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To cite this article: M F Rizkiana *et al* 2021 *IOP Conf. Ser.: Mater. Sci. Eng.* **1053** 012007

Fabrication of magnetic activated carbon from spent coffee ground by hydrothermal synthesis for methylene blue removal

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Abstract. Spent coffee ground-based magnetic activated carbon (MSC) was prepared using hydrothermal synthesis and utilized for the adsorption of methylene blue (MB). The MSC was made using the following conditions: the molar ratio of ferrous/ferric ions was 1:1.5, the hydrothermal treatment at 126°C for 2 h. The prepared MSC was investigated for surface morphology and chemical structure using FTIR and SEM. Batch adsorption studies were performed at 308 K; 318 K and MB concentration of 50-400 mg L^{-1} to evaluate the adsorption behaviour. The results showed as follows: there were C=O, C=C, C-O, Fe-O groups on the MSC surface and magnetite existed in the pores and surfaces of the MSC. Sorption behaviour at different temperatures were evaluated using the Langmuir, Freundlich, Temkin models, confirming Freundlich model was fitted on MSC. First and second order kinetic models were tested and the data fitted the first order behaviour. The adsorption process was a spontaneous, endothermic, and more reactive upon raising the temperature. After adsorption, MSC could be separated by applying magnetic field. Magnetic removal would allow convenient tool for adsorbent separation from contaminated water.

1. Introduction

In recent years, depletion of freshwater resources has become a global attention worldwide. Water pollution produced by industrial manufacturers or daily activities, is a serious threat to the environment and public health. The presence of synthetic dyes in water resources are generated by many industrial applications such as textile, leather, paper, and cosmetic industries [1]. It is estimated that approximately 10,000 tons per year of synthetic dyes with 100,000 different dyes are produced and used worldwide annually [2] and about 10-15% of these dyes are discharged into the environment without proper treatments [3]. With the increasing depletion of freshwater, it is significant to control water pollution and protect water resources.

Wastewater must ensure fulfill the standard requirement from government before discharged into the environment. Among various methods available, adsorption is more preferable due to its ease of operation and cost effectiveness [4]. Activated carbon provides inexpensive and attractive option for treating wastewater. Its adsorption capacity was influenced by activated carbon pore volume, pore

surface area, pore surface chemistry and surface chemical functionality [5]. The problem of using activated carbon to remove contaminants is separating the spent adsorbent. Traditional method, filtration indicate that some obstacles have existed, such as blockage in filters and loss of carbon in the sludge [4]. These issues will generate secondary pollution. Therefore, combining magnetic nanoparticles separation and activated carbon to remove contaminants from wastewater is an opportunity to achieve desirable adsorption process and effective separation by an external magnetic field [6].

The main raw material of activated carbon is coal, a non-renewable resource. Many researchers have taken interests to fabricate magnetic activated carbon using renewable resources such as corn cob [4], almond shells [5], sawdust [7], waste cotton textiles [8], rice straw [15], rice husk [16], coconut shell [20], etc. Since agriculture yield high quantities of by-product waste, their conversion into activated carbon would add value to agricultural commodities, reduce waste, and provide inexpensive replacement of commercial adsorbents derived from nonrenewable sources [5].

Magnetic activated carbon has been shown to remove various environmental contaminants from solutions, such as chromium [4], trinitrophenol [5], tetracycline [11,13, 16], methylene blue [7], sunset yellow [14], triclosan [15], lead ions [19] and phenol [20]. Fabrication of magnetic activated carbon has been widely reported [4-8, 13-15]. There are commonly methods for the synthesis of magnetic activated carbon, i.e. co-precipitation [4-5, 16, 18-20] and hydrothermal [9]. In both methods, the fabrication involves the preparation of activated carbon, followed by iron-impregnation into the activated carbon, and pyrolysis of iron/carbon composite materials [14]. Synthesis magnetite (Fe_3O_4) nanoparticles using hydrothermal method is considered a promising method to produce well-controlled morphology and narrow particle size distribution [10]. As an alternative, magnetic activated carbon has also been developed and synthesized by pyrolysis activation (simultaneous activation and magnetization). The purposes for simultaneous methods are expected to enhance pollutant removal efficiency and reduce synthetic steps [11,14].

