The characteristic of East Kalimantan's low-rank coal as an adsorbent for Methylene Blue (MB) dye removal from simulated textile wastewater

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Abstract. As the interest in developing and applying low-cost adsorbents is growing, the purpose of this paper is to introduce East Kalimantan's low-rank coal as an adsorbent that is abundant in nature but underutilized. This adsorbent was used in a batch adsorption process to remove Methylene Blue (MB) from simulated textile wastewater. The study was conducted at a range of pH values (from 3 to 13) using a variety of low-rank coal adsorbents (60, 80, 100, 120, 140, and 160 mg). Approximately 100 mg/L of MB was added to 100 mL of simulated textile wastewater over 60 minutes using a shaker set to 150 rpm. The pH value and the amount of adsorbent used have a significant effect on removing MB dye. The pH results indicated that the removal of MB dye is relatively constant between pH 3 and 11. However, the removal rate increased when the pH was increased to 12—increased the pH to 13, which resulted in a significant decrease in MB dye removal. Meanwhile, as the adsorbent dosage increased from 60 to 100 mg at pH 12, the removal of MB dye increased and then decreased. At pH 12 and adsorbent dosage of 100 mg, the maximum removal of MB dye was 99.40 %. Thus, East Kalimantan's low-rank coal is an intriguing alternative for removing MB dye from simulated textile wastewater.

1. Introduction

Water pollution is one of the significant environmental problems that threaten all living organisms' health. Water pollution is generally related to human activities such as industrial and agricultural applications. Textile industrial wastewater is one of the significant worldwide concerns, primarily because of emerging substances, such as synthetic dyes, heavy metals, and other toxic contaminants[1,2]. These pollutants are constantly discharged in the environment with poor or no treatment and may cause severe environmental problems[3].

To address this issue, it is necessary to remove these dyes from textile wastewater to deal with biological, ecological, and environmental concerns. Adsorption using carbon materials (such as clay composite, coconut shells, biomasses, activated carbon from agriculture waste, etc.) is widely regarded as the most effective and economical method for removing various organic and inorganic toxic contaminants from an aqueous solution[4]. Coal is a well-known carbonaceous raw material that has the potential to act as a low-cost adsorbent for toxic water contaminants [5].

Several authors studied the adsorption of dyes using several ranks of coal[6–8]. However, no prior art or literature study has examined the treatment of textile wastewater containing dyes such as methylene blue (MB). The majority of research to date has concentrated on medium and high-rank coals, with little attention paid to low-rank coals. Low-rank coal must be modified and developed as an adsorbent in developing low-cost adsorbents with high adsorption capacity.

This paper aims to introduce East Kalimantan's low-rank coal as an adsorbent that is abundant in nature but underutilized. This adsorbent was used to purify simulated textile wastewater of methylene blue (MB).

2. Materials and Methods

2.1 Materials
The raw material of low-rank coal was supplied by Tribhakti Inspektama Samarinda Company, East Kalimantan Province, Indonesia. The simulated textile wastewater was prepared using a methylene blue (MB) dye solution purchased from a local vendor.

2.2 Preparation of Low-rank Coal as Adsorbent
Low-rank coal that has been prepared to a mesh of -100 +120 was carbonized at 600^0C for 3 hours and then cooled for 8 hours before being activated with a 30% concentration of H_3PO_4 for 8 hours. After washing the immersion results to neutral pH, the heating process was continued at 800^0C for 2.5 hours.

2.3 Experiment
The study was performed in a batch adsorption process at room temperature and various pH (from pH 3 to 13) with different dosages of low-rank coal adsorbents (60, 80, 100, 120, 140, and 160 mg). The various pH was adjusted with 0.10 mol/L of HCl or NaOH solution. Approximately 100 mg/L of MB was added to 100 ml of simulated textile wastewater with a shaker at 150 rpm for 60 minutes. At the end of the process, the shaker was stopped, and the remaining MB dye concentrations of the simulated textile wastewater were determined using UV-Vis Spectrophotometer at a maximum wavelength (λmax) 664 nm of MB adsorption.

2.4 Material characterization
The characteristics of low-rank coal to be processed into adsorbent is 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), Fourier Transform InfraRed Spectroscope analysis using FTIR-Shimadzu IR Prestige 21 to detect the functional groups of low-rank coal, Field-Emission Scanning Electron Microscope analysis using Phenom Desktop ProXl to investigate the surface structure/morphology of low-rank coal before and after processed to be adsorbent, and Brunauer-Emmett-Teller (BET) analysis using Surface Area Analyzer (SAA) Quantachrome Novatouch Lx4 to investigate the surface area, pore size and pore volume of low-rank coal adsorbent.

