Adsorption kinetics of malachite green by activated low cost carbon

S.Arivoli*1, P.Martin Deva Prasath2, M.Hema1
1Department of Chemistry, M.R.Government Arts College, Mannargudi 614 001, (INDIA)
2Department of Chemistry, T.B.M.L. College, Porayar 607309, (INDIA)
E-mail: arivu3636@yahoo.com
Received: 25th October, 2007 ; Accepted: 30th October, 2007

ABSTRACT

A carbonaceous adsorbent prepared from an indigenous waste by acid treatment was tested for its efficiency in removing Malachite green. The 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 intra-particle diffusion. Freundlich and Langmuir isotherm models were applied to the equilibrium data. The adsorption capacity (Qm) obtained from the Langmuir isotherm plots were 63.41, 63.86, 64.43 and 67.06 mg/g respectively at an initial pH of 7.0 at 30, 40, 50 and 60°C. The temperature variation study showed that the Malachite green adsorption is endothermic and spontaneous with increased randomness at the solid solution interface. Significant effect on adsorption was observed on varying the pH of the Malachite green solutions. Almost 90% removal of Malachite green was observed at 60°C. The Langmuir and Freundlich isotherms obtained, positive ΔH° value, pH dependent results and desorption of dye in mineral acid suggest that the adsorption of Malachite green on MCC involves physorption mechanism.

INTRODUCTION

The concentration and effective utilization of activated carbon generated from natural plant material have attracted worldwide attention in a view of the large disposal problem without detriment to environment. Many investigators have studied the feasibility of using inexpensive alternative materials like pearl millet husk, date pits, saw dust buffing dust of leather industry, coir pith, crude oil residue tropical grass, olive stone and almond shells, pine bark, wool waste, coconut shell etc., as carbonaceous precursors for the removal of dyes from water and wastewater[1,2,3].

The present study undertaken to evaluate the efficiency of a carbon adsorbent prepared from acid activated morinda coreia buch-ham bark carbon(MCC) for removal of Malachite green dye in aqueous solution. In order to design adsorption treatment systems, knowledge of kinetic and mass transfer processes is essential. In this paper, we have reported the applicability of kinetic and mass-transfer models for the adsorption of Malachite green onto acid activated carbon.

Material
Adsorbent material

The dried morinda coreia buch-ham bark was carbonized with concentrated sulphuric acid in the weight ratio of 1:1 (w/v). Heating for twelve hours in a furnace at 400°C has completed the carbonization and activation. The resulting carbon was washed with distilled water until a constant pH of the slurry was reached. Then the carbon was dried for four hours at 120°C in a hot air oven. The dried material was ground well to a fine powder and sieved.

Adsorption dynamic experiments

Batch equilibration method

The adsorption experiments were carried out in a batch process at 30, 40, 50 and 60°C temperatures. The known weight of adsorbent material was added to 50 ml of the dye solutions with an initial concentration of 20 mg/L to 100 mg/L. The contents were shaken thoroughly using a mechanical shaker rotating with a speed of 120 rpm. The solution was then filtered at preset time intervals and the residual dye concentration was measured.

Effect of variable parameters

1. Dosage of adsorbent

The various doses of the adsorbents are mixed with the dye solutions and the mixture was agitated in a mechanical shaker. The adsorption capacities for different doses were determined at definite time intervals by keeping all other factors constant.

2. Initial concentration of dye

In order to determine the rate of adsorption, experiments were conducted with different initial concentrations of dyes ranging from 20 to 100 mg/L. All other factors are kept constant.

3. Contact time

The effect of period of contact on the removal of the dye on adsorbent in a single cycle was determined by keeping particle size, initial concentration, dosage, pH and concentration of other ions constant.

