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# Adsorption of Methyl Violet Dye by Thermally Modified *Ceiba Pentandra* Sawdust

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## Abstract

The disposal of synthetic dyes into the environment can cause water pollution. Methyl violet, a typical cationic dye widely applied in industries, can cause bad effect to the aquatic life due to its stability and biodegradability. It also reduces photosynthetic activity. In this study, modified *Ceiba pentandra* sawdust has been investigated as an adsorbent for the removal of methyl violet dye from aqueous solutions. The modification has been carried out using heating treatment at 110°C and 200°C for one hour. The FTIR spectra of raw and modified *Ceiba pentandra* sawdust were recorded using an FTIR technique (Perkin Elmer, USA) by the KBr pellet method. The spectrum was scanned in the range of 400 to 4000 $cm^{-1}$ wavenumbers. The photomicrography of the exterior surface of raw and modified *Ceiba pentandra* sawdust was obtained by SEM (JEOL, Japan). Batch studies were performed to investigate various experimental parameters including pH, contact time, and initial concentration for the removal of this dye. The results show that heating treatment increases the amount of methyl violet adsorbed. Effective pH for methyl violet adsorption was 7. A greater percentage of dye was removed with a decrease in the initial concentration of dye. Quasi-equilibrium reached in 30 min. Equilibrium isotherms were analysed by Langmuir and Freundlich isotherm equations. Freundlich equation is found to best represent the equilibrium data for methyl violet-modified *Ceiba pentandra* sawdust system.



## INTRODUCTION

The industrial wastewater usually contains a variety of heavy metals and organic compounds which are harmfull to the aquatic life. The disposal of synthetic dyes from paint, ink and textile industries into the stream not only inhibits photosynthesis of aquatic plants, but also increases damage to natural ecosystem because most of dyes may be highly toxic, carcinogenic and mutagenic (Rahchamani et al., 2011). Dyes can be classified as anionic, cationic and nonionic. Methyl violet is a member of the cationic dyes, a group with high intensity of colors that inhibit photosynthesis of aquatic plants (Xu et al., 2011). Although not strongly hazardous, methyl violet is even more toxic because it can easily interact with negatively charge of cells membrane surface and can enter into cells and concentrate in the cytoplasm (Li, 2010). Therefore, it is necessary to remove these dyes from wastewater. Numerous physicochemical and biological methods have been used to decolorize dyes in wastewater including aerobic (Tan et al., 2016) and anaerobic (Cao et al., 2017) degradation, filtration (Guo et al., 2016), coagulation (Li et al., 2016), membrane separation (Wang et al., 2016) and oxidation-softening (Zheng et al., 2015) and adsorption (Hanafiah et al., 2012). Among of these, adsorption process is an attractive and favorable alternate that has been successfully employed for dye removal from wastewater due to its simplicity of design and easy to operate. A number of organic and inorganic adsorbents have been used to remove it including activated carbon (Gao et al., 2016), fly ash (Lin et al., 2016) and polymer (Li, 2010). Agricultural wastes have been proven to be low cost alternative adsorbents due to their accessibility and abundantly availability.

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On the other hand, *Ceiba pentandra* is belonged to the family of Bombaceae and grow in Asia including Indonesia, Africa, and South America. *Ceiba pentandra* wood is variable in colors from white to light brown. The major components of the wood are cellulose 40-55%, lignin 15- 35% and hemicelluloses 20-35%, called as lignocellulosic materials (Walia et al., 2009). The existence of active sites in the materials lead to *Ceiba pentandra* can be used as an adsorbent. The objective of the present study is to investigate the feasibility of *Ceiba pentandra* sawdust as an adsorbent for the removal of methyl violet from aqueous solutions. To increase the adsorption capacity of *Ceiba pentandra* sawdust need to be modified by heating method to change the surface structure.

