After treatment with 1M hydrochloric acid, Indian rosewood sawdust (Dalbergia Sissoo), an inexpensive agricultural by-product showed excellent adsorption properties for synthetic dye, Methylene blue (MB). A systematic study of adsorption behavior of acid treated sawdust (ATS) was carried out in terms of various parameters such as contact time, adsorbent dose, initial dye concentration, initial pH of dye solution and particle size of adsorbent. Langmuir and Freundlich adsorption isotherm models were used to analyze the equilibrium data at different temperatures and the thermodynamic parameters such as $\Delta G^\circ$, $\Delta H^\circ$ and $\Delta S^\circ$ were evaluated by applying standard equations. ATS was further characterized by Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR) and XRD Analysis. The adsorption capacity of ATS was found to be 52.4 mg/g at initial pH 7 for the particle size in the range of 0-212µm. The adsorption of MB followed the pseudo-second order kinetics. The studies identified that ATS possess favorable adsorptive properties for its application in the treatment of effluents from the industries.

Keywords
Indian rosewood
Sawdust
Adsorption
Methylene blue
Langmuir Isotherm
Freundlich Isotherm

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efficient physicochemical water treatment methods as it is simple to operate, economical and does not require bulky instrumentation (Pengthamkeerati et al. 2008). It employs locally available inexpensive materials and involves simple pretreatment of material before applying as adsorbent. Initially, the removal of dyes by adsorption on activated carbon came into existence (Hameed et al. 2007; Tan et al. 2007) but the heavy cost of activated charcoal limit its application for commercial purposes. The agricultural by-products such as sugarcane bagasse (Abdullah and Salleh 2007), rice husk ash (Mane et al. 2007; Ong et al. 2007; Han et al. 2008), modified silk cotton hull waste (Thangamani et al. 2007), yellow passion fruit peel (Pavan et al. 2008), and maize cob (Sonawane and Shrivastava 2009) have been successfully applied for the dye removal from wastewater. The use of rattan sawdust (Hameed et al. 2007), treated pine sawdust (Özacar and Şengil 2005), beech sawdust (Batzius and Sidiras 2007), poplar sawdust (Pekkuz et al. 2008), wood sawdust (Qasimullah et al. 2011), meranti sawdust (Ahmad and Rafatullah 2009) and certain low cost adsorbents (Rafatullah et al. 2011) are reported in literature. The research papers reporting the use of Indian rosewood sawdust (Dalbergia Sissoo) as adsorbent are limited in number (Garg et al. 2003, 2004). The main aim of the present study was to investigate the enhanced adsorption properties of the Indian rosewood sawdust after treatment with 1M HCl for synthetic cationic dye, Methylene blue (MB). The experimental data was analyzed by applying Langmuir and Freundlich isotherm models at different temperatures to evaluate the isotherm constants. The thermodynamic parameters such as $\Delta G^\circ$, $\Delta H^\circ$ and $\Delta S^\circ$ were calculated by applying standard equations. The morphology of the adsorbent was examined by Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). XRD analysis was carried out to investigate the internal structure of adsorbent. Further, acid treated sawdust (ATS) was also investigated for its adsorption behavior for anionic dye, Congo red (CR). The comparative study showed that ATS exhibit superior capacity to remove cationic dye, MB in comparison to anionic dye, CR under similar experimental conditions.

2. Materials and Methods

2.1. Pretreatment of Sawdust

The Indian Rosewood sawdust (Dalbergia Sissoo) was collected from National Saw Mill, Amritsar. The crude sawdust was washed several times with deionized water to remove the surface adhered substances such as dirt, foreign particles and water soluble impurities. It was then dried in hot air oven at 120°C overnight. After drying, the sawdust was sieved to obtain two size fractions i.e. 212µm and 500µm using ASTM standard sieves.

