

# The Effect of Unburned Carbon on Coal Fly Ash toward its Adsorption Capacity for Methyl Violet

Widi Astuti, Agus Prasetya, Endang Tri Wahyuni, and I Made Bendiyasa

**Abstract**—Coal fly ash (CFA) generated by coal-based thermal power plants is mainly composed of quartz, mullite, and unburned carbon. In this study, the effect of unburned carbon on CFA toward its adsorption capacity was investigated. CFA with various carbon content was obtained by refluxing it with sulfuric acid having various concentration at various temperature and reflux time, by heating at 400-800°C, and by sieving into 100-mesh in particle size. To evaluate the effect of unburned carbon on CFA toward its adsorption capacity, adsorption of methyl violet solution with treated CFA was carried out. The research shows that unburned carbon leads to adsorption capacity decrease. The highest adsorption capacity of treated CFA was found  $5.73 \times 10^{-4} \text{ mol.g}^{-1}$ .

**Keywords**—CFA, carbon, methyl violet, adsorption capacity.

## I. INTRODUCTION

LARGE quantities of coal fly ash are produced during the combustion of coal in the production of electricity. In Indonesia, more than 1 million tons of fly ash is being generated annually [5]. Most of this ash is used in low level applications including landfill. Two approaches have been made for proper utilization of CFA, either to reduce the cost of disposal or to minimize the environmental impact. One application of CFA is used as adsorbent [4].

On the other hand, the presence of dyes in liquid effluents generated by textile, paper, ceramic, printing and plastic industries is undesired and harmful, so it must be eliminated or reduced to an allowable limit. Adsorption process is one of the effective techniques that have been successfully employed for color removal from wastewater. Many adsorbent have been tested to reduce dye concentrations from aqueous solutions, including activated carbon [8] and agricultural waste [3].

CFA is mainly composed of some oxides such as  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , having active sites, and unburned carbon as mesopore [2], so it is a potential adsorbent. But, the existence of unburned carbon in coal fly ash can generate two possibilities.

W. Astuti is with the Chemical Engineering Department, Semarang State University, Semarang, Indonesia and Ph.D student at the Chemical Engineering Department, Gadjah Mada University, Yogyakarta, Indonesia (e-mail: wiwied.unnes@gmail.com).

A. Prasetya is with the Chemical Engineering Department, Gadjah Mada University, Yogyakarta, Indonesia.

E.T. Wahyuni is with the Chemistry Department, Gadjah Mada University, Yogyakarta, Indonesia.

I M. Bendiyasa is with the Chemical Engineering Department, Gadjah Mada University, Yogyakarta, Indonesia.

It can improve the adsorption capacity or contradictionly hinder the adsorption. Therefore, this paper will discuss the effect of unburned carbon toward its adsorption capacity for methyl violet.

## II. MATERIALS AND METHODS

### A. Sample Preparation and Characterization

Methyl violet and hydrochloric acid (HCl) in extra pure grade were purchased through Merck. pH adjustments were carried out by 0.1M hydrochloric acid (HCl) and 0.1M sodium hydroxide (NaOH).

CFA was obtained from Tanjungjati power plant, Jepara, Indonesia. Before any treatment, it was washed with deionized water and dried. CFA was further treated with various sulfuric acid concentrations (50 to 75 w/w), temperatures (60 to 90°C) for three to six hours to reduce the carbon content. The ratio of CFA weight to sulfuric acid volume was 1g of CFA to 6mL of sulfuric acid. For each run, one variable was varied and two others were fixed. Finally the CFA was filtered, washed several times with deionized water until pH of the filtrate was around 7, dried at 110°C overnight, characterized and used as an adsorbent in the sorption experiments. The carbon content of CFA also was reduced by heating at 400-800°C, for 1 hour. In addition, the effect of carbon content was also evaluated by reducing mineral content on CFA through a BSS Tyler Sieve of 100-mesh size. CFA that do not pass 100 mesh sieve was used, because it had quite high unburned carbon content.

The chemical compositions of original CFA were analyzed using x-ray fluorescence (XRF). X-ray diffraction (XRD) patterns for original and treated CFA were obtained by powder method using Cu K $\alpha$  radiation (Schimadzu XRD-6000).