In this study, the activated carbon was prepared from spent coffee grounds by chemical activation. Fabrication activated carbon by chemical activation is considered an efficient method [12] due to high yield, low temperature, and short activation time [8]. The activated carbon was magnetized by coating magnetite nanoparticles on the surface of the activated carbon using hydrothermal method. This fabricated magnetic activated carbon (MSAC) was used for the adsorption of methylene blue. Methylene blue was selected as representative of synthetic dyes. Scanning Electron Microscopy (SEM), Fourier transform-infrared (FTIR), and adsorption behavior were used to characterize adsorbents.

2. Materials and Methods

2.1. Materials

The spent coffee grounds (SCG) were taken from convenience store at Shobara district, Hiroshima, Japan. The SCG was put in an oven at 105°C for 24 hours, then sieved with 40 mesh screens, and these particles were selected as the precursor for production of activated carbon. Ferric trichloride hexahydrate ($FeCl_3.6H_2O$), ferrous dichloride tetrahydrate ($FeCl_2.4H_2O$), methylene blue, sodium hydroxide, and phosphoric acid were purchased from Kanto Chemical Co., Inc. (Japan). All chemicals were of analytical grade and produced in Japan.

2.2. Methods

2.2.1. Preparation of activated carbon. Activated carbon was prepared through a chemical activation. The SCG (5 g) was immersed with H_3PO_4 50wt% with a ratio 1:1 for 24 hours. Afterward, the mixtures were placed into a furnace at 170°C for 30 minutes and continue with temperature 450°C for 1 hour. The carbonized materials were washed with deionized water until pH of the washing solution reached 6-7, filtered and finally dried at 60°C for 24 h. After being dried, the activated carbon was obtained, weighed, and stored in tightly closed bottles. The yield of activated carbon was calculated according to equation (1).

$$Yield\ (\%) = M_{AC}/M_0 \times 100 \quad (1)$$

In which M_{AC} is the weight of the activated carbon and M_0 is the weight of the spent coffee grounds.

2.2.2. Preparation of MSC. $FeCl_2.4H_2O$ (0.1305 g) and $FeCl_3.6H_2O$ (0.2690 g) were mixed with a mole ratio of 1:1.5. The solutions were stirred for 10 minutes until a homogeneous mix solution. Afterward, NaOH aqueous solution were added dropwise until pH reached 12. Black precipitates have formed. Then, 2 g of activated carbon was added to the mixture and stirred for 30 minutes. The mixture was transferred to an autoclave and heated to 126°C for 2 h. After cooling to room temperature, the MSC were washed with deionized water until pH of the washing solution reached 6-7, filtered and finally dried at 60°C for 24 h. After being dried, the activated carbon was obtained, weighed, and stored in tightly closed bottles. The yield of magnetic activated carbon was calculated according to equation (2).

$$Yield\ (\%) = M_{MSC}/M_0 \times 100 \quad (2)$$

In which M_{MSC} is the weight of the magnetic activated carbon and M_0 is the weight of the spent coffee grounds.

2.2.3. Characterization of the prepared MSC. The surface functional group of activated carbon and the prepared MSC sample was measured using Fourier Transform Infrared Spectroscopy (FTIR). The surface appearance and the pores of spent coffee grounds, activated carbon, and the prepared MSC sample were analysed using Scanning Electron Microscope (SEM).