## METHODS

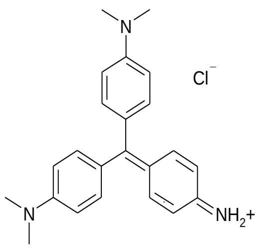


Figure 1. Structure of methyl violet dye

The sawdust of *Ceiba pentandra* was sieved and the fractions with the particle size less than 0.149 mm were used for experiments. Further, the sawdust was filtered, washed several times with deionized water until pH of the filtrate was around 7, dried at 110°C and 200°C for one hour, characterized and used as an adsorbent in the sorption experiments. The FTIR spectra of raw and modified *Ceiba pentandra* sawdust were recorded using an FTIR technique (Perkin Elmer, USA) with the KBr pellet method. The spectrum was scanned in the range of 500 to 4000 $cm^{-1}$ wavenumbers. Batch adsorption experiments were carried out at constant temperature (26±1°C) by adding 0.5 g of raw or modified *Ceiba pentandra* sawdust to 100 $cm^{-3}$ Erlenmeyer containing 50 $cm^{-3}$ aqueous solutions with varying initial methyl violet concentration (10-300 mg/$dm^{-3}$). The structure of this dye is shown in Figure 1. pH values of sawdust-methyl violet aqueous solution system were adjusted to desired levels (pH 3-9) using 0.1N HCl or 0.1N NaOH. The Erlenmeyer was shaken at 115 rpm for varying contact time (5-180 min). After specified contact times, suspended solids were filtered through Whatman paper No.5 and the filtrates were analyzed for residual methyl violet using a UV-Visible spectrophotometer at $\lambda_{max}$ of 581 nm.

## RESULT AND DISCUSSION

### Characteristic of *Ceiba Pentandra* Sawdust

To confirm the presence of functional groups in the adsorbent which are capable of adsorbing dye ions, FT-IR analysis was conducted. The FT-IR spectra before and after heating process are shown in Figure 2. Before adsorption process, it can be seen that there is a broad and strong band at 1793 $cm^{-1}$, which indicates the presence of C = O group (Hanafiah et al., 2012). The broad absorption peaks at 3761 $cm^{-1}$ indicate the existence of bonded

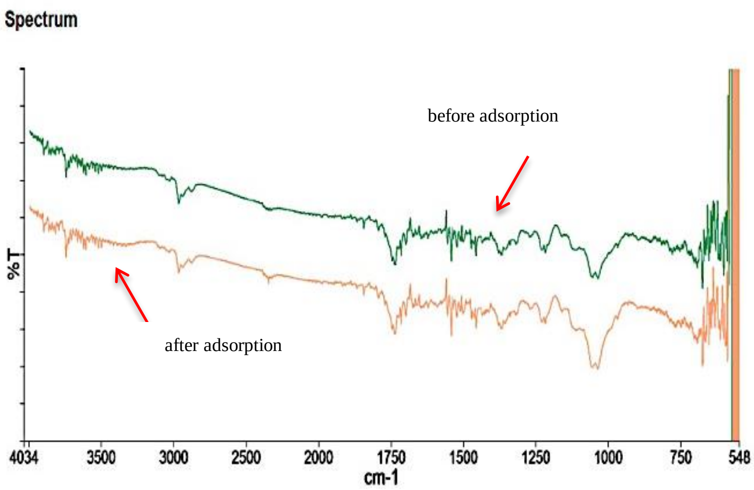


Figure 2. FTIR spectra of heated *Ceiba pentandra* sawdust at 200°C before and after adsorption process