2.2. Preparation of Acid treated sawdust

The reagent bottle (500ml) containing 10g pretreated sawdust in 100ml of 1M HCl solution was sealed and placed in an orbital shaker. The contents were stirred at 150 rpm for 4 hours at 30°C. The sawdust was then filtered and washed with double distilled water several times to remove excess of acid. The ATS was then dried at 120°C in hot air oven for 24 hours and preserved in a desiccator before applying as an adsorbent for the removal of synthetic dyes; Methylene blue and Congo red from aqueous solution.

2.3. Preparation of dye solution

Methylene blue and Congo red employed in the present study were procured from SD Fine Chemicals Ltd, India and used without any purification. The experimental dye solutions of desired concentration were freshly prepared at the time of use by dissolving an accurately weighed amount of dye in double distilled water. The physical and chemical characteristics of the dye are listed in (Table 1).

2.4. Batch mode adsorption studies

The batch adsorption studies were carried out by shaking appropriate amount of ATS with MB dye solution of known concentration in the reagent bottles. The bottles were sealed and covered with black polythene bags to prevent photochemical degradation of MB dye. Further, the reagent bottles were shaken at 150 rpm and 30°C in a temperature controlled shaker. The dye concentration was measured by subtracting the absorbance of ATS from that of the reagent solutions.

### Table 1: Physical Characteristics and molecular structure of Methylene Blue

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Properties</th>
<th>Dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Chemical formula</td>
<td>$\text{C}<em>{15}\text{H}</em>{11}\text{N}_3\text{Cl.3H}_2\text{O}$</td>
</tr>
<tr>
<td>2.</td>
<td>Chemical Structure</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>3.</td>
<td>Molecular weight</td>
<td>373.5g</td>
</tr>
<tr>
<td>4.</td>
<td>Wavelength $\lambda_{\text{max}}$</td>
<td>668 nm</td>
</tr>
<tr>
<td>5.</td>
<td>IUPAC Name</td>
<td>3,7-bis (dimethylamino)-phenothiazin-5-ium chloride</td>
</tr>
<tr>
<td>6.</td>
<td>Class</td>
<td>Thiazin</td>
</tr>
<tr>
<td>7.</td>
<td>Type</td>
<td>Basic dye</td>
</tr>
<tr>
<td>8.</td>
<td>Color</td>
<td>Blue</td>
</tr>
<tr>
<td>9.</td>
<td>Solution pH</td>
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</tr>
<tr>
<td>10.</td>
<td>Solubility</td>
<td>Soluble in water</td>
</tr>
</tbody>
</table>
controlled orbital shaker for pre-determined time intervals. After shaking the bottles for definite time intervals, ATS was separated from the solution by filtration. The final concentration of MB in the supernatant solution was calculated by recording the absorbance of the supernatant solution at $\lambda_{\text{max}}$ (668nm) by UV-vis Spectrophotometer (Shimadzu Model UV-160) using 1cm quartz cuvette.

The effect of pH of the initial solution of MB on the efficiency of ATS was examined over a pH range from 1 to 7. The pH of the solution was adjusted using 0.1 M HCl and 0.1M NaOH solutions. The adsorption experiments were conducted to analyze the effect of various parameters such as adsorbent dose, initial dye concentration, particle size and temperature. The percentage removal of MB by ATS was calculated using the equation:

\[
\text{Percentage removal of MB dye} = \left( \frac{C_i - C_e}{C_i} \right) \times 100
\]

where, $C_i$ and $C_e$ are the initial and equilibrium concentrations of dye (mg/L) in the solution. The adsorption capacity was calculated by using the mass balance equation for the adsorbent stated as

\[
q_e = \frac{(C_i - C_e)V}{W}
\]

where, $q_e$ (mg/g) is the adsorption capacity, $V$ (L) is the volume of dye solution and $W$ (g) is the mass of the adsorbent.