4. pH

Adsorption experiments were carried out at pH 3, 4, 5, 6, 7, 8, 9 and 10. The acidic and alkaline pH of the media was maintained by adding the required amounts of dilute hydrochloric acid and sodium hydroxide solutions. The parameters like particle size of the adsorbents, dye concentration, dosage of the adsorbent and concentration of other ions have kept constant while carrying out the experiments. The pH of the samples was determined using a portable pH meter, Systronics make. The pH meter was calibrated with 4.0 and 9.2 buffers.

5. Chloride

The experiments were done in the presence of varying chloride environments using various sodium chloride solutions. While doing the experiments, the absence of other anions has ensured.

6. Temperature

The adsorption experiments were performed at four different temperatures viz., 30, 40, 50 and 60°C in a thermostat attached with a shaker, Remi make. The constancy of the temperature was maintained with an accuracy of ± 0.5°C.

7. Zero point charge

The pH at the potential of zero charge of the carbon (pH zpc) was measured using the pH drift method [4]. The pH of the solution was adjusted by using 0.01 M sodium hydroxide or hydrochloric acid. Nitrogen was bubbled through the solution at 25°C to remove the dissolved carbon dioxide. 50 mg of the activated carbon was added to 50 ml of the solution. After stabilization, the final pH was recorded. The graphs of final pH versus initial pH used to determine the zero point charge of the activated carbon.

8. Titration studies

According to Boehm [4] only strong acidic carboxylic acid groups are neutralized by sodium bicarbonate, while as those neutralized by sodium carbonate are thought to be lactones, lactol and carboxyl group. The weakly acidic phenolic groups only react with strong alkali, sodium hydroxide. Therefore, by selective neutralization using bases of different strength, the surface acidic functional group in carbon can be characterized both quantitatively and qualitatively. Neutralization with hydrochloric acid characterizes the amount of surface basic groups that are, for example, pyrones and chromenes. The basic properties have described to surface basic groups and the π electron system of carbon basal planes. The results indicate that the activated
carbon used may possess acidic oxygen functional group on their surface and this is supported well by their respective zeropoint charge values. The results obtained from the above characterization studies are given in the TABLE 1.

9. Desorption studies

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the dye. The effect of various reagents used for desorption are studied.

RESULTS AND DISCUSSIONS

Characterization of the adsorbent

Activated carbons are a widely used adsorbent due to its high adsorption capacity, high surface area, microporous structure and high degree of surface respectively. The wide usefulness of carbon is a result of their specific surface area, high chemical and mechanical stability. The chemical nature and pore structure usually determines the sorption activity. The physico chemical properties are listed in TABLE 1

Effect of contact time and initial dye concentration

The experimental results of adsorptions of at various concentrations (10, 20, 30, 40, 50 and 60mg/L) with contact time are shown in representative figure 1. The equilibrium data were collected in TABLE 2 reveals that, percent adsorption decreased with increase in initial dye concentration, but the actual amount of dye adsorbed per unit mass of carbon increased with increase in dye concentration. It means that the adsorption is highly dependent on initial concentration of dye. It is because of that at lower concentration, the ratio of the initial number of dye molecules to the available surface area is low subsequently the fractional adsorption becomes independent of initial concentration. However, at high concentration the available sites of adsorption becomes fewer and hence the percentage removal of dye is dependent upon initial concentration[5,6]. Equilibrium have established at 40 minutes for all concentrations. Figure 1 reveals that the curves are single, smooth, and continuous, leading to saturation, suggesting the possible monolayer coverage of the dyes on the carbon surface.

