

The Effect of Coal Fly Ash Crystallinity toward Methyl Violet Adsorption Capacity

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Coal fly ash (CFA) generated by coal-based thermal power plants is mainly composed of some oxides having high crystallinity, like quartz and mullite. In this study, the effect of CFA crystallinity toward methyl violet (MV) adsorption capacity was investigated. To decrease crystallinity of CFA, the solution of sodium hydroxide (NaOH) of 1-7 M was used to treat CFA at various temperatures and reflux time. Then, to evaluate the effect of NaOH-treated CFA with respect to adsorption capacity, the original and NaOH-treated CFA were tested its MV adsorption capacity in batch experiments. Original or NaOH-treated CFA was contacted with 50 mL of MV solution at temperature of 26°C. The effects of contact time, pH of solution, adsorbent dose and initial concentration of dye on the adsorption of MV were investigated. The results show that CFA treated with low NaOH concentration (1-3 M), temperature of 60°C and 2 hours reflux time, the crystallinity of quartz and mullite decreases, but its capacity on MV adsorption increases from 34% to 97%. At higher NaOH concentration (>3M), in the range of studied reflux temperature and time, it is found that decreasing quartz and mullite crystallinity are followed by a hydroxysodalite formation which causes the decreasing of MV adsorption from 97% to 83%. The highest adsorption capacity of NaOH-treated CFA was found $1.24 \times 10^{-5} \text{ mol g}^{-1}$. Adsorption kinetics of MV onto NaOH-treated CFA could be approximated with a pseudo second order kinetic model with the rate constant was $3.2 \times 10^3 \text{ g mol}^{-1} \text{ min}^{-1}$.

Keywords: coal fly ash, crystallinity, quartz, mullite, methyl violet, adsorption

INTRODUCTION

The combustion of coal in the power plant generates a large quantity of CFA that causes a big problem to environmental. 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 as adsorbent (Woolard et al. 2000).

On the other hand, the presence of dyes in liquid effluents generated by textile, paper, printing and plastic industries is undesired and harmful, and must be eliminated or reduced to an allowable limit. Many adsorbent have been tested to reduce dye concentrations from aqueous solutions, such as activated carbon (Al-Degs et al. 2008) and some agricultural waste (Ofomaja 2008; Mall et al. 2005). In order to improve the efficiency of adsorption process, it is necessary

to develop an adsorbent that is cheaper but has high adsorption capacity.

CFA is mainly composed of some oxides such as Al_2O_3 , SiO_2 and unburned carbon that make it as a potential adsorbent. At high coal combustion temperature often produces Al_2O_3 and SiO_2 having high crystallinity like quartz and mullite. As a result it will reduce the adsorption capacity of the adsorbent. Therefore, this paper will discuss the effect of CFA crystallinity toward MV adsorption capacity.

EXPERIMENTAL

Sample preparation and characterization

CFA was obtained from Tanjungjati power plant, Jepara, Indonesia. It was treated with various NaOH concentrations (1 to 7M), temperatures (40 to 90°C) for one to six hours to reduce quartz and mullite contents in a batch reactor. The ratio of CFA weight to NaOH was 1 gram of CFA to 6 mL of NaOH. NaOH-treated CFA was filtered, washed several times with deionized water until pH of the filtrate was around 7, dried, characterized and used as an adsorbent in the sorption experiments. The chemical compositions of original CFA were analyzed using X-ray fluorescence (XRF). X-ray diffraction (XRD) patterns were obtained by powder method using Cu K α radiation (Schimadzu XRD-6000). Scanning Electron Microscopy (SEM) micrographs for original and treated CFA were obtained from SEM (JEOL, Japan). Specific surface area for both original

and treated CFA was measured by N_2 physisorption at 77 K using a NOVA 1200 microanalyzer (QUANTACHROME).

Batch adsorption experiment

Approximately 1 g of original or treated CFA was put into an erlenmeyer that had contained 50 mL of MV solution (MV solution concentrations were varied from 2.5 to 25 ppm). 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 240 minutes. Subsequently, suspended solid was filtered and filtrate was analyzed its MV concentration using a spectrophotometer at $\lambda_{\text{max}} = 581$ nm.

To investigate the effect of pH on adsorption, 1 g of original or treated CFA was added to an erlenmeyer contained 50 mL of 10 ppm MV solution. The pH was adjusted with base/acid to an appropriate pH (pH range of 3 to 11). The erlenmeyer contained the mixture was placed in a waterbath at 26°C and shaken mechanically for 240 minutes. The ash was separated from the solution and filtrate was analyzed its MV concentration using a spectrophotometer at $\lambda_{\text{max}} = 581$ nm.