3. Results and Discussion

In preliminary studies, sawdust prior to the acid treatment was employed as adsorbent for the removal of MB and the results showed that high dose of 20g/L can remove only 48.3% of MB after 2 hours of contact time. In comparison to untreated sawdust, ATS showed superior response as it can remove 98.6% of the dye with an adsorbent dose of 4g/l. Hence, ATS was investigated for its adsorption behavior for synthetic dyes, MB and OR in aqueous solution.

3.1. Effect of contact time and adsorbent dose

The effect of contact time and adsorbent dose (1-20g/L) on adsorption of Methylene blue by ATS at 30°C was studied. The percentage sorption of MB increased with increase in contact time and reached equilibrium after 2 hours for different adsorbent doses. The initial rate of adsorption was greater in the first 30 minutes and later it slowed down gradually until it reaches equilibrium. It is because the large number of vacant sorption sites is available on the surface of adsorbent for the dye molecules during initial stage, and after the time lapses, the repulsive forces between sorbed dye molecules on the sorbent surface and dye molecules in the solution prevents further adsorption of dye molecules.

By increasing the adsorbent dose from 1g/L to 4g/L, the percentage dye removal increases from 85.6% to 98.6% and it remained constant upon further increase in adsorbent dose for an equilibrium time of 2 hours. Hence, 4g/L was fixed as optimum dose for further studies. The increase in percentage adsorption of dye with increasing adsorbent dose could be attributed to increase in surface area and availability of more adsorption sites.

3.2. Effect of initial dye concentration

The effect of initial dye concentration was studied for 50 to 500mg/L MB and it was observed that the dye sorption percentage on ATS sharply decreased from 98.64 to 38.0%. This is because for the constant number of adsorption sites, when initial concentration of dye increases, the ratio of sorption sites/ sorbate decreases so the vacant sites are not available for increased number of dye molecules.

3.3. Effect of initial pH of dye solution

The influence of pH was investigated at different pH values ranging from 2.0-7.0. The results indicated that the maximum percentage removal of MB occurs in the pH range of 4.0 to 7.0. The pH of 50mg/L MB solution is 7.0. Hence, MB solutions were used as such for further studies. The percentage adsorption is less at acidic pH because of the presence of excess of H+ ions in the solution competing with dye cations for the adsorption sites.

3.4. Effect of particle size of adsorbent

In present study, the effect of particle size was investigated using two different particle sizes i.e. 0-212µm and 0-500µm. The experiments were carried out for three different initial dye concentrations; 30mg/L, 50mg/L and 100mg/L with an adsorbent dose of 4g/L for an equilibrium time of 2 hours. The results showed that the percentage removal of MB decreased with increase in the particle size of adsorbent for a fixed concentration of dye solution. With the increase in particle size from 0-212µm to 0-500µm, the percentage sorption of MB showed a slight decrease from 99.1% to 98.5% in case of 30mg/L dye solution. Similar trends were observed for 50mg/L and 100mg/L dye solutions. This is because increase in the particle size would lead to decrease in surface area which in turn decreases the availability of adsorption sites at the surface and thereby decreasing the adsorption capacity.

3.5. Effect of temperature

The effect of temperature on MB adsorption by ATS was investigated at three different temperatures as 303, 313 and 323K. The reagent bottles containing adsorbent dose of 4g/L and initial dye concentration 50, 100, 150, 200 and 250 mg/L were agitated in a temperature controlled orbital shaker. After shaking for 2 hours, the acid treated sawdust was separated by simple filtration and the filtrate was analyzed for the remaining MB concentration by UV-vis spectrophotometer at $\lambda_{\text{max}}$ 668nm. The adsorption...
Adsorption of methylene blue on sawdust: Page 61

data so obtained was analyzed by using Langmuir and Freundlich isotherm models.

