Application of Various Activated Carbons in the Adsorptive Removal of Methylene Blue from Aqueous Solution

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ABSTRACT
Adsorption of methylene blue had been done by using various activated carbons. The char derived from Acacia auriculiformis scrap wood was activated by using hydrochloric, phosphoric, sulphuric and nitric acid. The adsorption capacity of the prepared carbon was further compared with the adsorption capacity of the carbon prepared by microwave activation and it was found that the activated carbon developed by phosphoric acid activation had the highest adsorption capacity towards methylene blue. The characterization of the adsorbent was done through surface area analyzer and scanning electron microscopy. A typical honeycomb pattern with pores of varying size were observed on the surface of the scrap wood char whereas, the size of the existing micropores were increased when they were activated in presence of nitric acid. Besides, the roughness of the existing pore walls increased upto a certain extent when it was activated by using a domestic micro oven. The batch adsorption study of methylene blue was carried out by varying initial dye concentrations, agitation speed, adsorbent particle size and temperatures. The adsorption process was found to be exothermic in nature. The maximum removal of methylene blue was achieved at an agitation speed of 2000 rpm and a particle size of -100+250 mesh. The monolayer adsorption capacity of the phosphoric acid activated carbon was found to be 250 mg g⁻¹. The adsorption capacity of the prepared adsorbent was compared different commercially available adsorbents and the present adsorbent was found to have maximum removal efficiency for the basic dye methylene blue.

Key words: Methylene blue, adsorption, acid activation, equilibrium study

INTRODUCTION
Indiscriminate discharge of colored substances into various waste streams cause serious environmental concern. Dyes are mostly designed to resist the severities of environmental attack like microbial attack, light and pH (Fagga and Taeger, 1994; Rajeswari et al., 2011; Wanchanhtuek and Thapol, 2011). They have high solubility and partition coefficient indicating their potential for bio accumulation (Anliker et al., 1981; Wanchanhtuek and Nunrung, 2011; Rajendran et al., 2011). They also increase the COD of the water bodies. Dyes may also be problematic if broken down an aerobically in the sediment, leading to the production of toxic amines. Lethal levels may be reached affecting aquatic systems and associated flora and fauna. The above mentioned reasons necessities the treatment of dye containing waste water. Many treatments have been investigated so far regarding their effectiveness in removing the dyes from
dye-containing effluent such as, coagulation and flocculation (Amin, 2008), oxidation (Malik and Saha, 2003), membrane separation (Ciardelli et al., 2001) and adsorption (Wu and Tseng, 2008) but adsorption is worth mentioning amongst all. Wide verities of adsorbents are used commercially such as, activated carbon (El-Qada et al., 2006), pineapple leaf powder (Weng et al., 2009), rosewood sawdust (Garg et al., 2004) and montmorillonite clay (Almeida et al., 2009). But, Activated carbon is proved as the most efficient adsorbent because of its large surface area and highly porous structure (Karacan, et al., 2007) although it has high cost limits its’ widespread use. Therefore, development of activated carbon from comparatively low cost raw materials has become a growing field of interest. Generally, the activated carbon is manufactured from coal and coconut-shell. Besides, activated carbon is also manufactured from agricultural wastes such as rice husk (Bishnoi et al., 2004) and sugarcane bagasse (Mohan and Singh, 2002). But in comparison to all these materials, activated carbon prepared by carbonization of different scrap wood offers large surface area and total pore volume (Tancredi et al., 2004). In the present investigation, the char developed from Acacia auriculiformis scrap wood was used to remove a basic dye methylene blue from its aqueous solution. The removal capacity of the prepared adsorbent was compared with differently treated activated carbons. The effects of various parameters on the dye adsorption were studied through batch adsorption study.

MATERIALS AND METHODS
Raw materials: The scrap wood of Acacia auriculiformis selected for this work, was collected from local saw mill. Methylene Blue (MB), hydrochloric, phosphoric, sulphuric and nitric acid, zinc chloride, sodium hydroxide and ammonia were procured from Merck Specialities Private Limited, Mumbai, India.

Adsorbate: Methylene Blue (MB) has the following structure (Fig. 1) and its reported projected area is 130 Å² and it can be considered as a rectangular volume of 17 Å x 7.6 Å x 3.25 Å (Brindley and Hang, 1973).

Preparation of char: The char was prepared by carbonization of Acacia Auriculiformis scrap wood in an inert atmosphere. The wood scrap was first cut into small pieces of 2 mm width and 40 mm of length, cleaned with distilled water and was sun dried for 24 h prior to the carbonization.

