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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 the composing of 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 for the removal of methylene blue (MB) from the aqueous solution. Magnetic activated carbon/chitosan was fabricated with the subsequent circumstances: the molar ratio of ferrous/ferric ions was 2:1, coprecipitation temperature was at 60°C for 5 h. Adsorption parameters for MB were investigated. The adsorption by MACC was evaluated thermodynamically for the discharge of MB from an aqueous solution as adsorption reckons on 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, a process commonly known as endothermic. Based on R2 values, the adsorption of MB onto MACC was found best fitted to the Freundlich model. The maximum adsorption capacity of the MACC was counted as 24.5 mg/g. The adsorption process is spontaneous, which was concluded from the calculation of 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 sea without being processed, disposing of livestock, agricultural waste, and disposing of mining waste. Industrial waste is one of the main causes of polluted water, for instance, the textile industry. They produce liquid waste containing dyes in large volumes that are not treated properly and impact a water body. This liquid waste is generated from the textile refinement process and obtained from chemical liquids in printing motifs on fabrics.

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Dyes have complex chemical structures, toxic and carcinogenic substances. The dyes can cause serious effects on humans and 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, in-expensive, ease of operation, can be recycled, and non-toxic [6]. Various adsorbents have been used for the adsorption process, such as activated carbon. Activated carbon has a high absorption capacity and large surface area. However, the price of activated carbon is very expensive, and the fabrication of activated carbon from biomass waste such as spent coffee grounds are 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., difficult to separate in the downstream separation process, and difficult to reuse after the adsorption process. Many researchers proceed to combine the magnetic particles in the form of Fe_3O_4 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 due to its versatile application, abundance, cheapness, good affinity with pollutants, non-toxic, biodegradable, and safe for the environment [5]. However, chitosan-based adsorbents become saturated, toxic, and non-biodegradable after adsorption [11]. The combination of chitosan, magnetic particle, and activated carbon is expected to increase the effectiveness of removing dyes [10] and the economic utilization due to adsorbents recycling and regeneration. Therefore, a combination of chitosan-magnetic activated carbon is required to produce a higher adsorption capacity, more efficient, and inexpensive. Magnetic-activated carbon/chitosan (MACC) was synthesized by the coprecipitation method [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_3PO_4 0,1 M, acetic acid 3%, Fe(III) $FeCl_3.6H_2O$ and Fe(II) $FeCl_2.4H_2O$, NaOH 10% were used for fabrication MACC.

2.2 Preparation of Activated Carbon From Spent Coffee Grounds

SCG was dried in the oven at 105°C for 5 h and carbonized at 600°C for 4 hours, 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_3PO_4 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 stirred at 60°C for 30 minutes to produce a soluble solution. Fe (III) (as $FeCl_3.6H_2O$) and Fe (II) (as $FeCl_2.4H_2O$) 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 stirred for 24 hours to solidify, then separate the precipitate from the NaOH solution, and washed with demineralized water several times. The washing process was performed until the filtrate becomes 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 with demineralized water. MB solutions with a concentration of 5 to 50 mg/L 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 different temperatures of 35 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 filtrate and adsorbent [14]. The filtrate concentration of each solution was measured absorbance (MB adsorption wavelengths = 665 nm) using a UV/vis spectrophotometer. Calculation of adsorption capacity at equilibrium q_e in mg/g was conducted using equation (1).

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

where C_0, Ce 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 these Langmuir and 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, there are many cavities on the surface of MACC. The surface resembles a honeycomb structure. The pore structure indicates the presence of chitosan which contributed to the formation of a bead-like structure [16]. Figure 1 shows that Fe_3O_4 nanoparticles are distributed between the chitosan polymer chains [17]. Surface elements were analysed by EDX. Based on the graph and EDX analysis data, shows the presence of elements C, O, and Fe as the three main components. EDX results confirm the presence of Fe_3O_4, chitosan and activated carbon, while other elements such as Zn, Cu, and Mg are impurities [10].