Effect of carbon concentration

<table>
<thead>
<tr>
<th>Properties</th>
<th>MCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size (mm)</td>
<td>0.055</td>
</tr>
<tr>
<td>Density (g/cc)</td>
<td>0.3575</td>
</tr>
<tr>
<td>Moisture content (%)</td>
<td>2.25</td>
</tr>
<tr>
<td>Loss on ignition (%)</td>
<td>82</td>
</tr>
<tr>
<td>Acid insoluble matter (%)</td>
<td>2.5</td>
</tr>
<tr>
<td>Water soluble matter (%)</td>
<td>0.32</td>
</tr>
<tr>
<td>pH of aqueous solution</td>
<td>6.85</td>
</tr>
<tr>
<td>pH_{zpc}</td>
<td>6.35</td>
</tr>
<tr>
<td>Surface groups (m equiv/g)</td>
<td></td>
</tr>
<tr>
<td>(i) Carboxylic acid</td>
<td>0.325</td>
</tr>
<tr>
<td>(ii) Lactone, lactol</td>
<td>0.049</td>
</tr>
<tr>
<td>(iii) Phenolic</td>
<td>0.061</td>
</tr>
<tr>
<td>(iv) Basic (pyrones and chromenes)</td>
<td>0.036</td>
</tr>
</tbody>
</table>

Figure 1: Effect contact time on the adsorption of malachite green; [MG]=60mg/L; adsorbent dose=50mg/50ml; pH=7

Figure 2: Effect of adsorbent dose on the adsorption of malachite green; [MG]=60mg/L; Contact time=60min; pH=7

The adsorption of the Malachite green dye on carbon was studied by varying the carbon concentration (10-250mg/50ml) for 60mg/L of dye concentration. The percent adsorption increased with increase in the car-
Adsorption kinetics of malachite green by activated low cost carbon

An Indian Journal

Materials Science

Table 2: Equilibrium parameters for the adsorption of dye onto activated carbon

<table>
<thead>
<tr>
<th>[MG]₀</th>
<th>Cₑ (mg/L)</th>
<th>Qₑ (mg/g)</th>
<th>Dye removed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30°C</td>
<td>40°C</td>
<td>50°C</td>
</tr>
<tr>
<td>20</td>
<td>1.8546</td>
<td>1.6428</td>
<td>1.4357</td>
</tr>
<tr>
<td>40</td>
<td>8.4547</td>
<td>8.0015</td>
<td>7.6129</td>
</tr>
<tr>
<td>60</td>
<td>20.5492</td>
<td>19.9817</td>
<td>19.3149</td>
</tr>
<tr>
<td>80</td>
<td>31.8592</td>
<td>31.0924</td>
<td>30.3057</td>
</tr>
<tr>
<td>100</td>
<td>48.4757</td>
<td>41.5045</td>
<td>40.4968</td>
</tr>
</tbody>
</table>

Table 3: Langmuir isotherm results

<table>
<thead>
<tr>
<th>Dye</th>
<th>Temp °C</th>
<th>Statistical parameters/constant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>r²</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.9782</td>
</tr>
<tr>
<td>MG</td>
<td>40</td>
<td>0.9777</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.9768</td>
</tr>
</tbody>
</table>

Table 4: Freundlich isotherm results

<table>
<thead>
<tr>
<th>Dye</th>
<th>Temp °C</th>
<th>Statistical parameters/constant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>r²</td>
</tr>
<tr>
<td>MG</td>
<td>30</td>
<td>0.9941</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.9942</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.9942</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.9902</td>
</tr>
</tbody>
</table>

Figure 3: Langmuir isotherm for the adsorption of malachite green

This was attributed to increased carbon surface area and availability of more adsorption sites\[5,6\]. Hence the entire studies are carried out with the adsorbent dose of 50mg of adsorbent /50ml of the adsorbate solution.

