Comparative studies of removal of hazardous dyes, methylene blue (MB) and malachite green (MG) from solutions by low cost activated carbon

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The removal of two hazardous dyes, MB and MG newly synthesized economic activated carbon. The adsorbent was synthesized from an agro waste material. The activated carbon has been characterized by XRD, FTIR, SEM, and surface area. A comparative study of the removal of selected dyes was reported. The process of removal for both the dyes is optimized for important parameters. It has been observed that removal of the dyes is maximum in alkaline range of pH. Both for MB and MG, the removal is controlled by first order kinetics. Mass transfer studies for both the dyes have been reported and the values of coefficient of mass transfer are found to be 2.25×10⁻⁵ cm/s and 1.92 cm/s respectively at 30°C. The rates of transfer of dyes onto the adsorbent surface were significant both the cases. The process of removal is endothermic and in both the cases higher temperature favoured the removal. Equilibrium data fitted Freundlich adsorption isotherm and the values of constants are found to be 0.59 and 3.01 mg/g for the removal of selected dyes. The results show suitability of the synthesized material for both the systems and can serve as baseline data for dyes removal.

Keywords: Activated carbon, Adsorption, Agro waste, Malachite green, Methylene blue

Many industries like textile, leather, paint and paper manufacture industries regularly use large amount of coloured effluents for their different processes during manufacture and generate large amounts of effluents containing high levels of dyes. These industries are of main concern as they contribute largely to pollution of ground and surface water contaminating them with variety of organics and non-degradable dye molecules. These dyes may cause several types of health problems, affecting not only human also aquatic lives1-3. When conditions are anaerobic, the azo dyes are decomposed and give rise to carcinogenic effects and warrant a proper decontamination of these dyes prior to their release anywhere3-5. Removal of the dyes from the effluents is mandatory to keep the environment safe. Because of large scale application, ~7×10⁵ ton of effluents are discharged by these industries, approximately 10% of the mixture of dyes’ effluent is discharged6. The traditional methods of dye removal from effluents may be divided as physical, chemical and biological treatment. Though all these methods are regularly employed for dyes removal from waste waters, the physical methods have been most popular because of their ease in handling7-9. Filtration, coagulation, chemical precipitation, ultrafiltration and electrochemical methods have been employed for decontamination of dyestuff effluents10-13. Adsorption has been the most common and efficient removal process for dyes and other pollutant species from effluents and adsorption on activated carbon has been most popular14,15. But because of high cost, application of activated carbon has limited application at large scale, especially in developing economies like India [mmm]. Because of high cost of activated, scientists explored series of materials as alternates of activated carbon12. Several minerals, and waste materials have been reported to be potential materials for treatment of dyes and metallic pollutants from effluents16.

Present work reports synthesis of activated carbon by rice husk and its subsequent application for the decolouration of selected dyes (MB and MG) containing effluents. The synthesized adsorbent was characterized for various physicochemical characteristics. Adsorption experiments were conducted in batches and the process of removal of both the dyes was optimized for better removal. Kinetics and
isotherm studies for sequestration of dyes were examined and reported.

Experimental Section

Materials

The analytical grade reagent reagents were used in the experiments without further purification. The reagents were purchased from Merck (India). The dye-stock solution was prepared using distilled water. Methylene blue and malachite green are represented by chemical formulae, C₁₈H₁₉N₅S·3H₂O, and C₅₂H₃₈N₃O₁₂, respectively with respective molecular weights of 373.91 and 927.00 g·mol⁻¹, and λ_max of 663 nm and 618 nm (measured value). Rice husk, the precursor for activated carbon, was obtained from a local rice mill located at Varanasi, India.

Synthesis and characterization of the adsorbent

Adsorbent used in present investigation has been synthesized by an agro-waste rice husk in optimized conditions. Details of the synthesis method has been reported elsewhere. The synthesized material was characterized by sophisticated equipment like X-ray diffractometer (XRD), Infrared spectroscopy (FTIR), etc. The synthesized adsorbent was also characterized for various other parameters also.