3.5.1. Langmuir Adsorption Isotherm
This model assumes that adsorption takes place at specific homogenous sites present on adsorbent which are equivalent to each other in terms of energy. Langmuir adsorption isotherm is represented by the following equation (Madhavakrishnan et al. 2009).

\[ \frac{C_e}{q_e} = \frac{1}{Q_m} \left( \frac{1}{b} \right) + \frac{1}{Q_m} \cdot C_e \]

where, \( C_e \) (mg/L) is the equilibrium concentration of dye solution, \( q_e \) (mg/g) is the amount of dye adsorbed per specified amount of adsorbent at equilibrium, \( Q_m \) (mg/g) is the Langmuir equilibrium constant and \( b \) (L/mg) is the amount of adsorbate required to form a monolayer. The plot of \( C_e/q_e \) vs \( C_e \) give a straight line with a slope \( (1/Q_m) \) and an intercept as \( (1/bQ_m) \) as shown in (Figure 1). The values of constants \( Q_m \) and \( b \) were calculated from the Langmuir plot.

Significance of \( R_L \):
The essential characteristic of Langmuir isotherm can be expressed in terms of dimensionless equilibrium parameter \( R_L \). It is defined as \( R_L = [1/(1+bC_0)] \) where \( C_0 \) is the initial dye concentration (mg/L) and \( b \) is the Langmuir constant (L/mg). The \( R_L \) value indicates the type of adsorption process involved. \( R_L \) represents favourable adsorption if its value lies between 0-1 while \( R_L > 1 \) represents unfavourable adsorption and \( R_L = 1 \) represents linear adsorption while the adsorption process is irreversible if \( R_L = 0 \). The values of Langmuir constants, \( R_L \) and related correlation coefficient are summarized in (Table 2).

It seems clear from (Figure 1) that the adsorption of MB on ATS followed Langmuir isotherm as the plot is linear which is consistent with the Langmuir straight line equation. Also, the high values of correlation coefficient obtained (\( R^2 = 0.994 \) to 0.998) shows pretty good agreement within the parameters and indicates the monolayer adsorption of MB onto ATS. Moreover, the value of \( R_L \) remained between 0 and 1 hence satisfying the condition for favourable adsorption.

3.5.2. Freundlich Adsorption Isotherm
This model assumes that surface of adsorbent is heterogenous, non-specific and non-uniform in nature. It specifically deals with multilayer adsorption of a substance onto adsorbent. Freundlich proposed the following adsorption model:

\[ \ln q_e = \ln K_f + \frac{1}{n} \ln C_e \]

where, \( K_f \) is the adsorption capacity of adsorbent \([\text{mg/g(L/mg)}]^n \), \( n \) is an empirical constant and rest of the terms have the usual significance. Thus, a plot of \( \ln C_e \) vs \( \ln q_e \) should give a straight line with a slope \( 1/n \) and an intercept as \( \ln K_f \) as shown in (Figure 2). The values of Freundlich constants so calculated listed in (Table 2).

Significance of \( 1/n \)
The slope \( 1/n \) ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero (Talman and Atun 2006). The linearity of plot \( \ln C_e \) vs \( \ln q_e \) as shown in (Figure 2) indicates that the experimental data also obeys Freundlich isotherm. The low values of \( 1/n \) lie in the range of 0.24 to 0.29, confirming that the surface of ATS is heterogeneous thereby causing multilayer adsorption of MB.

From the results summarized for Langmuir and Freundlich isotherms, Langmuir type adsorption isotherm is better obeyed by ATS as is evident from the good values of \( R^2 \). Further, it can be concluded that the surface of sawdust was originally heterogeneous which becomes more and more heterogeneous on treatment with acid. The heterogeneous surface of sawdust consists of adsorption sites which are similar w.r.t. adsorption and act as good adsorbent for the removal of MB.

