Removal of Methylene blue from aqueous solution by *Achyranthes aspera* leaf powder (AALP)

4.1 Introduction

In recent decades, research interest was focused on easily available, abundant and low cost agriculture by-products, as an alternative adsorbent for the removal of dye from aqueous solution. Agriculture by-products are high volume and complex materials contain high levels of cellulose (60 %), hemicellulose (15-17 %) and lignin (7-9 %) as major constituents [1]. Agricultural wastes have many surface functional groups such as carboxylic, phenolic, and aldehyde which makes it possible for the adsorption of dyes. Recently, numerous agricultural materials such as rice husk [2], Indian rosewood saw dust [3], peat [4], oil palm trunk fiber [5], grape fruit peel [6], pomelo (*Citrus grandis*) peel [7], coffee bean [8], coconuthusk [9], coir pith [10], wheat straw [11], pine cone powder [12], cotton stalk [13] have been successfully employed for the adsorption process. *Achyranthes aspera* is an discarded agriculture waste weed belonging to the family of Amaranthaceae and has received considerable attention as an economical adsorbent for removal of cationic dye from aqueous solution due to its abundance in nature, availability and low cost.

In the present study, the adsorption potential of *Achyranthes aspera* leaf powder (AALP) was investigated for removal of MB from aqueous solution. The effect of various parameters such as adsorbent dose, pH, contact time, and initial concentration on removal performance of AALP was also investigated.
4.2 Materials and methods

4.2.1 Preparation of adsorbate solution

Methylene blue dye was used as an adsorbate. A stock solution (1000 mg/L) of MB was prepared by dissolving an appropriate amount of dye in double distilled water.

4.2.2 Preparation of adsorbent

*Achyranthes aspera* leaves were collected from the University campus. They were first washed thoroughly with double distilled water to remove color components, dust, dirt and other impurities. The leaves were firstly dried at room temperature and then in hot air oven at 70-80°C. The dried leaves were ground to a fine powder and sieved to obtain a 0.25 mesh size and stored in an airtight container for further use.

4.2.3 Batch equilibrium studies

The adsorption experiments were carried out in a batch process using stock solution of MB. Stock solution of MB was diluted to desired concentration (15-45 mg/L). All experiments were performed by adding a 0.2 g/L of AALP to a 50 mL of dye solution taken in a 250 mL conical flask. The pH was adjusted using 0.1M HCl and 0.1M NaOH solution with the help of Digital pHmeter. Conical flasks containing solution were shaken with the help of orbital shaker for desired time at constant temperature and after that solutions was centrifuged and then final concentration of dye in supernatant solution was determined at $\lambda_{max}=665$ nm using double beam UV-visible spectrophotometer. The optimum equilibrium concentration and contact time were determined and found to be 15 mg/L and 60 minutes respectively for further studies.

The percent removal of dye obtained on AALP was calculated by following equation:

$$\%\text{Removal} = \frac{C_0 - C_e}{C_0} \times 100$$

where, $C_0$ and $C_e$ are the initial and final concentration (mg/L) of dye respectively.

The amount of dye adsorbed on AALP at equilibrium (mg/g), was calculated by:
\[ q_e = \left( \frac{C_0 - C_e}{W} \right) V \]

where, \( q_e \) is the quantity of dye adsorbed on the adsorbent at time of equilibrium (mg/g), \( C_0 \) and \( C_e \) are the liquid-phase concentrations of dye at initial and equilibrium respectively, \( V \) is the (l) of solution and \( W \) is the mass of adsorbent (g).

4.3 Result and discussion

4.3.1 Characterization of the adsorbent

The textural properties such as BET surface area, pore volume, average pore diameter, physical properties and elemental composition of the AALP are shown in Table 4.1. The BET surface area was measured through adsorption-desorption N\(_2\) isotherm. The physical properties of the AALP were analyzed using proximate analysis. The prepared AALP material had a specific surface area and high pore volume. The elemental analysis demonstrated that the carbon is the major constituents (51.02 %), which indicated the carbonaceous nature of the adsorbent.

