Basic dye adsorption on a low cost carbonaceous sorbent – Kinetic and equilibrium studies

B Stephen Inbaraj & N Sulochana*
Department of Chemistry, Regional Engineering College, Tiruchirappalli 620 015, India
Received 5 March 2001; revised received 17 March 2002; accepted 20 March 2002

A carbonaceous sorbent prepared from an indigenous agricultural waste, jack fruit peel, by acid treatment was tested for its efficiency in removing basic dyes. Malachite green, a common basic dyestuff of triphenyl methane series used for dyeing silk and wool directly and cotton mordanted with tannin to deep green, was chosen for investigation. The process parameters studied include agitation time, initial dye concentration, carbon dose, pH and temperature. The adsorption followed first order reaction equation and the rate is mainly controlled by intraparticle diffusion. Freundlich, Langmuir and Redlich-Peterson isotherm models were applied to the equilibrium data. The adsorption capacity \( Q_0 \) obtained from the Langmuir isotherm plot was 166.37 mg g\(^{-1}\) at an initial \( \text{pH} \) of 6.0 and at 32 ± 0.5°C. The influence of \( \text{pH} \) on dye removal was not significant and the adsorption capacity increased with increase in temperature. A portion of the dye was recovered from the spent carbon using 50% acetic acid (v/v).

The discharge of highly coloured effluents into natural water bodies is not only aesthetically displeasing, but it also impedes light penetration, thus upsetting biological processes within a stream. In addition, many dyes are toxic to some organisms causing direct destruction of aquatic communities\(^1\). Some dyes can cause allergic dermatitis, skin irritation, cancer and mutation in man\(^2\). Recent estimates indicate that, approximately, 12 % of synthetic textile dyes used each year are lost during manufacture and processing operation and 20 % of these dyes enter the environment through effluents that result from the treatment of residual industrial waters\(^3\). Among the various classes of dyes, basic dyes were found to be the brightest class of soluble dyes used by the textile industry as their tinctorial value is very high\(^4\).

Wastewaters from dyeing industries are released into nearby land or rivers without any treatment because the conventional treatment methods are not cost effective in the Indian context. On the other hand, low cost technologies don't allow a wishful colour removal or have certain disadvantages\(^5\). Adsorption is one of the most effective methods and activated carbon is the preferred adsorbent widely employed to treat wastewater containing different classes of dyes\(^6\). However, recognising the economic drawback of commercial activated carbon, many investigators have studied the feasibility of using inexpensive alternative materials like pearl millet husk\(^7\), date pits\(^8\), saw dust\(^9\), buffing dust of leather industry\(^9\), coir pith\(^10\), crude oil residue\(^11\), tropical grass\(^12\), olive stone and almond shells\(^13\), pine bark\(^14\), wool waste\(^15\), coconut shell\(^16\) etc., as carbonaceous precursors for the removal of dyes from water and wastewater.

The present study is undertaken to evaluate the efficiency of a carbonaceous sorbent prepared from jack fruit peel, an agricultural waste, for the removal of basic dyes from aqueous solution. Malachite green, a common basic dyestuff of triphenyl methane series used for dyeing silk and wool directly and cotton mordanted with tannin to deep green, was chosen for investigation. Batch-mode adsorption studies were carried out systematically involving process parameters such as agitation time, initial concentration, adsorbent dose, \( \text{pH} \) and temperature. Jack fruit (Artocarpus heterophyllus) is one of the most popular fruits in South India, where per hectare production is higher than any other fruit. A jack tree produces about 200-500 fruits annually, with each fruit weighing about 23-40 kg. The outer peel (rind), which is mostly fibrous, constitutes about 59 % of the ripe fruit\(^17\). Apart from its use as a table fruit, jack is popular for making vegetable, pickles, for dehydration into thin round papad and many culinary preparations. Hence, significant amount of peel is expected to be discarded as waste. Earlier work on its efficiency in removing Cu(II)\(^18\) and Hg(II)\(^19\) from aqueous solution has shown an adsorption efficiency...
of 92.59 mg g⁻¹ and 125 mg g⁻¹, respectively at pH 5.0 and at 32 ± 0.5°C.

