Chapter − 3

Adsorption Studies of Hazardous Malachite Green

onto Treated Ginger Waste

3.1. Introduction

The textile industries are the greatest generators of liquid effluent, due to the high quantity of water used in the dyeing processes [1]. Fifteen percent of the total world production of dyes is lost during the dyeing process and released in textile effluent [2]. Malachite Green (MG) is a cationic dye and widely used for the dyeing of leather, wool and silk, distilleries, jute, paper, as a food-coloring agent, food additive, in medical disinfectant and fish industries [3-6]. Discharge of MG into the hydrosphere can cause environmental degradation as it gives undesirable colour to water and reduces sunlight penetration. The consumption of MG has many adverse effects due to its carcinogenic, genotoxic, mutagenic and teratogenic properties [7]. The carcinogenic properties of MG are due to presence of the nitrogen [5].

Many advanced treatment methods have been developed to remove dyes from wastewater, which can be divided into physical, chemical and biological method such as photo-degradation [8, 9], photocatalytic degradation [10-12], biodegradation [13, 14] and adsorption [15, 16]. Adsorption techniques have potential for removing organic and inorganic pollutants from wastewater due to their high efficiency and ability to separate a wide range of compounds [17, 18]. A considerable amount of interest has recently been focused on the adsorption technique for the removal of dyes from wastewater onto various adsorbent such as sepiolite [19-21], kaolinite [22], montmorillonite [23, 24], bentonite [25], bottom ash [4], peat [26], activated carbon [27, 28], polymers [29], de-oiled soya [30], hen feathers [31], rice straw [32] etc.

In this paper, we have studied the adsorption properties of ginger (*Zingiber officinale*) waste material treated with zinc chloride and sulfuric acid for the removal of malachite green (MG) from aqueous solution. The ginger waste was treated in order to increase its adsorption capacity. According to Huang and Huang [33], acid treatment results not only in a clean-up of the surface impurities, but also increases the surface area by opening the available sites for adsorption. Batch and column
processes were used to study the adsorption process.

3.2. Materials and Methods

3.2.1. Adsorbate

Malachite green hydrochloride [C.I. = 42,000, M.F. = C_{23}H_{26}N_{2}Cl, M.W. = 364.92, \lambda_{\text{max}} = 617 \text{ nm}] was supplied by CDH, New Delhi, India. Solutions of MG were prepared by dissolving accurately weighed amount of the dye in double distilled water. The molecular structure of the MG is illustrated in Fig. 3.1.

![Fig. 3.1. Structure of malachite green.](image)

3.2.2. Preparation of Adsorbent

The ginger waste material (rhizome) used in this study was collected locally. The material was washed with double distilled water and dried in an oven at 60°C for 12 h. The dried ginger waste material was converted into 100 (≈0.15-0.08 mm) mesh BSS particle size. The powdered material was soaked for 24 h in solution prepared from H_{2}SO_{4} and ZnCl_{2} in the ratio of 1:1 and it was again washed with double distilled water to remove the excess of acid, dried at 60°C for 24 h and used as such for further studies.

3.2.3. Characterization of Treated Ginger Waste (TGW)

The morphology of the TGW surface was obtained by the scanning electron microscope (LEO 435 VP model). The FTIR spectra of untreated and treated ginger waste in the range of 400-4000 cm\(^{-1}\) were taken and compared with each other to study the change in surface functional groups. The FTIR analysis was carried out by an Inter- spec 2020, Spectro lab, (U.K.) spectrometer.

Determination of point of zero charge (pH\(_z\)) was done to investigate the surface charge of TGW. For the determination of pH\(_z\), 0.1 M KCl was prepared and it’s initial pH was adjusted between 2.0 and 12.2 using NaOH and HCl. Then, 50 ml of 0.1 M KCl was taken in 250 ml flasks and 0.05 g of TGW was added to each
solution. These flasks were kept for 24 h and the final pH of the solutions was measured with a pH meter. Graphs were plotted between pH\text{final} and pH\text{initial} [34].

Acidic and basic sites on TGW were determined by the chemical titration method proposed by Boehm [35]. The amount of oxygen containing groups (carboxyl, lactonic and phenol) on the TGW was determined by neutralization with 0.1 N NaHCO$_3$, 0.1 N Na$_2$CO$_3$ and 0.1 N NaOH solutions, respectively. The basic group contents of the TGW were determined with 0.1 N HCl. The acidic and basic sites were determined by adding 50 ml of 0.1 N titrating solutions and 1 g of TGW into a 250 ml volumetric flask. The flask was left for 36 h at 30 °C. Afterward, a sample of 10 ml was titrated with 0.1 N HCl or NaOH solutions. The carboxylic and lactonic sites were titrated with a 0.1 N Na$_2$CO$_3$ solution while carboxylic sites were determined with 0.1 N NaHCO$_3$ solution and the phenolic sites were estimated by difference [36].