3. Results and Discussion

3.1 Characteristics of low-rank coal of East Kalimantan as adsorbent
The moisture content, ash content, and volatile matter of East Kalimantan Province low-rank coal were reduced from their initial values following an activation process that significantly increased the surface area of low-rank coal. The Indonesian standard for activated carbon as an adsorbent was applied to investigate the characteristics of East Kalimantan low-rank coal as an adsorbent, and the proximate analysis results are presented in Table 1.

Table 1. Characteristics of low-rank coal of East Kalimantan as adsorbent.

Parameters	Values	Indonesian Standards
Moisture content, %	0.45	Max.15
Ash content, %	1.12	Max. 10
Volatile matter, %	4.2	Max. 25
Fixed carbon, %	84.23	Min. 65
Iodine adsorption number, mg/g	761.4	Min. 750

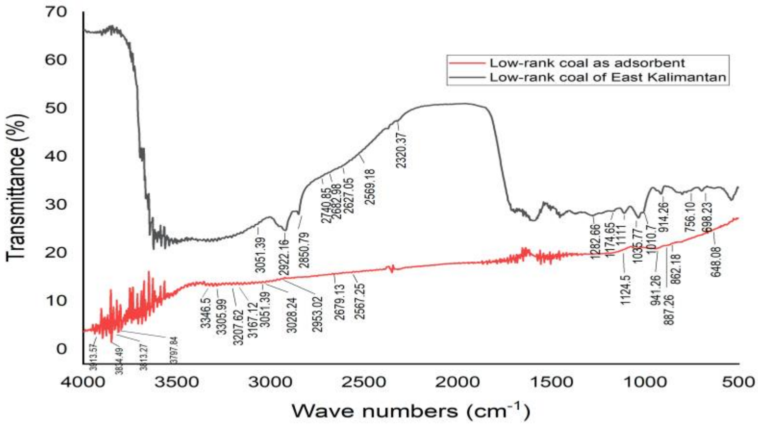
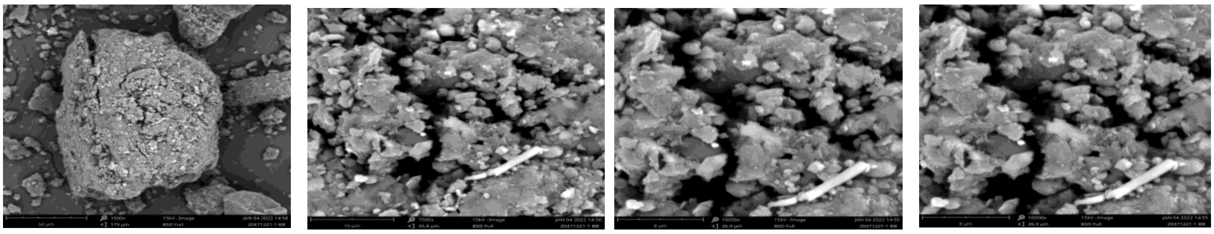
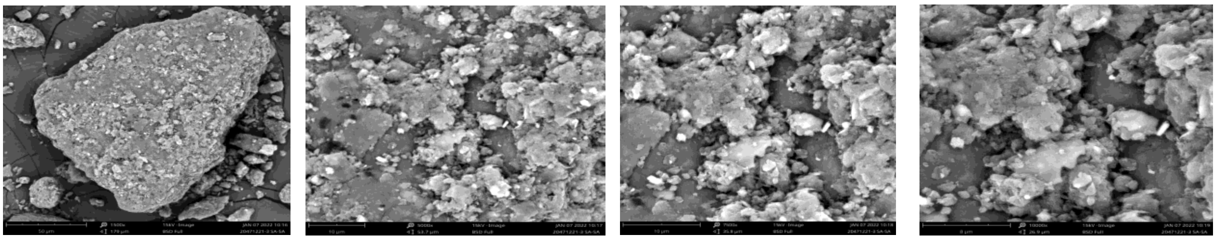


Figure 1. FTIR spectra of different conditioned low-rank coal.