The wood pieces were kept on a ceramic boat which was placed at the center of a 40 mm tubular furnace. The material was then heated from ambient temperature to the carbonization temperature at the rate of 4°C min⁻¹ in a continuous flow of N₂ and then it was kept at this temperature for 1h for subsequent activation. It was then allowed to cool to ambient temperature in presence of N₂ flow. The product was sieved to obtain the desired size fractions and stored in a desiccator over silica gel.

Preparation of activated carbon by acid treatment of C750N: The acid treated activated carbon was prepared by impregnating 5 g of ground C750N with 2 N of different acid solutions and

![Fig. 1: Structure of MB molecule](image-url)
kept the mixture for about 12 h at room temperature. The impregnation ratio (w/w) of acid to C750N ratio was adjusted to 1:1. The wet solid was then placed in an air oven at 105°C for 2 h. The resulting char was washed with distilled water followed by washing with dilute ammoniacal solution unto remove the excess acid. Finally, the sample was dried and stored in a desiccator over silica gel. The activated carbon prepared by chemical activation using hydrochloric, sulphuric and nitric acid was denoted as AC750NHCl, AC750NH2SO4 and AC750NHNO3, respectively.

Characterization of char: The surface area and the total pore volume of the prepared char and activated carbons were determined by using N2 adsorption-desorption method by using Brunauer Emmett Teller (BET) apparatus (Autosorb-1, Quantachrome). The surface morphology of the adsorbents was investigated by using Scanning Electron Microscope (SEM) (Hitachi, model SU-70).

The zero surface charge characteristics of the char was determined by adding 0.1 g of adsorbent in a series of volumetric flasks containing 100 mL 0.01 M NaCl solutions of different pH (Nethaji et al., 2010). The pH values of the NaCl solutions were adjusted between 2 and 10 by adding either 0.1 M HCl or dilute ammoniacal solution. The suspension were placed in a shaker incubator and shaken for 40 h. The final pH (pHf) was measured and it was plotted against the difference between the initial pH (pH0) and final pH (pHf).

Batch adsorption study: The effect of contact time and initial concentration on the amount of dye adsorbed were investigated at an initial dye concentration of 50-100 mg L⁻¹ and at different temperatures (298, 313 and 323K) whereas, the contact time was varied from 10-140 min. The particle size was varied from -36+44 mesh size to -100+150 mesh sizes. Besides, the stirrer speed was also varied from 500-2000 rpm to study the mass transfer effect. The monolayer adsorption capacity of the prepared adsorbents for MB was determined by the equilibrium study. The equilibrium study was carried out by adding 0.1 g of adsorbent into a series of 250 mL conical flask containing 100 mL solution of MB and was shaken for 36 h at room temperature. After this the samples were centrifuged and the concentrations were analyzed in a UV-Vis spectrophotometer. The kinetic study was carried out by analyzing adsorptive uptake of the dye from aqueous solution at different time intervals. The adsorptive capacity of different adsorbents was compared through batch adsorption. The equilibrium adsorption capacity was calculated from the relationship:

\[ q_e = \frac{(C_0 - C_e) \times V}{W} \]  

where, \( q_e \) (mg g⁻¹) is the equilibrium adsorption capacity, \( C_0 \) is the dye concentration at equilibrium (mg L⁻¹), \( V \) is the volume of solution (l) and \( W \) is the weight of adsorbent (g).

RESULTS AND DISCUSSION

Comparison of surface properties of activated carbons: The BET surface area (\( S_{BET} \)), total pore volume (\( V_{t,p} \)) and average pore size of C750N, AC750NHCl and AC750NH2SO4 were determined from the physical adsorption data of N2 at 77 K and the corresponding values are shown in Table 1. It can be seen from Table 1 that the activated carbon prepared by hydrochloric (HCl) and sulphuric acid (H2SO4) activation had lower surface area and total pore volume. The activated carbon prepared by HCl activation (AC750NHCl) had a surface area and total pore volume of 488.0 m² g⁻¹ and 0.37 \( \times \) g⁻¹, respectively whereas, the carbon developed by H2SO4...
activation (AC750NH₄SO₄) was found to have a surface area and total pore volume of 541 m² g⁻¹ and 0.40 cc g⁻¹, respectively. In case of H₂SO₄ activation, the decrease in surface area may be caused due to the strong oxidative nature of H₂SO₄ which ruptures the walls of existing micropores and breakdown the lignin from inside of the adsorbent (Mui et al., 2010). The char activated by HCl had the lowest surface in comparison to other carbons. This phenomenon may be partially attributed to the fact that after treatment with HCl some chlorine remained chemi-sorbed on the surface of the AC750NHC1 resulting in decreased surface area and narrower micropores (Nadeem et al., 2006). Besides, the activated carbons prepared by nitric and phosphoric acid activation was found to have comparatively higher surface area and total pore volume.