Adsorption isotherm

The experimental data analyzed according to the linear form of the Langmuir and Freundlich isotherms\[7,8\]. The Langmuir isotherm represented by the following equation

\[ Cₑ/Qₑ = 1/Qₑ + Cₑ/Qₑ \]

Where \(Cₑ\) is the equilibrium concentration (mg/L), \(Qₑ\) is the amount adsorbed at equilibrium (mg/g) and \(Qₑ\) and \(b\) is Langmuir constants related to adsorption efficiency and energy of adsorption, respectively. The linear plots of \(Cₑ/Qₑ versus Cₑ\) suggest the applicability of the Langmuir isotherms (Figure 3). The values of \(Qₑ\) and \(b\) were determined from slope and intercepts of the plots and are presented in TABLE 3. From the results, it is clear that the value of adsorption efficiency \(Qₑ\) and adsorption energy \(b\) of the carbon increases on increasing the temperature. From the values we can conclude that the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on adsorbent surface with constant energy and no transmission of adsorbate in the plane of the adsorbent surface. The observed \(b\) values shows that the adsorbent prefers to bind acidic ions and that speciation predominates on sorbent characteristics, when ion exchange is the predominant mechanism takes place in the adsorption of Malachite green, it confirms the endothermic nature of the process involved in the system\[9,10,11\]. To confirm the favourability of the adsorption process, the separation factor (\(R₇\)) was calculated and presented in TABLE 4. The values were found to be between 0 and 1 and confirm that the ongoing adsorption process is favorable\[12\].

The Freundlich equation was employed for the adsorption of Malachite green dye on the adsorbent. The Freundlich isotherm was represented by

\[ \log Qₑ = \log Kₑ + 1/n \log Cₑ \]

Where \(Qₑ\) is the amount of Malachite green dye adsorbed (mg/g), \(Cₑ\) is the equilibrium concentration of dye in solution (mg/L) and \(Kₑ\) and \(n\) are constants incorporating the factors affecting the adsorption capacity and intensity of adsorption, respectively. Linear plots of \(\log Qₑ versus \log Cₑ\) shows that the adsorption of Malachite green dye obeys the Freundlich adsorption isotherm (Figure 4). The values of \(Kₑ\) and \(n\) given in the
TABLE 5 shows that the increase in negative charges on the adsorbent surface that makes electrostatic force like Vanderwaal’s between the carbon surface and dye ion. The molecular weight, size and radii either limit or increase the possibility of the adsorption of the dye onto adsorbent. However, the values clearly show the dominance in adsorption capacity. The intensity of adsorption is an indication of the bond energies between dye and adsorbent and the possibility of slight chemisorptions rather than physisorption[10,11]. However, the multilayer adsorption of Malachite green through the percolation process may be possible. The values of n is greater than one indicating the adsorption is much more favorable[12].

**Effect of temperature**

The adsorption capacity of the carbon increased with increase in the temperature of the system from 30°C-60°C. Thermodynamic parameters such as change in free energy($\Delta G^o$(kJ/mol)), enthalpy($\Delta H^o$(kJ/mol) and entropy($\Delta S^o$(J/K/mol)) were determined using the following equations

$$K_0 = \frac{C_{solid}}{C_{liquid}}$$
$$\Delta G^o = -RT \ln K_0$$
$$\log K_0 = \frac{\Delta S^o}{(2.303RT)} - \frac{\Delta H^o}{(2.303RT)}$$

Where $K_0$ is the equilibrium constant, $C_{solid}$ is the solid phase concentration at equilibrium (mg/L), $C_{liquid}$ is the liquid phase concentration at equilibrium (mg/L), T is the temperature in Kelvin and R is the gas constant. The $\Delta H^o$ and $\Delta S^o$ values obtained from the slope and intercept of Van’t Hoff plots have presented in TABLE 6. The values $\Delta H^o$ are with in the range of 1 to 93KJ/mol indicates the physisorption. From the results we could make out that physisorption is much more favorable for the adsorption of Malachite green. The positive values of $\Delta H^o$ show the endothermic nature of adsorption and it governs the possibility of physical adsorption[11,13]. Because in the case of physical adsorption, while increasing the temperature of the system, the extent of dye adsorption increases, this rules out the possibility of chemisorption[13]. The low $\Delta H^o$ value depicts dye is physisorbed onto adsorbent MCC.