2.2.4. Adsorption behavior of MB on the prepared MSC. The adsorption behavior of MB on the prepared MSC was evaluated with batch experiment. The adsorption experiments were observed using 50 mg of MSC with 50 mL of methylene blue solutions with concentrations 50-400 mg L^{-1} (concentration gradient of 50 mg L^{-1}). The mixtures were placed in Erlenmeyer flask and the flask was put into a water-bath shaker at 100 rpm at temperature (308, 318 K) for 24 hours to reach equilibrium. The absorbance of filtrate was measured using a UV/VIS spectrophotometer at MB maximum adsorption wavelengths of 665 nm. The adsorption capacity at equilibrium q_e in mg/g was calculated using equation (3).

$$q_e = \frac{(C_0 - C_e)V}{1000 \times M_{MSC}} \quad (3)$$

Where C_0, C_e were the initial and equilibrium concentration (mg L^{-1}) of the MB solution, V was the volume of the MB solution (mL), and M_{MSC} was the mass of the added MSC.

The relationship between MB concentration and the absorbance was plotted according to the Lambert-Beer law. The adsorption process of MB on the prepared MSC was analysed using the adsorption isotherm, Langmuir, Freundlich, and Temkin [7]. The thermodynamic behavior was evaluated using thermodynamic parameters such as Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) [7].

3. Results and Discussion

3.1. Characterization of the prepared MSC

3.1.1. FTIR of the activated carbon and MSC. The FTIR spectrum of the activated carbon and the prepared MSC is shown in Figure 1. The FTIR spectrum of activated carbon and MSC were observed that many functional groups from spent coffee grounds disappeared after modification during chemical activation process. When phosphoric acid was used as activation precursor followed by heating treatment, volatile compounds on the carbon surface encountered decomposition, and resulted in an efficient surface modification [17]. The peak at 1704 cm^{-1} was assigned to the C=O stretching vibration from the carbonyl and carboxyl group. The peak at 1575 cm^{-1} was identified as the C=C stretching vibration. The peak at 1152 cm^{-1} was regarded as being from the C-O stretching vibrations. The peaks at 625 and 559 cm^{-1} were attributed to the Fe-O bending vibrations of Fe_3O_4 or γ-Fe_2O_3. A

peak for Fe-O emerged, compared with the FTIR spectrum of activated carbon. These characteristic adsorption peaks showed that the presence of iron oxides in the prepared carbon material [18].

