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# Adsorption of Methylene Blue by Magnetic Activated Carbon/Chitosan Composites Prepared from Spent Coffee Grounds

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**Abstract.** Spent coffee grounds were used as the main ingredient for composing magnetically activated carbon/chitosan (MACC) composites and synthesized using the coprecipitation method. The SEM-EDX characterization was used to understand the elemental identification and morphology of the adsorbent before the MACC was applied to remove methylene blue (MB) from the aqueous solution. Magnetic activated carbon/chitosan was fabricated under the following circumstances: the molar ratio of ferrous/ferric ions was 2:1, and the coprecipitation temperature was 60 °C for five hours. Adsorption parameters for MB were investigated. The adsorption by MACC was evaluated thermodynamically for the discharge of MB from an aqueous solution as a function of temperature. Calculations of thermodynamic parameters were conducted. Batch adsorption experiments were operated at 308 K, 318 K, and MB concentration of 5-50 mg L-1 to investigate the adsorption behavior. According to the results, MACC has a porous structure. The adsorption process is more reactive upon raising the temperature, commonly known as endothermic. Based on R<sup>2</sup> values, the adsorption of MB onto MACC was found to fit the Freundlich model best. The maximum adsorption capacity of the MACC was counted as 24.5 mg/g. The adsorption process is spontaneous, which was concluded from calculating thermodynamic parameters.

**Keywords:** adsorption, magnetic activated carbon/chitosan, methylene blue, spent coffee grounds

#### 1. Introduction

Water pollution in Indonesia is atrocious. This pollution is caused by human activities such as throwing garbage into rivers, draining industrial waste into rivers or the sea without being processed, disposing of livestock, agricultural waste, and mining waste. For instance, industrial waste is one of the leading causes of polluted water in the textile industry. They produce liquid waste containing dyes in large volumes that are improperly treated and impact a water body. This fluid waste is generated from the textile refinement and obtained from chemical liquids that print motifs on fabrics.

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Dyes have complex chemical structures, are toxic, and carcinogenic. The dyes can cause serious effects on humans and the water. Methylene blue is a cationic dye widely used in the textile industry to improve artistic points and have a higher selling value. Methylene blue is usually used for dyeing cloth, paper, and wood [1].

Several methods have been used to remove dye waste, such as the adsorption method, chemical oxidation [2], electrochemical treatment [3], microbiological or enzymatic decomposition [4], chemical and physical precipitation, and photocatalyst [5]. The adsorption method is the most applicable due to its efficiency, being inexpensive, easy to operate, recyclable, and non-toxic [6]. Various adsorbents, such as activated carbon, have been used for the adsorption process. Activated carbon has a high absorption capacity and a large surface area. However, activated carbon is costly, and the fabrication of activated carbon from biomass waste such as spent coffee grounds is promising. Their high carbon content of about 50% is used to reduce the cost of fabricating activated carbon [1]. The previous carbon sources converted to activated carbon were palm waste [7], orange peel waste [8], bagasse, wheat straw [9], etc. Activated carbon has disadvantages, i.e., separating in the downstream separation process and reusing after the adsorption process is complex. Many researchers combine the magnetic particles in the form of Fe<sub>3</sub>O<sub>4</sub> nanoparticles, which can increase the adsorption capacity of pollutants and simplify the downstream separation process [10].

The removal of dyes in waste by the adsorption method was combined with chitosan. Chitosan is utilized for its versatile application, abundance, cheapness, good affinity with pollutants, non-toxic, biodegradable, and environmental safety [5]. However, after adsorption, chitosan-based adsorbents become saturated, toxic, and non-biodegradable [11]. The combination of chitosan, magnetic particles, and activated carbon is expected to increase the effectiveness of removing dyes [10] and the economic utilization due to the recycling and regeneration of adsorbents. Therefore, a combination of chitosan-magnetic activated carbon is required to produce a higher adsorption capacity, more efficiency, and a more expensive product. The coprecipitation method synthesized magnetic-activated carbon/chitosan (MACC) [12]. This paper will discuss the fabrication of magnetic-activated carbon/chitosan. Furthermore, we examine the adsorption behavior of methylene blue.

