

Surface Chemical Structure and Morphological Analysis of Fallen Teak Leaves (*Tectona grandis*) Powder for Methylene Blue Adsorption

*Analisis Struktur Kimia dan Morfologi Permukaan Serbuk Guguran Daun Jati (*Tectona grandis*) untuk Adsorpsi Metilen Biru*

Dwi Ima Hikmawati^{1*}, Embun Rachma Haqiqi²⁾

^{1,2)}Universitas PGRI Madiun, Department of Chemical Engineering

*email: di_hikmawati@yahoo.com

Received: 16/05/19; Revised: 27/06/19; Accepted: 27/06/19

Abstract

In recent year, the research focus has been shifted toward developing of an environmentally friendly system to eliminate any pollutants from Waste. The potential of fallen teak leaves powder for removal of methylene blue has been successfully carried out by batch adsorption system. The purpose of this study is to characterize an adsorbent obtained from local fallen teak leaves. The characterization focused on the surface of chemical structure analysis obtained from Fourier Transform Infrared (FTIR) spectroscopy and morphological analysis by Scanning Electron Microscopy (SEM) in order to get an idea functional group as active site and textural properties. The FTIR results have explained the presence of some functional groups such as $-OH$, $C=C$, COO^- , CO , NO_2 on FTLP surface that could be potential adsorption sites for interaction with MB molecules. The SEM photographs morphology of FTLP surface has a rough surface with almost more non-uniform.

Keywords: Chemical Structure Analysis, Morphological Analysis, Fallen Teak Leaves, Environmentally Friendly Adsorbent, Methylene Blue

Abstrak

Dalam beberapa tahun terakhir, fokus penelitian telah beralih pada pengembangan sistem ramah lingkungan untuk mengurangi polutan dalam limbah. Potensi jaun jati kering untuk mengurangi metilen biru dalam air telah diteliti dan memberikan kinerja yang baik. Tujuan penelitian ini adalah karakterisasi adsorben yang diperoleh dari limbah daun jati lokal. Karakterisasi material difokuskan pada struktur kimia dan morfologi permukaan material untuk mendapatkan struktur kimia dan tekstur permukaan adsorben. Hasil analisis kualitatif berdasarkan spektrum IR menunjukkan bahwa permukaan adsorben mengandung gugus fungsi seperti $-OH$, $C=C$, COO^- , CO , NO_2 yang berpotensi menjadi sisi aktif adsorben. Hasil foto SEM menunjukkan bahwa FTLP memiliki morfologi permukaan yang kasar dan tidak seragam.

Kata kunci: adsorbent ramah lingkungan, analisis morfologi permukaan, analisis struktur kimia permukaan, daun jati kering, metilen biru

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INTRODUCTION

Adsorption has been used as a physico-chemical process over last decades. Adsorption is defined as physically attached or ions and molecules bonding onto another molecules surface, ie. onto two-dimensional surface (Gadd, 2009). Adsorption is the most common form of sorption used in conventional clean up technologies. Adsorption process involved the role of adsorbent.

Activated carbon has been widely used as an adsorbent, but its production cost is expensive and regeneration difficulties make it useful to research about use of natural adsorbents such as *Moringa oleifera* leaf (Bello *et al.*, 2017), *Imperata cylindrica* leaf (Bello & Semire, 2012), peel and bunch of banana (Prachpreecha *et al.*, 2016), chicken eggshell powder and rice husk composite (Haqiqi, 2018), *Salacca zalacca* seed powder (Hikmawati, 2018^b), and teak leaf (Rajendiren *et al.*, 2017).

On the other hand, Teak (*Tectona grandis*) tree belongs to the family of *Verbenaceae*, and several species of *Verbenaceae* have been quite effective remedies for different diseases. Thus a survey was carried out, to record the traditional health care remedies currently practiced by the local people. The teak self has a unique characteristic that the teak's wood usually famous used as furniture and teak leaves also used as food wrap. Despite, the tremendous used of teak tree, but leaves are not fully utilized, they are left to decay and become new constituting wastes in the environment. However, to the best of our knowledge, some studies have been reported on the characterization and use of teak leaf as adsorbent, but need more exploration.