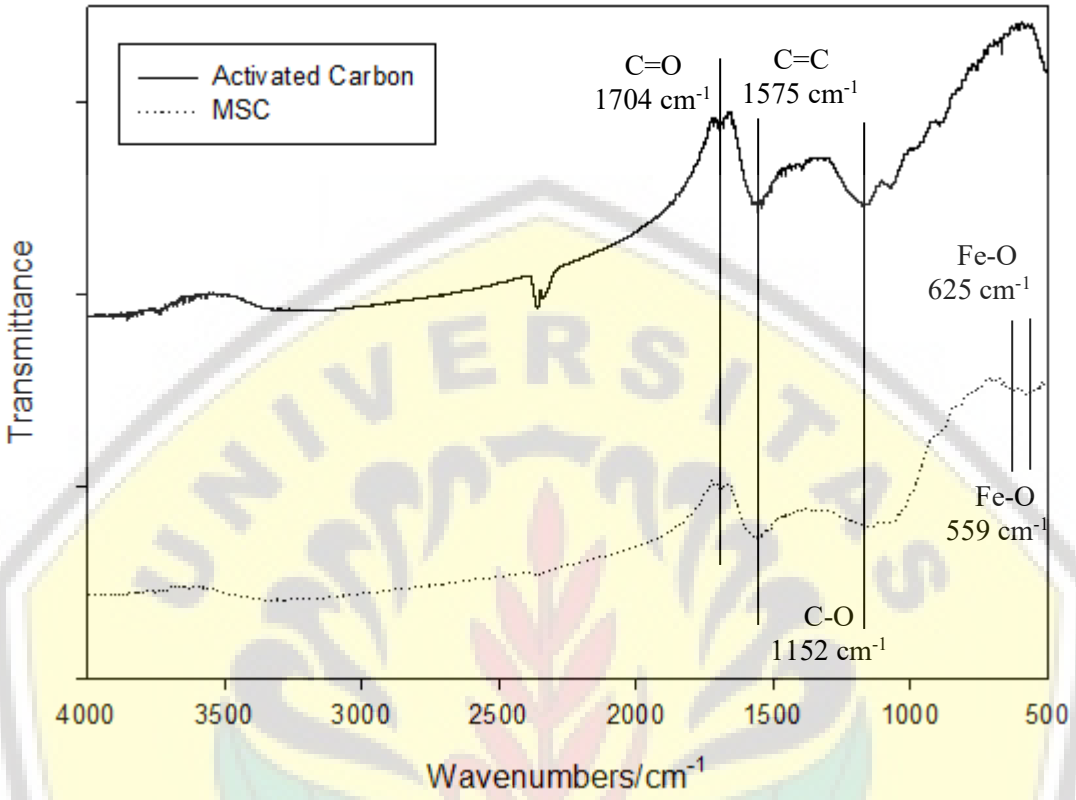

Figure 1. FTIR spectrum of the activated carbon-based spent coffee grounds and MSC

3.1.2. SEM of SCG, activated carbon and MSC. Porous and high surface areas are important features of a good adsorbent for wastewater treatment. The surface topography of the prepared MSC was investigated using scanning electron microscopy (SEM). Figure 2 shows the SEM images of spent coffee grounds, activated carbon, and MSC at different factors magnification. The surface of these scaffolds exhibits a morphology containing pores with a spherical appearance/cellular. As shown in Figure 2E-F, the surface topography of MSC is found to be different from activated carbon. The MSC shows magnetic materials existed on the surface of activated carbon. Some magnetic particles present aggregated into large particles as shown in Figure 2E.

3.2. Adsorption behavior of MB on the prepared MSC

3.2.1. Adsorption isotherms. The standard calibration curve of methylene blue, absorbance and concentration have been plotted at the maximum wavelength of 665 nm, and the linear equation was A=0.195C-0.0287, in which A is the absorbance, C is the concentration of MB, and R is the correlation coefficient. The value of R^2 was 0.9985, which indicated a good relation between absorbance and concentration [7].

