Synthetic Dye Removal of Methylene Blue on Adsorption Process using Low-rank Coal of East Kalimantan

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Abstract: Adsorption of synthetic dyes using low-rank coal as an adsorbent needs to be applied considering that adsorption is the best technology available and low cost to remove some toxic contaminants, both organic and inorganic contained in wastewater. In addition, the great potential of low rank coal in East Kalimantan is still abundant and not fully utilized because so far, several studies have focused on medium and high rank coal. This study aims to determine the dye removal of methylene blue (MB) on adsorption process using low rank coal as an adsorbent. 100 mg low rank coal adsorbent was added to 100 mL of 100 mg/L methylene blue dye solution at 30 °C. Initial pH effect adjusted with 0.10 mol/L of HCl or NaOH. Then the synthetic dye solution of methylene blue was shaker at 150 rpm based on different contact times (10 - 90 min). At the end of the period, the shaker was stopped, and the supernatants were filtered through a Whatman 40 filter paper to separate the liquid from the solid phase. The remaining synthetic dye concentrations of methylene blue were determined using UV-Vis Spectrophotometer at maximum wavelength (λ_{max}) of adsorption. The experiment was repeated for different initial concentrations of synthetic dye methylene blue (50 – 250 mg/L). The best results were obtained using 100 mg low-rank coal adsorbent of East Kalimantan at optimum pH, initial concentration, and contact time, respectively as follows 12, 150 mg/L, and 10 minutes with methylene blue dye removal of 98.41%.

1 INTRODUCTION

Dyestuff waste generally has non-biodegradable properties because it contains complex aromatic compounds that are difficult to decompose by microbes. The dye waste is harmful to human health and biota that live around polluted water bodies. Generally, these organic compounds are also teratogenic (causing defects in the fetus during pregnancy), carcinogenic and mutagenic, so that they can pose a serious threat to human health (Irawati et al., 2018). One of the dyes that are very dangerous for human health is methylene blue. Methylene blue can cause skin irritation, irritation to the digestive tract. If inhaled, it can cause cyanosis (Fayazi et al., 2016).

To reduce environmental pollution caused by the use of methylene blue, it is important to treat the dye wastewater before being discharged into the environment. One of the methods used to reduce methylene blue dye wastewater that is easy and economical is the adsorption process. Adsorption is an efficient technique to remove odors and reduce the concentration of dyes from solutions perfectly without converting them into more dangerous compounds.

Adsorption based on carbon materials is considered the best available and low-cost technology for the removal of several organic and nonorganic toxic contaminants from aqueous solutions (Yanagisawa et al., 2010). Coal is one of the widely-known carbonaceous raw materials that could be act as a potentially low-cost adsorbent material for toxic water contaminants (A. Gu¨ rses et al, 2014).

The adsorption of dyes using several ranks of coal as adsorbent was studied by several authors. Most research so far has focused on medium and high rank coals, thus paid less attention to low rank coals. In this research the dye removal of methylene blue use low-rank coal of East Kalimantan as adsorbent.

A good adsorption performance for methylene blue also achieved by Yu et al. (2020) in their research "Adsorptive removal of cationic methylene blue and anionic Congo red dyes using wet-torrefied microalgal biochar : Equilibrium, kinetic and mechanism modeling". The maximum adsorption capacities and percent removal for methylene blue were 113.00 mg/g and 26.23% respectively.

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Research was conducted by Myneni et al. (2019) has studied "Modelling and Optimization of Methylene Blue (MB) Adsorption onto Magnesium Oxide Nanoparticles loaded onto Activated Carbon (MgONP-AC): Response Surface Methodology and Artificial Neural Networks" obtained MB removal of 94.34% at pH 5.91, MgONP-AC dosage 0.47 g/L, initial concentration of MB in solution 15mg/L and temperature 313 K and 207 mg/g for MgONP-AC adsorption capacity.

The other research has done by Shokry and Elkady (2019) used Maghara coal which impregnates to nano-activated carbon was inspected for the removal of methylene blue (MB) dye from aqueous solutions. This study obtained the adsorption equilibrium of MB onto prepared nano-activated carbon (NAC) was fitted well with the Langmuir isotherm indicating monolayer coverage of dye molecules on NAC with a maximum mono-layer adsorption capacity of 28.09 mg/g. NAC produced from Maghara coal is an effective adsorbent and low cost material for removal of organic pollutants from wastewater.