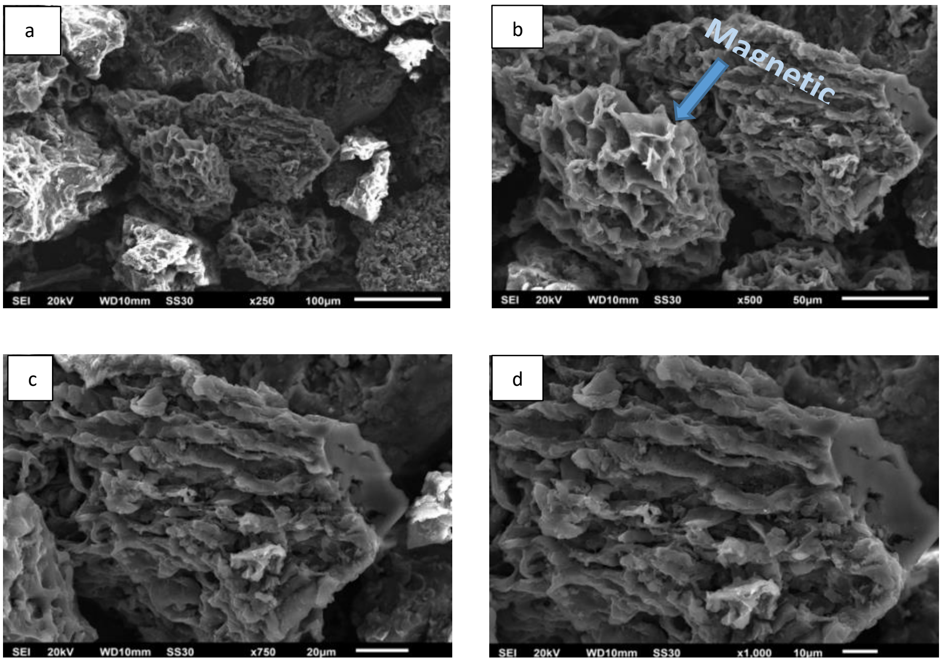

Figure 1. SEM images of MACC (a) 250x (b) 500x (c) 750x (d) 1000x

Table 1. EDX analysis data of MACC

Element	Mass %
C	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

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3.2 Adsorption Experiments

3.2.1 Adsorption Isotherm

Langmuir and 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. Figure 2 shows plot of the curve obtained from experimental data.