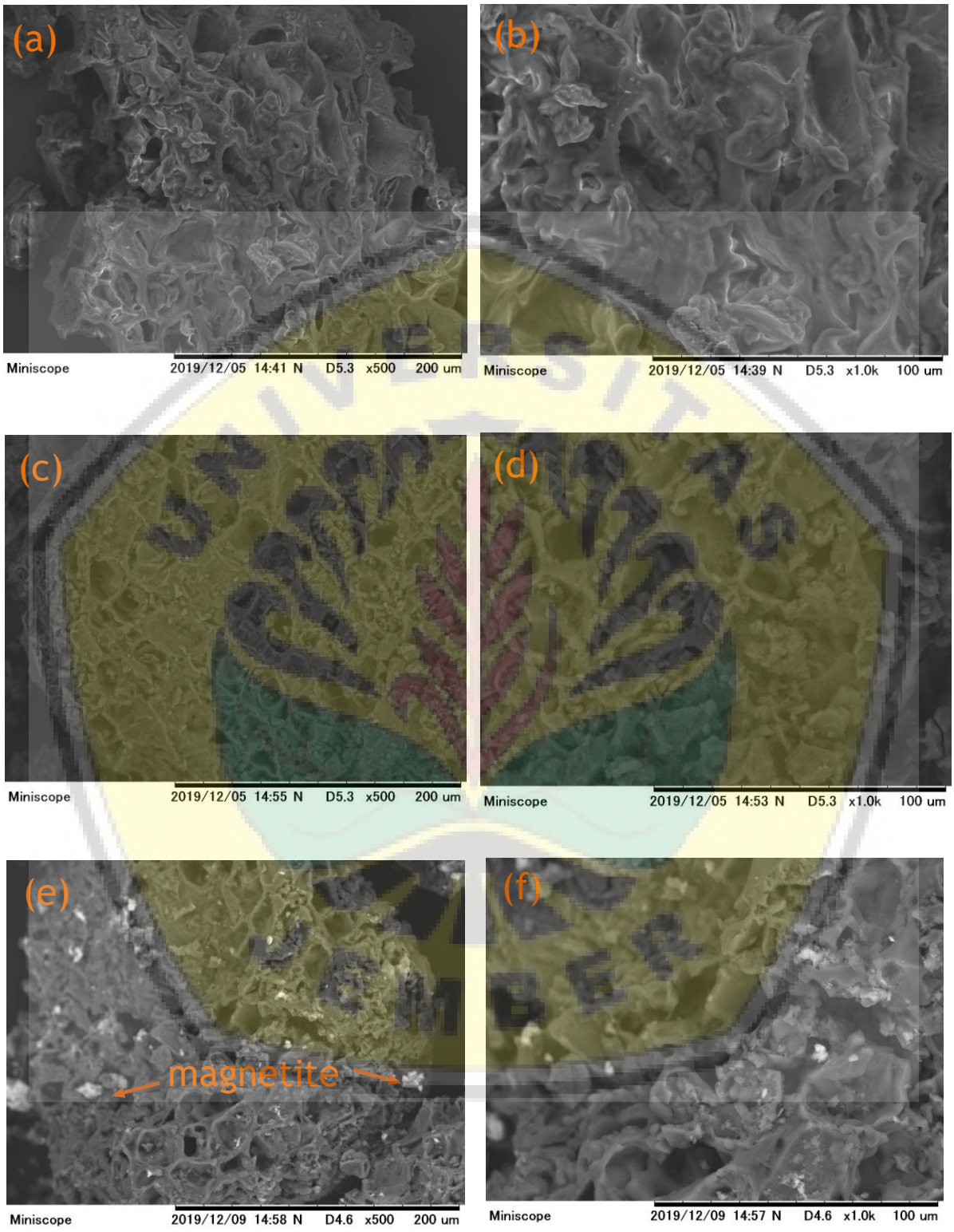

Figure 2. SEM images o spent coffee grounds (a) 500x (b) 1000x; activated carbon (c) 500x (d) 1000x; MSC (e) 500x (f) 1000x