3.2.4. Batch Adsorption Studies

Batch adsorption experiments were conducted in order to evaluate the effect of various operation parameters such as contact time, solution pH, initial MG concentration and temperature. In each batch experiment, 50 ml dye solution of known concentration (5–20 mg/l) and known amount (0.05 g) of TGW was taken in 250 ml standard flask at the constant temperature. Kinetic studies were carried out at three different initial dye concentrations 5, 10 and 20 mg/l using 0.05 g dose of TGW and agitated for the fixed time intervals. The effect of the solution pH on MG removal was investigated over a pH range of 2–9. The solution pH was measured by pH meter (Elico SL 120). The pH was adjusted using dilute HCl and NaOH solution. After adsorption, the dye remaining in the solution was measured at the maximum wavelength of MG ($\lambda_{\text{max}} = 618$ nm) using double beam UV–vis spectrophotometer (Elico SL 164 India). The adsorbed amount of MG at equilibrium, $q_e$ (mg/g) was determined by:

$$ q_e = (C_0 - C_e)V/W $$

where $C_0$ and $C_e$ are the concentrations (mg/l) of MG dye at initial and equilibrium, respectively. $V$ is the volume (l) of the solution and $W$ is the weight (g) of the adsorbent used.
3.2.5. Column Adsorption Studies

Fixed bed column studies were performed by varying dose of adsorbent 0.2, 0.3 and 0.5 g, supported by glass wool in three separate glass columns of 30 cm in length and 1 cm in internal diameter. Each column was then loaded with an adsorbate solution of known concentration at the flow rate of 1 ml/min. The column was operated till the effluent concentration matched with the concentration of the loaded dye.

3.2.6. Desorption Studies

Desorption studies were performed by column process. The column of length 30 cm and internal diameter 1 cm and a flow rate of 1 ml/min was used. 0.05 g of TGW was used to adsorb MG solution of concentration 10 mg/l. The column was then washed several times with double distilled water in order to remove the traces of MG unadsorbed. 0.1 M and 1 M CH₃COOH solutions were used to elute the MG from the exhausted adsorbent. The amount of MG desorbed in acidic solution was determined by spectrophotometer.

3.3. Results and Discussion

3.3.1. Surface Characterization of the TGW

Scanning electron microscope was used to study the surface morphology of TGW. SEM image of TGW shows texture and porous structure of TGW (Fig. 3.2). SEM images clearly showed that the pores were completely filled after the adsorption of MG.

The concentration of total acidic and basic sites determined by the Boehm titration method onto the TGW are 1.12 mequiv/g (carboxylic and lactonic site—0.94 mequiv/g and carboxylic site—0.18 mequiv/g) and 0.044 mequiv/g, respectively.

The FTIR spectra of the untreated and treated ginger waste are presented in Fig. 3.3. The absorption band at 3418 cm⁻¹ represents the presence of –OH and –NH groups. The absorption band observed at 2926 cm⁻¹ is associated to asymmetric stretches of –CH group. However, a small peak 2926 cm⁻¹ is associated to asymmetric stretches of –CH group and a small peak located around 2883 cm⁻¹, is assigned for symmetric stretching vibrations of –CH group. Atmospheric CO₂ bands are present at 2366 cm⁻¹ (antisymmetric C=O stretch). The dual bands at 1662 and 1457 cm⁻¹.
indicates the presence of –COO, –C=O and –NH groups for the untreated and treated ginger waste. Another absorption bands appearing around 1156, 1047 and 672 cm\(^{-1}\) can be attributed to the C–O stretching, sulfonic group and C–S stretching vibration, respectively. The peak present at 806 cm\(^{-1}\) indicates the presence of aromatic heterocyclic molecules, which is absent in TGW. This indicates that there is a possibility of ring cleavage after the acid treatment [37, 38]. Fig. 3.4 shows the point of intersection of the curves at 6, thus, pH\(_z\) of TGW is 6.