### B. Batch Adsorption Experiment

Original or treated CFA (dose varied from 0.1-2.0g) was put into an erlenmeyer filled 50mL of methyl violet solution (methyl violet solution concentrations were varied from 10 to 1000mg.dm<sup>-3</sup>). The adsorption was carried out at pH of 9. The erlenmeyer contained the mixture was placed in a waterbath at 26°C and shaken mechanically for 5 to 180min. Subsequently, suspended solid was filtered and the filtrate was analyzed to determine methyl violet concentration using UV-visible spectrophotometer at  $\lambda_{\text{max}} = 581\text{nm}$ .

To investigate the effect of pH on adsorption, 1g of original or treated CFA was added to an erlenmeyer filled 50mL of

10ppm methyl violet solution. The pH was adjusted with base/acid to an appropriate pH (pH range of 3 to 11). The erlenmeyer filled the mixture was placed in a waterbath at 26°C and shaken mechanically for 180 minutes. The ash was separated from the solution and the filtrate was analyzed to determine methyl violet concentration using UV-visible spectrophotometer at  $\lambda_{\text{max}} = 581\text{nm}$ .

### III. RESULTS AND DISCUSSION

#### A. Chemical Composition

The chemical compositions obtained from x-ray fluorescence (XRF) analysis are presented in Table I. It shows that the major components of CFA are silica ( $\text{SiO}_2$ ), alumina ( $\text{Al}_2\text{O}_3$ ) and unburned carbon. To confirm the existence of silica and alumina, CFA is analyzed using x-ray diffraction (XRD). The XRD pattern of CFA can be seen from Fig. 1. It shows that CFA contains crystalline phases including quartz ( $\text{SiO}_2$ ), mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) and amorphous components. Thus, there is suitability between the result of XRF analysis and XRD pattern.

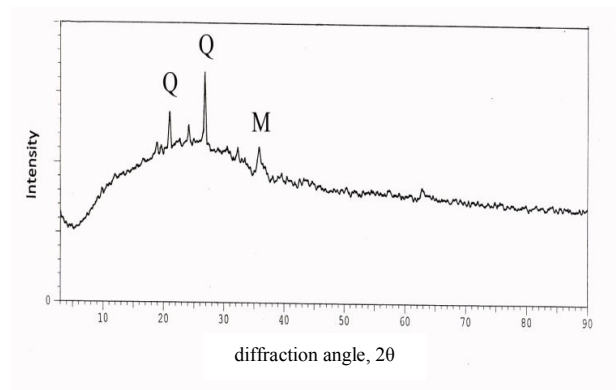


Fig. 1 XRD patterns of tanjungjati fly ash  
Symbols: Q-quartz, M-mullite

#### B. Effect of Sulfuric Acid, Heating, and Sieving Treatment toward Carbon Content

Diffractogram of CFA treated with sulfuric acid is shown in Fig. 2. It shows several sharp diffraction peaks that are different from diffractogram of the original CFA. Besides quartz, there is hydroxysodalite in the treated CFA.

Fig. 3 demonstrates that the sulfuric acid treatment causes the decrease of unburned carbon content in the CFA. For the sulfuric acid concentration and the processing time are constant, the higher temperature of the process, the lower unburned carbon content is. For the temperature of process and the processing time are constant, the higher sulfuric acid concentration, the lower unburned carbon content is. The longer processing time, the lower unburned carbon content is, for the temperature of process and the sulfuric acid concentration are constant. The heating from 400°C to 800°C also causes the decreasing of unburned carbon content. The higher the temperature gives the lower unburned carbon

content. The decreasing of unburned carbon content caused by heating is more than it caused by sulfuric acid treatment.

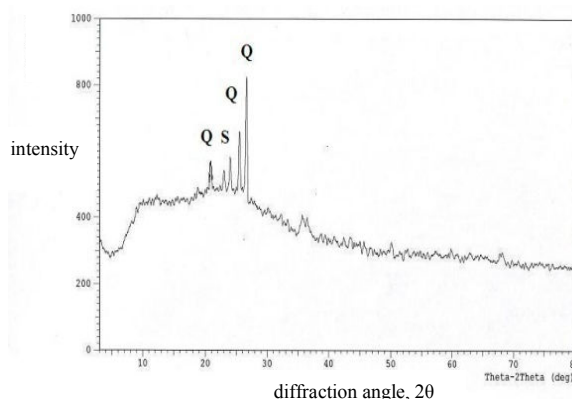


Fig. 2 XRD patterns of treated coal fly ash  
Symbols: Q-quartz, S-hydroxysodalite