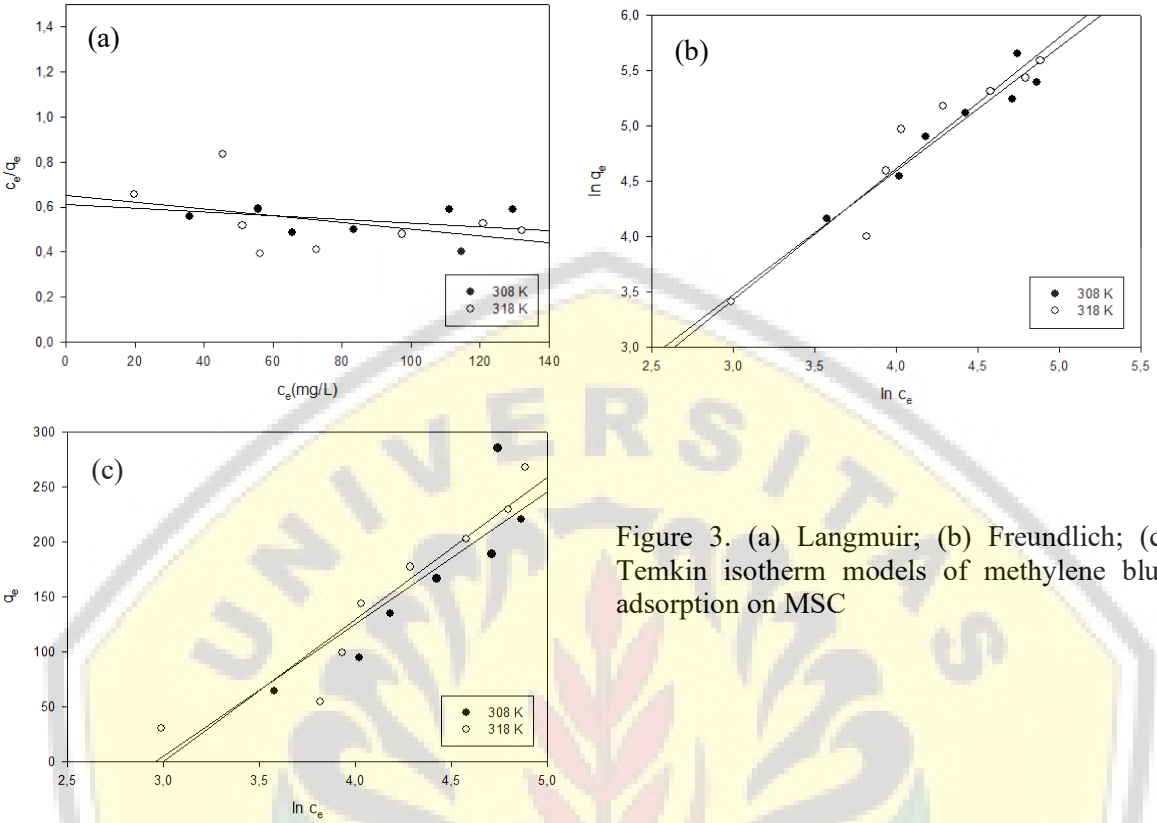

Figure 3. (a) Langmuir; (b) Freundlich; (c) Temkin isotherm models of methylene blue adsorption on MSC

Table 1. The adsorption isotherm parameters

	Langmuir				Freundlich			Temkin		
T (K)	q_{max}	K_L	R_L	R^2	K_F	n	R^2	b_T	a_T	R^2
308	909	0.00254	0.67-0.86	0.7855	1.123	0.894	0.967	21.325	0.052	0.8454
318	588	0.00568	0.57-0.76	0.8611	0.887	0.845	0.918	20.417	0.050	0.9009

The adsorption isotherms described the distribution of adsorbate molecules between the liquid phase and the solid phase when the system reached an equilibrium, and the fitting of the isotherm data to different adsorption models was important in order to obtain the best isotherm model that described the adsorption process [18].

The isotherm data of the MB adsorption on the prepared MSC were fitted to three adsorption isotherm models, namely Langmuir, Freundlich, Temkin. Figure 3 shows the fitted isotherm. The isotherm parameters are shown in Table 1. Table 1 shows that the experimental data fits Freundlich isotherm and gave R^2 values of 0.97 and 0.92 at 308, 318 K. Fitted to Freundlich isotherm model demonstrates that the adsorption of MB on MSC is applicable at low to intermediate concentrations. The Freundlich isotherm model describes the equilibrium at heterogeneous surface and does not assume any monolayer adsorption [20].

The Langmuir isotherm model gave R^2 values of 0.78 and 0.86 at 308, 318 K. Langmuir model assumes that the adsorption occurs on monolayer adsorption. The R_L values of 0.57-0.86 from the Langmuir isotherm indicate that the nature of adsorption of MB on the prepared MSC was favorable ($0<R_L<1$) [7]. For the results, the Freundlich isotherm model is most suitable for explaining the adsorption process of MB on MSC.

3.2.2. Adsorption thermodynamics. The thermodynamic parameters, including Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) were evaluated. The results are displayed in Table 2 and Figure 4. The negative values of Gibbs free energy propose that the adsorption process was spontaneous, and the increase of ΔG values suggested that the adsorption was more favorable at higher temperatures. The value of ΔH positive, which implied the adsorption process was endothermic. The positive value of ΔS indicated that enhancement the randomness of the adsorption system at the liquid/solid interface and degree of freedom enhanced during adsorption process. The adsorption process involving activated carbon have similar results (ΔG negative, ΔH positive, ΔS positive values) [7].