**Experimental Procedure**

Carbon was prepared by treating air-dried jack fruit peel (after removing the carpel fibers) with concentrated sulphuric acid in a weight ratio of 1:1.8 (peel:acid). The resulting black product was kept in an air-oven maintained at 160 ± 5°C for 6 h followed by washing with water until free of excess acid and dried at 105 ± 5°C. The carbon product obtained from jack fruit peel (JPC) was ground and the portion retained between 44 and 89 µm sieves was used in all the experiments. The characteristics of the carbon such as pH, moisture content, bulk density, ash content, water soluble matter, acid soluble matter, decolourising power, ion exchange capacity and iron content were determined according to ISI methods. Surface area was measured using direct reading Carlo Erba Sorptomatic-1800 by assuming that the adsorbed nitrogen forms a monolayer and possess a molecular surface texture and porosity of JPC clearly reveals the surface texture and porosity of JPC with holes and small openings found on the surface indicating that it would increase the contact area and facilitate pore diffusion during adsorption.

Malachite green dye was supplied by Bayer Ltd. All adsorption experiments were carried out by agitating the carbon with 100 mL dye solution of desired concentration at pH 6.0 and at room temperature (32 ± 0.5°C) in a mechanical shaker (200 rpm). After the defined time intervals, samples were withdrawn from the shaker, centrifuged and the supernatant solution was analysed for residual dye concentration using a Jasco Double Beam Spectrophotometer (UV/1240) at 620 nm. Kinetic study was carried out by taking three dye concentrations viz., 20, 40 and 60 mg L⁻¹ and agitating with 25 mg of carbon dose at predetermined intervals of time. Effect of adsorbent dosage was studied by varying the carbon dose from 5 to 60 mg, taking 60 mg L⁻¹ as initial dye concentration. For studies on the effect of pH, the initial pH of 20 mg L⁻¹ dye solution was adjusted to a desired value using small amounts of dilute hydrochloric acid or sodium hydroxide and agitated with 25 mg of the carbon. For temperature variation study, 25 mg of the carbon was agitated with 60 mg L⁻¹ dye solution using a temperature-controlled water bath-cum-shaker. Freundlich isotherm was derived from the studies on the effect of carbon dosage on the percent dye removal. Langmuir and Redlich–Peterson isotherm study was carried out with dye solutions of different initial concentrations ranging from 20 to 100 mg L⁻¹ and agitating with a fixed carbon dose (25 mg), until equilibrium was reached. Control experiments were carried out to examine possible adsorption of dye in the absence of adsorbent by container walls. It was found that there was no dye adsorption by the container walls. Experiments were repeated at least three times and mean values are reported. Standard deviations and analytical errors were calculated and the maximum error was ± 5 %.

After adsorption of 60 mg L⁻¹ of malachite green by 60 mg 100 mL⁻¹ of the carbon, the carbon loaded with dye was separated and gently washed with distilled water to remove any unadsorbed dyes. The dye-laden carbons were agitated with 100 mL of neutral pH water, 1 M sulphuric acid, 1 M sodium hydroxide, 10 % acetic acid (v/v) and 50 % acetic acid (v/v) separately for 60 min.

**Results and Discussion**

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

The kinetics of adsorption of malachite green by JPC is shown in Fig. 2, with smooth and single plots indicating monolayer adsorption of dye on the
The removal of dye increases with the lapse time and attains equilibrium in 45 min for 20 mg L\(^{-1}\) and 180 min for 40 and 60 mg L\(^{-1}\). With increase in dye concentration from 20 to 60 mg L\(^{-1}\), the amount of dye adsorbed increased from 77.6 to 167.6 mg g\(^{-1}\) while the per cent removal decreased from 97 to 69.8, indicating that the dye removal by adsorption on JPC is concentration dependent.

### Adsorption rate constant

The rate constant of adsorption of malachite green on JPC was determined using the following rate expression given by Lagergren\(^{24}\):

\[
\log(q_e - q) = \log q_e - \frac{K_{ad} t}{2.303}
\]

where \(q_e\) is the amount of solute adsorbed per unit weight of the adsorbent (mg g\(^{-1}\)) at equilibrium time, \(q\) is the amount adsorbed (mg g\(^{-1}\)) at time \(t\) (min) and \(K_{ad}\) is the rate constant (min\(^{-1}\)). Linear plots of \(\log(q_e - q)\) versus \(t\) suggest the applicability of the Lagergren equation (Fig. 3). The rate constants \((K_{ad})\) were calculated from the slope and are presented in Table 2. \(K_{ad}\) was found to decrease from 0.1195 to 0.0159 min\(^{-1}\) with the increase in the initial concentration from 20 to 60 mg L\(^{-1}\). An examination of the effect of dye concentration on the rate constant \((K_{ad})\) helps to describe the mechanism of removal taking place\(^{26}\). In cases of strict surface adsorption, a variation of rate should be proportional to the first power of concentration. However, when pore diffusion limits the adsorption process, the relationship between initial solute concentration and the rate of reaction will not be linear\(^{26}\). Fig. 4 shows that a direct linear relationship does not exist in the adsorption of dye on JPC. It seems likely that pore diffusion limits the overall rate of dye adsorption.

