BIOCHAR FROM COCONUT FROND AS ADSORBENT FOR MALACHITE GREEN DYE REMOVAL

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ABSTRACT
The use of low cost and eco-friendly adsorbent has been explored as alternatives to the current expensive pollutants removal methods. In this study, biochar from coconut frond (BCF), an agricultural waste was investigated as an adsorbent for the removal of cationic dye, Malachite green (MG) from aqueous solution. Factors affecting dye adsorption such as adsorbent dosage, initial dye concentration, contact time and pH were investigated in a batch mode. BCF was prepared at a carbonization temperature of 800°C which resulted in the best percentage of MG removal (> 99%) at the optimized condition. The Langmuir and Freundlich isotherms have been employed to study the adsorption mechanism and favorability. The adsorption of MG dye using BCF was best explained based on the Langmuir model with the adsorption capacity of 126.58 mg/g. The result showed that the BCF has the potential as an efficient adsorbent for MG dye removal in aqueous solution.

Keywords: biochar from coconut frond, adsorption, dye removal, Malachite green, isotherms.

INTRODUCTION
Dyes are widely utilized in various industries especially in the textile industries, and they comprise mainly of synthetic dyes since the synthetic versions are industrial friendly compared to natural dyes. MG is one of the dyes that have been widely used in the dyeing industry. It is a triarylmethane which is a basic cationic dye with a molecular formula C_{23}H_{22}ClN_{2}. It is used to dye cotton, wool, silk, jute, leather, paper, and acrylics. Besides that, it is used as a food coloring agent, food additives and medical disinfectant. Also, it is significantly used in aquaculture to control fungal attack, protozoan infection and other disease caused by helminths. However, recently MG has been reported to contain toxic effects (Srivastava et al., 2004). The ability of MG to accumulate in the tissues of aquatic life will cause adverse health effects due to its carcinogenic, mutagenic, genotoxic, and teratogenic properties. Human beings will be directly affected upon consumption of the polluted water or indirectly by consuming affected aquatic livings. Since water pollution caused by dyes has a continuous impact starting from the producer until the end consumer, covering the whole ecosystem and nature, it should be systematically treated. This is given the fact that access to clean and safe water has become a challenge for people in some parts of the world. This global issue of water pollution is always given serious attention by various authorities so effective methods in waste water treatments can be executed. Government legislation requires every industry to treat their effluent before disposing it to the environment making the demands for effective wastewater treatment methods prevalent. Effectively removing dyes from water is difficult since the complex aromatic molecular structure of dyes made them very stable to the oxidizing agent, light and resistant to aerobic digestion.

There are considerable methods to treat water namely by utilizing the filtration, ion exchange, precipitation, solvent extraction and electrochemical treatments (Dezhanspanah et al., 2014). However, these methods are considered expensive, not eco-friendly and sometimes not effective in treating water on a massive scale. Adsorption is one of the alternative methods widely used to remove organic and inorganic contaminants either from an aqueous solution or gaseous environment due to its effectiveness. However, there is a financial downside because commercial activated carbons made from petroleum coke; bituminous coal and lignite are expensive. Hence, there is a growing need to develop low-cost adsorbent for wastewater treatment.

Biochar is one of the adsorbents based on agricultural waste which is a solid that has carbon-rich produced from heating biomass like wood, manure with the absence of oxygen (Sohi, 2012). It is traditionally used as soil amendment, is getting popular as a low-cost adsorbent. Biochar has a porous structure similar to activated carbon, but processing biochar is comparatively much cheaper and requires lower energy (Tan et al., 2015). The feedstock for biochar production is usually low-cost by products such as agricultural waste. Hence, the utilization of agricultural waste can create a cradle to cradle practice. Rice straw (Hameed & El-Khaiary, 2008b), wood, oak, pine, hazelnut, corn, soy, bamboo (McBeath et al., 2014), wheat straw (Liu et al., 2012), palm bark, eucalyptus (Sun et al., 2013), canola, soybean and peanut straw (Xu et al., 2011) have been studied for their potential to be developed into biochars.