**Fig. 3.2.** SEM images of TGW (a) before adsorption (b) after adsorption.

**Fig. 3.3.** FTIR spectra of (a) untreated ginger waste and (b) treated ginger waste.
3.3.2. Batch Adsorption Studies

3.3.2.1. Effect of Initial Dye Concentration and Contact Time

The uptake of dye increased from 4 to 15.5 mg/g with the increase in dye concentration from 5 to 20 mg/l. This may be attributed to an increase in the driving force of the concentration gradient with the increase in the initial dye concentration [39, 40]. The effect of contact time in the range 15–180 min were studied in the concentration range 5–20 mg/l of MG solution. The uptake of MG as a function of contact time is shown in Fig. 3.5. The uptake increased with the increase in contact time. The maximum removal of MG from aqueous solution was obtained after contact time of 150 min. Initially adsorption was rapid due to the adsorption of dye onto exterior surface, after that dye molecules enter into pores (interior surface) which is a relatively slow process. The removal of MG increased with an increase in concentration and remained constant after the equilibrium time [41].

3.3.2.2. Effect of pH

The adsorption capacity of TGW increased with an increase in solution pH and the maximum adsorption capacity for MG was observed at pH 9 as depicted in Fig. 3.6. When solution pH increases, high OH\(^-\) ions accumulate on the adsorbent surface. Therefore, electrostatic interaction between negatively charged adsorbent surface and cationic MG molecule caused an increase in adsorption. Furthermore, the solution pH is above the point of zero charge (pHz 6) and hence the negative charge
density on the surface of TGW increased which favors the adsorption of cationic dye [42].

![Graph showing the effect of contact time on MG adsorption.](image)

**Fig. 3.5.** Effect of contact time on MG adsorption.

![Graph showing the effect of pH on MG adsorption.](image)

**Fig. 3.6.** Effect of pH on MG adsorption.

### 3.3.2.3. Effect of Temperature

The adsorption studies were carried out at 30, 40 and 50 °C and the results of these experiments are shown in Fig. 3.7. It was observed that as the temperature increased, the adsorption capacity also increased, indicating that the process was endothermic in nature. The enhancement in adsorption with temperature may be due to the increase in the mobility of the dye molecule with increase in their kinetic energy as well as the enhanced rate of intraparticle diffusion of adsorbate with the rise in temperature [43].
3.3.2.4. Determination of Thermodynamic Parameters

The Gibbs free energy change ($\Delta G^0$) indicates the degree of the spontaneity of the adsorption process. For significant adsorption, the free energy change ($\Delta G^0$) of adsorption must be negative. The Gibbs free energy, entropy and enthalpy changes of adsorption were calculated by Van’t Hoff and Gibbs-Helmholtz equations

$$K_c = \frac{C_{ac}}{C_e}$$  \hspace{1cm} (2)

$$\Delta G^0 = -RT \ln K_c$$  \hspace{1cm} (3)

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$  \hspace{1cm} (4)

where $K_c$ is the thermodynamic equilibrium constant. $C_{ac}$ and $C_e$ are the initial and equilibrium concentration (mg/l) of dye in solution. $\Delta H^0$ and $\Delta S^0$ can be determined from the slope and the intercept of the linear plot of $\ln K_c$ vs $1/T$ (Fig. 3.8). The positive $\Delta H^0$ value (Table 3.1) suggests the endothermic nature of adsorption and the negative $\Delta G^0$ values indicates the feasibility and spontaneity of the adsorption process. The positive value of $\Delta S^0$ shows an increase in randomness at solid-solution interface during adsorption.
Table 3.1. Thermodynamic parameters for MG adsorption onto TGW.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>∆G° (kJ/mol)</th>
<th>∆H° (kJ/mol)</th>
<th>∆S° (kJ/mol K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>-1.515</td>
<td>47.491</td>
<td>0.167</td>
</tr>
<tr>
<td>40</td>
<td>-2.133</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>-3.016</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

![Fig. 3.8. ln Kc vs 1/T plot for MG adsorption](image)

3.3.2.5. Adsorption Isotherms

Langmuir and Freundlich adsorption isotherm equilibrium models were used for the analysis of the MG–TGW adsorption system. The Langmuir adsorption isotherm model, to evaluate the monolayer adsorption phenomena, is depicted in eq.5:

\[
\frac{1}{x/m} = \frac{1}{\Theta_0 b C_e} + \frac{1}{\Theta_0} \tag{5}
\]

where \(x/m\) is the dye uptake per unit weight of adsorbent (mg/g), \(C_e\) is the concentration of dye in aqueous phase at equilibrium (mg/l), \(\Theta_0\) and \(b\) are Langmuir constants related to the adsorption capacity and adsorption energy, respectively. The values of these constants can be evaluated from the intercept and the slope of the linear plots of \(1/x/m\) vs. \(1/C_e\). The values of Langmuir parameters are listed in Table 3.2.