Batch adsorption experiments

Experiments for the uptake of MB and MG from solutions were performed in batch. The solid powders of MB and MG were dissolved in distilled water for stock solutions. Working solutions of the dyes were prepared by diluting stock solutions by distilled water to the stock solutions. 0.1M HCl/0.1M NaOH solutions were used to maintain pH of the working solutions. For running the batches, 50 mL solutions of the dyes were taken in 125 mL glass bottles (BOROSIL). The parameters like initial concentration, pH, agitation speed and adsorbent dose were fixed. The study was conducted at The removal experiments were conducted at 30, 40 and 50 °C (± 0.5). Adsorbent was added to the solutions and the solutions were agitated on a shaking machine. After equilibrium, a centrifuge (Remi 24, New Delhi, India) was used for separation of adsorbent from solutions. Rate of centrifugation was maintained at ten thousand for 10 min. The residual concentrations of the dyes in filtrates was examined by a spectrophotometer (UV 7000, Shimadzu, Japan) at 663 and 618 nm respectively. Following expression was used for calculating the mass of dyes (mg/g) by the adsorbent:

\[
\text{Amount adsorbed } (q_e) = \frac{C_o - C_e}{W} V
\]

% removal = \(\frac{C_o - C_e}{C_o} \times 100\)

Results and Discussion

Characterization of the adsorbent

XRD of the adsorbent was carried out to study crystal lattice. The diffractogram was recorded within the range 2θ = 10° to 90° with scanning rate 2° min⁻¹ and step function 0.02° presented. XRD diffraction profile of the synthesized catalyst has displayed in Fig. 1. In this diffractogram the strong and weak peak, positioned at 2θ = 23.4° and 43.3° correspond to the (201) and (304) planes respectively. These are in good agreement with characteristic peaks of the hexagonal lattice of carbon nanoparticle, supported by the ICPDS database (File no. 22-1069). In this X-ray diffractogram, the broad and noisy nature of such characteristic peaks implies the amorphous nature of the catalyst. The similar peak pattern has also been reported by Xie et al. (2014) and Xu et al. (2014).

FT-IR analysis

The FTIR analysis of as synthesized activated carbon and methylene blue adsorbed activated carbon

Fig. 1 — XRD synthesized activated carbon
is depicted in Fig. 2. The spectra illustrate that the vibration bands around 3700 and 3420 cm\(^{-1}\) presence of absorbed water and it was indicated by stretching OH vibrations in spectra. Presence of C=O was confirmed by peak appearing at 1650 cm\(^{-1}\). And non symmetric C=O vibrations are confirmed by bands (~around 1750 cm\(^{-1}\)). Furthermore, the strong absorption band at 1520 cm\(^{-1}\) is conforms to vibrations (stretching) of aromatic carbonaceous C=C band\(^{19}\). The observed vibrations are in accordance with the previously reported FTIR spectra of such an adsorbent material. Further, because of MB adsorption, absorption pattern and it shifted from 1800 –1000 cm\(^{-1}\) because of presence of C=N, C=S and C-N vibration bands, whereas the range 1800-4000 cm\(^{-1}\) remains unchanged. The vibration bands observed at 1130 cm\(^{-1}\), 1330 cm\(^{-1}\), 1378 cm\(^{-1}\) are attributes to the adsorption of the dye(MB) on adsorbent\(^{19}\). The material displayed a specific surface area of 180.50 m\(^{2}\)/g (Table 1). This surface area is significant, indicating the activated carbon to be a superior adsorbent.

**Effect of contact time and concentration**

The pollutants’ concentration (starting) have significant impact on its sequestration from the contaminated solutions. In present case also, this study was performed for removal of MB and MG by synthesised adsorbent. For the studies, the respective initial concentrations of MB and MG were taken as 16.04×10\(^{-2}\) and 6.47×10\(^{-2}\) mol/L. The results of the removal have been presented as Fig. 3 a, b. The figures display that the removal of both the dyes increased by increasing the contact time of the dyes with the adsorbent. The removal of MB increased from 77.25 to 93.20 and that for MG, the removal increased from 93.75 to 94.91%. Its also noteworthy that % removal of the dyes increased with decreasing the initial concentrations and this finding has industrial relevance as invariably, a lower concentration of the dyes is encountered in the effluents\(^{15,16}\).