King *et al.* (2006) utilized teak leaf powder to remove Cu(II) from aqueous solutions, but no characterization method has been reported. Vilvanathan & Shanthakumar (2016) used teak leaf powder to remove Co(II) and Ni(II) from aqueous solutions. Rajendiren *et al.* (2017) studied on teak leaves for detergent industrial waste water treatment.

Physical and chemical characteristics of these adsorbent such as the surface functional group, texture, and morphology have been reported. Dwivedi *et al.* (2016) investigated the teak leaf on the removal cyanide from solution. They have been observed SEM and FTIR characterization that indicated the teak leaf has good potential on sorptions processes of cyanide.

The adsorption of process is mainly dependent on the surface properties of the adsorbent and adsorbate's structure and properties (Dávila-Jiménez, 2005). Okada *et al.* (2003) investigated the adsorption properties of active carbons from waste newspaper to remove methylene blue with chemical and physical activation. They showed that the chemically activated products have amounts of functional groups in the surface were found to be higher than the physically activated product. The results showed that adsorption was found higher in the chemically activated products than the physically activated products. Tsai *et al.* (2008) demonstrated that the beer brewery waste as a porous material used to adsorbent for treating industrial waste water containing basic dye. The result observed that the pore properties of adsorbent were higher also deals with the measured adsorption capacities. Due to adsorption is a process that involves a

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material interface, so surface characterization is very necessary to find allegations of interactivity capabilities. The chemical, structural, and elemental composition of any adsorbents play certainly crucial role and have paramount significant in adsorption process (Shrestha, 2016).

Hikmawati (2018^a) has been prepared fallen teak leaf adsorbent for removal methylene blue from aqueous solutions. It was reported that it gave a good performance. The aim of this study was to reveal the nature surface of local fallen teak leaves powder characteristic that prepared as natural adsorbent for methylene blue adsorption. This study provides evidence of relationship between the surface properties of adsorbent and methylene blue in aqueous solution.

MATERIALS AND METHODS

1. Adsorbate

The basic dye used in this study was a technical grade of methylene blue (MB) purchased by merck and used without further purification. Stock solution was provided by dissolving 1.0 g of MB in 1 L of distilled water. The sample solutions were made by diluting it with distilled water to the desired concentrations. The calibration curves were prepared by serial dilutions (1.0 ppm to 5.0 ppm).

2. Adsorbent

The Fallen Teak Leaves Powder (FTLP) used for the preparation of adsorbent was collected from botanical waste that abundantly available at Madiun, Indonesia. The light brown colored dry teak leaves used in this study. The collected leaves were washed with tap water several time to disposal dirt particle and completely dried in sunlight. Leaves

were cut into small pieces, dried, and powdered. Then, the powdered material washed with water tap several time to eliminate adhering dirt until washed water colorless, then followed by rinsing with distilled water. Every washed time, the powder was dried at 67 °C for 24 h. In this present study, the powdered material's fraction having average particle size ~ 40 mesh was used. The resulting product was used as adsorbent without any pre-treatment.

3. Batch Experiment

Batch experiments were undertaken in a 100 mL bottle at ambient temperature in hot plate stirrer at 400 rpm. The adsorbent dose was 1 g FTLP/50 mL working volume of MB solution at pH 5.5. The contact time effect was studied in the range of 15-30 minutes.

In each case sample was separated through centrifuge. Filtrate was analyzed for the MB concentration at 664 nm wavelength using single beam UV/visible spectrophotometer. The percentage removal of MB and equilibrium adsorption capacity (Q_e) was included to Eq.(1) and (2).

$$\% \text{ removal MB} = \frac{C_i - C_f}{C_i} \times 100 \dots \text{Eq. 1}$$

Where C_i is initial MB concentration and C_f is final MB concentration.

$$Q_e = \frac{(C_i - C_f)V}{w} \dots \text{Eq 2.}$$

Where Q_e is amount of MB adsorbed (mg/g), w is adsorbent weight, V is volume of solution (L), C_i is initial MB concentration and C_f is final MB concentration.