3.5.3. Evaluation of thermodynamic parameters
The thermodynamic parameters such as \( \Delta G^\circ \), \( \Delta H^\circ \) and \( \Delta S^\circ \) for the adsorption process were evaluated using the Van’t Hoff equation and Gibbs-Helmholtz equation (Gong and Feng 2009) and

![Fig.1 Langmuir isotherm plots for MB adsorption at different temperatures by ATS.](image)

![Fig.2 Freundlich isotherm plots for MB adsorption at different temperatures by ATS.](image)
results are summarized in (Table 2). Van’t Hoff equation is represented as
\[ \ln \frac{q_e}{C_p} = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}. \]
The values of standard enthalpy change \( \Delta H^o \) and standard entropy change \( \Delta S^o \) were obtained from the slope and intercept of plot of \( \ln q_e/C_p \) versus 1/T, respectively. The values of standard Gibbs free energy change were evaluated from Gibbs Helmholtz equation which is represented as \( \Delta G^o = -RT \ln K \)
where \( R \) is the absolute temperature and \( K \) is the equilibrium constant (K= \( q_e/C_p \)). It is clear from the results that with the rise in temperature, the value of \( \Delta S^o \) becomes more negative which indicates that the adsorption process becomes more favorable and spontaneous with rise in temperature. The positive value of \( \Delta H^o \) signifies that the adsorption process is endothermic in nature and higher temperature will favor the adsorption process. The positive value of \( \Delta S^o \) also reflect the favorable nature of adsorption process. Hence, thermodynamic parameters showed that the ATS possess a great potential to adsorb MB from aqueous solution.

3.5.4. Kinetic Studies
The kinetics of adsorption is an important parameter to evaluate the efficiency of adsorbent being used in the process of adsorption. The kinetic studies are carried out by applying the standard equations such as pseudo first order (Lagergren, S. 1898), the pseudo second order (Ho and Mckay 1998), and Weber-Morris intraparticle diffusion model (Weber and Morris 1963). The rate constants of first order adsorption \( (K_1) \), the rate constants of second order adsorption \( (K_2) \) and intraparticle diffusion rate constant \( (K_p) \) are presented in (Table 3). The pseudo first order rate equation is given as:
\[ \ln (q_e - q_t) = \ln q_e - K_1 t. \]
where, \( q_e \) and \( q_t \) are the amount of dye adsorbed (mg/g) on ATS at equilibrium and at time \( t \), respectively. \( K_1 \) is the rate constant of pseudo first order adsorption (min\(^{-1}\)). The values of \( q_e \) and \( K_1 \) for first order equation were determined from the slope and intercept of the plot of \( \ln (q_e - q_t) \) versus \( t \). It was observed that the above equation does not fully describe the adsorption kinetics because the values of \( q_e \) obtained from the slope of the graph are too less than the experimental values obtained for different dye concentrations ranging from 5-25 mg/L.
Therefore, pseudo second order equation was applied on experimental data which is
\[ \frac{t}{q_t} = \frac{1}{K_2 q_e} + \frac{t}{q_e}, \]
where, \( q_e \) is the equilibrium adsorption capacity (mg/g) and \( K_2 \) is the pseudo second order rate constant (g/mg/min). The values of \( q_e \) and \( K_2 \) for second order equation were determined from the slope and intercept of the plot \( t/q_t \) versus \( t \). The linear plot as shown in (Figure 3) shows good agreement of experimental data for different initial dye concentrations 5-25 mg/L and the calculated values of \( q_e \) from graph lies close to experimental values which confirms that the experimental data follows pseudo second order model.

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>303</td>
</tr>
<tr>
<td>( Q_0 ) (mg/g)</td>
<td>43.3</td>
</tr>
<tr>
<td>( b ) (L/mg)</td>
<td>0.43</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.998</td>
</tr>
<tr>
<td>( R_L )</td>
<td>0.044</td>
</tr>
<tr>
<td>Freundlich</td>
<td></td>
</tr>
<tr>
<td>( K_f ) [mg/g(L/mg)(^{1/n})]</td>
<td>15.3</td>
</tr>
<tr>
<td>( 1/n )</td>
<td>0.23</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.974</td>
</tr>
</tbody>
</table>