The spectra differences between the low-rank coal of East Kalimantan before and after processed to be adsorbent were compared to understand and identify the nature of functional groups on the adsorbent surface. The significant differences were observed for the raw low-rank coal of East Kalimantan at the wavenumber range from approximately 3600 to 3900 cm^{-1} (showing the stretching vibration of hydroxyl group, O-H bond), 3010 to 3100 (showing the stretching of aromatic C-H group), 2850 to 2970 cm^{-1} (showing the stretching of aliphatic C-H group), 1500 to 1600 cm^{-1} (showing the stretching of aromatic C=C group), 1050 to 1300 cm^{-1} (showing the stretching of C-O alcohol/eter/carboxyl acid), and 690 to 900 cm^{-1} (showing the stretching of aromatic C-H group). After they were processed to be adsorbent, some changes can be observed in the spectra of the low-rank coal adsorbent, especially in the areas of stretching vibration of hydroxyl group, O-H bond (3600 to 3900 cm^{-1}), aromatic C-H group (3010 to 3100 cm^{-1}), aliphatic C-H group (2850 to 2970 cm^{-1}) and aromatic C=C group (1500 to 1600 cm^{-1}) that decreases obviously. This occurred due to the adsorbent being processed, which resulted in the decomposition of organic compounds contained in the low-rank coal structure.



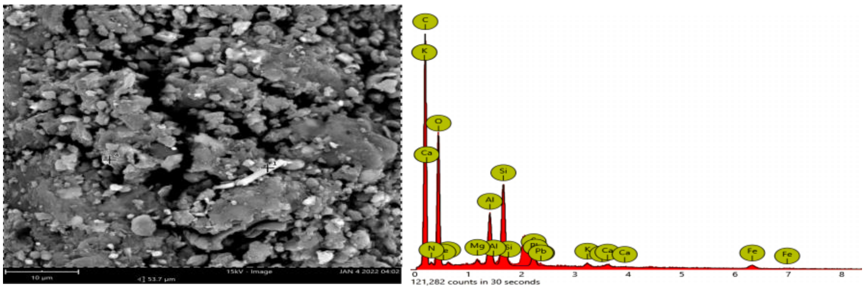
(a) (b) (c) (d)



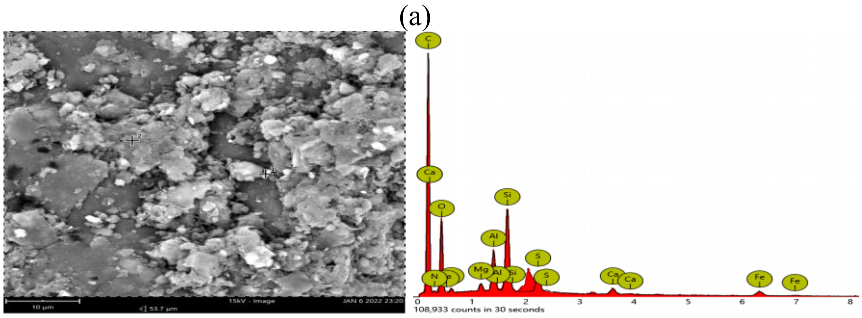
(e) (f) (g) (h)

Figure 2. Morphology structure of low-rank coal (a) - (d) before processed at magnification of 1000x, 5000x, 7500x and 10000x, (e) - (h) after processed to be adsorbent at magnification of 1000x, 5000x, 7500x and 10000x.

In Figure 2, the Field Emission Scanning Electron Microscope (FESEM) analysis revealed that the structures of low-rank coal used as an adsorbent had changed from their initial state. This was confirmed by X-ray spectroscopy analysis of mineral traces. The X-ray spectrum is depicted in Figure 3.



(a)



(b)

Figure 3. SEM-Energy dispersive X-Ray (EDX) (a) Element compositions at the initial surface structure of low-rank coal, (b) Element compositions at the surface structure of low-rank coal as adsorbent.

These analyses revealed the presence of several elements such as carbon (C), oxygen (O), silicon (Si), aluminum (Al), nitrogen (N), sulfur (S), iron (Fe), kalium (K), calcium (Ca), magnesium (Mg), and lead (Pb) in East Kalimantan's low-rank coal at the following concentrations: 62.41%, 28.8%, 2.36%, 1.77%, 2.77%, 0.4%, 0.44%, 0.14%, 0.12%, 0,18% and 0.01%. However, the activation process of low-rank coal resulted in the disappearance of the elements kalium (K), calcium (Ca), and lead (Pb), while the element carbon (C) increased from 62.41% to 71.28%. The activation process increased the stability of the carbonaceous material[9] and revealed changes in the surface morphology of low-rank carbonaceous materials following activation (Figures 2 and 3). The activation process altered the surface properties of the adsorbents.

Table 2. Breunauer Emmet-Teller (BET) analysis of low-rank coal of East Kalimantan as adsorbent.