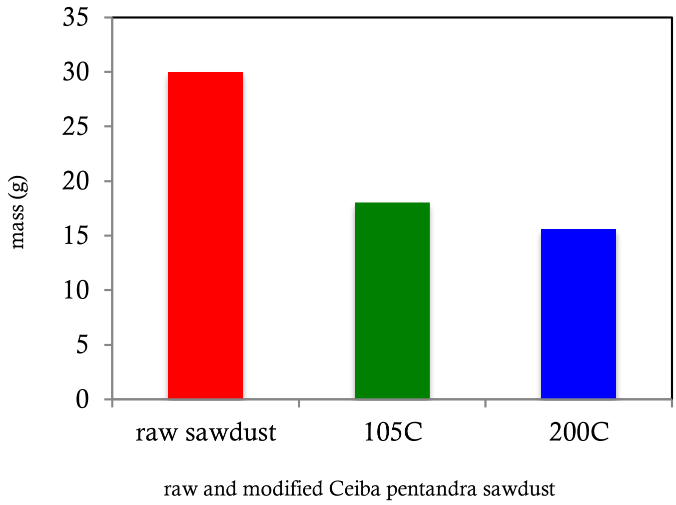


Figure 3. Effect of heating toward yield of *Ceiba pentandra* sawdust

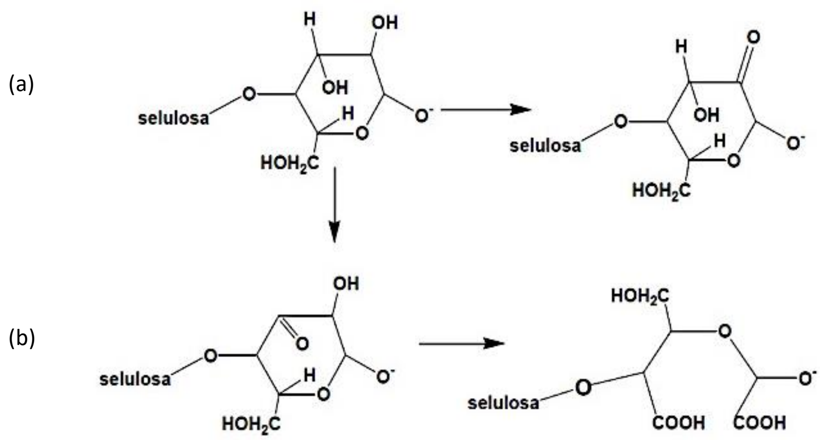


Figure 4. The degradation of cellulose by heating at (a) 105°C and (b) 150°C

hydroxyl groups on the surface of sawdust. This band is associated with the OH stretching of the phenolic group of cellulose and lignin (Hanafiah et al., 2012). After used to absorb methyl violet, there is a shift of peak from 3761 cm$^{-1}$ to 3671,55 cm$^{-1}$. This suggests a change in the absorption peak that may be due to methyl violet bound to the OH group. The shift of the absorption peak was also seen from 1793 cm$^{-1}$ to 1735.67 cm$^{-1}$ while the intensity of peak at 1035.30 cm$^{-1}$ indicates methyl violet is also absorbed at C-O and C = O.

**Effect of Heating toward Yield of Adsorbent**

Heating of *Ceiba pentandra* sawdust at 105°C and 200°C decreases the mass of adsorbent, as can be seen in Figure 3. It can be explained by the fact that there is a degradation of some celluloses to the vaporizing compound due to chain-breaking, dehydration and oxidation reactions (Suyati, 2008). The reaction is illustrated in Figure 4.

**Effect of Heating toward Methyl Violet Adsorbed**

The effect of heating temperature toward the amount of methyl violet adsorbed is illustrated in Figure 5. The amount of methyl violet adsorbed by thermally modified sawdust at 200°C was higher than that of thermally modified sawdust at 105°C due to the active site on the thermally modified sawdust at 200°C was more accessible by the adsorbate since it had more open structure.

