

# Equilibrium and Kinetic Study of Methylene Blue (MB) Adsorption on the Activated East Kalimantan's Low-Rank Coal

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Several studies have been conducted on the adsorption of Methylene Blue (MB) dye using carbon-based materials as an adsorbent. However, there has yet to be a reported study investigating MB removal using the activated East Kalimantan's Low-Rank Coal (LRC). This research aims to investigate the MB dye adsorption behavior onto activated East Kalimantan's LRC to develop a novel low-cost adsorbent. Batch experiments were performed on the adsorption of 50, 100, 150, 200, and 250 mg/L MB dye (100 mL) with different adsorbent dosages (60, 80, 100, 120, and 140 mg) at room temperature, natural pH (3 – 13) and 5, 10, 20, 30, 40, 50, and 60 min contact time. The findings revealed that the optimum condition of the MB dye adsorption was 100 mg of LRC, 100 mg/L of MB concentration, pH of 12, and 5 min of contact time. The adsorption isotherm modeling result showed that the  $R^2$  coefficient was the highest for the model fit provided by the Langmuir isotherm = 0.9474, and the highest possible MB adsorption capacities were 196.08 mg/g. The findings from the experiment fit best by the pseudo-second-order model. The results suggested that an affordable activated LRC from East Kalimantan could remove MB from wastewater.

## 1. Introduction

Organic dyes, metal ions, pesticides, and pharmaceuticals are just a few examples of the hazardous and non-biodegradable chemical pollutants discharged into wastewater, leading to severe and significant environmental problems in the water bodies. Methylene blue (MB) is a cationic thiazine dye that, at room temperature, forms a stable solution in water. MB is widely recognized as a toxic chemical that poses serious problems to human health. Because of the widespread use of MB, this hazardous chemical accumulates in wastewater from textile wastewater. Consequently, developing a practical strategy for treating MB from wastewater is crucial. Some of the technologies that can be used to treat dye wastewater are nano-filtration, reverse osmosis, photocatalysis, aerobic and anaerobic treatments, chemical oxidation, coagulation, biological degradation, ion exchange, flocculation, and adsorption (Khairol et al., 2019). Particularly, adsorption is regarded as one of the most efficient techniques for removing colors because its design is relatively straightforward.

Among the most popular adsorbents used in environmental applications, activated carbon (AC) is the most extensively employed in industries, considering its significant adsorption rate, mechanical force, thermal balance, porous structure, and desirable surface area. Scientists are now concentrating on creating AC as adsorbents from plentiful, low-cost precursors like coal, peat, sawdust, coconut shell, etc. The use of LRC for getting rid of the stubborn MB dye from wastewater, mainly the LRC found in East Kalimantan, as an adsorbent has not been thoroughly investigated until now. Coal is a popular raw carbon source because it can serve as an affordable adsorbent for contaminants in water. In Indonesia, coal is one of the abundant natural resources, particularly in the East Kalimantan province, which is 16.07 billion t or 41.42 % of the total coal in Indonesia. However, around 70 % of the total available resources are generally dominated by low-rank coal.

There are some reported studies on MB dye removal. For instance, Shokry et al. (2019) reported a study on the adsorption of MB dye from aqueous solutions using nanoactivated carbon from industrial mining coal. Jawad et al. (2019) demonstrated the adsorption of MB using Malaysian LRC and used models (e.g., Langmuir) and kinetic analysis for their study. Gokce et al. (2020) also investigated the removal of MB dyes utilizing demineralized LRC from Rawdon Collaery Moira, UK, and described the adsorption mechanism through the adsorbent structure characteristics. Gürses et al. (2014) utilized untreated lignite to adsorb the MB dye, and Shaban et al. (2017) used coal for the adsorption of Safranin-T dye.

There is currently a scarcity of literature on the adsorption of dye removal utilizing activated LRC found in East Kalimantan. As a consequence, the main objective of this study is to fulfill a research gap by investigating a new type of low-cost adsorbent, the East Kalimantan activated LRC, to remove MB's dye from wastewater. The adsorbent's surface morphology and pore characteristics were characterized as part of the research. Furthermore, in batch mode, the influence of crucial adsorption parameters, for example, the dosage of adsorbent, initial pH, contact duration, and initial concentration, were investigated. Finally, kinetic models and experimental data fitting with adsorption equilibrium isotherms (Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich) were applied to examine the adsorption processes on MB dyes through activated East Kalimantan LRC.