The negative values of $\Delta G^o$(TABLE 6) shows the adsorption is highly favorable and spontaneous. The positive values of $\Delta S^o$ (TABLE 6) shows the increased disorder and randomness at the solid solution interface of Malachite green with MCC adsorbent, while the adsorption there are some structural changes in the dye and the adsorbent occur. The adsorbed water molecules, which have 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. The enhancement of adsorption capacity of the activated carbon at higher temperatures was attributed to the enlargement of pore size and activation of the adsorbent surface[12,13,14].

**Kinetics of adsorption**

The kinetics of sorption describes the solute uptake rate, which in turn governs residence time or sorption reaction. It is one of the important characteristics in defining the efficiency or sorption. In the present study,
TABLE 7: Rate constants for the adsorption of Malachite green dye ($10^3 k_{ad}$, min$^{-1}$) and the constants for forward ($10^3 k_1$, min$^{-1}$) and reverse ($10^3 k_2$, min$^{-1}$) process

<table>
<thead>
<tr>
<th>[D]$_0$</th>
<th>$k_{ad}$</th>
<th>$k_1$</th>
<th>$k_2$</th>
<th>$k_1$</th>
<th>$k_2$</th>
<th>$k_1$</th>
<th>$k_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30°C</td>
<td>50°C</td>
<td>60°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>345.88</td>
<td>653.86</td>
<td>1084.98</td>
<td>313.81</td>
<td>600.18</td>
<td>53.71</td>
<td>-7.54</td>
</tr>
<tr>
<td>40</td>
<td>115.15</td>
<td>129.42</td>
<td>155.79</td>
<td>90.82</td>
<td>103.54</td>
<td>25.88</td>
<td>-4.21</td>
</tr>
<tr>
<td>60</td>
<td>45.71</td>
<td>48.98</td>
<td>51.56</td>
<td>54.74</td>
<td>30.06</td>
<td>32.64</td>
<td>16.31</td>
</tr>
<tr>
<td>80</td>
<td>34.15</td>
<td>53.81</td>
<td>37.63</td>
<td>52.18</td>
<td>20.55</td>
<td>21.90</td>
<td>13.91</td>
</tr>
<tr>
<td>100</td>
<td>30.39</td>
<td>31.45</td>
<td>33.11</td>
<td>34.54</td>
<td>17.49</td>
<td>18.40</td>
<td>13.05</td>
</tr>
</tbody>
</table>

The determination of rate constants as described in literature given by

\[ K_{ad} = k_1 + k_2 = k_1 + (k_1/K_0) = k_1 [1 + 1/K_0] \]

The overall rate constant $k_{ad}$ for the adsorption of dye at different temperatures are calculated from the slopes of the linear Natarajan-Khalaf plots. The rate constant values are collected in TABLE 7 shows that the rate constant ($k_{ad}$) increases with increase in temperature suggesting that the adsorption process in endothermic in nature. Further, $k_{ad}$ values decrease with increase in initial concentration of the dye. 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 dye concentration and rate of reaction will not be linear. Thus, in the present study pore diffusion limits the overall rate of dye adsorption. The over all rate of adsorption is separated into the rate of forward and reverse reactions using the above equation. The rate constants for the forward and reverse processes are also collected in TABLE 7 indicate that, at all initial concentrations and temperatures, the forward rate constant is much higher than the reverse rate constant suggesting that the rate of adsorption is clearly dominant\cite{11,13}.