**Adsorbent dose**

Adsorbent dose affected the removal of the selected dyes, MB and MG. The effect was

![Fig. 3 — Effect of initial concentration on removal of MB and MG species; Temperature, 303 K; dose, for MB 5 g·L\(^{-1}\); for MG 10 g·L\(^{-1}\)100 rpm. (a) MB removal onto rice husk activated carbon for 16.04×10\(^{-2}\) mol/L, (b) MG removal onto rice husk activated carbon for 6.47×10\(^{-2}\) mol/L.](image-url)

<table>
<thead>
<tr>
<th>Adsorbent dose</th>
<th>Effect of adsorbent dose on removal of the selected dyes, MB and MG. The effect was...</th>
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<td>Effect of dose on removal of the selected dyes, MB and MG. The effect was...</td>
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<td>Effect of dose on removal of the selected dyes, MB and MG. The effect was...</td>
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<td>7.5</td>
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<td>20</td>
<td>Effect of dose on removal of the selected dyes, MB and MG. The effect was...</td>
<td>25</td>
<td>Effect of dose on removal of the selected dyes, MB and MG. The effect was...</td>
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<tr>
<td>10</td>
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<td>50</td>
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<td>100</td>
<td>Effect of dose on removal of the selected dyes, MB and MG. The effect was...</td>
</tr>
</tbody>
</table>

**Table 1 — Characterization of rice husk activated carbon**

<table>
<thead>
<tr>
<th>Surface area (m(^{2})/g)</th>
<th>Moisture(%)</th>
<th>Ash content(%)</th>
<th>Volatile matter(%)</th>
<th>Fixed carbon(%)</th>
<th>pHzpc</th>
<th>Density(g/m(^{3}))</th>
<th>Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>180.5</td>
<td>7.3</td>
<td>39.2</td>
<td>78.9</td>
<td>13.2</td>
<td>6.27</td>
<td>2.14</td>
<td>0.51</td>
</tr>
</tbody>
</table>

![Fig. 2 — FTIR of the adsorbent material synthesized from rice husk.](image-url)
investigated by varying dose of adsorbent materials between 8-12 g/L for MB and that for MG, 3-7 g/L, respectively. The desired amounts of the activated carbon were mixed in simulated solutions. The initial concentration, temperature and pH were kept constant and the dose was varied for the different batches. The trend of concentration variation with time has been important (Fig. 4). Uptake of the dyes, MB and MG gradually increased from 86.75 to 99.85 for MB and 85.33 to 99.08% for MG by enhancing the doses from 8 to 12 g/L for MB and that for MG, 3 to 7 g/L, respectively. Thereafter, the removal did not increase substantially and it may be because of unavailability of substantial effective site on the adsorbent surface. The increased removal can be correlated to the enhanced number of free surface spaces for the dye molecules by increasing the adsorbent dose.

pH effect

Solution pH is a significant parameter controlling the dyes removal. Because of its importance, this parameter has been termed as ‘master variable’. A system can be controlled by controlling this parameter. In present studies, effect of this parameter on system was undertaken by changing values of pH in 2 to 8.0 range. Other parameters were kept constant. The influence of pH could be understood on the basis of acid-base characteristics of the adsorbent and the dyes solutions. In both the cases, removal of dyes was 'appreciable' in alkaline pH range and was maximum (100%) at pH 10.0, whereas, the removal was low, 83% at 2.0 pH for both the dyes (Fig. 5). The reason for less removal in acidic range seems to be repulsion of the dye molecules with the surface functional groups.

Effect of temperature

Adsorption has significant impact on adsorption of dyes from the solutions and it decides degree of decontamination of the dye stuff industry effluents. The experiments for the study of effect of temperature were conducted at 30, 40 and 50°C. The uptake of MB and MG increased almost up to 100% (99.16%) from 93.2% and that of MG 94.91 to 96.5% by increasing from 30 to 50°C (Fig. 6). All other reaction parameters were kept constant. The initial concentrations of the dyes were 16.04×10^{-2} and 6.47×10^{-2} mol/L for the dyes, methylene blue and malachite green. This is noteworthy that unlike most adsorption processes, these cases are typical examples of endothermic adsorption.