## 2. Methodology

### 2.1 East Kalimantan LRC

East Kalimantan LRC was used in the activation process, obtained from Tribakti Inspektama Company, East Kalimantan, Indonesia. Phosphoric acid (Merck) was used as an activator, and Methylene Blue (C.I. 52015, Merck) was used to evaluate the adsorbent's performance.

### 2.2 Preparation of activated LRC

The preparation of LRC refers to the optimum conditions for the activation process to generate activated LRC of East Kalimantan, as established by previous research (Patmawati et al., 2020). 500 g East Kalimantan LRC was processed by crushing, screening, and cleaning in a 100 +120 mesh immediately preceding the activation with a 30 % concentration of  $H_3PO_4$  for 8 hours after the carbonization at 600°C for 3 hours. After neutralizing the pH with water until a pH of 7, the heating process was continued for another 2.5 hours at 800°C. The characteristics of activated LRC adsorbent were investigated using Field-Emission Scanning Electron Microscope (FESEM), Brunauer Emmet Teller (BET), and Fourier Transform Infra-Red (FTIR).

### 2.3 Batch adsorption studies

Batch adsorption experiments were performed in Erlenmeyer flasks with agitation maintained at 150 rpm at 30°C. At the end of the process, the shaker was turned off, and the concentration of MB was measured using a Hitachi-double beam UV-Vis spectrophotometer U-2900/2910 at a wavelength of 664 nm. The initial pH was adjusted from 3 to 13 under 100 mg/L of MB with 100 mg of adsorbent dosage. Different amounts of activated LRC, such as 60, 80, 100, 120, and 140 mg, were used in the experiment. About the MB dye solution, around 100 mL was used to prepare 50, 100, 150, 200, and 250 mg/L under an optimum pH of 12 until the equilibrium was reached. The activated LRC was placed in contact with the solution of MB dye in the required time (5, 10, 20, 30, 40, 50, and 60 min), and the dye concentration was monitored by taking samples at predetermined time intervals.

### 2.4 Experimental data and model fitting

The dye removal efficiency and adsorption capacities are measured using Eq(1) and (2):

$$\text{MBye removal percentage,} = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (1)$$

$$\text{Adsorption capacity, } q_e = \frac{(C_0 - C_e)}{W} \times V \quad (2)$$

$C_0$  represents the initial dye concentration (mg/L),  $C_e$  represents the equilibrium concentration (mg/L),  $V$  is the total volume of dye solution (L),  $W$  is the weight of adsorbent (g), and  $q_e$  is adsorption capacity (mg/g). The kinetic constants were evaluated using pseudo-first order and pseudo-second order. Meanwhile, four adsorption isotherm types were employed to investigate the adsorbent's adsorption capacity and surface properties.

### 3. Result and Discussion

#### 3.1 Characterization of the activated East Kalimantan's LRC

Proximate analysis showed a moisture content of 0.45 %, ash content of 1.12 %, volatile matter of 4.52 %, and fixed carbon of 84.23 %. Meanwhile, the adsorbent's surface morphology was examined utilizing a FESEM under 10,000 magnifications, with a scale bar represented 8  $\mu\text{m}$ . Figure 1(a) shows that the texture of the pore surface is rough and has a large pore on the adsorbent surface.

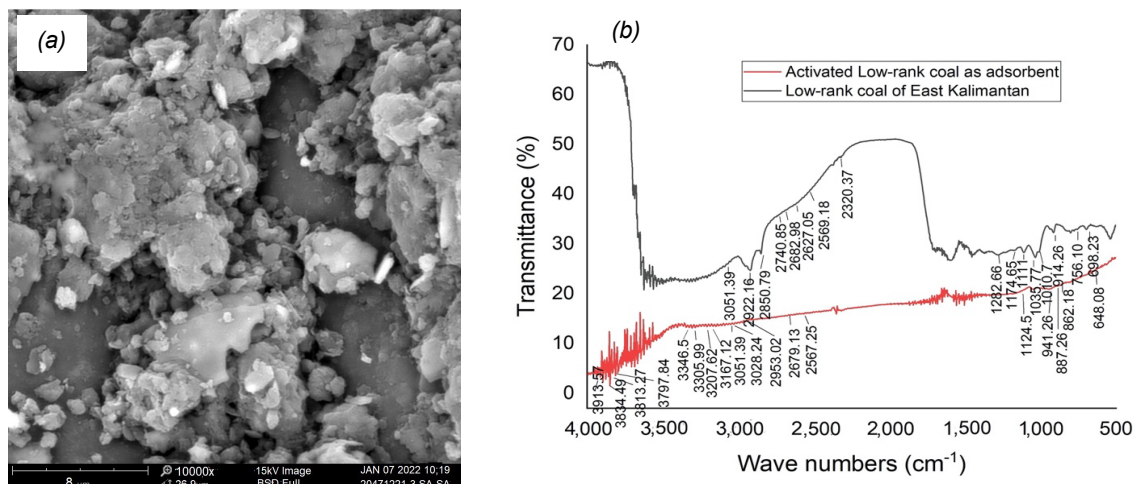


Figure 1: (a) FESEM image of the activated East Kalimantan's LRC; (b) FTIR spectra