4. Characterization

The surface structure of the prepared FTLP was recorded by scanning

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electron microscopy (SEM) measurement, and to analyze the functional groups present on the prepared FTLP surface that performed by fourier transform infrared (FTIR) spectra of the adsorbents were developed between the wavenumber range of 500 cm^{-1} to 4500 cm^{-1} .

RESULT AND DISCUSSION

Methylene blue was chosen for this study because of its known strong interaction onto interface solid material. Methylene blue has a chemical formula $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$ with molecular weight is 319.86 g/mol .

The effect of contact time on the MB removal by FTLP at initial concentration 50 mg/L showed rapid adsorption of dye in range work time. Figure 1. shows a plot of the amount of MB adsorbed (Q_e) versus contact time for room temperature.

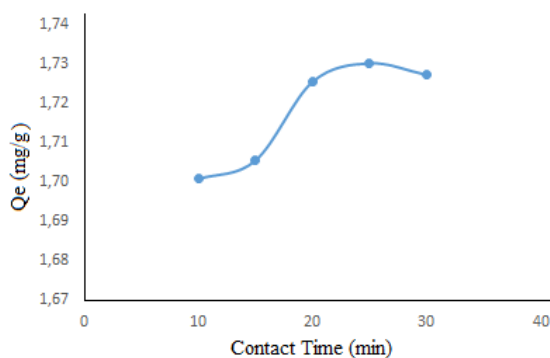


Figure 1. Effect of Contact Time

It was observed that the maximum amount of dye adsorption was achieved at 25 minutes. Further, the rapid adsorption of MB occurred in the fifteenth minutes to the twentieth minutes. Thereafter it proceeds at a lower rate. At 25 minutes adsorption process, it happened optimum contact time of MB adsorption. It showed that the amount of MB adsorption by FTLP

and remained in the solution were in equilibrium. After 25 minutes application until 30 minutes, the ability of FTLP to adsorb MB decreased. As shown in Figure 1, adsorption of MB onto FTLP increased upon time and reached equilibrium after 25 minutes of contact time.

Table 1. Effect of Contact Time on MB Removal

Contact Time	C_i (mg/L)	C_f (mg/L)	Removal (%)
10	50	1,4025	97,19
15	50	1,2681	97,46
20	50	0,6966	98,61
25	50	0,5622	98,88
30	50	0,6462	98,71

It is understood from Table 1 that final concentration of MB in the residual process decreases steeply from the tenth minutes to twenty-fifth minutes, then increase to thirtieth minutes. The maximum amount of MB adsorption by FTLP is found to be 98,88% for a weight 1 gr adsorbent. This shows that as a contact time increase, the MB adsorption also increases. In addition, increasing the contact time increases the number of collision between particle of MB and FTLP surface was bigger.

Surface Morphology Analysis by SEM

The surface morphology of the starting FTLP was studied by employing scanning electron microscopy (SEM). SEM is a primary tool for characterizing the morphology and physical properties of the adsorbent surface. The FTLP was scanned by electron microscope at different magnifications.

Figure 2. shows the SEM photographs of the prepared FTLP at magnifications (a) 1000 and (b) 4000 respectively. Figure 2a, it can be noted that

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prepared FTLP has a heterogeneous surface. It was observed that there are some prominent part on the surface, dense, and there were a series of overlaps. A series that overlap was a rough surface with an almost not uniform structure, there is a smooth and rough part that allows the attachment of dissolved species to the surface.

It is revealed from the SEM figure at larger magnifications (Figure 2b), that the FTLP surface is found contains a number of rough parts. The prominent part observed in various shape (rough, dense, flower-like, root-like and ruptured). The overlapping series also observed in the non-uniform structure. It formed clusters

with various shapes. The cavities might form by connecting structure and the rough part. The cavities structure could be observed in a cylinder and oval form.

That the FTLP surface is found contains cavities and rough series, where this condition allows the MB molecules to have adhered and adsorbed into these surfaces. It has a similarity with the reference that has been reported in the previous study. The SEM photographs of the referenced adsorbents showed that the teak leaf powder surface has a rough surface with an almost more non-uniform property (Mishra *et al.*, 2015; Jafar & Balasubramanian, 2010).