This research aims to study the efficiency of biochar-based on coconut frond as an adsorbent for basic cationic MG dye. Coconut shell (Banat et al., 2003; Demirbas, 2008; Gupta et al., 2011; Sek et al., 2004) coir pith (Gupta et al., 2011; Kadirvelu & Namasiyavam, 2003), husk (Tan et al., 2008), tree saw dust (Kadirvelu et al., 2003) have been studied for their efficiency in adsorbing pollutants. However, studies of coconut frond as an adsorbent are still lacking in the current literature. The
optimization of parameters such as adsorbent dosage, initial dye concentration, contact time and pH were investigated in the batch mode. Adsorption mechanism and favorability were determined based on Langmuir and Freundlich isotherms.

MATERIALS AND METHOD

Chemicals
The chemicals used in this study are Malachite Green (MG) dye, C<sub>26</sub>H<sub>26</sub>ON<sub>2</sub> (R&M Chemicals), citric acid-1-hydrate, C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>·H<sub>2</sub>O (Bendensen), Sodium citrate 2-hydrate, Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>·2H<sub>2</sub>O (Bendensen), di-Sodium hydrogen phosphate, Na<sub>2</sub>HPO<sub>4</sub> (Merek), Sodium tetraborate-1-hydrate/Borax, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O (HmbG), Potassium dihydrogen phosphate, KH<sub>2</sub>PO<sub>4</sub> (HmbG), Sodium hydroxide pellet, NaOH (HmbG) and Hydrochloric acid, HCl (Scharlau).

Preparation of Adsorbate
Coconut fronds were obtained from Jeli district in the state of Kelantan. Only the coconut frond’s cushion (CFCP) was cut, washed and sun-dried. Then, it was ground and sieved to obtain a particle size of 0.125 mm (Mohammad et al., 2017). The CFCP powder was then placed in 100 mL crucibles and carbonized at 800°C with 10°C/min heating rate for 4 h, (modified from Yuan et al., 2014). The samples were left to cool down and placed in zipper bags for further studies.

Preparation of Adsorbate
1.0 g of MG dye powder was diluted in distilled water to prepare a stock solution of 1000 mg/L. The stock solution was transferred into the reagent bottle and kept inside a light proof cupboard to prevent dye degradation.

Calibration Curve
A series of standard calibration solutions were prepared in a concentration range of 0.5-12.0 mg/L by diluting from a stock solution using distilled water. The absorbance reading of these standard solutions was measured using UV spectrophotometer (Thermo Scientific/GENESYS 20) at a wavelength of 617 nm.

Adsorption Studies
The adsorption study was carried out by mixing a fixed dosage of BCF with 100 mL of MG solution at specific initial concentration. The mixture of BCF and MG dye solution were stirred using a glass rod for 2 minutes and left for 4 hours at room temperature. After 4 hours, the mixture was filtered using filter paper, and the filtrate was measured using a UV-Visible Spectrophotometer at a wavelength of 617 nm. The same procedure was used for subsequent studies.

A few parameters have been studied in a certain range i.e. BCF dosage 0.02-2.0 g; initial MG dye concentrations 10-800 mg/L; contact time 20 minutes -7 hours and pH 3-11. Other parameters were fixed according to the optimum conditions obtained from previous experiments.

The percentage of dye removal and the adsorption capacity (q<sub>e</sub>) were calculated using the following equation (Salleh et al., 2012): 

\[
\text{Percentage of dye removal} = \frac{C_0 - C_e}{C_0} \times 100
\]

Where \( C_0 \) = initial dye concentration (mg/L) and \( C_e \) = dye concentration at equilibrium (mg/L)

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

Where q<sub>e</sub> = amount of dye adsorbed (mg/g), C<sub>0</sub> = initial dye concentration (mg/L), C<sub>e</sub> = equilibrium dye concentration (mg/L), V = initial volume of dye solution (L) and W = weight of biochar (g)

RESULTS AND DISCUSSIONS

Effect of Adsorbent Dosage
Based on Figure-1, the percentage of MG dye removal increases from 98.37% to 99.91% when the amount of adsorbent dosage is increased from 0.02 g to 0.1 g for 100 mL of solution. Whereas, a further increase in the adsorbent dosage of more than 0.1 g does not show any significant difference in the percentage of MG dye removal. The constant percentage of MG dye removal beyond 0.1 g shows that the equilibrium has been achieved between the adsorbate and adsorbent. 0.3 g has provided sufficient adsorption sites for the adsorption of most of the MG particles. Hence, a dosage of 0.3 g is selected as the optimum dosage to be used in the subsequent parameters. Lower adsorbent dosage is not enough to provide a sufficient number of specific sites for the adsorbate particles. Only some MG dye molecules are adsorbed by a limited amount of biochar, and the remaining MG dye molecules are left in the reaction mixture. When the adsorbent dosage increases, the surface area increases and this creates more specific adsorption sites available for adsorption (Kolodyńska et al., 2012).
Effect of Initial Dye Concentration

Based on Figure-2, the percentage of MG removal is constant at the concentration of 10 mg/L until 500 mg/L and decreases with the increase in the initial dye concentration.