The contact-time experimental results can be used to study the rate-limiting step in the adsorption process, as shown by Weber and Morris\(^{27}\). Since the particles are vigorously agitated during the adsorption period, it is probably reasonable to assume that the rate is not limited by mass transfer from the bulk liquid to the particle external surface. One might then postulate that the rate-limiting step may be either film or intraparticle diffusion. As they act in series, the slower of the two will be the rate-determining step.
Fig. 3—Lagergren first order kinetic plots. Dye concentrations: (●) 20 mg L⁻¹, (■) 40 mg L⁻¹, (▲) 60 mg L⁻¹.

Fig. 4—Effect of dye concentration on the observed rate of adsorption.

The rate constant for intraparticle diffusion is obtained using the equation

$$q = K_p t^{1/2}$$  \hspace{1cm} (2)

where $K_p$ (mg g⁻¹ min⁻¹) is the intraparticle diffusion rate constant. The nature of the plots in Fig. 5 suggests that the initial curved portion is attributed to the film or boundary layer diffusion effect and the subsequent linear portion to the intraparticle diffusion effect.  \cite{23,28}. Fig. 5 also depicts that the intraparticle diffusion is the slow and the rate-determining step. $K_p$ values were obtained from the slope of the linear portions of the curves at each dye concentration (Table 2). The $K_p$ values increased with increase in the dye concentration, which reveals that the rate of adsorption is governed by the diffusion of adsorbed dye within the pores of the adsorbent.

Assuming spherical geometry for the adsorbent, \cite{29}, the adsorption rate constant for the process can be correlated to the pore diffusion coefficient in accordance with the expression, \[ D_p = \frac{0.03 (r_0^3)}{t_{1/2}} \], where, $t_{1/2}$ = time for half change (s), $D_p$ = pore diffusion coefficient (cm² s⁻¹) and $r_0$ = radius of the adsorbent (cm). According to Micheelsen et al., \cite{30}, for the pore diffusion to be the rate-limiting step in an adsorption process, the pore diffusion coefficient values obtained should fall in the range of $10^{-11}$ to $10^{-13}$ cm² s⁻¹. The average value of pore diffusion coefficients (Table 2) calculated for different dye concentrations is $0.415 \times 10^{-11}$ cm² s⁻¹. This again confirms that intraparticle or pore diffusion is the rate-controlling step.

Effect of carbon mass

The amount of dye adsorption increased with the increase in carbon dose and reached a maximum value after a particular dose (Fig. 6). Taken an initial dye concentration of 60 mg L⁻¹, complete dye removal was obtained at a maximum carbon dose of 60 mg 100 mL⁻¹. The increase in the adsorption of...
dye with carbon dose was due to the introduction of more binding sites for adsorption.

**Adsorption isotherms**

The distribution of dye between the liquid phase and the adsorbent is a measure of the position of equilibrium in the adsorption process and can be generally expressed by three of the most popular isotherm theories viz., the Freundlich\(^{31}\), the Langmuir\(^{32}\) and the Redlich-Peterson isotherms\(^{33}\).

The equilibrium data obtained at varying carbon dosage and fixed initial dye concentration conform to the Freundlich equation (Fig. 7), which has the following forms:

\[ q_e = \frac{x}{m} = K_F C_e^n \]  \hspace{1cm} \ldots (3)

\[ \log q_e = \log K_F + \frac{1}{n} \log C_e \]  \hspace{1cm} \ldots (4)