Because of weak oxidizing properties of these acids the wall of the existing micropores on the activated carbon surface does not rupture to a large extent which results into comparatively higher surface area. The activated carbons prepared by nitric and phosphoric acid activation were designated as AC750NHNHO₃ and AC750NH₄PO₄. The comparison of methylene blue adsorption capacity is presented in Table 2.

**Surface morphology of activated carbons:** The surface morphology of activated carbons was investigated through Scanning Electron Microscope (SEM) analysis. The SEM images of various activated carbons are shown in Fig. 2a-d. It can be observed from Fig. 2a that a typical honeycomb structure with pores of different size was formed on the surface of char (C750N) when it was treated at optimum condition. The similar surface morphology could also be observed when

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Surface area (m² g⁻¹)</th>
<th>Total pore volume (cc g⁻¹)</th>
<th>Average pore diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C750N</td>
<td>514.2</td>
<td>0.36</td>
<td>27.99</td>
</tr>
<tr>
<td>AC750NHC1</td>
<td>488.0</td>
<td>0.37</td>
<td>30.18</td>
</tr>
<tr>
<td>AC750NH₄SO₄</td>
<td>541.0</td>
<td>0.40</td>
<td>29.70</td>
</tr>
<tr>
<td>AC750NHNHO₃</td>
<td>504.3</td>
<td>0.39</td>
<td>30.82</td>
</tr>
<tr>
<td>AC750NH₄PO₄</td>
<td>582.3</td>
<td>0.46</td>
<td>31.52</td>
</tr>
</tbody>
</table>

**Table 2: Comparison of methylene blue adsorption capacity**

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Methylene blue adsorption capacity (mg g⁻¹)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bamboo dust activated carbon</td>
<td>143.20</td>
<td>Kannan and Sundaram (2001)</td>
</tr>
<tr>
<td>Coconut shell activated carbon</td>
<td>277.90</td>
<td>Kannan and Sundaram (2001)</td>
</tr>
<tr>
<td>Groundnut shell activated carbon</td>
<td>164.90</td>
<td>Kannan and Sundaram (2001)</td>
</tr>
<tr>
<td>Jute fiber carbon</td>
<td>225.64</td>
<td>Tsai et al. (2001)</td>
</tr>
<tr>
<td>Almond shell-activated carbon</td>
<td>1.33</td>
<td>Aygun et al. (2003)</td>
</tr>
<tr>
<td>Walnut shell-activated carbon</td>
<td>3.53</td>
<td>Aygun et al. (2003)</td>
</tr>
<tr>
<td>F300 (calgon carbon Co.)</td>
<td>240</td>
<td>Stavropoulos and Zabaniotou (2006)</td>
</tr>
<tr>
<td>Activated carbon (sewage sludge-H₂SO₄ impregnated)</td>
<td>194.3</td>
<td>Rozada et al. (2003)</td>
</tr>
<tr>
<td>Tree leaves</td>
<td>133.33</td>
<td>Singh and Srivastava (1999)</td>
</tr>
<tr>
<td>NaOH-treated pure clay</td>
<td>122.0</td>
<td>Ghosh and Bhattacharyya (2001)</td>
</tr>
<tr>
<td>Carbon slurry waste</td>
<td>96.2</td>
<td>Jain et al. (2003)</td>
</tr>
<tr>
<td>Pure clay</td>
<td>91.87</td>
<td>Ghosh and Bhattacharyya (2001)</td>
</tr>
<tr>
<td>Activated carbon from waste rubber P-700</td>
<td>49.0</td>
<td>Miguel et al. (2002)</td>
</tr>
<tr>
<td>Saw dust</td>
<td>32.26</td>
<td>De and Basu (1998)</td>
</tr>
<tr>
<td>AC750NH₄PO₄</td>
<td>250</td>
<td>This work</td>
</tr>
</tbody>
</table>

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activated carbon was prepared from corncobs by chemical activation (Tseng, 2006). On the other hand, it was observed that acid treatment of char significantly alters the physico-chemical properties and porosity of the adsorbent. The SEM image of C750N treated by using HCl solution is shown in Fig. 2b. After treating with HCl some of the residue chlorine remains on the adsorbent surface which gives rise to narrower pore distribution and lower surface area (Cruz et al., 1997). The SEM image of char treated with H2SO4 solution is shown in Fig. 2c. As the char was treated with H2SO4 solution the protons are contributed onto the adsorbent surface upon ionization in aqueous solution which in turn produces a uniform pore size distribution (Shafeeyan et al., 2009). The surface morphology of activated carbon treated in presence of HNO3 is shown in Fig. 2d. It was observed that comparatively larger size pores were formed on the carbon surface which is not always favorable in case of adsorption of smaller dye molecules.

