Adsorptive removal of textile dye using carbonaceous material from waste biomass

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Key words: Dyes, Wastewater, Sagwan wood, Activated carbon, Methylene blue.

Abstract

Dyes are present in the waste waters due to waste mismanagement in industries. Due to its toxicity their removal from water bodies is necessary. These dyes can be removed by adsorption on activated carbon and this method is an alternative eco-friendly solution of dye removal compared to many other methods. In this study methylene blue (MB) dye was removed by using Tectonagrandis (Sagwan) wood which was activated chemically by using nitric acid (2ml per 100g). Several parameters such as dye concentration (10-60mg/100ml), activated carbon dosage (1-6g), contact time (30-210 minutes), temperature (25-45°C) and pH (2-10) were examined at 200rpm rotation speed in batch mode experiments. By increasing the initial dye concentration, the percentage dye removal was decreased while by increasing the adsorbent dosage, pH and temperature the percentage dye removal increased. Maximum dye removal was observed at 30min. Maximum percentage of dye removal observed was 99.27%. This was achieved at 60mg of dye concentration, adsorbent dosage of 6g and contact time of 150 minutes. According to the results it was observed that the sagwan wood sawdust has highest capacity for the removal of methylene blue dye.

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Introduction
One of the major global concerns is water pollution due to increasing urbanization, population and industrialization (Huang et al., 2015). Due to increasing population growth, demand for fabrics is also increasing at alarming rate. These dyes and pigments are also used by many other industries for products coloration like plastic, rubber, textile, paper, cosmetics, etc. (Raghuvanshi et al., 2005). Consequently, these dyes are regularly discharged in the industrial wastewaters (Malik, 2003). About 3600 different types of dyes are in use of textile industry. In discharge and drainage water, nearly 20% dyes are lost (Ahmed et al., 2012; Chequer et al., 2013). Dyes are toxic and resistant to degradation (due to molecular complexity), therefore their extraction from effluent and wastewater course is necessary. Dyes also inhibit incoming light and therefore the process of photosynthesis is inhibited which result in damage to aquatic plants (Regti et al., 2017). For dye removal, number of studies is carried out more specifically of methylene blue (MB) (Ardekani et al., 2017). Activated carbon is a carbonaceous material more widely used for treatment purpose because of having a large surface area, high porosity, micro porous structure and higher surface reactivity. It is widely used for different applications. Feed stocks for activated carbon production are peat, coal, wood, lignite, residues of petroleum, but they are non-renewable and expensive (Chen et al., 2011). Therefore, researchers are now focused to synthesize activated carbon by using sustainable and low-cost precursors, such as rice husk, bagasse, sawdust, corn straw, garden and food waste (Chen et al., 2011; Yahya et al., 2015).

Different Studies have shown that the adsorption capacity is different in many aspects such as type of biomass used, experimental conditions, and the usage of different gases/reagents during activation process. Nevertheless, the adsorbent which shows high adsorption capacity has been prepared by three-stages. Adsorption capacity of methylene blue, in comparison, has recorded to be very low i.e. 0.66 mg/g for lemon peels (sweet) without activation and on egg shell it is found to be 94.9 mg/g (waste) (Abdel-Khalek et al., 2017).

Preparation steps also have high significance on the performance of adsorbers. Lanasyngray (2.60×10³) and Lanasyn orange (2.60×10³) (mg/g) are usually used in carpet wool dyes. It is recorded to have extremely high adsorption, on nano-porous ACs extracted from bamboo cane which has been chemically activated (Pradhananga et al., 2017). Due to increased surface area, adsorption is also high (2130 m²/g) with pore volume of 2.69cc/g. Golden shower extracted activated carbons is also observed and for methylene green it shows high adsorption capacity (Tran et al., 2017), and this activation process is also carried out in three steps. However, experimental studies shows that ACs derived from different sources do no depend on their surface area but it is because of their biggest effect of π-π interaction between the two adsorbents and adsorbates.

Biowaste derived methylene blue adsorption and other adsorbents onto activated carbons has been studied widely. The range of MB for adsorption capacities onto ACs from various bio-waste is a 17.44-476.2mg/g. Methylene blue adsorption is highest (476.2mg/g) when AC is prepared from cotton. But it is less than that produced by using oven heating of H₃PO₄ (487.4 mg/g) (Hao et al., 2014). Those prepared from micro oven heating of bio waste shows high adsorption of methylene blue (Foo et al. 2012; Hao et al., 2014), and it can further be increased by using H₃PO₄.

The purpose of the present study was to prepare activated carbon from Tectonagrandis (Sagwan) and the use of this activated carbon as an adsorbent for the removal of methylene blue dye.

Materials and methods
Adsorbent preparation
Sagwan sawdust collected from a local timber market. To remove dust particles and dirt the sawdust was washed it thoroughly with distilled water. It was dried...
in oven at 100°C for 24hrs, grinded, crushed and weighed. Sawdust was segregated in 2 parts. One part was kept as raw form and the other part is chemically processed to form chemically activated carbon (Garg et al., 2004). Sawdust was treated with nitric acid to make it chemically activated. 2ml of Nitric acid was added in sawdust and mixed it properly.