#### 2. Method

#### 2.1 Materials

Spent Coffee Ground (SCG) was collected from a coffee shop near Universitas Jember. Chitosan, methylene blue, distilled water, HCl 0.1 M, H<sub>3</sub>PO<sub>4</sub> 0.1 M, acetic acid 3%, Fe(III) FeCl<sub>3</sub>.6H<sub>2</sub>O, and Fe(II) FeCl<sub>2</sub>.4H<sub>2</sub>O, NaOH 10% were used for the fabrication of MACC.

# 2.2 Preparation of Activated Carbon From Spent Coffee Grounds

SCG was dried in the oven at 105 °C for five hours, carbonized at 600 °C for 4 hours, and then cooled. Subsequently, the SCG was sieved with a size of 100 mesh. 30 g of coffee grounds were soaked in 100 ml of 0.1 M HCl and 0.1 M H<sub>3</sub>PO<sub>4</sub> activator solutions for 48 hours and filtered. Then the activated carbon was washed using demineralized water until neutral and dried at 110 °C for 3 hours [13].

## 2.3 Preparation of Magnetic Activated Carbon/Chitosan (MACC)

Upon addition of 100 ml of acetic acid (3% v/v), 3 g of chitosan dissolved at ambient temperature for 12 hours. Then, it was stirred at 60 °C for 30 minutes to produce a soluble solution. Fe (III) (as FeCl<sub>3</sub>.6H<sub>2</sub>O) and Fe (II) (as FeCl<sub>2</sub>.4H<sub>2</sub>O) in the ratio (0.02 mol: 0.01 mol) were dissolved and added to the mixed solution. The solution was then kept stirring for 2 hours. The mixed solution was blended with 3 g of activated carbon dissolved in 100 ml of acetic acid (3%) and stored at 60 °C with stirring at 800 rpm for 3 hours. A solution of NaOH (10%, w/v) was then added dropwise to the solution. Then, it was stirred for 24 hours to solidify, and the precipitate was separated from the NaOH solution and washed with demineralized water several times. The washing process was performed until the filtrate became neutral. The solid mixture was dried at 60 °C using an oven for 5 hours. The solids are then crushed with a mortar and stored in a desiccator [14].

## 2.4 Adsorption Experiments

A stock solution of methylene blue (MB) (1000 mg/L) was prepared by dissolving the required amount in demineralized water. MB solutions with a 5 to 50 mg/L concentration were prepared by diluting the stock solution. All adsorption tests were carried out in a 100 ml stopper Erlenmeyer flask and shaken in an incubator with temperature control at 120 rpm and natural pH (for MB: 7.73). The adsorption experiments were obtained by mixing 50 mg of adsorbent with 50 ml of dye solution with different initial concentrations (5-50 mg/L) in a 100 ml stopper Erlenmeyer flask at 35 °C and 45 °C. The mixtures were shaken at 120 rpm for 24 hours. Subsequently, the mixtures were centrifuged for 10 minutes at a speed of 2000 to separate the

filtrate and the adsorbent [14]. The filtrate concentration of each solution was measured by absorbance (MB adsorption wavelengths = 665 nm) using a UV/vis spectrophotometer. Calculating adsorption capacity at equilibrium, q<sub>e</sub>, in mg/g was conducted using equation (1).

$$q_e = \frac{(C_0 - C_e)V}{1000 \times M_{MACC}} \tag{1}$$

where  $C_0$ ,  $C_0$  was the initial and equilibrium concentration (mg  $L^{-1}$ ) of the MB solution, V was the volume of the MB solution (mL), and  $M_{MACC}$  was the mass of the added MACC.

Adsorption isotherm parameters for MB were investigated. The experimental data have been used to fit the Langmuir and the Freundlich isotherm model equations. Furthermore, the adsorption by MACC was examined thermodynamically for the removal of MB from an aqueous solution. Calculations of thermodynamic parameters were conducted [15].