TABLE I  
CHEMICAL COMPOSITION OF TANJUNGJATI FLY ASH

| Component               | Content (mass %) |
|-------------------------|------------------|
| $\text{SiO}_2$          | 36.47            |
| $\text{Al}_2\text{O}_3$ | 19.27            |
| $\text{CaO}$            | 6.56             |
| $\text{MgO}$            | 2.94             |
| $\text{Fe}_2\text{O}_3$ | 10.74            |
| $\text{MnO}$            | 0.07             |
| $\text{Na}_2\text{O}$   | 1.76             |
| $\text{K}_2\text{O}$    | 1.77             |
| $\text{CuO}$            | 0.01             |
| $\text{As}_2\text{O}_3$ | 0.01             |
| $\text{P}_2\text{O}_5$  | 0.25             |
| $\text{SO}_3$           | 1.04             |
| Unburned carbon         | 19.11            |

#### C. Methyl Violet Adsorption

##### 1. Effect of Unburned Carbon Content

Fig. 4 shows that the increase of carbon content on CFA leads to adsorption capacity decrease. It is because the role of the active sites on CFA is higher than that of unburned carbon pore. The great amount of unburned carbon can form aggregates and cover the active site on CFA surface, so chemical binding between the active sites and methyl violet cannot happen. The adsorption capacity increases with the increasing initial methyl violet concentration and then constant. It is because of equilibrium has been attained.

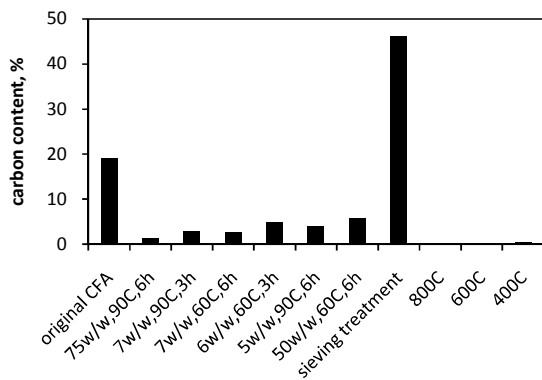


Fig. 3 Carbon content of original and treated CFA

Note: x w/w, yC, zh means sulfuric acid concentration (w/w), temperature (°C) and reflux time (hours)

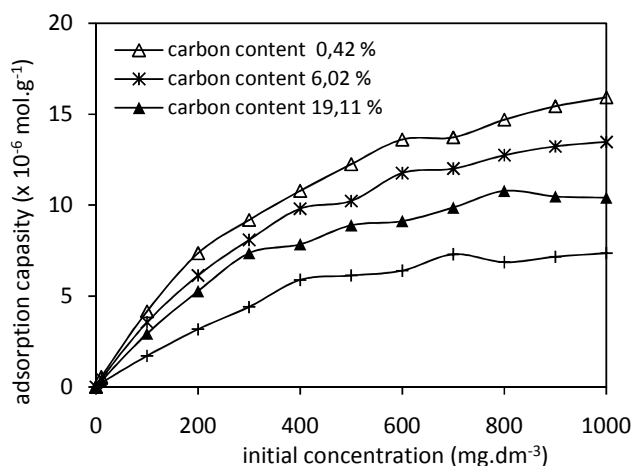


Fig. 4 Effect of carbon content toward adsorption capacity (CFA dose = 1 g/50mL solution, contact time = 180 minutes, pH 9)

## 2. Effect of CFA Dose toward Adsorption Capacity

The effect of CFA dose toward adsorption capacity is shown in Fig. 5. The adsorption capacity increases with the CFA dose up to a certain limit and then it reaches a constant value. Optimum CFA dose for methyl violet adsorption was 1 g of CFA per 50mL of solution. The increase of adsorption capacity with adsorbent dose was due to the availability of more active site for adsorption.

## 3. Effect of pH

pH of solution affect surface charge of the adsorbent as well as the degree of ionization of different pollutants. Fig. 6 shows the effect of solution pH toward adsorption capacity. The adsorption capacity increase until pH 9, and then constant with the increase of pH. At lower  $H^+$  concentrations, the CFA surface becomes more negatively charged, so the electrostatic binding between active site on coal fly ash and methyl violet becomes easier.