The sawdust was kept in oven for 24hrs. The carbonized material was then kept in furnace at 300°C for 2hrs for its physical activation. The sample was then washed to take out excess acid if present and dehydrated it in oven at 100°C. Then the material was crushed in a mortar and pestle to obtain a fine particle size (Garg et al., 2004).

Selection of dye
Methylene blue (MB) (analytical grade) was used in the experiment as an adsorbate. It is a cationic dye with molecular formula is C_{16}H_{18}CIN_{36} and 373.9g/mol is molecular weight. Distilled water was used for making all the regents and dye solution. Methylene blue is widely used dye in many textile and dyeing industries (Hameed et al., 2009).

Batch experiment
Dye removal experiment was conducted by batch method at different variables by taking different factors such as amount of AC dosage, different concentration of dye, different temperature, and variable time intervals and at different pH by changing the amount of parameter under examination while keeping the other parameters constant. By using 100ml of volume we performed the experiments in 250ml of flasks at 200rpm speed and at variable temperature.

By using ultraviolet spectrophotometer, we determined the dye concentrations at 665nm wavelength. Also, the pH effect was studied by taking range of 2 to 10. Adjustment of pH was done by using 0.1N NaOH and 0.1N H_{2}SO_{4}.

The percentage dye removal was determined by using the formula:

\[
\% \text{ Dye removal} = \frac{C_i - C_f}{C_i} \times 100
\]

Where, 
C_{i} is the Dye Concentration (Initial) 
C_{f} is the Dye Concentration (Final).

Results and discussion
Effect of different initial concentration of dye
The influence of initial dye concentration on the adsorption of methylene blue was studied using a dosage of 2g/100ml of activated carbon. In the current study 10-60 mg/100ml of methylene blue was tested. With the increase in initial dye concentration, it is observed that the percentage adsorption of methylene blue decrease (Table 1 and Fig.1).

Table 1. Variable dye concentration effects on adsorption of MB.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Concentration</th>
<th>Absorbance</th>
<th>Remaining Dye Conc. After 150min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Dye Conc.</td>
<td>10 (mg/100ml)</td>
<td>0.654</td>
<td>1.8713</td>
</tr>
<tr>
<td></td>
<td>20 (mg/100ml)</td>
<td>0.551</td>
<td>1.4770</td>
</tr>
<tr>
<td></td>
<td>30 (mg/100ml)</td>
<td>0.911</td>
<td>2.8549</td>
</tr>
<tr>
<td></td>
<td>40 (mg/100ml)</td>
<td>1.752</td>
<td>6.0738</td>
</tr>
<tr>
<td></td>
<td>50 (mg/100ml)</td>
<td>1.927</td>
<td>6.7436</td>
</tr>
<tr>
<td></td>
<td>60 (mg/100ml)</td>
<td>1.954</td>
<td>6.8469</td>
</tr>
<tr>
<td>Amount of Activated Carbon</td>
<td>1 (g/100ml)</td>
<td>0.491</td>
<td>1.2474</td>
</tr>
<tr>
<td></td>
<td>2 (g/100ml)</td>
<td>0.486</td>
<td>1.2283</td>
</tr>
<tr>
<td></td>
<td>3 (g/100ml)</td>
<td>0.412</td>
<td>0.9450</td>
</tr>
<tr>
<td></td>
<td>4 (g/100ml)</td>
<td>0.39</td>
<td>0.8608</td>
</tr>
<tr>
<td></td>
<td>5 (g/100ml)</td>
<td>0.296</td>
<td>0.5011</td>
</tr>
<tr>
<td></td>
<td>6 (g/100ml)</td>
<td>0.278</td>
<td>0.4322</td>
</tr>
<tr>
<td>Temperature</td>
<td>25 (°C)</td>
<td>2.757</td>
<td>9.9203</td>
</tr>
<tr>
<td></td>
<td>30 (°C)</td>
<td>2.756</td>
<td>9.9165</td>
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<tr>
<td></td>
<td>35 (°C)</td>
<td>2.632</td>
<td>9.5184</td>
</tr>
<tr>
<td></td>
<td>40 (°C)</td>
<td>2.412</td>
<td>8.3998</td>
</tr>
<tr>
<td></td>
<td>45 (°C)</td>
<td>2.173</td>
<td>7.6851</td>
</tr>
</tbody>
</table>

\( \Delta \ln K \) 2 3.768 13.7998
This decrease can be because of lesser number of adsorption sites of activated carbon available or it may be due to decrease in the driving force required for the adsorption of MB. With increase in MB concentration the sites will not be available for adsorption as when compared with low dye concentration where all active sites were fixed. Methylene orange has been removed using activated carbon and its efficiency has been studied (Danish et al., 2014).