## 3. Result and Discussion

# 3.1 Morphology of MACC

Magnetically activated carbon-chitosan sample was characterized using Scanning Electron Microscopy-Energy Dispersive X-ray Analysis (SEM-EDX) at the Integrated Laboratory of UNDIP. Figure 1 shows the morphology of MACC with different magnifications. SEM results indicate that the MACC has a porous framework and many cavities on its surface. The surface resembles a honeycomb structure. The pore structure suggests the presence of chitosan, which contributed to forming a bead-like structure [16]. Figure 1 shows that Fe<sub>3</sub>O<sub>4</sub> nanoparticles are distributed between the chitosan polymer chains [17]. EDX analysed surface elements. The graph and EDX analysis data show elements C, O, and Fe as the three main components. EDX results confirm the presence of Fe<sub>3</sub>O<sub>4</sub>, chitosan, and activated carbon, while other elements such as Zn, Cu, and Mg are impurities [10].

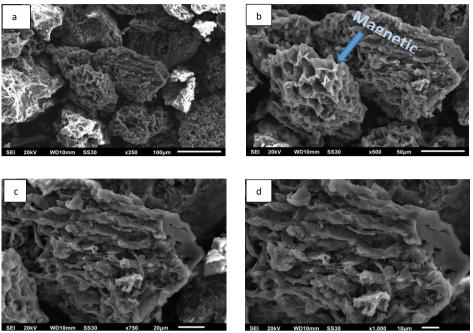


Figure 1. SEM images of MACC (a) 250x (b) 500x (c) 750x (d) 1000x

Table 1. EDX analysis data of MACC

Element	Mass %		
С	73.13		
O	21.38		
Na	0.14		
Mg	0.23		
P	0.19		
Cl	0.10		
K	0.12		
Ca	0.34		
Fe	3.65		
Cu	0.44		
Zn	0.28		
Total	100		

# 3.2 Adsorption Experiments

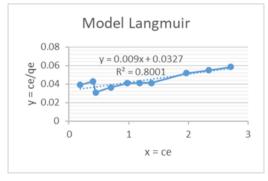
# 3.2.1 Adsorption Isotherm

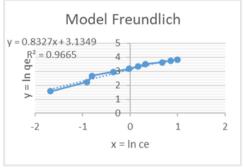
Langmuir and the Freundlich isotherm models are usually used to interpret adsorption isotherms. The results of the two isotherm models and each calculated parameter are shown in Table 2.

Model Isoterm	T	Parameter Value	
Langmuir	35 °C	qm (mg/g)	111,547
		Ka (L/mg)	0,2741
		$R_{L}$	0,06-0,4
		$\mathbb{R}^2$	0,8001
	45 °C	qm (mg/g)	78,067
		Ka (L/mg)	0,5023
		$R_{L}$	0,03-0,167
		$\mathbb{R}^2$	0,8909
Freundlich	35 °C	Kf	22,985
		1/n	0,8327
		$\mathbb{R}^2$	0,9665
	45 °C	Kf	24,4962
		1/n	0,75098
		R <sup>2</sup>	0,9369

Table 2. The adsorption isotherm parameters of MB on the prepared MACC

Table 2 shows the calculated parameter of MACC. The Kf value for MB increases with increasing temperature from 22.985 to 24.4962 mg/g. The result indicates a greater tendency for the adsorption of MB molecules by MACC at higher adsorption temperatures [1]. In addition, the values for n and 1/n at a temperature of 35 are 0.832 and 1.2. In contrast, at a temperature of 45 °C, namely 0.751 and 1.331, the result shows that the surface is more heterogeneous, and n>1 indicates the physical adsorption mechanism or physical adsorption process. Figure 2 shows a plot of the curve obtained from experimental data.





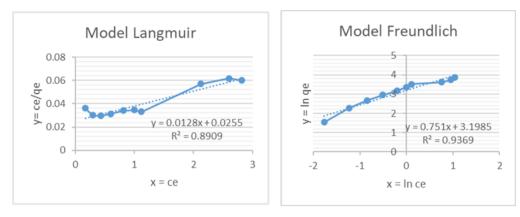


Figure 2. Langmuir and the Freundlich model at temperatures 35 °C (up) and 45 °C (below)

Figure 2 and Table 2 show that the Freundlich model is best qualified with a determination coefficient of  $R^2 = 0.9665$  compared to the Langmuir model, which has a determination coefficient of  $R^2 = 0.8001$ . The surface of the adsorbent is heterogeneous and multilayered. Likewise, at a temperature of 45 °C, the Freundlich model is also best fitted with a correlation coefficient of  $R^2 = 0.9369$  compared to the Langmuir model, which has a correlation coefficient of  $R^2 = 0.8909$ . The Freundlich model shows heterogeneous and multilayer adsorbents.