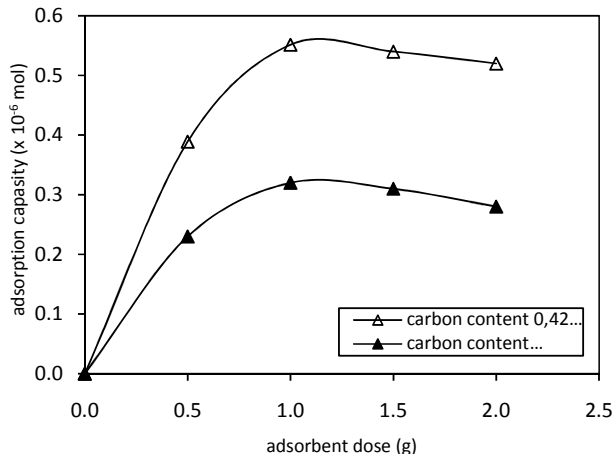


Fig. 5 Effect of adsorbent dose toward adsorption capacity (initial concentration = 10 ppm, contact time = 180 minutes, pH = 9)

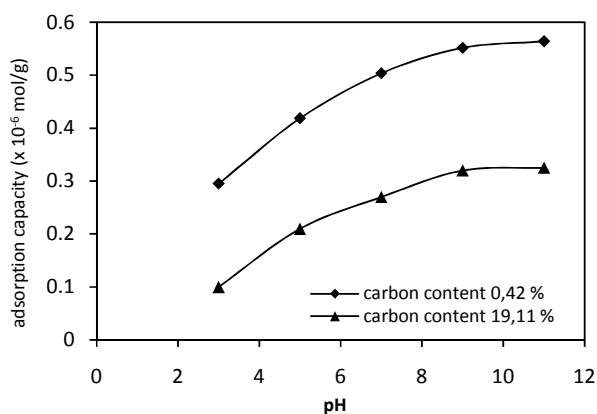


Fig. 6 Effect of solution pH toward adsorption capacity (CFA dose = 1 g/50mL solution, initial concentration = 10ppm, reaction time = 180 minutes)

## 4. Effect of Reaction Time

In the first few minutes, the adsorbate uptake is very fast and then it becomes slow and finally level off as can be see Fig. 7. In the initial stage of adsorption, a large number of vacant surface sites are available for adsorption and after some active sites are occupied by adsorbate, the adsorption process becomes difficult due to repulsive forces between the solute molecules on solid and bulk phases [3].

### D.Adsorption Kinetics

In order to clarify the adsorption kinetics of methyl violet onto CFA, pseudo-first and second order kinetic models were applied to the experimental data. The linearized form of the pseudo first order rate equation by Lagergren is given as [1]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

where  $q_e$  and  $q_t$  are amounts of the methyl violet adsorbed at equilibrium ( $\text{mol g}^{-1}$ ) and at time  $t$  ( $\text{mol g}^{-1}$ ), respectively,  $k_1$  is the rate constant ( $\text{min}^{-1}$ ),  $t$  is time (min). The adsorption rate

constants ( $k_1$ ) can be determined experimentally by plotting of  $\ln (q_e - q_t)$  versus  $t$ . Experimental data were also fitted for the pseudo second order [6]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \cdot t \quad (3)$$

where  $k_2$  ( $\text{g} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$ ) is the rate constant. Equation (3) is solved graphically by plotting  $t/q_t$  versus  $t$ . The value of  $q_e$  can be calculated from the slope of the straight line and  $k_2$  from its intercept. Table II illustrates the  $k_1$  and  $k_2$  for pseudo first and second order rate constants as well as  $q_e$  for both of them. It indicated that the experimental data fit with the pseudo second order model. It is because chemisorptions occurs involving ionic forces between active site on CFA and methyl violet [7].

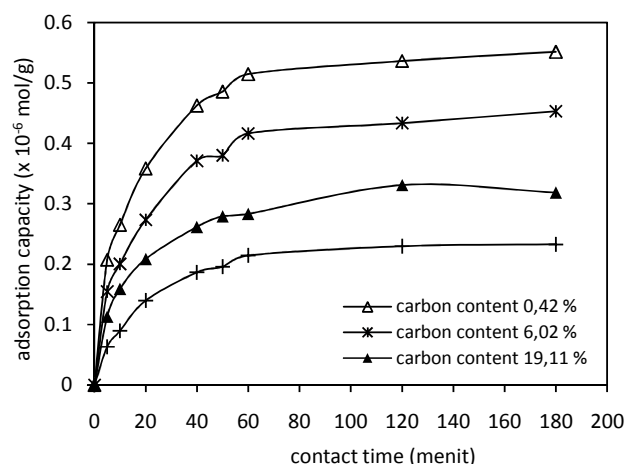


Fig. 7 Effect of reaction time on methyl violet removal (CFA dose = 1g/50 mL solution, initial concentration= 10ppm, pH 9)