Adsorption kinetic studies

The kinetic system for the adsorption of the contaminants involving rate of the reaction, mass transfer, time and the adsorbate-adsorbent interaction were used for adsorption kinetic studies of the present systems. The experimental data were tested for first as
well as second order kinetics for the removal of MB and MG. On the basis of R^2 values for the systems, it was clear that the data followed first order kinetics. To understand the kinetics, the Lagergren’s expression was used to fit the kinetic model for MB and MG removal.

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

\( q (\text{mg/g}) \) is amount of dye adhered to the surface at time, \( t \), whereas the amount adhered at equilibrium is \( q_e \) (mg/g). \( K_{ad} \) (min^{-1}) represents the kinetic parameter, the rate constant for the process of removal of dyes. The single undeviated graphs of \( \log (q_e - q_t) \) vs \( t \) (Figure not shown) confirmed that the data obeyed first order kinetics. Further, the slopes of straight line plots of the model were used to determine the value of an adsorption constant (\( K_{ad} \)). \( K_{ad} \) for removal of MB was recorded to be \( 1.40 \times 10^{-2} \text{ min}^{-1} \) at \( 16.04 \times 10^{-2} \text{ mol/L} \) initial 30°C. On the other hand, for adsorption of MG, the values of \( K_{ad} \) were obtained as \( 4.22 \times 10^{-2} \text{ min}^{-1} \) at 30°C. The values of \( K_{ad} \) for both the systems revealed suitability of the prepared adsorbent for the present systems.

**Mass transfer study**

Transfer of mass is important for any process. It describes how much of the species are going to the other phase, in this case solution phase to the solid adsorbent phase in present case. The mass transfer study was conducted using following well known expression:

\[
\ln \left( \frac{C_i}{C_o} - \frac{1}{1 + mk} \right) = \ln \left( \frac{mk}{1 + mk} \right) - \left( \frac{1 + mk}{mk} \right) \beta_L S_t \alpha \ln \left( \frac{C_i}{C_o} - \frac{1}{1 + mk} \right)
\]

where \( \beta_L \) is a product of adsorption efficiency and energy of adsorption, the isotherm parameters. The term \( S_t \) is specific surface area, and \( \beta_L \) (cm/s) indicates mass transfer from bulk to the solid surface. It is termed as mass transfer coefficient. M is mass of the adsorbent volume. Values of these parameters were determined using following expressions:

\[
m = \frac{W}{V}
\]

\[
S_t = \frac{6m}{\delta_p (1 - \epsilon_p)}
\]

where \( \delta_p \) is particle diameter of the activated carbon, \( \epsilon_p \) is porosity of the adsorbent, and \( \delta_p \) (g/cm^3), density of adsorbent particles. Values of \( \beta_L \) at different temperatures were calculated by using slopes and intercepts of \( \ln \left( \frac{C_i}{C_o} - \frac{1}{1 + mk} \right) \) vs. \( t' \) (Fig. 7) and these...
values of $\beta_L$ have been given in Table 2. It is clear from this table that that values of $\beta_L$ were found to 2.25×10^5 cm/s and 1.92×10^5 cm/s at 30°C for uptake of MB and MG by adsorption on the surface of synthesized adsorbent. Further, the values of $\beta_L$ increased with increasing temperature. At 50°C, the calculated values of $\beta_L$ were 5.67×10^5 cm/s and 2.94 ×10^5 cm/s for both the systems. The enhancing values of transfer of dyes from bulk further clarify that the process of removal of the dyes is endothermic.

Equilibrium Study

It is important to clarify the adsorption behaviour of the adsorbent-adsorbate system. Interaction of the adsorbate with adsorbent is quite a complex process and it can be explored by testing the equilibrium data in various adsorption isotherms. There have been several isotherm models which are based on different criteria. In present case, the equilibrium data for the removal of MB and MG from effluents were fitted in Languir’s isotherm model and Freundlich’s isotherm model. The analysis supported suitability of the synthesized material for removal of MB and MG.