Table 4.1 Textural properties of AALP

<table>
<thead>
<tr>
<th>Typical properties</th>
<th>AALP</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET surface area (m(^2) g(^{-1}))</td>
<td>72</td>
</tr>
<tr>
<td>Total pore volume (cm(^3) g(^{-1}))</td>
<td>0.029</td>
</tr>
<tr>
<td>Average pore diameter (Å)</td>
<td>27.68</td>
</tr>
<tr>
<td><strong>Proximate analysis</strong></td>
<td></td>
</tr>
<tr>
<td>Moisture content</td>
<td>7.43</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>80.5</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>2.75</td>
</tr>
<tr>
<td>Ash</td>
<td>8.7</td>
</tr>
<tr>
<td><strong>Elemental analysis (wt%)</strong></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>51.02</td>
</tr>
<tr>
<td>H</td>
<td>2.65</td>
</tr>
<tr>
<td>N</td>
<td>3.17</td>
</tr>
</tbody>
</table>
The FTIR technique is an important tool for identifying functional groups in adsorbent, which are capable of adsorbing dyes. The FTIR spectra were shown in Fig. 4.1. The broad adsorption peaks around 3400 cm\(^{-1}\) indicates the presence of –OH groups, –NH groups. The peak at 2927 and 2854 cm\(^{-1}\) was assigned to C–H stretching of the methyl groups. The peak at 1623 cm\(^{-1}\), 1245 cm\(^{-1}\) [14], and 1156 cm\(^{-1}\) indicated the presence of C=C stretching vibration, phenolic groups, and C-O-C stretching, respectively. The peak at 1041 cm\(^{-1}\) shows the stretching vibration of C-O group that may be attributed the cellulose structure of the AALP. The peak around 800-897 cm\(^{-1}\) depicted the C–H bending vibration. The peak at 777 cm\(^{-1}\) indicated C-Cl groups. After sorption of MB, the peaks are slightly shifted from their original positions and their intensity also changed. Thus the functional groups such as carboxylic, and phenolic etc. present on the surface in the deprotonated form, attract positively charged of MB dye.

![Fig. 4.1 FTIR spectra of (a) AALP and (b) MB loaded AALP](image)

SEM study was performed to interpret the surface morphology of the adsorbent. Fig. 4.2 (a) shows the SEM micrograph of AALP. It has been clear from the Figure, that the
surface of AALP is rough and highly corrugated. AALP is a heterogeneous material consisting of particles of irregular shapes having considerable layers with varying pore size which provide adsorption sites for the binding of dye.

![SEM Image of (a) AALP and (b) MB loaded AALP](image)

**Fig. 4.2 SEM Image of (a) AALP and (b) MB loaded AALP**

The XRD pattern of *Achyranthes aspera* (AALP) is presented in Fig. 4.3. XRD patterns that contains diffraction peak at $2\theta = 17.7^\circ$, $22.2^\circ$, and $34.7^\circ$ are the characteristics of highly crystalline cellulose with corresponding reflection peaks of (101), (002) and (040). All these diffraction peaks appear to be broad and diffused which suggest the amorphous nature of the adsorbent.
4.3.2 Effect of adsorbent dose

Adsorbent dose is an important parameter to investigate the effect of adsorbent dose on the adsorption of dye. The experiment was carried out by taking adsorbent doses ranging from 0.05 to 0.25 g/L with initial concentration of MB dye as 15 mg/L, without changing the volume of dye solution (50mL) at constant temperature. It can be seen that the percentage removal of dye increased with increasing adsorbent dose from 0.05 to 0.25g/L (Fig. 4.4). This is so because, the greater availability of the exchangeable sites or surface area at higher concentration of the adsorbent [15].
4.3.3 Effect of pH

The pH is an important factor that affects the adsorption of dye on adsorbent. The effect of pH on adsorption of MB was studied by varying pH from 2 to 12 which is shown in Fig. 4.5a. The percentage removal of dye increases with increasing pH. At lower pH adsorption of dye is low which is due to the H⁺ ions competing with cation groups on the MB for adsorption sites. At higher pH, the adsorption of dye is higher because surface charge density decreases with an increasing pH, electrostatic repulsion between the positively charged MB and the surface of AALP is lowered. From above results, higher percentage removal was occurred at pH 10. The uncertainty in the pH value was ±0.01.