Another study related to the absorption of methylene blue dye was carried out by Rizki et al. (2019). By using tamarind seeds as adsorbents with variations in contact time of 30, 60, 120, and 180 min, the adsorbent dosage was 0.3, 0.4, 0.6, and 0.9 g. The best sorption removal of methylene blue was 98.827% with a contact time of 120 min and pH 6 at 0.9 g biosorbent.

This article discusses the dye removal of methylene blue on adsorption process using low rank coal of East Kalimantan as an adsorbent.

2 METHODOLOGY

Firstly, Low rank coal is carbonized at 600^0C for 3 h, then after cold it was activated using 30% concentration of H_3PO_4 for 8 h. The immersion results were then washed to neutral pH and continued with the heating process at 800^0C for 2.5 h. Second, the investigation of the dye removal of methylene blue using the low rank coal as adsorbent runs in a batch adsorption process at room temperature with the adsorbent dosages 100 mg, variations in pH of methylene blue solution (3 to 13), the initial concentration of (50 to 250 mg/L) and the contact time (10 to 90 min). 100 mg of low rank coal adsorbent was added to 100 mL of methylene blue solution at 30 °C were shaker at 150 rpm based on different contact times and initial concentration of methylene blue. Initial pH effect adjusted with 0.10 mol/L of HCl or NaOH. At the end of the period, the shaker was stopped, and the supernatants were filtered through a Whatman 40 filter paper to separate the liquid from the solid phase. The remaining synthetic dye concentrations of methylene blue were determined using UV-Vis Spectrophotometer at 664 nm maximum wavelength (λ_{max}) of adsorption.

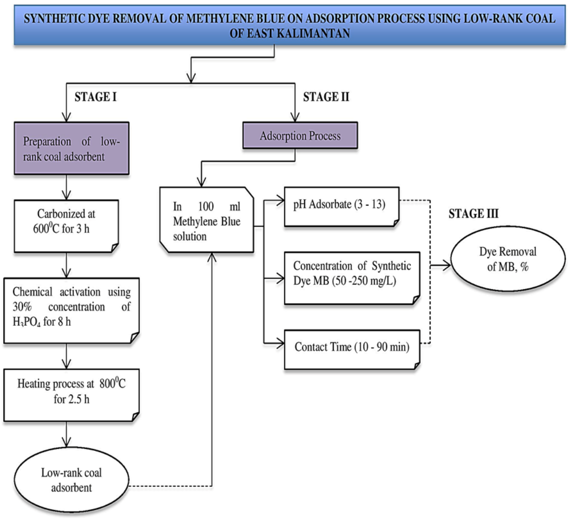

Figure 1: Research framework and design.

Third, determine of dye adsorption performance are expressed by methylene blue dye removal based on the amount of methylene blue adsorbed per gram of the low rank coal adsorbent at equilibrium, q_e (mg/g), were obtained using Equation (1) and Equation (2).

$$Removal, \% = \frac{(C_0 - C_e)}{C_0} x\ 100\% \quad (1)$$

$$q_e = \frac{(C_0 - C_e)xV}{W} \quad (2)$$

Where C_0 and C_e (mg/L) refer to methylene blue concentration at initial and equilibrium, respectively. Meanwhile, V symbol refers to the volume of methylene blue solution (Liter) and W symbol refers to the adsorbent dosage used (mg).

3 RESULT AND DISCUSSION

The low-rank coal of East Kalimantan is used as an adsorbent in the adsorption process of synthetic dye methylene blue. The characteristics of low rank coal to be processed into adsorbent are investigated by proximate analysis to determine the parameters of moisture content, ash content, volatile matter, fixed carbon, and calorific value respectively as follows 33.66%, 3.72%, 32.53%, 33.09%, and 4208 cal/g.

The characteristics of adsorbents were obtained after the activation process consists of moisture content, ash content, volatile matter, fixed carbon and iodine adsorption number respectively as follows 0.45%, 1.12%, 4.2%, 84.23%, and 761 mg/g.

The methylene blue adsorption process results at 100 mg/L concentration of methylene blue dye solution, pH 12, adsorbent dosage 100 mg, and different contact times can be seen in Table 1 and Figure 2.

Table 1: The effect of contact time on methylene blue dye removal.

Time (minute)	C_0 (mg/L)	C_e (mg/L)	Removal (%)
0	100	0	0
10	100	0.60	99.40
30	100	6.57	93.43
45	100	6.64	93.36
60	100	6.61	93.39
75	100	6.70	93.30
90	100	7.34	92.66

Contact time is one of the factors that affect the adsorption process of methylene blue. The reaction rate depends on the number of collisions per unit time. The more collisions that occur, the faster the reaction takes place until equilibrium conditions occur. The equilibrium occurs when the rate of adsorption is equal to the desorption rate.