<table>
<thead>
<tr>
<th>Time</th>
<th>4</th>
<th>2.657</th>
<th>9.5376</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>2.412</td>
<td>8.5998</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1.954</td>
<td>6.8469</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>1.752</td>
<td>6.0738</td>
<td></td>
</tr>
<tr>
<td>30 (min)</td>
<td>0.498</td>
<td>1.2742</td>
<td></td>
</tr>
<tr>
<td>60 (min)</td>
<td>0.491</td>
<td>1.2474</td>
<td></td>
</tr>
<tr>
<td>90 (min)</td>
<td>0.412</td>
<td>0.9450</td>
<td></td>
</tr>
<tr>
<td>120 (min)</td>
<td>0.401</td>
<td>0.9029</td>
<td></td>
</tr>
<tr>
<td>150 (min)</td>
<td>0.378</td>
<td>0.8149</td>
<td></td>
</tr>
<tr>
<td>180 (min)</td>
<td>0.352</td>
<td>0.7154</td>
<td></td>
</tr>
<tr>
<td>210 (min)</td>
<td>0.354</td>
<td>0.7231</td>
<td></td>
</tr>
</tbody>
</table>

Three synthetic dyes telon blue, astrazon blue, and methylene blue were removed by using activated carbon extracted from pinewood (Tseng et al., 2003).

Results showed that time was the main factor in activation because of pore size and surface area. Textile effluent dye is removed by using activated carbon obtained by Mahogany sawdust (Malik et al., 2004).

**Different dosage effects of activated carbon**

By changing the amount of activated carbon 1-6g/100ml and keeping the concentration of dye constant (60mg), adsorption of methylene blue was studied at constant time i.e. 150min and the results in the Table1 and Fig. 2. It shows that at 150min maximum dye absorption (99.27%) was attained and by increasing the amount of dose the percentage adsorption of methylene blue significantly increase from 97.92% to 99.27%.

This may be because more active sites are available for adsorption, which results in more removal of methylene blue and as the surface area of the activated carbon (adsorbent) increases there is more methylene blue adsorption.

The factor which play an significant part are surface area, pore size/volume. As a result different woods have different adsorption ability (Zuo et al., 2010).
Temperature effects on methylene blue adsorption

Temperature effect was studied at different temperature from (25°C to 45°C) to observe the adsorption efficiency of MB. It was observed from the results that by increasing the temperature the adsorption efficiency of the dye solution also increasedTable 1 and Fig.3. This is due to the fact that the bond strength between dye molecules and activated carbon increases at high temperature. The increased dye adsorption (at increased temperature) indicated that the process is endothermic in nature. Heidari et al., (2014) used H₃PO₄, KOH and ZnCl₂ during chemical activation for the formation of activated carbon from Eucalyptus camaldulensis wood. It was notice that the concentration and type of dehydrating agent in wood control the pore size and surface capacity in the AC.

Effect of pH

Results for the effect of pH on the dye removal was observed and is given in the Fig.4 and Table 1. Results depicts that when the pH of the dye solution increases the efficiency of removal of dye increases with increase of initial pH of dye solution. But for cationic dyes such as methylene green and methylene blue, the efficiency of dye removal is lower at lower pH which shows that this is because of high hydrogen ions concentration that offers competition with
cationic groups. Different concentration of dehydrating agent is added in wood biomass for activation. CaO, ZnCl₂, KOH, NaOH, H₂SO₄, H₃PO₄, etc. are usually used dehydrating agents during chemical activation. The ideal dehydrating agent is phosphoric acid (H₃PO₄), because it is effectively, economic, efficient and above all it is environmentally safe (Bhatnagar et al., 2015). Wood of Paulownia (Paulownia elongata) treated with H₃PO₄ (as activating agent) produce activated carbon having high surface area (Yorgun et al., 2015).

**Fig. 4.** pH effects on adsorption of MB.

**Fig. 5.** Contact time effects on adsorption of MB.

**Contact time effect on dye adsorption**

The influence of time on the adsorption of methylene blue was studied at different contact time (30 to 210 min).

The amount of dye adsorbed at various intervals of time is shown in Fig. 5 and Table 1. Initial dye removal increases as time increase but then it reaches to an equilibrium state within 150–180 min. It is found that adsorption process was initially very rapid, and therefore a large portion of the total dye concentration is removed but after sometime it becomes almost constant.
The maximum adsorption of dye was observed to be 99.27% at optimum conditions of temperature, pH, contact time of 150 min, 200 rpm speed, adsorbent dose of 6 g/100 ml. Zhang et al., (2004) reported that different temperature and time affect the size of pore and area of surface. Study illustrated that loosely bounded substances can be eliminate considerably to open the pore by variations of activation time (Konicki et al., 2015).

**Conclusion**

Dyes present in waste water are necessary to remove. Activated Carbon prepared from different biomass and agricultural by-products has great potential to treat waste water from dyes. These bio adsorbents are low in cost, are locally available and eco-friendly.

In this work removal of methylene blue dye has been successfully achieved by using activated carbon prepared from Sagwan wood sawdust. Different parameters such as effect of different dye concentration, contact time, dosage of adsorbents, pH and temperature were optimized to get maximum efficiency. Activated carbon may also used for the removal of trace metals from waste water.

There are several challenges in the use of activated carbon on large scale for dye removal. These challenges need to be overcome for use of activated carbon on large scale.

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