The pHzc of any adsorbent determines the pH at which the adsorbent surface has net electrical neutrality [16]. A series of solutions were prepared in which the concentration of KNO₃ was fixed at 0.1M and the pH of these solution were varied from 2 to 12 by adding 0.1M NaOH or 0.1M HCl, after the adjustment of pH 0.2 g/L adsorbent was added to 50 mL of 0.1M KNO₃ solution in 250ml of conical flask and agitated with the
help of orbital shaker for 2 hours. Fig. 4.5b depicted the pH_{ZPC} of the adsorbent. A graph was plotted between the initial and final pH (pH_{i} - pH_{f}) against the pH_{i}. If the pH is greater than pH_{ZPC}, the adsorbent surface negatively charged and favors uptake of basic dye to increased electrostatic force of attraction. If the pH is smaller than pH_{ZPC}, the surface becomes positively charged, cations were repelled and equilibrium uptake of dye was low. The pH_{ZPC} value of AALP was found to be 7.8. Thus MB adsorption of AALP is favored at higher pH than pH_{ZPC}. The plausible mechanism of the adsorption of MB on the basis of functional groups on the surface of the adsorbent as well as optimized pH was represented by following steps:

\[
\text{AALP} - \text{OH} \xrightarrow{\text{pH} > \text{pH}_{ZPC} (7.8)} \text{deprotonation} \quad \text{AALP} - \text{OH} \\
\text{Dye} - \text{MBCl} + \text{H}_{2}\text{O} \xrightarrow{\text{dissociation}} \text{Dye} - \text{MB}^{+} + \text{Cl}^{-} \\
\text{AALP} - \text{OH}^{-} + \text{Dye} - \text{MB}^{+} \xrightarrow{\text{electrostatic interaction}} \text{AALP} - \text{OH}^{-} \text{MB}^{+} - \text{Dye}
\]

Fig 4.5 Effect of pH on adsorption of MB on AALP (a), pH_{ZPC} of the AALP (b)

4.3.4 Effect of contact time and initial concentration
Fig. 4.6 shows the effect of contact time on the percentage removal of MB at 303 K and pH 8.0. The rate of adsorption of MB increases with time and attains constant time when the equilibrium was established. The rate of removal of MB is rapid at initial stage which due to the availability of large number of surface area of the adsorbent for the adsorption of MB. The adsorption rate gradually decreases with time until it reaches equilibrium. This decline is due to decrease in total adsorbent surface area and less available binding sites [17]. The optimum time was found to be 60 min., which was used for further experiments. The amount of dye adsorbed was not changed after optimum time.

In order to investigate the effect of initial concentration on adsorption behavior of MB by using three concentrations 15, 30, 45 mg/L agitated with appropriate amount of adsorbents at constant temperature (Fig. 4.6). We found that the adsorption of MB increases with increasing initial concentration but gradually decreases until the equilibrium is reached, whereas the percentage removal of MB decreases with increasing initial concentration. Initial concentration provides the driving force to overcome the resistance to the mass transfer of MB between liquid and solid phase. The increasing initial concentration of MB enhances the interaction between MB and AALP.

![Figure 4.6 Effect of contact time and initial concentration on adsorption](image_url)
4.3.5 Adsorption isotherms

Adsorption isotherms represent the useful data in order to investigate the mechanism of adsorption process and also describe how an adsorbate molecule interacts with an adsorbent surface. Langmuir, Freundlich isotherms model were tested with experimental data.

The linearized form of Langmuir model is represented as [18]:

\[
\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m}
\]  \quad (6)

where, \( q_e \) (mg/g) is the amount of the dye adsorbed per unit mass of adsorbent, \( C_e \) is the dye equilibrium concentration (mg/L) in solution at equilibrium, \( q_m \) is the monolayer adsorption capacity (mg/g) and \( b \) is the Langmuir constant related to the energy of adsorption. The values of \( q_m \) and \( b \) were calculated from the slopes \((1/q_m)\) and intercepts \((1/bq_m)\) of the linear plots of \( C_e/q_e \) vs. \( C_e \) (Fig. 4.7a) and are given in Table 4.2.