Freundlich adsorption isotherm

The Freundlich isotherm expression assumes that the surface of the adsorbent is heterogeneous and that the adsorbate molecules can adhere to the surface in non-uniform fashion. The Freundlich isotherm model is presented as follows:

\[
\log q_e = \log K_f + \frac{1}{n} \log C_e \quad \ldots (7)
\]

where, $q_e$ (mg/g) represents dyes adhered to the solid adsorbent surface when system is equilibrated, the amount of the adsorbed dyes at equilibrium, $C_e$ (mg/L), the dyes’ residual concentration in solutions at equilibrium. $K_f$ and $1/n$ represent isotherm constants. In the process of adsorption, the adsorption capacity and adsorption energy are represented by the constants.

The intercepts and slopes of Fig. 8 were used to determine the numerical values of Freundlich constants. Values of $K_f$ for both the systems were found to be 0.586 and 3.10 mg/g for the removal of MB and MG respectively at 30°C. The $n$ values for both the systems were found to be 0.272 and 1.86 L/g, respectively for the removal of MB and MG. Table 3 contains the values of the parameters.

The values of $K_f$ for both the dyes (MB and MG) at 303 K were determined as (0.586 and 3.01) mg/g. The values of $n$ for both the systems were (0.272 and 1.86) L/g respectively (Table 3). Values of the parameters suggest suitability of the adsorbents for both the systems, but the adsorbent was better for the removal of MG

Thermodynamic studies

Like most chemical reactions, adsorption of MB and MG was also temperature dependent. This dependence was further evaluated by looking into the variations of $\Delta G^o$, $\Delta H^o$ and $\Delta S^o$. Values of these parameters were calculated for both the systems and they fetched significant results. Their values were calculated at 30,40 and 50°C. Following expressions:

![Figure 8 — Freundlich plot for MB and MG removal by rice husk activated carbon. dye concentration of MB and MG 16.04×10^2 and 6.47×10^2 mol/L, respectively, dose of adsorbent 5 mg·L^1; 303 K temperature; Dose, for MB 5 g·L^1; for MG 10 g·L^1; 100 rpm](image)

<table>
<thead>
<tr>
<th>Dye Temperature(K)</th>
<th>Parameter $\beta_f$ (x10^5 cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB 303</td>
<td>2.25</td>
</tr>
<tr>
<td>313</td>
<td>2.50</td>
</tr>
<tr>
<td>323</td>
<td>5.67</td>
</tr>
<tr>
<td>MG 303</td>
<td>1.92</td>
</tr>
<tr>
<td>313</td>
<td>2.34</td>
</tr>
<tr>
<td>323</td>
<td>2.94</td>
</tr>
</tbody>
</table>

Table 2 — Values of $\beta_f$ for sequestration of MB and MG by adsorption on synthesized adsorbent

<table>
<thead>
<tr>
<th>Dye Temperature(K)</th>
<th>Parameter</th>
<th>$K_f$ (mg/g)</th>
<th>$1/n$ (L/g)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB 303</td>
<td>0.59</td>
<td>0.272</td>
<td>0.9808</td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>0.61</td>
<td>0.292</td>
<td>0.9911</td>
<td></td>
</tr>
<tr>
<td>323</td>
<td>0.66</td>
<td>0.516</td>
<td>0.9891</td>
<td></td>
</tr>
<tr>
<td>MG 303</td>
<td>3.01</td>
<td>1.86</td>
<td>0.9946</td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>3.74</td>
<td>2.11</td>
<td>0.9944</td>
<td></td>
</tr>
<tr>
<td>323</td>
<td>3.99</td>
<td>3.14</td>
<td>0.9955</td>
<td></td>
</tr>
</tbody>
</table>

Table 3 — Comparison of Freundlich constants for the adsorptive removal of MB and MG at different temperature
The studies presented results that show it was a suitable material for sequestration of selected dyes from solutions.

The removal increased from (77.25 to 93.20) % for MB and (93.75 to 94.91) % for MG by decreasing concentration and these data is of industrial application.

pH studies revealed that both MB and MG favours alkaline range.

Adsorption of selected dyes (MB and MG) shows the process of removal is endothermic.

The results of present research investigation confirm the usefulness of the synthesized activated carbon was a low cost and thus economically viable for removal both the selected dyes, methylene blue and malachite green. The result displayed that the activated carbon could be used for large scale treatment of dye rich wastewaters and the material could be used for the removal of other dyes and contaminants.

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References