Based on BET analysis performed, there was an increase in the surface area, micropore area, and micropore volume of the adsorbent after the activation process, respectively, as follows from 7.872  $\text{m}^2/\text{g}$ , 21.318  $\text{m}^2/\text{g}$  to 321.026  $\text{m}^2/\text{g}$ , 237.73  $\text{m}^2/\text{g}$  and 0.0049  $\text{cc}/\text{g}$  to 0.122  $\text{cc}/\text{g}$ . This proves the activation with a phosphoric acid solution opens the surface and forms many pores on the adsorbent surface. As a result, it will allow the adsorbate to be adsorbed more effectively and increase its adsorption capacity. In addition to FESEM and BET analysis, an FTIR examination was performed to identify the functional groups on the adsorbent surface, as shown in Figure 1 (b). At wave number intervals, significant changes in East Kalimantan LRC as an adsorbent can be observed. Stretching vibration of hydroxyl group, O-H bond (3,600 to 3,900  $\text{cm}^{-1}$ ), aromatic C-H group (3,010 to 3,100  $\text{cm}^{-1}$ ), aliphatic C-H group (2,850 to 2,970  $\text{cm}^{-1}$ ), and aromatic C=C group (1,500 to 1,600  $\text{cm}^{-1}$ ) reduces noticeably. This occurred mainly because of the activation, triggering the decomposition of organic molecules in the LRC structure.

#### 3.2 Adsorption study

##### 3.2.1 Effect of pH and adsorbent dosage

The effect of pH on dye adsorption can reveal details about the adsorption mechanism. Figure 3 (a) shows the dye removal at various pH. The findings revealed that the MB dye removal is nearly constant between pH 3 - 11. However, as the pH raised to 12 and 13, the removal efficiency increased. The lower MB dye removal at pH 3-11 indicates an excess of  $\text{H}^+$  ions over the adsorbent surface. Nevertheless, increasing the pH of the solution causes a decrease in ions with positive charges, favoring ions with negative charges through electrostatic attraction. As a consequence, the negatively charged surface of the adsorbent attracts the positive ions and functional groups of the MB dye, increasing the percentage of MB dye removal by activated East Kalimantan LRC at higher pH. These findings are comparable to those of Ahmad et al. (2021), whereby there was an increase in the removal of MB dyes and a rise in the pH of the solution. Meanwhile, based on Figure 3 (b), the removal efficiency of the MB increased from 94.60 % to 99.40 % when the adsorbent dosage was raised from 60 mg to 100 mg. This signifies that as the adsorbent dose was raised, so were the adsorbent particles, which increased the adsorbent surface area where the dye could be permeated. A further rise in the adsorbent dosage may cause more collisions between the adsorbent particles. On the other hand, as the adsorbent dosage was increased from 60 mg to 140 mg, the MB's adsorption capacity decreased from 157.67  $\text{mg}/\text{g}$  to 70.86  $\text{mg}/\text{g}$ . Considering the removal percentage and the adsorption capacity, the optimum adsorbent dosage for MB adsorption is 100 mg with a 99.4 % MB dye removal and an adsorption capacity of 99.40  $\text{mg}/\text{g}$ .