where \(x\) (mg L\(^{-1}\)) is the amount of solute adsorbed, \(m\) (g L\(^{-1}\)) is the weight of the adsorbent used, \(C_e\) (mg L\(^{-1}\)) is the equilibrium solute concentration in solution and \(K_F\) (mg g\(^{-1}\)) and \(n\) are constants incorporating factors affecting the adsorption process such as adsorption capacity and intensity of adsorption, respectively. The correlation coefficient, \(r^2\), obtained for the linear plot (Fig. 7) is 0.968. The constants \(K_F\) and \(n\) obtained from the intercept and slope of the plot are 116.49 mg g\(^{-1}\) and 6.69, respectively. According to Treybal\(^{34}\), it has been shown using mathematical calculation that \(n\) values between 1 and 10 represent beneficial adsorption. The sorption equation arrived

\[(x/m = 116.49C_e^{0.15})\]  can be employed to determine the volume of wastewater that could be treated. Substituting the concentration of dye to be treated for \(C_e\), the respective sorption capacity can be calculated, which on dividing by the actual amount of dye to be removed gives the volume of wastewater that could be treated. About 16.5 L of wastewater, containing 10 mg L\(^{-1}\) of the dye under study, can be treated by using 1 g of JPC.

The adsorption isotherms frequently employed for single-solute systems are the 2-parameter Langmuir and 3-parameter Redlich-Peterson models that obey the correct thermodynamic boundary condition of Henry’s law in the range of infinitely dilute concentrations\(^{35,36}\). The Langmuir and the Redlich-Peterson isotherms models for liquid-phase adsorption are written as follows:

\[ q_e = \frac{Q_s b C_e}{1 + b C_e} \]  \hspace{1cm} \ldots (5)

\[ q_e = \frac{\alpha C_e}{1 + \beta C_e^\gamma} \]  \hspace{1cm} \ldots (6)

In the Langmuir model, \(Q_s\) and \(b\) represent monolayer adsorption capacity and a constant related to energy of adsorption, respectively, while \(\alpha\), \(\beta\) and \(\gamma\) are empirical constants for the Redlich-Peterson model.

The equilibrium adsorption results obtained at different initial dye concentrations were fitted with 2-parameter Langmuir and 3-parameter Redlich-Peterson models. Fitted curves of both models are
shown in Fig. 8 for comparison with the adsorption data. The isotherms obtained were of the type 137, which were very close to irreversible adsorption. Such isotherms are characteristic of strong adsorbate-adsorbent interactions, probably due to nonpolar interactions. The adsorption parameters of both models were obtained by a nonlinear optimization method15,36 using GNUPLOT program (Version 3.7 for MS-Windows) that involves Marquardt-Levenberg algorithm. Adopting this method, $Q_0$ and $b$ values were found to be 166.37 mg g$^{-1}$ and 2.0902 L mg$^{-1}$, respectively. Similarly, empirical constants, $a$, $\beta$ and $\gamma$, involved in Redlich-Peterson model were found to be 298.91 L g$^{-1}$, 1.6423 (L mg$^{-1}$)$^\gamma$ and 1.0267, respectively. As a measure of degree of fitness, the correlation coefficient, $r^2$ was computed from the following equation38:

$$r^2 = \frac{\sum q_i^2 - \sum (q_i - q_\theta)^2}{\sum q_i^2} \ldots (7)$$

In the above equation, $q_i$ and $q_\theta$ denote the experimental adsorption data and the fitted results of each adsorption model for a solute, respectively.

The correlation coefficient obtained for Langmuir and Redlich-Peterson isotherm models were 0.997 and 0.998, respectively. This indicates that both models were in good agreement with the actual data ($r^2 > 0.99$), although 3-parameter Redlich-Peterson model shows a little better fit to adsorption data than the 2-parameter Langmuir model.

The influence of isotherm shape has been considered with a view to predicting if an adsorption system is "favourable" or "unfavourable". The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, $R_L$, which is defined as $R_L = 1/(1+bC_0)$, where $b$ is the Langmuir constant and $C_0$ is the initial dye concentration. $R_L$ values obtained (0.0048-0.0234) were between 0 and 1, which indicate favourable adsorption of dye on JPC for the concentration range studied.