The essential characteristics of the Langmuir isotherm can be expressed by means of \( R_L \), a dimensionless constant, called separation factor or equilibrium parameters. \( R_L \) can be calculated from the following equation [19].

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

where, \( C_0 \) is the initial concentration of sorbate.

The linear form of the Freundlich isotherm can be expressed by the following equation [20]:

\[
\ln q_e = \ln K_F + \frac{1}{n} \ln C_e
\]  \quad (8)

The value of \( K_F \) and \( n \) were calculated from the intercepts \((\ln K_F)\) and slopes \((1/n)\) of linear plots of \( \ln q_e \) vs. \( \ln C_e \) (Fig. 4.7b). If value of \( n \) is greater than 1 then adsorption condition
is favorable. By comparing correlation coefficient values of Langmuir and Freundlich isotherms model it can be observed that Langmuir isotherms was better fit than Freundlich but the value of $K_F$ fit in the range of 1-10 which shows that the adsorption process is also favorable. From the above discussion it can be concluded that surface of AALP have both homogenous and heterogeneous active sites.

Fig. 4.7 Langmuir plot for the removal of MB on AALP (a), Freundlich plot for the removal of MB on AALP (b)

Table 4.2 Isotherm parameter for adsorption of MB on AALP

<table>
<thead>
<tr>
<th></th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_{max}$</td>
<td>37.03</td>
<td></td>
</tr>
<tr>
<td>$B$</td>
<td>0.149</td>
<td></td>
</tr>
<tr>
<td>$R_L$</td>
<td>0.118</td>
<td></td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.998</td>
<td></td>
</tr>
<tr>
<td>$K_F$</td>
<td>5.08</td>
<td></td>
</tr>
<tr>
<td>$n$</td>
<td>1.44</td>
<td></td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.991</td>
<td></td>
</tr>
</tbody>
</table>

4.3.6 Adsorption kinetics

In order to investigate the kinetics of sorbate on to adsorbent, the adsorption dynamic data were analyzed by using pseudo first order, pseudo second order kinetics models.

The linear form of the pseudo-first order model can be written as [21]:
\[
\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t
\]  

(9)

where, \(q_e\) and \(q_t\) are the amounts of the dye adsorbed at equilibrium and at time \(t\) (mg/g), respectively and \(k_1\) is rate constant of adsorption. The values of \(k_1\) and \(q_e\) were calculated from slopes and intercepts of linear plot of \(\ln(q_e - q_t)\) vs. \(t\). Figure was not shown because plot was not appropriate to describe the

The pseudo-second order kinetic model [22] can be written as:

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t
\]  

(10)

where, \(k_2\) is the rate constant of adsorption (g/mg min). The value of \(q_e\) and \(k_2\) can be determined experimentally from slope and intercepts of plot of \(t/q_t\) vs \(t\) (min.) and shown in Fig. 4.8. The values of \(q_e\) and \(k_2\) are reported in Table 4.4. From Table, we found that the pseudo-first order was not fit to describe the kinetic data because the correlation coefficients value \((R^2)\) were relatively low and the experimental values \(q_e\) did not agree with the calculated values. The correlation coefficients for pseudo-second order were relatively high, indicates the experimental values agreed with the calculated values. The pseudo-second order kinetic model is adequate to describe.
Fig. 4.8 pseudo-second order kinetics model for adsorption of MB on AALP

Table 4.3: Kinetics for adsorption of MB on AALP

<table>
<thead>
<tr>
<th>Initial concentration (mg/L)</th>
<th>$q_{e,exp}$ (mg $g^{-1}$)</th>
<th>Pseudo-first order</th>
<th>Pseudo-second order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_1$</td>
<td>$q_{e,cal}$</td>
<td>$R^2$</td>
</tr>
<tr>
<td>15 mg/l</td>
<td>6.73</td>
<td>0.018</td>
<td>1.17</td>
</tr>
<tr>
<td>30 mg/l</td>
<td>13.17</td>
<td>0.015</td>
<td>1.37</td>
</tr>
<tr>
<td>45 mg/l</td>
<td>18.85</td>
<td>0.058</td>
<td>10.71</td>
</tr>
</tbody>
</table>

4.3.7 Thermodynamics

Thermodynamic studies were performed in order to understand the effect of temperature on the adsorption of MB on AALP carried out by different temperature at 30, 40, 50°C,
and parameters such as Gibbs free energy $\Delta G^\circ$, enthalpy $\Delta H^\circ$ and entropy $\Delta S^\circ$ were calculated using the following equations [23]:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

(11)

$$\ln K = \frac{\Delta G^\circ}{RT} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R} \cdot \frac{1}{T}$$

(12)

$\Delta H^\circ$ and $\Delta S^\circ$ were calculated from the slope and intercept from the plot of $\ln K_d$ and $1/T$, respectively and were shown in Fig.4.9.