RESULTS AND DISCUSSION

Characterization of adsorbents

The chemical compositions obtained using XRF show that the major components of CFA are SiO_2 , Al_2O_3 and carbon (See Table 1). The XRD traces (Fig 1) shows that CFA contains

Table 1. Chemical Compton of Tanjungjati CFA

Component	Content (mass %)
SiO_2	36.47
Al_2O_3	19.27
CaO	6.56
MgO	2.94
Fe_2O_3	10.74
MnO	0.07
Na_2O	1.76
K_2O	1.77
CuO	0.01
As_2O_3	0.01
P_2O_5	0.25
SO_3	1.04
Carbon	19.11

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crystalline phases like quartz (SiO_2), mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and amorphous components. The XRD pattern of treated CFA can be seen in Fig 2a, b, c, d, e, f and g. At lower NaOH concentration, lower temperature and shorter reflux time, intensity of quartz and mullite decrease, or in other words, the amorphous component of CFA increases (See Fig 2a,b,c). However, at higher NaOH concentration, higher temperature and longer reflux time, the decreasing of quartz and mullite intensity are

followed by formation of hydroxysodalite ($\text{Na}_6(\text{Si}_6\text{Al}_6\text{O}_{24}) \cdot 8\text{H}_2\text{O}$) (See Fig 2d,e,f,g). The crystallinity of hydroxysodalite increases with increasing NaOH concentration, as can be seen in Fig 4.

CFA treated with NaOH causes the increasing of specific surface area of the CFA, due to the increasing of amorphous formation. For NaOH concentration of 3M, reflux temperature of 60°C and 2 hours, specific surface area of treated CFA is $84.88\text{ m}^2 \cdot \text{g}^{-1}$. This

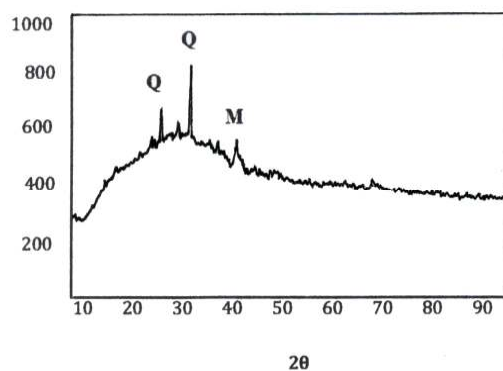


Figure 1. XRD patterns of Tanjungjati fly CFA Symbols : Q-quartz, M-mullite

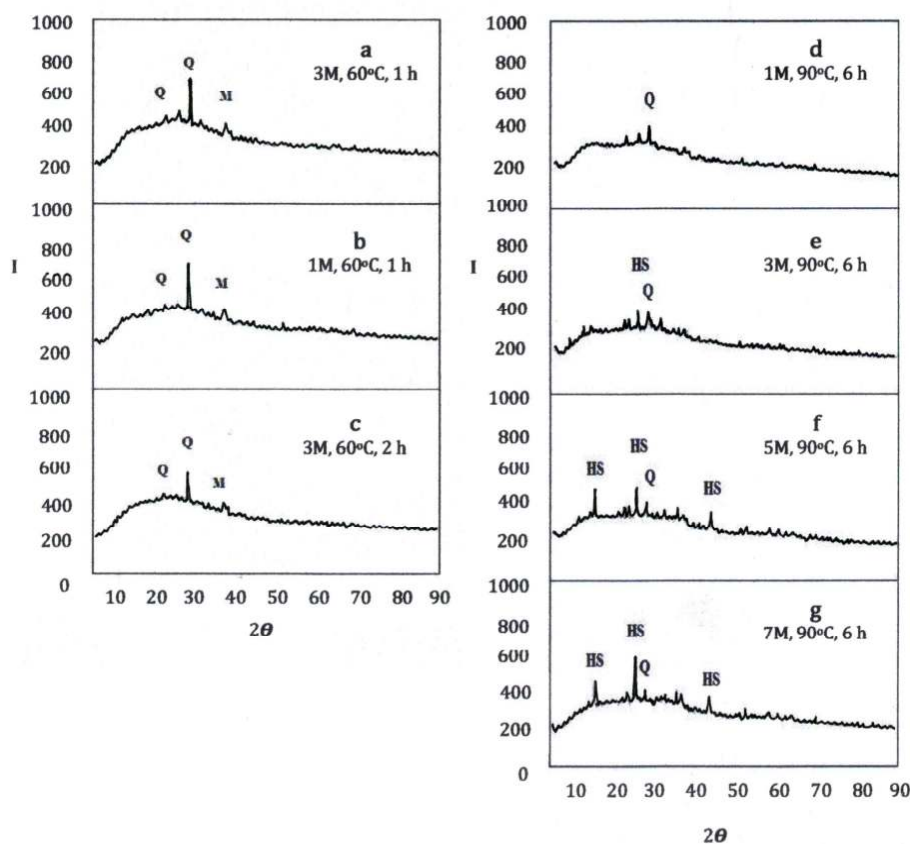


Figure 2. XRD patterns of various treated CFA Symbols : Q-quartz, M-mullite, HS-hydroxysodalite