Thermodynamic parameters
\[ \Delta G^o (kJmol^{-1}) = -24.22 \]
\[ \Delta H^o (kJmol^{-1}) = 15.47 \]
\[ \Delta S^o (kJmol^{-1}) = 0.131 \]

Further, Weber-Morris model was also applied to investigate the intraparticle diffusion mechanism. The equation used in this case is:
\[ q_t = K_{pt^{1/2}} + C \]
Where, \( K_p \) (mg/g min\(^{1/2}\)) is intraparticle diffusion rate constant. If intraparticle diffusion is rate limited, then plots of adsorbate uptake \( q_e \) versus the square root of time \( (t^{1/2}) \) would result in a linear relationship. If the plot of \( q_e \) versus \( t^{1/2} \) is linear and passes through the origin, then intraparticle diffusion is the sole rate determining step. However, in the present work, the linear plot between \( q_e \) and \( t^{1/2} \) as shown in (Figure 4) did not pass through the origin which indicates some degree of boundary layer control is present and also that the intraparticle diffusion is not the only rate controlling step. The value of constant \( C \) in the above equation gives an idea about the thickness of the boundary layer, i.e., the larger the intercept, the greater is the boundary layer effect (Kannan and Sundaram 2001).

![Fig.3 Pseudo second order kinetic plot for MB sorption by ATS.](image_url)
3.6. SEM studies

Scanning Electron Microscopy (SEM) is a widely known surface diagnostic tool which enables us to examine the structural network existing in the adsorbent. The SEM micrographs of raw sawdust, ATS and MB loaded ATS are recorded at JEOL JSM-6100 Scanning Electron Microscope and are presented in (Figure 5). The surface of raw sawdust (Figure 5a) consists of vacant adsorption sites which are smaller in size and are arranged in a longitudinal pattern. After treating the raw sawdust with 1M HCl acid for 4 hours, the sawdust becomes more porous showing vacant sorption sites containing oblong pores within the circular segments arranged symmetrically (Figure 5b). It can be seen that after adsorption of MB, the surface of sawdust changed to a greater extent due to the filling of all available adsorption sites but the sawdust still retained the heterogeneous surface (Figure 5c).

3.7. Fourier Transform Infrared Spectroscopy Analysis

The FTIR analysis of ATS before and after adsorption of methylene blue is carried out. In the spectra of ATS, the strong peaks at 3441 cm\(^{-1}\) and 2927 cm\(^{-1}\) represent the \(-\text{OH}\) stretching of phenol group of cellulose and lignin and \(\text{CH}_2\) stretching of aliphatic compound, respectively. The appearance of peaks at 1734 cm\(^{-1}\) and 1615 cm\(^{-1}\) indicates the presence of \(\text{C=O}\) stretching of aldehyde group and \(\text{C=C}\) stretching of phenol group, respectively. The position of the peaks of characteristic functional groups of ATS shifted to a smaller extent after the adsorption of MB. In comparison to ATS spectra, no new peak appeared in MB loaded ATS spectra which confirm that the process of adsorption is entirely a physical phenomenon.