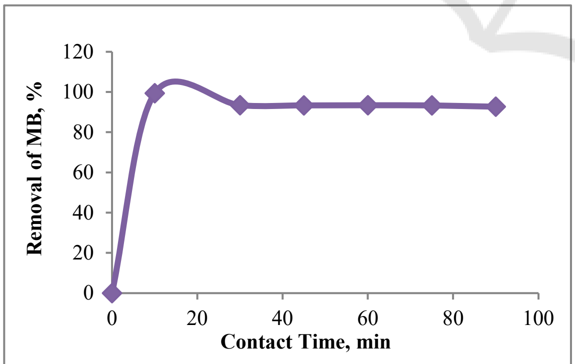

Figure 2: The effect of contact time on methylene blue dye removal.

Figure 2 shows that the methylene blue dye removal increased with the increase of contact time until a certain time and then tends to be constant. In Figure 2, methylene blue dye solution adsorption using low-rank coal as adsorbent occurs very quickly in the first 10 minutes. After that, the methylene blue dye removal decreased slowly and could be assumed to be constant at 30 minutes of the adsorption process. After the adsorption reached equilibrium at the optimum contact time, the addition of the contact time between the adsorbent and the adsorbate further did not significantly affect the absorption of the dye. Hastuti et al. (2012) said that too long physical contact between the dye and the adsorbent causes the dye to be released from the solution over time (desorption). The optimum contact time was obtained at 10 minutes of the adsorption process. Furthermore, the adsorption process for the synthetic dye methylene blue was carried out with variations in the initial concentration of methylene blue at 10 minutes of contact time. The pH of the dye solution was 12 and 100 mg adsorbent dosage.

Table 2: The effect of initial concentration on methylene blue dye removal.

No	C_0 (mg/L)	C_e (m/L)	*Removal (%)*
1	0	0	0
2	50	21.90	56.20
3	100	5.26	94.74
4	150	2.38	98.41
5	200	3.28	98.36
6	250	4.62	98.15

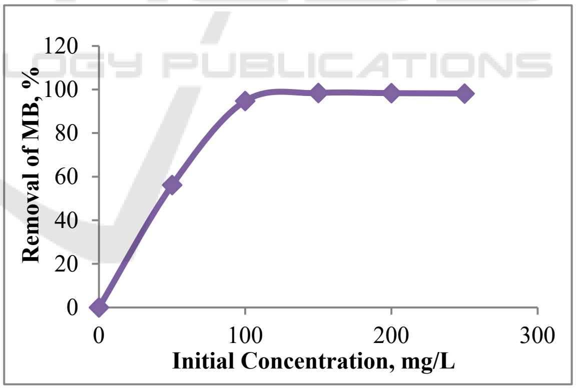

Figure 3: The effect of initial concentration on methylene blue dye removal.

Based on Figure 3, the dye removal increases as the initial concentration of the methylene blue dye solution increases. At 50 mg/L concentration, the methylene blue dye removal was 56.20 %. It is due to the large number of empty spaces on adsorbent surfaces or pores that dyes have not occupied. At 100 mg/L concentration, the percent removal has increased to 94.74%. It indicates that there are still empty spaces on the surface of the adsorbent, namely the availability of active groups from the adsorbent to bind the methylene blue dye. At 150 mg/L concentration, the increase of methylene blue dye removal was not significant because almost all the pores of the low-rank coal adsorbent had been filled with methylene blue (almost saturated). Meanwhile, at a concentration of more than 150 mg/L, the adsorbent is already saturated, so adding the dye concentration will decrease the adsorption ability. The concentration of the dye is related to the active sites on the surface of the adsorbent. If the number of active sites is large enough compared to the amount or concentration of dye, the dye removal will be high until the number of active sites is the same as the dye concentration. Therefore, when the optimum concentration has been reached, increasing the concentration can reduce the adsorption ability. From this research, the optimum methylene blue dye removal of 98,41% was obtained at 150 mg/L concentration, 12 pH of dye solution, 100 mg adsorbent dosage, and 10 minutes contact time of adsorption process.

4 CONCLUSIONS

1. Characteristics of low-rank coal adsorbents used in the methylene blue adsorption process have moisture content, ash content, volatile matter, fixed carbon, and iodine adsorption number respectively as follows 0.45%, 1.12%, 4.2%, 84.23%, and 761 mg/g.
2. The optimum synthetic dye removal of methylene blue of 98,41% was obtained at 150 mg/L concentration, 12 pH of dye solution, 100 mg adsorbent dosage, and 10 minutes contact time of adsorption process.

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