The essential characteristics of the Langmuir isotherm can be expressed in terms of either a dimensionless constant separation factor or equilibrium parameter, \(R_L\):
where $R_L$ is a dimensionless separation factor, $C_0$ is the initial dye concentration (mg/l) and $b$ is the Langmuir constant (l/mg). The parameter $R_L$ indicates the shape of isotherm, as follows: $R_L > 1$ unfavorable, $R_L = 1$ linear, $0 < R_L < 1$ favorable, $R_L = 0$ irreversible. The results show that the values of $R_L$ are between zero and one, indicating the favorable adsorption of MG onto TGW (Table 3.2).

The Freundlich equation was employed to study the adsorption isotherm of MG onto TGW. The linear Freundlich equation is:

$$\log \left( \frac{x}{m} \right) = \left( \frac{1}{n} \right) \log C_e + \log K_f$$

where $K_f$ and $n$ are Freundlich constants indicating the adsorption capacity and intensity, respectively. The values of Freundlich parameters were calculated from plots, $\log \left( \frac{x}{m} \right)$ vs. $\log C_e$ and are mentioned in Table 3.2. The adsorption isotherms predict that the values of $\Theta^0$ and $n$ increases with increasing temperature. At $50^\circ$C, the value of $n$ is greater than unity, indicating favorable adsorption and support the endothermic nature of adsorption process for MG adsorption onto TGW.

### Table 3.2. Langmuir and Freundlich isotherm parameters of MG adsorption onto TGW.

<table>
<thead>
<tr>
<th>Temperature ($^\circ$C)</th>
<th>$\Theta^0$ (mg/g)</th>
<th>$b$ (l/mg)</th>
<th>$R_L$</th>
<th>$R^2$</th>
<th>$K_f$ (mg/g)(mg/l)$^{1/n}$</th>
<th>$n$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>84.03</td>
<td>0.010</td>
<td>0.826</td>
<td>0.999</td>
<td>1.14</td>
<td>0.93</td>
<td>0.986</td>
</tr>
<tr>
<td>40</td>
<td>163.9</td>
<td>0.005</td>
<td>0.901</td>
<td>0.999</td>
<td>1.11</td>
<td>0.97</td>
<td>0.999</td>
</tr>
<tr>
<td>50</td>
<td>188.6</td>
<td>0.005</td>
<td>0.905</td>
<td>0.995</td>
<td>1.04</td>
<td>1.007</td>
<td>0.994</td>
</tr>
</tbody>
</table>

### 3.3.2.6. Adsorption Kinetics

In order to find out the potential rate-controlling steps involved in the process of adsorption, kinetic models were also applied. Pseudo-second order kinetic model was used to fit the experimental data at different initial dye concentrations at $30^\circ$C. The pseudo-second order kinetic rate equation [44] is expressed as:

$$\frac{t}{q_t} = \left( \frac{1}{k_2 q_e^2} \right) + \frac{t}{q_e}$$

where $q_t$ and $q_e$ are the amount of dye adsorbed (mg/g) at ant time and equilibrium,
respectively. $k_2$ is the pseudo-second order rate constant. By plotting $t/q_t$ against $t$ for the different concentrations, straight lines were obtained as shown in Fig. 3.9. The pseudo-second order rate constants $k_2$ and $q_e$ values were determined from the slope and intercept of plots. The results showed that the values of correlation coefficients ($R^2$) for the pseudo-second order kinetic model are very high (Table 3.3). The values of experimental $q_e$ and calculated $q_e$ were close in agreement showing the applicability of pseudo-second order kinetic model.

![Fig. 3.9. Pseudo-second order kinetics for MG adsorption](image)

### Table 3.3. Pseudo-second order kinetic constants for MG adsorption onto TGW.

<table>
<thead>
<tr>
<th>Concentration (mg/l)</th>
<th>$k_2$ (g/mg min)</th>
<th>$q_e$ exp (mg/g)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1.11</td>
<td>4.36</td>
<td>0.996</td>
</tr>
<tr>
<td>10</td>
<td>0.045</td>
<td>10.25</td>
<td>0.987</td>
</tr>
<tr>
<td>20</td>
<td>0.020</td>
<td>21.69</td>
<td>0.974</td>
</tr>
</tbody>
</table>