### Table 3: Kinetic model parameters for MB adsorption by ATS

<table>
<thead>
<tr>
<th>Conc. (mg/L)</th>
<th>(q_e) (exp) (mg/g)</th>
<th>(q_e) (cal) (mg/g)</th>
<th>(K_1) (min(^{-1}))</th>
<th>(R^2)</th>
<th>(q_e) (cal) (mg/g)</th>
<th>(K_210^{-2}) (g/mg/min)</th>
<th>(R^2)</th>
<th>(K_p) (mg/g/min(^{1/2}))</th>
<th>(C)</th>
<th>(R^2)</th>
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</thead>
<tbody>
<tr>
<td>5</td>
<td>1.226-1.233</td>
<td>0.0462</td>
<td>-0.0649</td>
<td>0.999</td>
<td>1.235</td>
<td>5.128</td>
<td>0.999</td>
<td>0.00127</td>
<td>1.22</td>
<td>0.795</td>
</tr>
<tr>
<td>10</td>
<td>2.435-2.462</td>
<td>0.0608</td>
<td>-0.0270</td>
<td>0.999</td>
<td>2.472</td>
<td>2.079</td>
<td>0.999</td>
<td>0.00524</td>
<td>2.40</td>
<td>0.929</td>
</tr>
<tr>
<td>15</td>
<td>3.637-3.684</td>
<td>0.130</td>
<td>-0.0339</td>
<td>0.982</td>
<td>3.699</td>
<td>1.897</td>
<td>0.999</td>
<td>0.00838</td>
<td>3.59</td>
<td>0.941</td>
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<tr>
<td>20</td>
<td>4.850-4.910</td>
<td>0.120</td>
<td>-0.0231</td>
<td>0.977</td>
<td>4.928</td>
<td>1.795</td>
<td>0.999</td>
<td>0.01049</td>
<td>4.79</td>
<td>0.979</td>
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<tr>
<td>25</td>
<td>5.981-6.101</td>
<td>0.586</td>
<td>-0.0506</td>
<td>0.999</td>
<td>6.153</td>
<td>1.284</td>
<td>0.999</td>
<td>0.0238</td>
<td>5.87</td>
<td>0.843</td>
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</table>

### Table 4: Comparison of MB and CR adsorption by ATS

<table>
<thead>
<tr>
<th>Methylene blue</th>
<th>Congo Red</th>
</tr>
</thead>
<tbody>
<tr>
<td>%R in time intervals (min)</td>
<td>%R in time intervals (min)</td>
</tr>
<tr>
<td>30</td>
<td>60</td>
</tr>
<tr>
<td>4</td>
<td>97.6</td>
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<tr>
<td>10</td>
<td>98.0</td>
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<tr>
<td>20</td>
<td>98.3</td>
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<table>
<thead>
<tr>
<th>Initial dye concentration (mg/L)</th>
<th>Methylene blue</th>
<th>Congo Red</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>97.6</td>
<td>98.0</td>
</tr>
<tr>
<td>50</td>
<td>97.3</td>
<td>97.8</td>
</tr>
<tr>
<td>75</td>
<td>95.3</td>
<td>96.0</td>
</tr>
</tbody>
</table>

\*AdSORbent dose (g/L)

\*Initial dye concentration (mg/L)

Conditions: (a) 30mg/L initial dye concentration, (b) 4g/L adsorbent dose
3.8. XRD Analysis

The XRD pattern of the adsorbent showed typical spectrum of cellulose material having main and secondary peaks at 20 of 22.8° and 35.2° respectively. The main peak is taken as indicative of the presence of highly organized crystalline cellulose while the secondary peak is the measure of polysaccharide structure (Gong et al. 2005).

3.9. Desorption Studies

The regeneration of the adsorbent makes the treatment more economical. Attempts were made to regenerate the used ATS for another application by using CH₃COOH in the concentration range of 0.5-1N. The percentage desorption increased with increasing CH₃COOH concentration in the aqueous medium (Figure 6) and attained the maximum desorption at 10 N CH₃COOH solution. The effect of percentage desorption was inversely correlated to pH effect, indicating that ion exchange was probably the major mode of adsorption process. Similar results were reported for the adsorption of Crystal violet dye from aqueous solution using Ricinus Communis Pericarp carbon as an adsorbent (Madhavakrishnan et al. 2009).