**Effect of temperature**

The adsorption capacity of JPC increased with increase in the temperature of the system from 32 to 50°C (Table 3). Thermodynamic parameters such as change in free energy ($\Delta G^o$), enthalpy ($\Delta H^o$) and entropy ($\Delta S^o$) were determined using the following equations40·42:

$$K_c = \frac{C_{ae}}{C_0} \ldots (8)$$

$$\Delta G^o = -RT \ln K_c \ldots (9)$$

$$\log K_c = \frac{\Delta S^o}{2.303 R} - \frac{\Delta H^o}{2.303 RT} \ldots (10)$$

where $K_c$ is the equilibrium constant, $C_{ae}$ is the solid-phase concentration at equilibrium (mg L$^{-1}$), $T$ is the temperature in Kelvin and $R$ is the gas constant. $\Delta H^o$ and $\Delta S^o$ were obtained from the slope and intercept of van't Hoff plot (Fig. 9) and are presented in Table 3. Positive value of $\Delta H^o$ (Table 3) shows the
endothermic nature of adsorption. This rules out the possibility of physical adsorption. Because in the case of physical adsorption, while increasing the temperature of the system the extent of dye adsorption decreases, as desorption increases with temperature\textsuperscript{43}. As chemisorption is mainly an irreversible process, the high positive $\Delta H^\circ$ value (135.72 kJ mol$^{-1}$) depicts that malachite green dye is chemisorbed onto JPC\textsuperscript{43}. This is in agreement with the type I isotherm (Fig. 8) obtained which is close to irreversible adsorption.

The negative values of $\Delta G^\circ$ (Table 3) indicate that the dye adsorption is spontaneous. The positive value of $\Delta S^\circ$ shows increased randomness at the solid-solution interface during the adsorption of dye on JPC. The adsorbed water molecules, which are displaced by the adsorbate species, gain more translational entropy than is lost by the adsorbate molecules, thus allowing the prevalence of randomness in the system\textsuperscript{44}. Enhancement of adsorption capacity of JPC at higher temperatures may be attributed to the enlargement of pore size and/or activation of the adsorbent surface\textsuperscript{45}.

**Effect of pH**

The experiments carried out at different pH show that there was no change in the per cent removal of dye over the entire pH range, except that there was 4% decrease when the pH was lowered from 3 to 1. This indicates the strong force of interaction between the dye and JPC that either $H^+$ or $OH^-$ ions could not influence the adsorption capacity. In other words, the adsorption of malachite green dye on JPC does not involve ion exchange mechanism. If the adsorption would have occurred through ion exchange mechanism there should have been an influence on the dye adsorption while varying the pH\textsuperscript{44}. This observation is in line with the type I isotherm (Fig. 8) and high positive $\Delta H^\circ$ value obtained, which indicates irreversible adsorption probably due to nonpolar interactions.

**Desorption studies**

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the dye. If the adsorbed dye can be desorbed using neutral pH water, then the attachment of the dye on the adsorbent is by weak bonds. If sulphuric acid or alkaline water can desorb the dye, then the desorption is by ion exchange. If organic acids, like acetic acid can desorb the dye, then the dye is held by the adsorbent through chemisorption\textsuperscript{47}. Neutral pH water, 1 M sulphuric acid and 1 M sodium hydroxide did not show any desorption of the dye. However, 10% acetic acid (v/v) and 50 % acetic acid (v/v) solubilized 9 and 56% of malachite green, respectively, from the dye-adsorbed carbon. The nonreversibility of adsorbed dye in mineral acid or base is in agreement with the pH independent results obtained. The desorption of dye in acetic acid (organic medium) indicates that malachite green dye is adsorbed onto JPC through chemisorption mechanism.

**Conclusion**

Carbon prepared from waste jack fruit peel was found effective in removing malachite green dye from aqueous solution. The adsorption is faster and the rate is mainly controlled by intraparticle diffusion. Using the sorption equation obtained from the Freundlich isotherm, it was found that about 16.5 L of wastewater, containing 10 mg L$^{-1}$ of malachite green dye could be treated by 1 g of JPC. The equilibrium data conformed well with the Langmuir and Redlich-Peterson isotherm models and the adsorption capacity of JPC is 166.37 mg g$^{-1}$ at an initial pH of 6.0 and at 32 $\pm$ 0.5°C. The temperature variation study showed that the dye adsorption is endothermic and spontaneous with increased randomness at the solid-solution interface. No significant effect on adsorption was observed on varying the pH of the dye solution. The type I isotherm obtained, high positive $\Delta H^\circ$ value, pH independent results and desorption of dye in organic medium suggest that the adsorption of malachite green dye on JPC involves chemisorption mechanism.
The encouraging results obtained prompted to work on the removal of other basic dyes that pose real challenge to the conventional methods of treatment.

Acknowledgement
The authors thank Rajiv Gandhi National Drinking Water Mission, Ministry of Rural Development, Government of India for the financial assistance.

References