/l range. The corresponding results obtained are listed in Table 2.
Effect of particle size range

The results of contact time investigations using several adsorbent particle size ranges were analysed, the amount of dye adsorbed increasing as the particle size decreased. This may be attributed to the larger external surface available with smaller particles at a constant total mass of adsorbent in the system. Figure 4 depicts the results obtained and indicates that there was no marked effect of particle size variation on the contact time necessary to attain saturation.

### Figure 3
Effect of dyestuff concentration on the adsorption of Crystal Violet and Rhodamine B from aqueous solution to sugar cane dust. Experimental conditions: temp., 30 ± 1°C; pH, 7.5.

### Table 2. Amounts and Percentages of Dyestuffs Adsorbed

| Dye conc. (mg/l) | Malachite Green | Crystal Violet | Methylene Blue | Rhodamine B |
|------------------|----------------|---------------|---------------|------------|
|                  | mg/g | %     | mg/g | %     | mg/g | %     | mg/g | %     |
| 6.0              | 2.315| 96.48 | 2.229| 92.89 | 2.178| 90.78 | 1.950| 81.25 |
| 8.0              | 2.978| 93.05 | 2.879| 89.98 | 2.725| 85.15 | 2.442| 76.32 |
| 12.0             | 3.999| 83.32 | 3.798| 79.13 | 3.745| 78.02 | 3.240| 67.50 |

*At 30 ± 1°C and pH = 7.5.
Crystal Rhodamine B Particle

\[ 0 < 80 \text{ mesh}, \quad > 80 \text{ mesh} \]

Time (min)

2.0
1.0
0.0

4.0
3.0
2.0
1.0
0.0

Crystal
Violet

| Rhodamine B |
|------------|
| ●          |
| △          |
| □          |

Particle size

- < 80 mesh
- 80 mesh
- > 80 mesh

Figure 4. Effect of particle size of sugar cane dust on the adsorption of Crystal Violet and Rhodamine B from aqueous solution. Experimental conditions: dye conc., 12 mg/l; temp., 30 ± 1°C.

Adsorption dynamics

The adsorption rate constant, \( k_{\text{ad}} \), for the removal of Malachite Green and Rhodamine B by sugar cane dust at temperatures of 25°C, 35°C and 45°C were determined using the following first-order expression:

\[
\log(q_e - q) = \log q_e - \frac{k_{\text{ad}}}{2.303} t \tag{1}
\]

where \( q_e \) and \( q \) (both in mg/g units) are the amounts of dye adsorbed at equilibrium and any time \( t \), respectively. The linear Langergren plots of \( \log(q_e - q) \) versus \( t \) obtained (Figures 5 and 6) indicate the applicability of the above equation to the systems studied. The values of \( k_{\text{ad}} \) at different temperatures were calculated from the slopes of the respective linear plots and are listed in Table 3. It may be concluded from the values of \( k_{\text{ad}} \) that a first-order process is occurring in all the systems.

Besides adsorption on the outer surface of the adsorbent, there is also the possibility of adsorbate ion transport from the solution into the pores of the adsorbent due to the rapid stirring employed in the batch reactors. This possibility was tested in terms of a graphical relationship between the amount of the dye adsorbed and the square root of the time (Figures 7 and 8). The dual nature of
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Figure 5. Langergren plot for the adsorption of Malachite Green on sugar cane dust from aqueous solution. Experimental conditions: dye conc., 8 mg/l; pH, 7.5.

TABLE 3. Adsorption Kinetic Parameters at Different Temperatures for Malachite Green and Rhodamine B

| Temperature (°C) | Malachite Green | Rhodamine B |
|-----------------|-----------------|-------------|
|                 | $10^3k_{ad}$ (min$^{-1}$) | $k_p$ [mg/(g min$^{1/2}$)] | K | $10^3k_{ad}$ (min$^{-1}$) | $k_p$ [mg/(g min$^{1/2}$)] | K |
| 25              | 11.02           | 0.672       | 19.618 | 8.55 | 0.511 | 3.819 |
| 35              | 10.67           | 0.600       | 8.551  | 8.02 | 0.501 | 2.790 |
| 45              | 10.20           | 0.525       | 4.147  | 7.70 | 0.492 | 2.117 |

these plots may be explained by the initial curved portions being attributed to boundary layer diffusion effects while the final linear portions are due to intraparticle diffusion effects (McKay et al. 1980). The rate constants for intraparticle diffusion, $k_p$, at different temperatures were determined from the slopes of the linear portions of the respective plots and are listed in Table 3.
Figure 6. Langergren plot for the adsorption of Rhodamine B on sugar cane dust from aqueous solution. Experimental conditions: dye conc., 8 mg/l; pH 7.5.

Effect of temperature

The effect of temperature on the adsorption of Malachite Green and Rhodamine B on sugar cane dust is shown in Figure 9. The uptake of each dye was found to decrease with increasing temperature, indicating that dye adsorption on the adsorbent surface was favoured at lower temperatures. The changes in the standard free energy, enthalpy and entropy of the adsorption processes were calculated using the following equations:

\[ \Delta G^0 = -RT \ln K \]  
\[ \Delta H^0 = R \left[ \frac{T_2 T_1}{T_2 - T_1} \right] \ln \left( \frac{K''}{K'} \right) \]  
\[ \Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \]
where $R$ is the gas constant and $K$, $K'$ and $K''$ are the equilibrium constants at temperatures of $T$, $T_1$ and $T_2$, respectively. The equilibrium constant can be determined as:

$$K = \frac{\text{concentration of dye present on the adsorbent surface}}{\text{remaining concentration of dye in solution}}$$  \hspace{1cm} (5)

The values for $\Delta G^0$, $\Delta S^0$ and $\Delta H^0$ are listed in Table 4, the negative values of $\Delta G^0$ indicating a spontaneous process with a high affinity of the dye for the surface of the adsorbent. Furthermore, the negative values of the enthalpy and entropy changes suggest that the adsorption process is exothermic and that the system exhibits random behaviour.