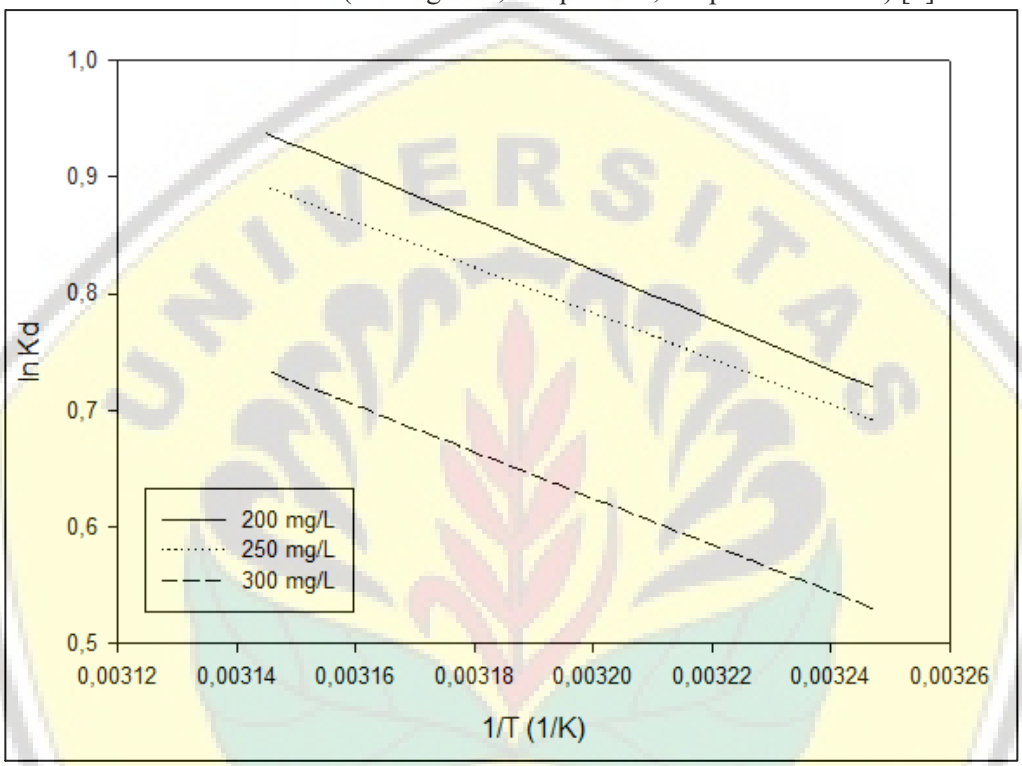

Figure 4. Plot of thermodynamics parameters for methylene blue adsorption on MSC

Table 2. Thermodynamics parameters for methylene blue adsorption on MSC

C_0 (mg L^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	ΔG (kJ mol^{-1})		Plotted Equation
			308 K	318 K	
200	17.78	63.70	-1.84	-2.48	ln Kd = -2138.2/T + 7.6619
250	16.36	58.85	-1.77	-2.36	ln Kd = -1967.2/T + 7.0782
300	16.60	58.30	-1.36	-1.94	ln Kd = -1996.3/T + 7.0118

4. Conclusions

Spent coffee grounds were converted into magnetic activated carbon (MSC) using hydrothermal method. The MSC were characterized and used for methylene blue removal. Freundlich isotherm model best fitted with isotherm data. FTIR results showed that peak Fe-O emerged and these characteristic adsorption peaks indicated the presence of iron oxides in the prepared carbon material. Based on SEM results, the MSC shows magnetic materials existed on the surface of activated carbon. The adsorption process of MB on the prepared MSC was spontaneous, more favorable at higher temperatures and endothermic chemisorption.

Acknowledgements
The authors are grateful for financial support from Islamic Development Bank (IsDB). This project was done when corresponding author enrolled Non-Degree Training at Prefectural University of Hiroshima, Japan.

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