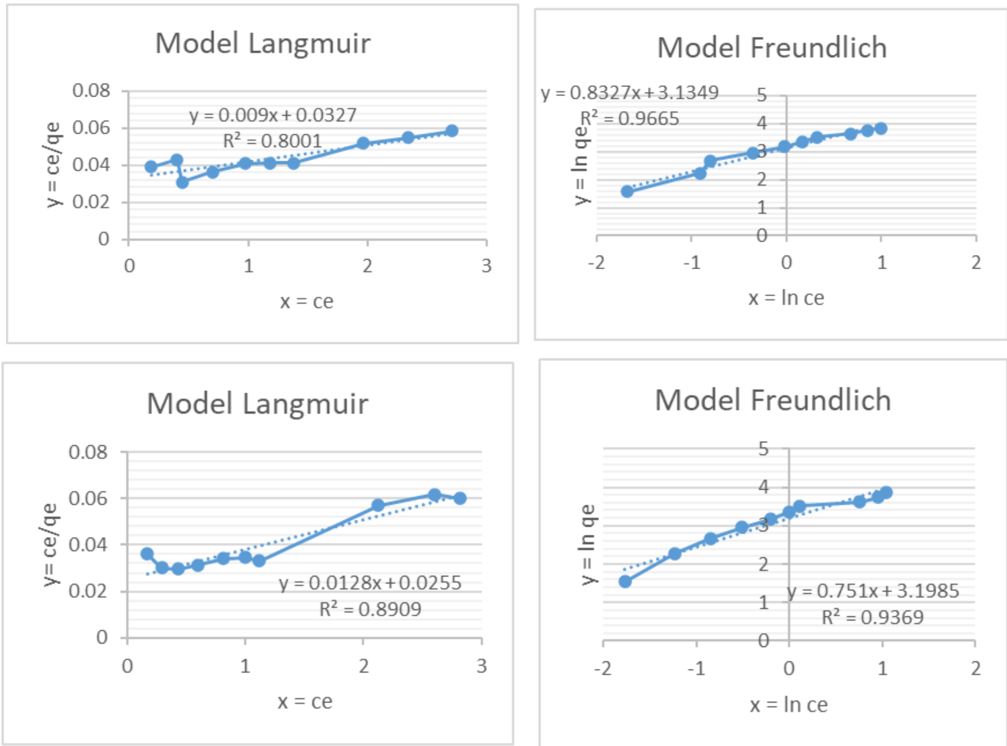

Figure 2. Langmuir and Freundlich model at temperatures 35°C (up) and 45°C (below)

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

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

Based on 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 multilayer. 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.

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, while at a temperature of 45, 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.

As for the Langmuir model, the R_L value for MB adsorption using magnetic activated carbon for a temperature of 35°C is between 0.06-0.4, while for a temperature of 45°C is between 0.03-0.167. This result indicates that there is 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 important 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 magnitude of the H^o value indicates the type of adsorption process, the H^o 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 S^o on MB adsorption indicates an increase in irregularity and randomness at the adsorbent-solution interface during the adsorption process. If the resulting S^o is negative, then there is no randomness in the adsorption process [18]. The value of Gibbs free energy G^o is negative for both concentration and temperature variations, indicating that the adsorption takes place spontaneously, is very favorable, and is profitable. The value of G^o becomes negative with increasing temperature indicating that higher temperatures are suitable for MB adsorption and high temperature is the most important factor to increase the active adsorption capacity of chitosan species. In addition, for physical adsorption, the literature explained that G° 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 to -9 kJ/mol (according to Table 3), the type of adsorption is physical adsorption. 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 results in an increase in the vibrational energy of the dye ion to react with the activated carbon-chitosan type at high temperatures [20]. If the resulting G° value is overall positive, this indicates that the reaction does not take place spontaneously and energy is needed to continue the reaction [18].

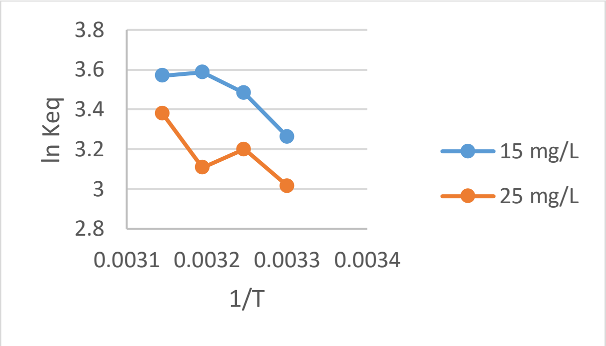

Figure 4. Thermodynamic chart temperature 30, 35, 40, 45 °C

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

Konsentrasi MB (mg/L)	ΔH^0 (kj/mol)	ΔS^0 (kj/mol/K)	ΔG^0 (J/mol)			
			30 ^{0}C	35 ^{0}C	40 ^{0}C	45 ^{0}C
15	16,51661	0,0821	-8220,14	-8920,70	-9333,37	-9438,07
25	15,90915	0,0776	-7598,07	-8195,48	-8086,61	-8933,75

4. Conclusions

Coprecipitation method, as one of nanoparticle synthesis, 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, a process commonly known as endothermic. The experimental data were fitted to Langmuir and Freundlich isotherms models. The results showed that based on R^2 values, Freundlich model correspond with 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 the calculation of thermodynamic parameters.

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