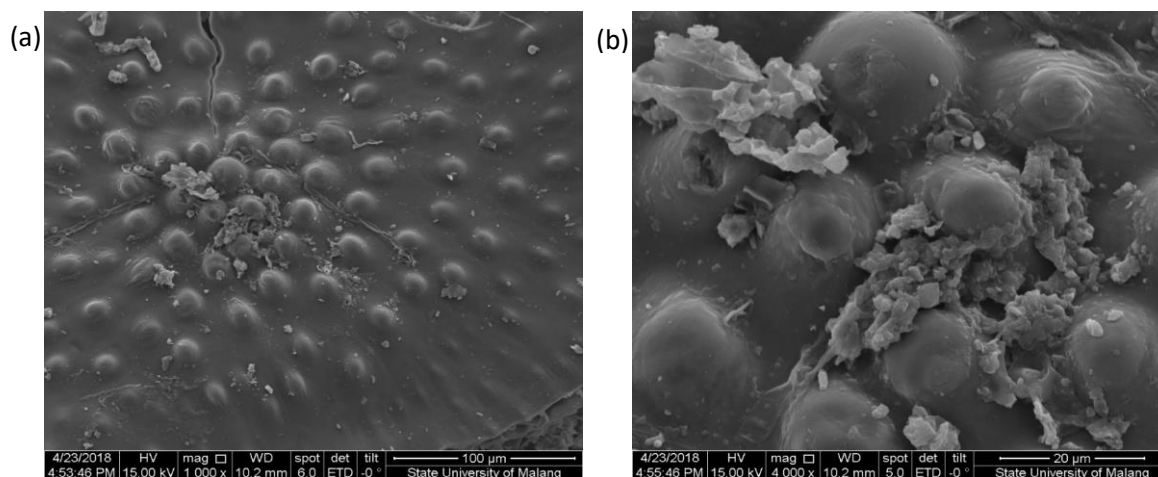


Figure 2. SEM Photographs of Adsorbent FTLP at Different Magnifications

Surface Chemical Structure by FTIR

To understand the mechanism of MB adsorption using Fallen Teak Leaves Powder (FTLP), FTIR result was carried out to analyze the starting and final treatment of the materials. The FTIR spectra of FTLP display a number of absorption peaks, indicating the complex nature of the material.

The FTIR spectroscopic analysis of starting FTLP shows a sharp and

broadband at 3426 cm^{-1} representing stretching of hydroxyl bonded ($-\text{OH}$) or $-\text{NH}$ groups. The presence of bands located at the region on $2973\text{--}2867\text{ cm}^{-1}$, which correspond to the position of asymmetrical and symmetrical stretching of methyl and methylene groups in the aliphatic and cyclic hydrocarbons. The bands located at 1752 cm^{-1} indicated to carbonyl groups and other functional groups. The band at 1642 cm^{-1} represent the aromatic ring vibration assigned to

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aromatic carbonyl and carbonyl motion in carboxylic acid with intermolecular hydrogen bonding. Several bands appearing in the range of 1518 until 1106 cm^{-1} were assigned to the position of C=C stretching vibration of cycloalkenes, S=O symmetric stretching frequency of organic

sulphates, and C–O alcoholic stretching vibrations. Bands seen between 807-629 cm^{-1} likely shows NO_2 bending vibrations. The band at region 486 cm^{-1} assigned to C–C bending vibrations of normal alkenes.