TABLE II  
PARAMETERS FOR ADSORPTION KINETICS OF METHYL VIOLET

| Pseudo first order               |                                |       | Pseudo second order              |  |       |
|----------------------------------|--------------------------------|-------|----------------------------------|--|-------|
| $q_e$<br>( $\text{mol g}^{-1}$ ) | $k_1$<br>( $\text{min}^{-1}$ ) | $R^2$ | $q_e$<br>( $\text{mol g}^{-1}$ ) | $k_2$<br>( $\text{g mol}^{-1} \text{min}^{-1}$ ) | $R^2$ |
| $3.64 \times 10^{-4}$            | 0.03                           | 0.933 | $5.73 \times 10^{-4}$            | 0.122  | 0.996 |

#### IV. CONCLUSION

It is concluded that unburned carbon hinder methyl violet adsorption. The increase of carbon content on CFA leads to adsorption capacity decrease. The amount of methyl violet adsorbed depends on the initial concentration of methyl violet solution, pH of solution, contact time and adsorbent dose. Adsorption kinetics of methyl violet onto CFA could be approximated with pseudo second order kinetic model which the rate constant is  $0.122 \text{ g mol}^{-1} \text{ min}^{-1}$ .

#### ACKNOWLEDGMENT

We are grateful to Directorate for Research and Community Service, Directorate General of Higher Education, Ministry of National Education Republic Indonesia and Gadjah Mada University for doctorate research grant with grant number lppm-ugm/1200/2009.

#### REFERENCES

- [1] J.A. Hefne, W.K. Mekhemer, N.M. Alandis, O.A. Aldayel, T. Alajyan, "Kinetic and Thermodynamic study of the Adsorption of Pb(II) from Aqueous solution to The Natural and Treated Bentonite", *International Journal of Physical Sciences*, vol. 3, pp. 281-288, 2008.
- [2] J.Y. Hwang, X. Sun, Z. Li, "Unburned Carbon from Fly Ash for Mercury Adsorption : I. Separation and Characterization of Unburned Carbon", *Journal of Minerals and Materials Characterization & Engineering*, vol 1, no. 1, pp. 39-60, 2002.
- [3] M. Dogan, Y. Ozdemir, M. Alkan, "Adsorption Kinetics and Mechanism of Cationic Methyl Violet and Methylene Blue Dyes onto Sepiolite", *Dyes and Pigments*, vol.75, pp. 701-713, 2007.
- [4] P. Ricou, V. Hequet, I. Lecuyer, P. Le Cloirec, "Removal of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  in Aqueous Solutions by Sorption onto Fly Ash and Fly Ash Mixtures (Published Conference Proceedings style)," in *Proc. International Ash Utilization Symposium*, University of Kentucky, 1999.
- [5] Sukandarrumidi, *Batubara dan Pemanfaatannya* (Book style). Yogyakarta : Gadjah Mada University Press, 2006.
- [6] Y.S. Ho, G. McKay, "Batch Lead (II) Removal from Aqueous Solution by Peat : Equilibrium and Kinetics", *Trans IChemE*, vol. 77 part B, pp. 165-173, 1999.
- [7] Y.S. Ho, "Review of Second-Order Models for Adsorption Systems," *Journal of Hazardous Materials*, B136, pp. 681-689, 2006.
- [8] Y.S. Al-Degs, M.I. El-Barghouthi, A.H. El-Sheikh, G.M. Walker, "Effect of Solution pH, Ionic Strength, and Temperature on Adsorption Behaviour of Reactive Dyes on Activated Carbon", *Dyes and Pigments*, vol.77, pp.16-23, 2008.

**Widi Astuti** is Ph.D student at the Chemical Engineering Department, Gadjah Mada University, Yogyakarta, Indonesia. She also serve as a faculty member at the the Chemical Engineering Department, Semarang State University, Semarang, Indonesia. In recent years, she focuses on the application of coal fly ash for adsorbant.