Figure 5 also shows that the amount of methyl violet adsorbed increases with the increase of methyl violet concentration and remain constant after equilibrium reached. The initial concentration provides an important driving force to overcome all mass transfer resistance of methyl violet between

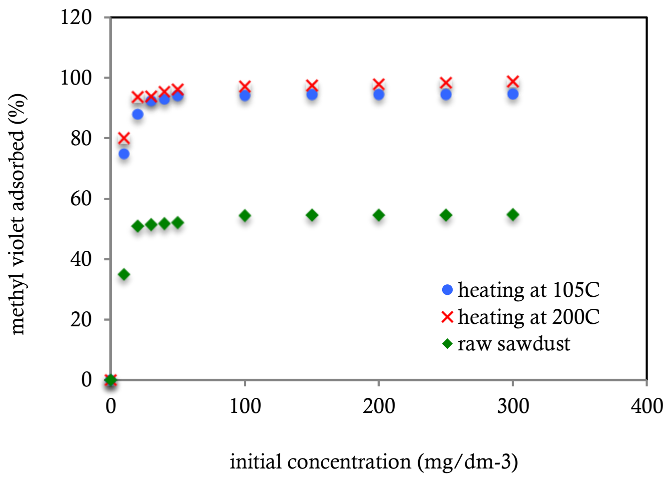


Figure 5. Effect of initial concentration on methyl violet adsorption by raw and modified *Ceiba pentandra* sawdust (pH of 5, contact time of 90 minutes, dose of adsorbent of 2gr/100cm$^{-3}$ solution)

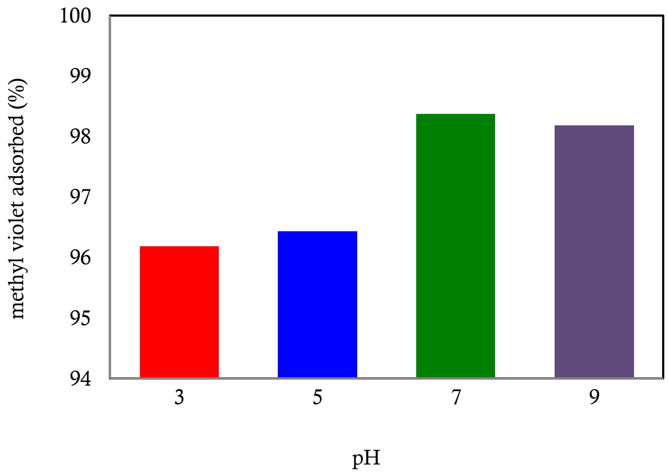


Figure 6. The effect of pH toward methyl violet adsorbed (Initial concentration of 50 mg/dm$^{-3}$, time of 90 minutes, dose of adsorbent of 2gr/100cm$^{-3}$ solution)

aqueous and solid phase. Hence, the higher initial concentration of methyl violet will enhance the adsorption process.

**Effect of pH toward Methyl Violet Adsorbed**

pH has been referred as an important influencing factor for dyes adsorption on sawdust (Ansari et al., 2012). Solution pH would affect both aqueous chemistry and surface binding sites of the adsorbent. Therefore, there is a favorable pH range for the adsorption of every dye on a specific adsorbent. In this study, the effect of pH on methyl violet adsorption by thermally modified sawdust at 200°C was investigated by varying the pH of methyl violet solution-sawdust suspension from 3 to 9. The results are described in Figure 6. The amount of methyl violet adsorbed increases until pH 7 and then decreases with the increase of pH. The increase may be related to the formation of negative surface charges on the adsorbent which is influenced by the pH. In the acid medium, the positively charged species start dominating and sawdust surface tends to acquire positive charge while the adsorbate species are still positively charged. The increase of solution pH lead to the decrease of positively charged species and sawdust surface tends to acquire the negative charge. The increase of electrostatic attraction between positively charged of adsorbate species and negatively charged of sawdust lead to the increase of the adsorption of methyl violet dye. The decrease in adsorption beyond pH 7 is due to the formation of soluble hydroxy complexes between the adsorbent and the dye.