At lower dye concentrations, most of the MG particles are able to interact with adsorption sites facilitating maximum adsorption (Gupta et al., 2011). Whereas at higher dye concentrations, MG particles have to compete for available active sites which are limited (Singh et al., 2013). Hence, the rate of adsorption process between the adsorbent and dye molecule slows down (Sharma & Nandi, 2013). Although the percentage of MG removal decreases, the amount of MG adsorbed per unit mass of adsorbent increases with the increased $C_0$ (Garg et al., 2004; Wong et al., 2009). This is because of the driving force to overcome the mass transfer of MG dye uptake from the solution increases with the increase of $C_0$ (Mall et al., 2005; Salleh et al., 2012).

Most of the related findings showed that the increase in $C_0$ caused a decrease in the removal percentage of the MG dye, as reported in removal of MG dye using zea mays dust activated carbon (Baskaran et al., 2011), rice husk activated carbon (Sharma et al., 2009), Prosopis cineraria waste (Garg et al., 2004), sugarcane bagasse (Wong et al., 2009) and modified rice husk (Dezhampanah et al., 2014). Although the percentage of MG removal decreases, the adsorption capacity increases with the increase of $C_0$ in this study (Figure-2b). It was supported by similar findings in the removal of MG dye using bagasse fly ash (Mall et al., 2005), mentha plant biochar (Rawat & Singh, 2018) and rattan sawdust (Hameed & El-Khairy, 2008b). Therefore, the initial dye concentration of 400 mg/L was chosen as the optimum value to be used in the subsequent study.
Effect of Contact Time

Based on Figure-3, the percentage of MG dye removal shows a significant increase from 20 min (94.73%) to 4 h (99.14%) and became constant beyond 4 h. Further increase in contact time does not show an increase in the percentage of MG dye removal as equilibrium is reached between the adsorbate and adsorbent. However, the maximum MG dye removal is obtained in 6 h (99.84%). Hence, further studies were carried out in 6 h to allow the maximum adsorption of MG dye molecules on the biochar.

In a more extended period of time, only a few numbers of surface active sites become available for the dye uptake. Also, the increase in contact time causes aggregation of the dye molecules. The mesopores which get saturated by initially adsorbing the dye molecules creates resistance or repulsion force to the aggregated dye molecules in the bulk phase. Hence, it prevents the aggregated dye molecules from diffusing deeper into the adsorbent. This phenomenon supports MG monolayer formation on the adsorbent surface results in a constant percentage of MG removal particularly towards the end of
this experiment (Singh et al., 2013). Similar trends were reported in the removal of MG dye using activated carbon from rambutan peel (Ahmad & Alrozi, 2011), treated ginger waste (Ahmad & Kumar, 2010), rice husk biochar (Leng et al., 2015), activated carbon from oil palm fruit fibre (Bello, 2013) and bagasse fly ash (Mall et al., 2005).

**Effect of pH**

pH has an effect on the surface charge of the adsorbent and the chemistry of the aqueous solution imparted by the ionization process of the dye molecules. The effect of the initial pH on the removal of MG was studied by varying the pH (3-11) under the optimum condition of other parameters. Based on Figure-4, the percentage of MG removal is almost constant from pH 3 till pH 7 and starts to increase beyond pH 7. It can be seen that the removal of the MG dye is optimum in alkaline condition. In the acidic condition, excess H⁺ ions are competing with cationic dye molecules for the adsorbent binding sites causing less favored adsorption. However, based on the result, the percentage of MG removal is still more than 90% in a very acidic medium which is considered as good adsorption. This may be caused by π-π dispersion interactions between the dye molecule and graphene layer of biochar which becomes dominant in this case (Liu et al., 2012; Qiu et al., 2009).