As for the Langmuir model, the R<sub>L</sub> value for MB adsorption using magnetic activated carbon at 35 °C is between 0.06 and 0.4, while at a temperature of 45 °C, it is between 0.03 and 0.167. This result indicates an interaction between the dye and the adsorbent surface in the monolayer [10]. The adsorption experiment showed that the adsorption capacity increased at high temperatures. Qm is an essential constant in the Langmuir isotherm model. The maximum adsorption capacity of the adsorbent in this experiment was not too large, namely 24,4962 mg/g. The lower adsorption performance of activated carbon observed in this study suggests that this adsorbent has a low affinity to methylene blue.

## 3.2.2 Adsorption Thermodynamic

As illustrated in Table 2, the resulting enthalpy change is positive at different temperatures. The result indicates that MB adsorption by MACC is an endothermic reaction and supports MB adsorption at high temperatures [18]. The results of MB adsorption by MACC are endothermic reactions, and support that MB adsorption at high temperatures can be seen in Table 3.

Konsentrasi	$\Delta \mathbf{H}^0$	$\Delta S^0$	∆G <sup>0</sup> (J/mol)			
MB (mg/L)	(kj/mol)	(kj/mol/K)	30 °C	35 °C	40 °C	45 °C
15	16,51661		-	-	-	-
			8220,14	8920,70	9333,37	9438,07
25	15,90915	0,0776	-	-	-	-
			7508.07	210542	808661	2033.75

Table 3. The adsorption thermodynamic parameters of MB on the prepared MACC

The magnitude of the H<sup>o</sup> value indicates the type of adsorption process; the H<sup>o</sup> value (15-16 kJ/mol) is lower than the range of adsorption enthalpy according to the literature, which is < 20 kJ/mol. The result indicates the type of adsorption is physical adsorption [19]. The positive value of So on MB adsorption suggests an increase in irregularity and randomness at the adsorbent-solution interface during the adsorption process. If the resulting So is negative, then there is no randomness in the adsorption process [18]. The value of Gibbs free energy, G<sup>o</sup>, is negative for both concentration and temperature variations, indicating that the adsorption occurs spontaneously, is very favorable, and is profitable. The value of Go becomes negative with increasing temperature, suggesting that higher temperatures are suitable for MB adsorption, and high temperature is the most critical factor in increasing the active adsorption capacity of chitosan species. In addition, for physical adsorption, the literature explained that Go ranges from -20 to 0 kJ/mol, and for chemical adsorption, it ranges from -80 to -400 kJ/mol. The value of G° in this experiment produces between -7 and -9 kJ/mol (according to Table 3), and the adsorption type is physical. This result is in accordance with the value of "n" obtained from the Freundlich isotherm model, namely, the value of "n" is more than 1. This physical adsorption causes the capacity of the carbon-chitosan adsorber to increase with increasing temperature. This increases the vibrational energy of the dye ion to react with the activated carbon-chitosan type at high temperatures [20]. If the resulting value is overall positive, the reaction does not occur spontaneously, and energy is needed to continue the reaction [18].

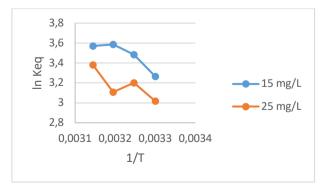


Figure 4. Thermodynamic chart temperature 30, 35, 40, 45 °C

## 4. Conclusions

The coprecipitation method, as one of the nanoparticle synthesis methods, was used to fabricate magnetic activated carbon/chitosan (MACC). Based on SEM, MACC has a porous structure. The adsorption process is more reactive upon raising the temperature, commonly known as endothermic. The experimental data were fitted to the Langmuir and the Freundlich isotherm models. The results showed that based on R<sup>2</sup> values, the Freundlich model corresponds with the adsorption behavior of MB onto MACC. The maximum adsorption capacity of the MAC was calculated as 24,5 mg/g. The adsorption process is spontaneous, which was concluded from calculating thermodynamic parameters.

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