Kinetics data were also analyzed by the procedure given by Reichenberg [45] using equation 9-11:

$$B_t = -2.303 \log (1-F) - 0.4977 \quad (9)$$

$$F = Q_t / Q_0 \quad (10)$$

$$B = \pi^2 D_i / r_0 \quad (11)$$

where $F$ is the fractional attainment of equilibrium at time $t$, $Q_t$ is the amount of
adsorbent taken up at time t, $Q_0$ is the maximum equilibrium uptake at infinite time, $D_i$ is the effective diffusion coefficient, $B$ is the time constant, $r_0$ is the radius of the adsorbent particle assumed to be spherical. The linearity test of $B_t$ vs. time plots were used to distinguish between the film- and particle-diffusion-controlled adsorptions. If the plot is a straight line passing through the origin, the adsorption rate was governed by the particle-diffusion, otherwise it was governed by film diffusion. The plots for all the concentration of MG are linear, but they do not pass through the origin as shown in Fig. 3.10, indicating the film-diffusion-controlled mechanism. The values of $B$ can be determined by the slope of the plot $B_t$ vs. $t$ (Table 3.4). The above observation was also supported by log $(1-F)$ vs. $t$ plot (Fig. 3.11) for different MG concentrations at 30 °C. The straight lines were obtained which support the fact that the adsorption of MG onto TGW occurs via internal transport. Similar results have also been reported for the adsorption of MG onto hen feather [31].

Table 3.4. The values of effective diffusion coefficient for Mg adsorption onto TGW.

<table>
<thead>
<tr>
<th>Concentration (mg/l)</th>
<th>$B$</th>
<th>$D_i$ (m$^2$/s)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.011</td>
<td>$1.621 \times 10^{-5}$</td>
<td>0.968</td>
</tr>
<tr>
<td>10</td>
<td>0.019</td>
<td>$2.804 \times 10^{-5}$</td>
<td>0.977</td>
</tr>
<tr>
<td>20</td>
<td>0.014</td>
<td>$2.059 \times 10^{-5}$</td>
<td>0.995</td>
</tr>
</tbody>
</table>

Fig. 3.10. Plot of $B_t$ vs. time for MG adsorption
3.3.3. Column Studies

3.3.3.1. Effect of Adsorbent Dosage on Breakthrough Capacity

Fixed bed columns were prepared by placing 0.2, 0.3 and 0.5 g of TGW in separate columns. 10 mg/l dye solution was allowed to pass through each column at the flow rate of 1 ml/min. The breakthrough curves at varying dosage are shown in Fig. 3.12 and the maximum breakthrough capacity and exhaustive capacity for 0.2, 0.3, 0.5 g of TGW were found to be 7.5, 11.9, 18.1 mg and 10.1, 15.9, 24.3 mg, respectively.

3.3.3.2. Desorption Studies

In order to make the process more economical and feasible, the adsorbent was regenerated. Exhausted columns were regenerated using 0.1 M and 1 M CH₃COOH as eluent at the flow rate of 1 ml/min. Results show that desorption increase from 40 to 60 % as the concentration of CH₃COOH increased from 0.1 to 1 M. Incomplete desorption of MG at different concentration of CH₃COOH confirmed that the chemisorption was the major mode of adsorption.
3.3.4. Adsorption Mechanism

Adsorption of MG may take place either by chemisorption or physisorption or both. There are many factors which influence the adsorption behavior such as structure of dye and adsorbent surface properties. MG is a cationic dye having two amino groups and one hydroxyl group. There are many forces which control the adsorption such as van der Waals, hydrogen bonding, steric effect etc. The formation of hydrogen bond between MG molecule and TGW surface is less because of the presence of only one oxygen atom. On the basis of above facts, it can be inferred that physisorption was not major mode of adsorption. The effect of pH shows that the optimum adsorption of MG is observed at pH 9. As the negative charge density increases on the surface of TGW, the interaction between positive charge MG and negative charge TGW also increases which conform chemisorption. Furthermore, chemisorption was also confirmed by incomplete desorption of MG by CH₃COOH under the reported experimental conditions.
34. Conclusion

The present study shows that TGW is an effective adsorbent for the removal of MG from aqueous solution. The adsorption of MG was endothermic and spontaneous in nature. The value of $\Delta H^0$ and $\Delta S^0$ are 47.49 kJ/mol and 0.167 kJ/molK, respectively. The results indicated that both Freundlich and Langmuir models can be used to fit the experimental data and to estimate the model parameters. The kinetics of adsorption followed pseudo-second order model and the adsorption was controlled by film diffusion.
Adsorption Studies of Hazardous Malachite Green

References