**Selection of adsorbent:** The adsorption capacity of different acid activated carbons was investigated for a basic dye methylene blue and it was found that AC750NH4PO4 had better adsorption capacity in comparison to other adsorbents (Fig. 3). The phenomenon may be attributed to the fact that after phosphoric acid activation the effective surface area increased which in turn increase the methylene blue adsorption capacity. Therefore, AC750NH4PO4 was used for the methylene blue adsorption in the present investigation.

**Batch adsorption study**

**Effect of initial concentration and contact time:** The contact time and initial concentration has significant effect on the adsorption of methylene blue and the effects are shown in Fig. 4. The
Fig. 3: Comparison of adsorption capacity of different activated absorbents

Fig. 4: Effect of initial methylene blue concentration (adsorbent dose = 1 g L\(^{-1}\), temperature 32\(^\circ\)C, volume of adsorbate = 100 mL)

effect was studied over a varied range of initial concentrations (100-500 mg L\(^{-1}\)). It is observed from Fig. 4 that the adsorption capacity increased very rapidly in the initial period of time and as the time progressed it gradually become constant. A quasi state equilibrium was reached after 2 h for all the concentration. At the time of adsorption the adsorbent surface come in contact with the dye molecules and the exterior surface of the adsorbent starts getting occupied. As the time passes more and more dye molecules get adsorbed and after a certain period of time the exterior surface become saturated. After the saturation of exterior surface the dye molecules are adsorbed in the interior surface of the adsorbent particle. But the time taken to reach the interior of an adsorbent particle is comparatively more as the individual dye molecules has to travel a long distance consisting various resistances of mass transfer.

The adsorption of methylene blue increased with increasing initial dye concentration and an adsorption capacity of 140 mg g\(^{-1}\) was achieved after 90 min with an initial concentration of 500 mg L\(^{-1}\). As the initial concentration increase the difference between initial and instantaneous
Effect of particle size: Adsorption of methylene blue by using three different particle size namely 44≤36, 65≤44, 80≤65 and 100≤80 mesh was studied for 100 mg L⁻¹ of initial dye concentration. The effect of particle size is shown in Fig. 5. It can be observed that as the particle size increased the adsorption of methylene blue decreased. This may be due to the increase in effective surface area with the decrease in particle diameter. In case of larger size particle the resistance due to mass transfer is high therefore, the entire internal surface of the adsorbent can be utilized which in turn leads to lower adsorption capacity (Senthilkumaar et al., 2005).

Effect of agitation speed: The effect of agitation speed was studied at different agitation speed ranging from 500-2000 rpm. It can be seen that the adsorption of methylene blue was increased with increase in agitation speed and the maximum removal was obtained at an agitation speed of 2000 rpm (Fig. 6). The phenomenon may be attributed to the fact that the rate of diffusion of dye
molecules from bulk liquid to the liquid boundary layer surrounding the adsorbent particle increased with increasing agitation speed (Fatih et al., 2011).

At higher rpm onset of turbulence takes place which in turn decreases the thickness of the liquid boundary layer around the activated carbon particle. Conversely, at lower rpm the resistance offered by the liquid boundary layer is large and as a result more contact time is required to obtain a higher adsorption capacity.

**Effect of temperature:** To study the effect of temperature the temperature was varied from 25-50°C. It can be seen from Fig. 7 that the adsorption capacity of methylene blue increased with decrease in temperature and the maximum adsorption was achieved at a temperature of 30°C. The result resembled the result obtained by Gaikwad and Misal, 2010. This behavior confirms the physical adsorption which is always an exothermic process. Conversely in some cases, the adsorption of methylene blue increased with decrease in temperature (Awala and El-Jamal, 2011).

**Comparison of removal efficiency of various activated carbons:** The char derived from the scrap wood of *Acacia auriculiformis* was further activated by using various chemical reagents namely zinc chloride and sodium hydroxide. The char is further activated in a domestic microoven by varying the input power supply. The removal efficiency of different activated carbons was also compared to the commercial activated carbons (Norit and E-mark carbons). The kinetic study was performed to compare the adsorption capacity of various adsorbent at a higher initial dye concentration namely 500 mg L⁻¹. It can be seen from Fig. 8 that the activated carbon prepared by phosphoric activation had highest removal capacity in comparison to other carbons.

**Comparison of adsorption capacity of differently activated carbon:** The adsorption capacity of the prepared adsorbent was further compared to the adsorption capacity of different activated carbon available in the literature and it was found that the prepared adsorbent has good adsorption capacity for methylene blue.
Fig. 8: Comparison of methylene blue adsorption capacity of various adsorbents

CONCLUSION
The activated carbon was prepared by phosphoric acid activation of the *Acacia auriculiformis* scrap wood char. The prepared carbon showed good adsorption towards a basic dye methylene blue in comparison to other adsorbents.

REFERENCES