### Intraparticle diffusion

The most commonly used technique for identifying the mechanism involved in the sorption process is by fitting the experimental data in an intraparticle diffusion plot. Previous studies by various researchers showed that the plot of $Q_t$ versus $t^{0.5}$ represents multi linearity, which characterizes the two or more steps involved in the sorption process. According to Weber and Morris, an intraparticle diffusion coefficient $K_p$ is defined by the equation:

\[ K_p = \frac{Q}{t^{0.5}} \]

Thus the $K_p$ (mg/g min$^{-0.5}$) value can be obtained from the slope of the plot of $Q_t$ (mg/g) versus $t^{0.5}$ for Malachite green. From figure 5, it was noted that the sorption process tends to be followed by two phases. The two phases in the intraparticle diffusion plot suggest that the sorption process proceeds by surface sorption and intraparticle diffusion\cite{15,16}. The initial curved portion of the plot indicates a boundary layer effect while the second linear portion is due to intraparticle or pore diffusion. The slope of the second linear portion of the plot has been defined as the intraparticle diffusion param-
was obtained at pH 3.0. However, when the pH of the solution was increased (more than pH 9), the uptake of Malachite green ions was increased. It appears that a change in pH of the solution results in the formation of different ionic species, and different carbon surface charge. At pH values lower than 6, the Malachite green ions can enter into the pore structure. At a pH value higher than 7, the zwitterions form of Malachite green in water may increase the aggregation of Malachite green to form a bigger molecular form (dimer) and become unable to enter into the pore structure of the carbon surface. The greater aggregation of the zwitterionic form is due to the attractive electrostatic interaction between the ionic groups of the monomer.

At a pH value higher than 9, the existence of MCC surface OH creates a competition between ionic dye and it will decrease the aggregation of Malachite green, which causes an increase in the adsorption of Malachite green ions on the carbon surface. The effect of the charge on the carbon surface and the electrostatic force of attraction and repulsion between the carbon surface and the Malachite green ions cannot explain the outcome.

Effect of the ionic strength on the adsorption of Malachite green

The effect of sodium chloride on the adsorption of Malachite green on MCC is shown in figure 7. In a low solution concentration NaCl had little influence on the adsorption capacity. At higher ionic strength the adsorption Malachite green will be increased due to the partial neutralization of the positive charge on the carbon surface and a consequent compression of the electrical double layer by the Cl\(^-\) anion. The chloride ion can also enhance adsorption of Malachite green ion onto MCC by pairing of their charges and hence reducing the repulsion between the Malachite green molecules adsorbed on the surface. This initiates carbon to adsorb more of positive Malachite green ions.

Desorption studies

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 using neutral pH water, then the attachment of the dye of the adsorbent is by weak bonds. If sulphuric acid or alkaline water desorp the dye then the adsorption is by ion exchange. If organic acids, like acetic acid can desorp
Adsorption kinetics of malachite green by activated low cost carbon

An Indian Journal
Materials Science

the dye, then the dye has held by the adsorbent through chemisorption. The effect of various reagents used for desorption studies indicate that hydrochloric acid is a better reagent for desorption, because we could get more than 65% removal of adsorbed dye. The reversibility of adsorbed dye in mineral acid or base is in agreement with the pH dependent results obtained. The desorption of Malachite green dye by mineral acids and alkaline medium indicates that the dyes were adsorbed onto the activated carbon through by physisorption mechanisms.[12,18]

CONCLUSIONS

The experimental data correlated reasonably well by the Langmuir and Freundlich adsorption isotherms and the isotherm parameters were calculated. The low as well high pH value pay the way to the optimum amount of adsorption of the dye. The amount of Malachite green adsorbed increased with increasing ionic strength and increased with increase in temperature. The dimensionless separation factor ($R_L$) showed that the activated carbon could be used for the removal of Malachite green from aqueous solution. The values of $\Delta H^0$, $\Delta S^0$ and $\Delta G^0$ results shows that the carbon employed has a considerable potential as an adsorbent for the removal of Malachite green.

ACKNOWLEDGMENT

The authors acknowledge sincere thanks to Mrs. Mala Arivoli, The Principal, M.R.Government Arts College, Mannargudi and The Director of Collegiate Education, Chennai for carrying out this research work successfully.

REFERENCES


Figure 7: Effect of other ions on the adsorption of malachite green; [MG]=60mg/L; Contact time=60 min; Adsorbent dose=50mg/50ml