The decrease in acidity of the solution is observed with the increase in pH which causes the deprotonation of the MG. As the pH increases, it causes the adsorbent surface to get negatively charged due to the deposition of the OH⁻ ions. It enhances the adsorption of MG dye (cationic dye) through the electrostatic force of attraction resulting in higher removal percentage of MG up to 99%. A similar trend is reported, which recommends that a higher pH of the solution will allow for the optimum adsorption of the cationic MG dye (Refer to Table-1).
Adsorption Isotherm

Adsorption isotherm is an equation which relates to the amount of solute adsorbed onto solid, and the concentration of solute at equilibrium in a solution. Langmuir and Freundlich isotherm models were employed in this study using the linear equation for both isotherms as stated by Dada et al. (2012). Langmuir adsorption model assumes that maximum adsorption is due to a saturated monolayer of the solute molecule on an adsorbent surface (Ahmad & Alrozi, 2011). Also, the surface of the adsorbent said to be homogenous, which means that it contains a constant number of identical adsorption sites. Hence, each site is capable of taking one molecule. There will be no interaction between the adsorbed molecules, or the interaction is negligible (Mohammadi et al., 2014). Freundlich isotherm model suggests non-ideal adsorption on the heterogeneous surface. The heterogeneity is due to the surface of the adsorbent which is made up of different types of functional groups. Hence, there will be various interactions between the adsorbent and adsorbate.

Based on Table-2, the equilibrium data is best fitted to the Langmuir adsorption model since the value of correlation coefficient \( R^2 = 0.9999 \) is higher compared to the Freundlich model \( R^2 = 0.8977 \). The \( n \) value of the Freundlich isotherm model indicates its favorability. Given that when \( 1 < n < 10 \), the condition is favorable towards heterogeneous adsorption (Velmurugan et al., 2011). However, the \( n \) obtained in the study was not in the range which is -66.67; shows that it does not support heterogeneous adsorption. Hence, the adsorption of MG

### Table 1. Optimum pH for MG dye removal by different types of adsorbents

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Form</th>
<th>Optimum pH</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sugarcane bagasse &amp; Rice husk</td>
<td>Raw</td>
<td>8</td>
<td>Dezhampanah et al., (2014)</td>
</tr>
<tr>
<td><em>Hydrilla Verticillata</em></td>
<td>Treated with HCl</td>
<td>8</td>
<td>Kannan et al., (2010)</td>
</tr>
<tr>
<td>Coconut peel</td>
<td>Activated carbon treated with KOH</td>
<td>8</td>
<td>Ahmad &amp; Alrozi, (2011)</td>
</tr>
<tr>
<td>Ginger waste</td>
<td>Treated with H&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt; and ZnCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>9</td>
<td>Ahmad &amp; Kumar, (2010)</td>
</tr>
<tr>
<td><em>Eucalyptus wood</em></td>
<td>Biochar</td>
<td>9</td>
<td>Singh et al., (2016)</td>
</tr>
<tr>
<td>Mentha plant</td>
<td>Biochar</td>
<td>10</td>
<td>Rawat &amp; Singh (2018)</td>
</tr>
<tr>
<td>Zea mays dust</td>
<td>Activated carbon treated with H&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>9</td>
<td>Baskaran et al., (2011)</td>
</tr>
<tr>
<td>Mosambi peel dust</td>
<td>Raw</td>
<td>11</td>
<td>Mary et al., (2015)</td>
</tr>
</tbody>
</table>
dye on biochar surface takes place as a monolayer adsorption.

**Table 2.** Langmuir and Freundlich parameters for adsorption of MG dye.

<table>
<thead>
<tr>
<th>Isotherm model</th>
<th>Values of constant</th>
</tr>
</thead>
</table>
| Langmuir      | $q_o = 126.58 \text{mg/g}$  
|               | $K_L = -8.78 \text{L/mg}$  
|               | $R^2 = 0.9999$         |
| Freundlich    | $K_F = 133.20 \text{mg/g}$  
|               | $n = -66.67$           
|               | $R^2 = 0.8977$         |

**CONCLUSIONS**

As a conclusion, biochar based on coconut frond has the potential to be developed as a novel adsorbent for MG dye removal. At an optimized condition (adsorbent dosage = 0.3 g, initial dye concentration = 400 mg/L, contact time = 6 h and pH = 10) the percentage of MG removal recorded is 99.27%. The equilibrium data were well described by the Langmuir model with a correlation of $R^2 = 0.999$, suggesting a monolayer adsorption mechanism. The maximum adsorption capacity was 126.58 mg/g.

**ACKNOWLEDGMENT**

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