4. Comparative study of Methylene blue and Congo red with 1M HCl treated sawdust

The ATS was also further investigated for its adsorption behaviour towards an anionic dye, Congo red (CR) and the results so obtained were compared with that of MB adsorption (Table 4). It seems clear that ATS possess an enhanced adsorption capacity for the cationic dye, MB in comparison to the anionic dye, CR. The data shows the adsorbent dose (4g/L) successfully adsorbed 98.6% MB whereas significantly less percentage of CR was adsorbed in an equilibrium time of 2 hours under similar conditions. Similar trends were observed on investigating the effect of initial dye concentration on adsorption of both the dyes. This can be attributed to deposition of Cl ions on the surface of crude sawdust which bind with MB more strongly than CR due to electrostatic interaction and ion exchange mechanism. Hence, it can be concluded that ATS possess better adsorption capacity for the cationic dye in comparison to the anionic dye.

Further, comparison was made of the adsorption behavior of ATS with that of the adsorbents previously reported in the literature (Table 5). It is clear from the data that the adsorption capacity of ATS for methylene blue is superior or comparable to many reports.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>q_max (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid treated sawdust</td>
<td>52.40</td>
<td>Present work</td>
</tr>
<tr>
<td>Gypsum</td>
<td>36.00</td>
<td>(Rauf et al. 2009)</td>
</tr>
<tr>
<td>Mansonia wood sawdust</td>
<td>20.77</td>
<td>(Ofomaja and Ho, 2008)</td>
</tr>
<tr>
<td>Neem leaf powder</td>
<td>8.76</td>
<td>(Bhattacharya and Sharma, 2005)</td>
</tr>
<tr>
<td>Beech sawdust</td>
<td>30.50</td>
<td>(Batzias and Sidiras, 2007)</td>
</tr>
<tr>
<td>Poplar sawdust</td>
<td>135.30</td>
<td>(Pekkuz et al. 2008)</td>
</tr>
<tr>
<td>Rattan sawdust</td>
<td>294.12</td>
<td>(Hameed et al. 2007)</td>
</tr>
<tr>
<td>Almond shell AC</td>
<td>1.33</td>
<td>(Aygün et al. 2003)</td>
</tr>
<tr>
<td>Ground eggshell waste</td>
<td>69.72</td>
<td>(Tsai et al. 2008)</td>
</tr>
</tbody>
</table>

5. Application of ATS for the removal of dyes from wastewater sample

The simulated wastewater sample was prepared by mixing equal volumes of solutions of three dyes such as methylene blue, malachite green and crystal violet (concentration of each solution was 30 mg/L). The reagent bottle containing optimum dose and simulated wastewater sample was shaken at 303K for 2 hours and then the filtrate was analyzed for the remaining dye concentration at corresponding λ_max 585nm, 615nm and 668nm for CV, MG and MB respectively. After adsorption, the blue colored dye solution become colorless. ATS effectively caused the removal of dyes from the ternary dye mixture simultaneously with highest % sorption for MB as 99.16%, for MG as 89.44% and for CV as 80%. The application of ATS to decolorize the woolen mill effluent further confirmed that it could be used as a low-cost alternative in wastewater treatment for dye removal.
Conclusion
Acid treated Indian rosewood sawdust exhibited enhanced adsorption capacity for the cationic dye, Methylene blue. The experimental data is in good agreement with Langmuir and Freundlich isotherm models indicating the heterogeneous surface of acid treated sawdust consist of similar adsorption sites which are responsible for the favorable adsorption phenomenon. The adsorbent shows high Langmuir monolayer adsorption capacity of 52.4 mg/g in comparison to other reports in literature. SEM micrographs, FTIR analysis and XRD analysis support the promising adsorption behavior of ATS. Hence, it can be concluded that HCl treated sawdust proved to be good adsorbent for the cationic dye, Methylene blue and suitable for its application for the waste water treatment.

Acknowledgement
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References
Adsorption of methylene blue on sawdust:


Qasimullah, Q., Ahmad, A., Rafatullah, M., Sulaiman, O., & Hashim, R. (2011). Role of sawdust in adsorption of \( \text{Zn}^{2+} \) and \( \text{Cd}^{2+} \) from aqueous system. Journal of Industrial Research and Technology, 1(1), 06-11.