**TABLE 4.** Thermodynamic Parameters for Malachite Green and Rhodamine B

| Temperature ($^\circ$C) | Malachite Green $\Delta G^0$ (kJ/mol) | Malachite Green $\Delta H^0$ (kJ/mol) | Malachite Green $\Delta S^0$ [1/(K mol)] | Rhodamine B $\Delta G^0$ (kJ/mol) | Rhodamine B $\Delta H^0$ (kJ/mol) | Rhodamine B $\Delta S^0$ [1/(K mol)] |
|-------------------------|--------------------------------------|--------------------------------------|--------------------------------|-------------------------------|--------------------------------|----------------------------------|
| 25                      | 7.358                                | 63.336                               | 184.38                          | 3.317                         | 23.961                         | 69.275                           |
| 35                      | 5.479                                | 59.037                               | 173.89                          | 2.627                         | 22.556                         | 64.704                           |
| 45                      | 3.754                                |                                      |                                 | 1.980                         |                                |                                   |
Figure 8. Intraparticle diffusion plot for the adsorption of Rhodamine B from aqueous solution on to sugar cane dust. Experimental conditions: dye conc., 8 mg/l; pH, 7.5.

Figure 9. Effect of temperature on the adsorption of Malachite Green and Rhodamine B from aqueous solution on to sugar cane dust. Experimental conditions: dye conc., 8 mg/l; pH, 7.5.
Adsorption isotherm

The study of adsorption isotherms is helpful in determining the adsorption capacity of an adsorbent for the removal of dyes at certain temperatures. The Langmuir adsorption isotherm model was applied to the adsorption equilibrium at all temperatures studied, i.e.

\[ \frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \]  \hspace{1cm} (6)

where \( C_e \) is the equilibrium concentration (mg/l), \( q_e \) is the amount adsorbed at equilibrium (mg/g) and \( Q^0 \) and \( b \) are Langmuir constants related to the adsorption capacity and the energy of adsorption, respectively. The linear plots of \( C_e/q_e \) versus \( C_e \) obtained (Figures 10 and 11) demonstrate the applicability of the Langmuir isotherm in all cases. Values of \( Q^0 \) and \( b \) as determined from the slope and intercept of the plots are presented in Table 5.

The equilibrium parameter, \( R_L \), has been calculated from the relationship:

\[ R_L = \frac{1}{1 + bC_0} \]  \hspace{1cm} (7)

where \( C_0 \) is the initial concentration of adsorbate (mg/l) and \( b \) is the Langmuir constant (1/mg). The values of \( R_L \) listed in Table 5 indicate that the adsorption of Malachite Green and Rhodamine B on to sugar cane dust was a favourable process since the \( R_L \) values lie between 0 and 1.

![Figure 10. Langmuir plot for the adsorption of Malachite Green from aqueous solution on to sugar cane dust at various temperatures.](image-url)
TABLE 5. Langmuir Constants for Malachite Green and Rhodamine B

| Temperature (°C) | Malachite Green | Rhodamine B |
|------------------|-----------------|-------------|
|                  | Q^0 (mg/g)      | b (l/mg)    | R_L         | Q^0 (mg/g) | b (l/mg) | R_L         |
| 25               | 4.879           | 9.345       | 0.013       | 4.261      | 0.696     | 0.152       |
| 35               | 4.575           | 5.102       | 0.023       | 4.040      | 0.579     | 0.191       |
| 45               | 4.080           | 2.994       | 0.040       | 3.821      | 0.508     | 0.197       |

Effect of pH

Sugar cane dust has proved to be an effective adsorbent for the removal of Malachite Green and Rhodamine B from aqueous solution at pH 7.5, at which pH almost quantitative adsorption was
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Figure 12. Effect of pH on the removal of Malachite Green and Rhodamine B from aqueous solution by adsorption on to sugar cane dust. Experimental conditions: dye conc., 8 mg/l; temp., 30 ± 1°C.

achieved (Figure 12). In alkaline medium, negatively charged species start to dominate and the surface tends to acquire a negative charge while the adsorbate species are still positively charged. As a consequence, the increasing electrostatic attraction between the positively charged adsorbate species and the negatively charged adsorbent particles would lead to increased dye adsorption (Khattri and Singh 1998).

CONCLUSIONS

The following conclusions may be drawn from the work described:

1. Sugar cane dust is an effective adsorbent for the removal of basic dyes. Such dust is widely available as a product of sugar milling. Activated carbon is an expensive material and regeneration is essential, whereas sugar cane dust is so cheap that regeneration is not necessary.
2. The ultimate capacity of sugar cane dust as an adsorbent decreases with increasing temperature and with increasing particle size.
3. The fact that the Langmuir model may be applied to the systems studied suggests monolayer coverage of the adsorbate on the outer surface of the adsorbent, the process being exothermic in nature.
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