The negative value of $\Delta G^\circ$ indicates the feasibility and spontaneous nature of adsorption process. The negative value of $\Delta H^\circ$ indicates the exothermic nature of the process. The negative value of $\Delta S^\circ$ shows decrease in degree of freedom of the adsorbed species. From this figure it can be concluded that the rate of adsorption capacity decrease with increasing temperature. The value of $\Delta G^\circ$, $\Delta H^\circ$, $\Delta S^\circ$ was shown in Table 4.5.

![Graph showing the effect of temperature on the removal of MB (dye concentration=15 mg/L, pH=10)](image)

**Fig. 4.9** Effect of temperature on the removal of MB (dye concentration=15 mg/L, pH=10)
Table 4.4: Thermodynamic parameter of free energy (ΔG°), entropy (ΔS°), and enthalpy (ΔH°)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>ΔG° (KJ/mol)</th>
<th>ΔH° (KJ/mol)</th>
<th>ΔS° (J/molK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 °C</td>
<td>-5345.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40 °C</td>
<td>-5521.71</td>
<td>-6.65</td>
<td>-17.62</td>
</tr>
<tr>
<td>50 °C</td>
<td>-5697.91</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.3.8 Desorption and regeneration

In order to investigate, the adsorption process more economical and feasible, desorption efficiency and regeneration potential of AALP was studied [24]. Desorption study was performed using three different solvents such as HNO₃ (0.1 M), HCl (0.1M), and distilled water. It was found that the maximum desorption value for MB (92.15 %) using HCl (0.1 M), whereas desorption value using HNO₃ (0.1 M) and distilled water are 83.00 % and 71.87 %, respectively. To test the reusability of AALP adsorbents, adsorption-desorption cycles were repeated 5 times. Fig. 4.10 shows the adsorption capacities of AALP for MB over five successive adsorption-desorption cycles. The results showed that the adsorption capacity of AALP for MB slightly decreased with increase in adsorption-desorption cycle, at the end of the fifth cycle. The regeneration ability of AALP decreased the operation cost and indicated the industrial applicability. Thus, AALP was a good reusable adsorbent and could be successfully applied for the recovery of MB from aqueous solution.
Fig. 4.10 Adsorption-Desorption studies of MB on AALP

4.4 Conclusion:

- Adsorption of MB was successfully carried out using *Achyranthes aspera* leave powder.
- AALP reveals mesoporous nature with average pore diameter of 26.78 Å and surface area of 72 m² g⁻¹.
- SEM study describes the porous surface of the adsorbent which is responsible for the absorption of dye.
- FTIR confirms the adsorption of MB on AALP.
- XRD peaks indicate the crystalline and amorphous nature of the adsorbent.
- Solution pH plays important role in the MB adsorption. Maximum adsorption was found at higher pH 10. The pH_{ZPC} of the adsorbent was 7.8. Initial contact time and concentration also influence the adsorption process. The optimum contact time and concentration was 60 min. and 15 mg/L, respectively.
• Equilibrium isotherms study suggested that the MB adsorption data well described through Langmuir isotherms model with monolayer adsorption capacity for MB was calculated as 37.03 mg/g.
• Adsorption kinetics demonstrated that the adsorption data was best fit with pseudo-second order model.
• Thermodynamic investigations suggested that the adsorption process is feasible, spontaneous, and exothermic nature.
• Desorption was carried out by using different solvents such as HNO₃ (0.1 M), HCl (0.1M), and distilled water. Maximum desorption value was found with HCl (0.1M). The regeneration of the adsorbent was performed by consecutive 5 times adsorption-desorption cycles.
References