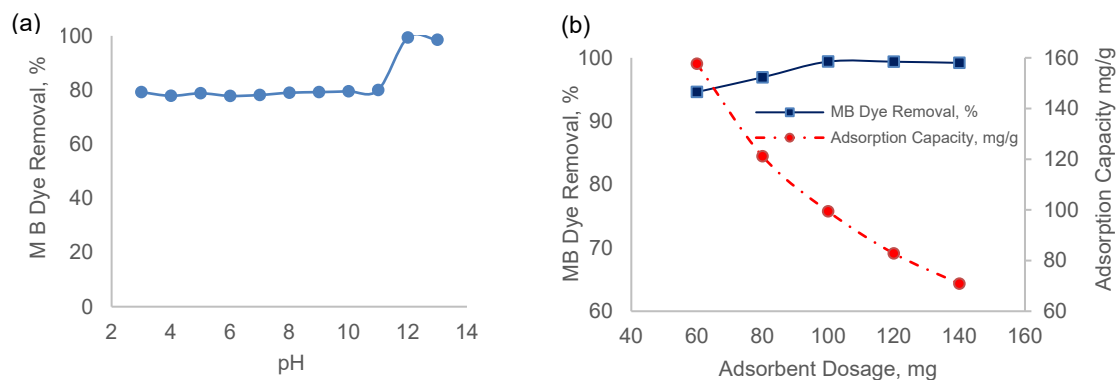


Figure 3: MB dye removal at (a) different pH and (b) different adsorbent dosage

### 3.2.2 Effect of contact time and initial concentration

The interaction time consequence offers an analysis of the adsorbed characteristics in the adsorption process at different interaction times, which applies to the kinetic model. Therefore, the equilibrium time for the optimum MB dye adsorption using the LRC as an adsorbent were studied by determining the removal efficiency at different initial dye concentration, as shown in Figure 4 (a). The MB's acidity solution remained at 12, and the adsorbent dosage was maintained at 100 mg, which is optimum for MB dye removal. As interaction time increased, a greater concentration of the MB dye was removed until equilibrium was reached and all available sorption sites were filled, where almost no additional adsorptive removal reaction could occur. Figure 4 (a) shows that at the initial dye concentration from 50 to 250 mg/L, MB dye removal reaches a plateau after 5 min of interaction. Further, increasing the interaction time (5 to 60 min), the MB dye removal has remained nearly constant. This information is useful for future kinetics modeling because it establishes a time of 5 min as the equilibrium time for MB dye removal using LRC as an adsorbent. This result is similar to other MB dye adsorption studies conducted by Gürses et al. (2014) employing untreated lignite from Askali, Turkey, whereby the equilibrium conditions were obtained in a 5 - 10 min adsorption process. The kinetic study evaluated the MB dye removal from the beginning of the adsorption process until the equilibrium time was reached.

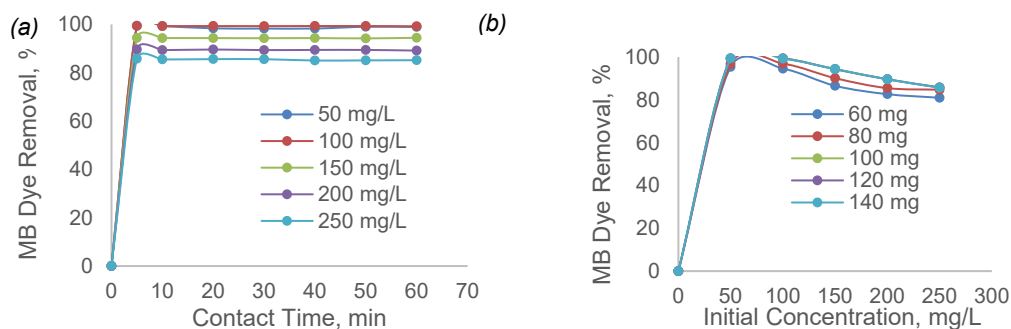


Figure 4: MB dye removal at (a) different contact times and (b) different initial MB concentration

The adsorbent's adsorption capacity relates to the initial concentration of the dye. Commonly, if the active site on the adsorbent surface is saturated, the removal tends to decline with increasing initial concentration. In contrast, if the active site is unsaturated, a higher initial concentration results in a more significant removal because the high dye concentration supplies greater stimulus energy for transferring mass toward the adsorbent. Figure 4 (b) depicts the removal efficiency of MB decreased from 95.40 % - 99.40 % to 80.99 % - 85.85 % when the initial concentration was higher from 50 to 250 mg/L for all the adsorbent dosages (60 mg - 140 mg). Table 1 provides some reported MB dye removal in several studies using different adsorbents, and for this study, the adsorption condition was used at MB dye solution pH of 3-13, 60-140 mg adsorbent dosage, 50-250 mg/L MB dye concentration and 5-60 min contact time.