Parameters	Low-rank coal of East Kalimantan	Low-rank coal as adsorbent
Surface area, m^2/g	7.872	321.026
Total pore volume, cc/g	-0.00501579	0.226554
Average pore size, nm	-1.27434	1.41144
Micropore area, m^2/g	21.318	237.732
Micropore volume, cc/g	0.00487657	0.121797

The surface area, pore size, and pore volume of low-rank coal were determined using Brunauer-Emmett-Teller (BET) analysis before and after it was processed to be adsorbent. These analyses in Table 2 demonstrated how low-rank coal's surface area, pore size, and pore volume changed over time. This is because the process used to create an adsorbent may be open, increasing the pore volume and diameter formed during the carbonization and activation processes. In this study, the surface area, total pore volume and pore size of low-rank coal adsorbent increased from 7.872 to 321.026 m^2/g, -0.00501579 to 0.226554 cc/g, and -1.27434 to 1.41144 nm. Specifically, the adsorbent synthesized from low-rank coal of East Kalimantan was observed to have a microporous surface with the micropore area, and the micropore volume is 237.732 m^2/g and 0.121797 cc/g, respectively. The larger the surface area of the low-rank coal adsorbent, which means the low-rank coal adsorbent has the potential for greater adsorption capacity[10].

3.2 Performance on Methylene Blue Dye Removal from Simulated Textile Wastewater

The pH and adsorbent dosage significantly influence the removal of MB dye. Figure 4 illustrates the findings on the pH revealed that the MB dye removal tends to be constant from pH 3 to 11 at 100 mg adsorbent dosage. However, the removal was increased when the pH was increased to 12. Further increase of the pH to 13 gave an interesting result, where the methylene blue dye removal dropped significantly.

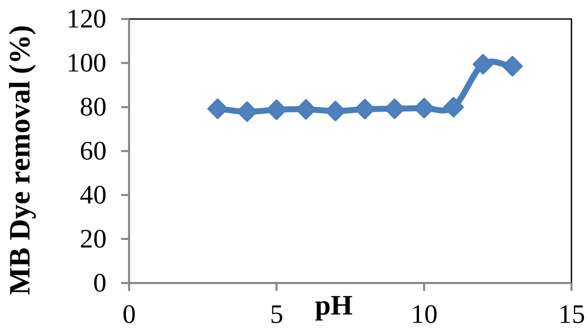


Figure 4. The dye removal of methylene blue at 100 mg adsorbent dosage and different pH.

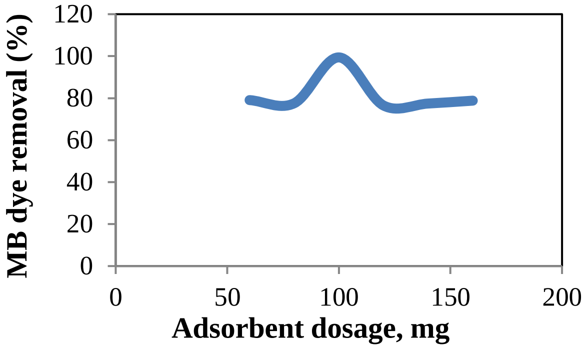


Figure 5. The dye removal of methylene blue at different adsorbent dosages.

The effects of adsorbent dosage on MB dye removal are depicted in Figure 5. The experimental results indicated that as the adsorbent dosage increased from 60 mg to 100 mg at pH 12, the MB dye removal increased and then decreased. The increased absorbent dosage results in a larger surface area and, as a result, more active binding sites for MB adsorption. Increases in the adsorbent dosage did not affect the amount of dye adsorbed, and dye removal remained nearly constant following this point. At pH 12 and adsorbent dosage of 100 mg, the maximum removal of MB dye was 99.40 %.

5. Conclusion

The low-rank coal of East Kalimantan adsorbent was characterized by proximate analysis (moisture content, ash content, volatile matter, fixed carbon and iodine adsorption number respectively as follows 0.45%, 1.12%, 4.2%, 84.23% and 761.4 mg/g). The surface morphology and pore size of low-rank coal adsorbent have been observed under FESEM and Brunauer-Emmett-Teller (BET) analysis and obtained 321.026 m^2/g of surface area, 0.226554 cc/g of pore volume, and 1.41144 nm of average pore size with the micropore area and micropore volume are 237.732 m^2/g and 0.121797 cc/g respectively. At pH 12 and adsorbent dosage of 100 mg, the maximum removal of MB dye was 99.40%. As a result, East Kalimantan's low-rank coal is an interesting alternative for removing MB dye from simulated textile wastewater.

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