Figure 6 also shows that the highest dyes adsorbed is at pH 7 (98.36%). Wang et al. (2013) states that the IEP (isoelectric point) of cellulose is 5.22. IEP is a condition in which the positive and

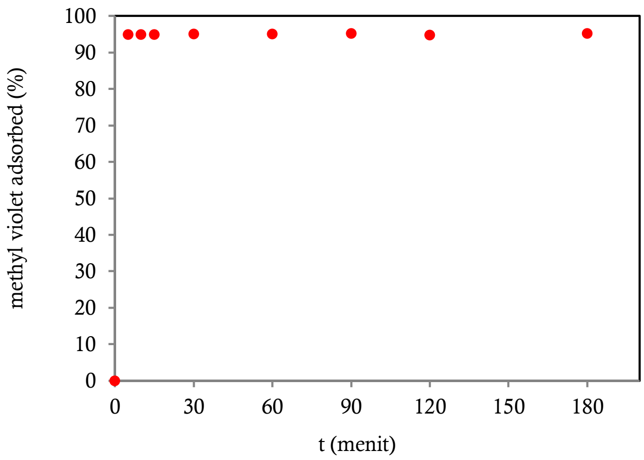


Figure 7. The effect of time (t) toward methyl violet adsorbed (% ) (Initial concentration of 50 mg/dm$^{-3}$, time of 90 minutes, dose of adsorbent of 2gr/100 cm$^{-3}$ solution)

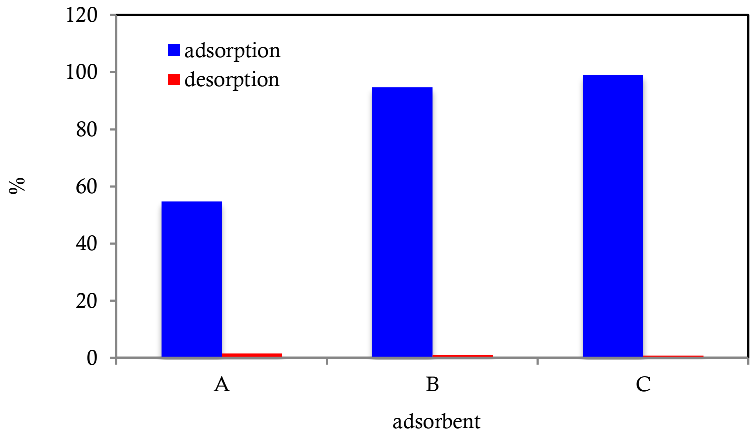


Figure 8. The amount of methyl violet adsorbed and desorbed (A= raw sawdust, B=thermaly modified sawdust at 105°C, C= thermally modified sawdust at 200°C)

negative charges are equal. It means at pH below IEP (pH 3), the active site tends to be protonated so it has positively charged. It causes a repulsive force between the active site and methyl violet which is also positively charged so adsorption was difficult to occur.

**Effect of Contact Time toward Methyl Violet Adsorbed**

The effect of contact time toward the amount of methyl violet adsorbed by thermally modified *Ceiba pentandra* sawdust at 200°C is investigated to study the rate of methyl violet removal, as can be seen in Figure 7. The removal of methyl violet is rapid but it gradually slows down until it reaches the equilibrium. This is due to a large number of vacant surface sites are available for adsorption during the initial stage, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases. Once the equilibrium was attained, the percentage sorption of dye did not change with the further increase of time. Therefore, the optimum contact time is 30 minutes.

**Desorption Study**

Desorption is an important issue to clarify the mechanism of adsorption. Desorption study of methyl violet onto raw and modified *Ceiba pentandra* sawdust was performed using distilled water. If methyl violet can be desorbed by distilled water, it indicates that methyl violet adsorption occurs with weak interaction (physisorption). Otherwise, if methyl violet can not be desorbed by distilled water, it indicates that methyl violet adsorption occurs in stronger interaction (chemisorption). Figure 8 shows that 0.34-0.72 % of methyl violet adsorbed into the sawdust can be desorbed by distilled water. It indicates that most of adsorption occurs through a chemisorption mechanism.