*Table 1: Comparison of MB dye removal using the activated East Kalimantan LRC as an adsorbent and other adsorbent reported in the literature*

Adsorbent	MB Removal percentage, %	Reference
Activated LRC of East Kalimantan	80.99 – 99.4	This study
Sawdust biochar	98.7	Ichipi et al., 2022
Wet- torrefied microalgal biochar	26.32 – 89.78	Yu et al., 2020
Lemongrass leaf activated carbon	64.36	Ahmad et al., 2021
Magnesium oxide nanoparticles (MgONP)	94.34	Myneni et al., 2019
Malaysian Coal	85.4 – 99.8	Jawad et al., 2019
Activated charcoal from the fruit peel of the plant <i>Hydnocarpus pentandra</i>	90 – 95	Nayak et al., 2020

### 3.3 Adsorption modelling

#### 3.3.1 Adsorption equilibrium isotherm

The adsorption behaviors for each isotherm model can be seen in Table 2, which presents the parameters for each isotherm, along with the  $R^2$  value that indicates which model provides the best fit. When compared to the Freundlich, Temkin, and Dubinin-Radushkevich isotherms, the Langmuir isotherm provided the most accurate description of the MB adsorption, with the accessibility of sites for adsorption determining the maximum possible adsorption capacity. The findings were similar to those of a previous analysis of MB adsorption by various types of coal as adsorbent.

*Table 2: Adsorption equilibrium isotherm model on MB using the activated East Kalimantan's as an adsorbent*

Isotherm Model	Model Parameters	Methylene Blue
Langmuir	qm (mg/g)	196.08
	KL (L/mg)	1.1860
	R2	0.9474
	RL	0.0084
Freundlich	Kf	84.9400
	nf	3.9063
	R2	0.8956
Temkin	B (J/mol)	29.460
	AT (L/g)	25.4240
	R2	0.9418
Dubinin-R	qm (mg/g)	176.60
	Kad (mol <sup>2</sup> / k <sup>2</sup> .J <sup>2</sup> )	9E-08
	E (KJ/mol)	2,357.02
	R2	0.9373

#### 3.4 Adsorption kinetic

Adsorption kinetic modeling assesses adsorbent effectiveness based on adsorption rate and mechanism. The frequent kinetic models used in this experiment are the pseudo-first-order and pseudo-second-order adsorption kinetics, which were employed to estimate the removal of MB dye by activated LRC. The kinetic model adsorption of MB's dye onto activated East Kalimantan's LRC is shown in Table 3.

*Table 3: Adsorption kinetic and mechanism model on MB using the activated East Kalimantan's LRC as an adsorbent under several initial concentrations*

Kinetic and mechanism model	Model parameters	MB dye initial concentration, mg/L				
		50	100	150	200	250
Pseudo first order	q <sub>e</sub> , exp (mg/g)	49.69	99.400	141.54	179.24	214.38
	q <sub>e</sub> , cal (mg/g)	1.950	1.8200	0.6200	2.3800	3.7900
	k <sub>1</sub> (1/min)	0.044	0.0683	0.0328	0.0429	0.0308
	R <sup>2</sup>	0.229	0.3495	0.0526	0.1380	0.1051
Pseudo second order	q <sub>e</sub> , cal (mg/g)	49.51	99.01	140.85	178.57	212.77
	k <sub>2</sub> (g/mg.min)	0.408	1.020	0.5041	0.1045	0.0552
	R <sup>2</sup>	1.0000	1.0000	1.0000	1.0000	1.0000

The experimental data and the pseudo-first-order model were unsavory for several MB dye concentrations because the correlation coefficient  $R^2$  was very low, and the difference between the adsorption capacity obtained from data from the experiment ( $q_e, \text{exp}$ ) and calculated data ( $q_e, \text{cal}$ ) values was large. However, the pseudo-second-order was the most appropriate model, with a high correlation coefficient,  $R^2 = 1.0000$ , and calculated data ( $q_e, \text{cal}$ ) closest to the result of the experimental ( $q_e, \text{exp}$ ) values. The adsorption rate was found to be a function of both the adsorbent and the adsorbate, and the entire performance was governed by chemisorption involving valance bonds, as indicated by a perfect fit to the pseudo-second-order model requirements through the transfer of electrons between MB and adsorbents.

#### 4. Conclusion

The activated East Kalimantan's LRC is a low-cost and environmentally friendly adsorbent. The results showed that at a pH of 12, an adsorbent dosage of 100 mg, and a contact time of 5 min, the MB dosage could be considered optimum at 100 mg/L. The removal efficiency of MB was 99.40 % under these conditions. The Langmuir and pseudo-second-order models explained the adsorption behavior according to the adsorption isotherm and kinetic models. The activated East Kalimantan is a highly effective adsorbent for removing MB dye from wastewater before disposal into the environment.

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