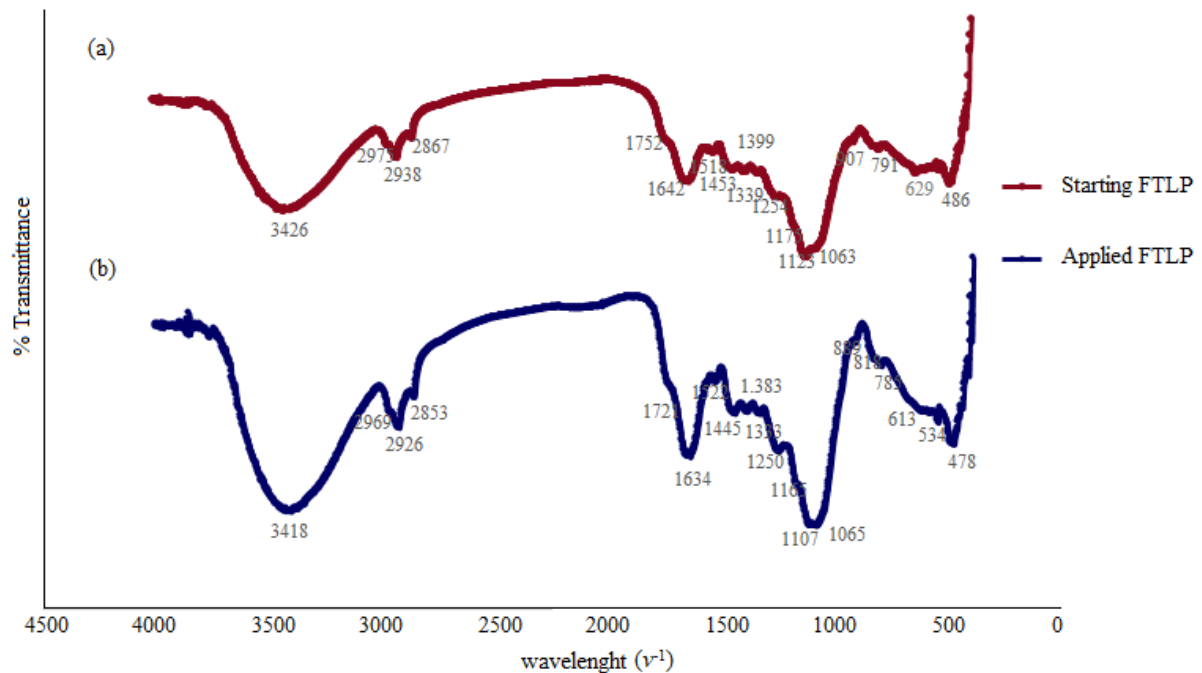


Figure 4. Profile FTIR Spectra of (a) FTLP before and (b) after MB Adsorption

Table 2. The FTIR Spectral Characteristic of the starting and applied FTLP

IR Peaks		Assignment
Starting FTLP (cm ⁻¹)	Applied FTLP (cm ⁻¹)	
3426	3418	Stretching of hidroxyl bonded (–OH) or –NH groups
2973-2867	2969-2853	Asymmetrical and symmetrical stretching of methyl and methylene groups in the aliphatic and cyclic hydrocarbons
1752	1727	Carbonyl groups and other functional groups
1642	1634	Aromatic ring vibration assigned to aromatic carbonyl and carbonyl motion in carboxylic acid with intermolecular hydrogen bonding
1518-1106	1522	C=C stretching vibration of cycloalkenes, S=O symmetric stretching frequency of organic sulphates, and C–O alcoholic stretching vibrations
807-629	889	NO_2 bending vibrations
486	478	C–C bending vibrations of normal alkenes

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Thus the FTIR result has confirmed the existence a number of some functional groups such as –OH, –NH, C=C, COO⁻, CO, NO₂ on the FTLP surface which could be potential active sites that interaction with MB molecules. The FTIR spectral characteristic of the starting and applied FTLP are labeled in Table 2.

The vibration peaks contained on applied FTLP surface located in these areas appear with a sharper band than peaks contained on starting FLTP. The peaks were shifted or appeared may correspond to the formation of a chemical bond between the functional groups present on the FTLP surface. This is the one can ascertain the feasibility of MB adsorption onto the FTLP surface with adequate and good performance of removal efficiency. The presence of shifted peaks deals with previous study reported by Mishra (2015) that adsorption of methylene blue onto teak leaf powder gave adsorption peak at lower and upper region.

CONCLUSION

In this research, an adsorbent prepared from local fallen teak leaves powder (FTLP) has been successfully done. The materials suggest the versatility to remove MB due to the surface characteristic. Furthermore, the SEM characterization result showed that the FTLP surface has a rough surface with an almost more non-uniform structure. The FTIR result has confirmed the presence of some functional groups such as –OH, C=C, COO⁻, CO, NO₂ on the surface of FTLP. The maximum amount of MB adsorption by FTLP is found to be 98,88% for a weight of 1 gr adsorbent.

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