Table 1. Correlation coefficients ($R^2$) of Langmuir and Freundlich isotherm models

| **Models** | **$R^2$** |
|---|---|
| Langmuir | 0.9984 |
| Freundlich | 0.9989 |

Table 2. Isotherm constans for methyl violet adsorption onto thermally modified *Ceiba pentandra* sawdust at 200ºC

| Constants | Value |
|---|---|
| Langmuir model | |
| $K_L$ | 0.1216 |
| $q_{max}$ | 15.3293 |
| Freundlich model | |
| $K_F$ | 2.0696 |
| $n_F$ | 0.6194 |

**Adsorption Isotherm**

Adsorption isotherms are important to describe the adsorption mechanism of solute on the adsorbent surface. In this study, the equilibrium data obtained from methyl violet adsorption using raw and modified *Ceiba Pentandra* sawdust were tested with two isotherm models, including Langmuir and Freundlich, to reveal the best fitting isotherm. The Langmuir isotherm is based on the fact that the monolayers adsorption occurs in homogeneous sites on the adsorbent surface. Other assumption, it is localized adsorption and once a dye molecule occupies a site, no further adsorption can take place at the site. In addition, the interaction between the adsorbate molecules is ignored. This model can be expressed as Eq. (1) and rearranged to the linear form is given by Eq. (2) (Astuti et al., 2016)

$$q_e = \frac{q_m\, K_L C_e}{1 + K_L\, C_e} \quad (1)$$

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_e}\frac{1}{C_e} \quad (2)$$

The amount of dye adsorbed per unit weight of adsorbent at equilibrium ($q_e$, mg/g) was calculated using equation (3).

$$q_e = \frac{(C_i - C_e)\, V}{m} \quad (3)$$

where $C_i$ and $C_e$ are the initial and residual concentration of methyl violet in mg/dm$^{-3}$, $q_e$ is the adsorption capacity in mg/g, $V$ is the volume of methyl violet solution (dm$^{-3}$), $m$ is the adsorbent mass in g, $K_L$ is the adsorption equilibrium constant in dm$^{-3}$/mg related to the energy of adsorption, $q_m$ is the quantity of adsorbate required to form a single monolayer on unit mass of adsorbent in mg/g and $q_e$ is the amount dye adsorbed on unit mass of the adsorbent (mg/g) when the equilibrium concentration is $C_e$. A plot of $1/q_e$ versus $1/C_{e^{`}1}$ should yield straight line if the model is obeyed by the adsorption equilibrium. It is marked by value of correlation coefficient is closer to unity. The value of $q_{max}$ and $K_L$ can be calculated from the intercept and slope of the graphed line, respectively.

The Freundlich isotherm is derived by assuming a heterogeneous surface. The Freundlich isotherm is expressed by Eq. (4) where $K_F$ (mg$^{1-1/n}$ dm$^{-3(1/n)}$g$^{-1}$) and n are the Freundlich equilibrium constants which can be determined from the plot of log $q_e$ versus log $C_e$ on the linear form, as can be seen in Eq. (5).

$$q_e = K_F C_e^{n_F} \quad (4)$$

$$\log q_e = \log K_F + n \log C_e \quad (5)$$

The applicability of the isotherms was judge of the value of the correlation coefficients as can be seen in Table 1. Data in Table 1 shows that Freundlich model is seen in accordance with experimental data due to the correlation coefficient for the Freundlich isotherm is closer to unity than that of Langmuir isotherms. It is an indication of surface heterogeneity of the adsorbent due to the presence of energetically heterogeneous adsorption sites. The value of Langmuir and Freundlich constants are given in Table 2.

## CONCLUSION

Heating process increases the the amount of methyl violet adsorbed. The optimum condition of methyl violet adsorption by thermally modified *Ceiba pentandra* is at pH of 7 and contact time of 30 minutes. The equilibrium adsorption data were tested with two isotherm models and were best fitted with Freundlich isotherm.

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