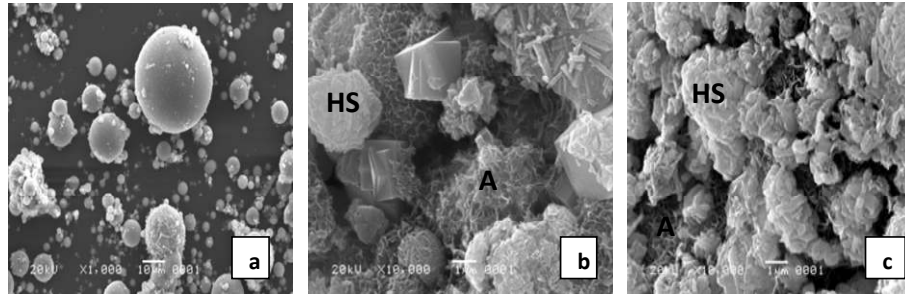


Figure 3. SEM image of treated CFA Symbols: HS-hydroxysodalite, A-amorphous. (a) original CFA, (b) treated CFA with reflux by 3M NaOH, 90°C, 6 hours, (c) treated CFA with reflux by 7 M NaOH, 90°C, 6 hours

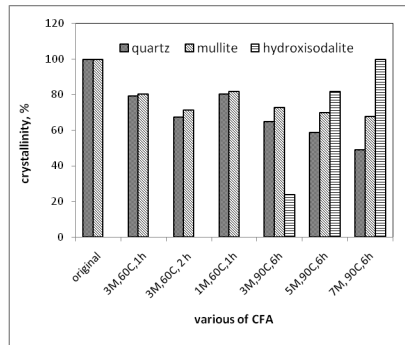


Figure 4. Crystallinity of original and NaOH-treated CFA

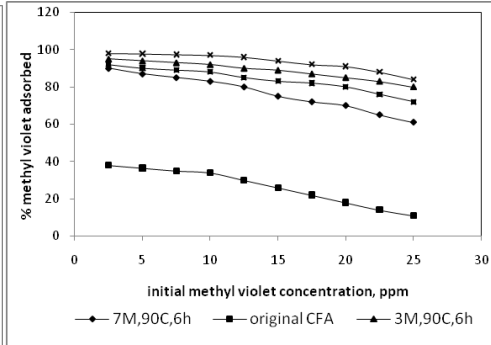


Figure 5. Effect of initial concentration on removal of MV by original and NaOH-treated CFA

(CFA dosage = 1g/50 mL MV solution, contact time = 240 minutes, pH = 9)

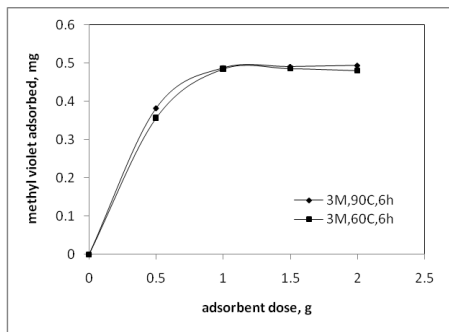


Figure 6. Effect of adsorbent dose for MV adsorption by NaOH-treated CFA (contact time = 240 min, pH = 9, initial MV concentration = 10 ppm)

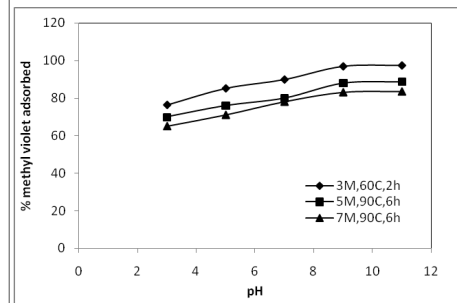


Figure 7. Effect of pH on MV adsorption by original and NaOH-treated CFA (CFA dose = 1g/50 mL MV solution, initial MV concentration = 10 ppm, time = 240 minutes)

is significantly higher than that of original CFA which is $10.4\text{m}^2\cdot\text{g}^{-1}$. If sodium hydroxide concentration increases to 7M, reflux temperature to 90°C , and time to 6 hours, specific surface area decreases from $84.88\text{ m}^2\cdot\text{g}^{-1}$ to $47.45\text{ m}^2\cdot\text{g}^{-1}$. The decrease in surface area indicates the formation of hydroxysodalite.

Fig 3 shows the SEM image of original and NaOH-treated CFA. When the NaOH-treated CFA are compared with the original CFA, a marked change in surface morphology can be observed. The original CFA comprises smooth spherical particles (Fig 3a). It can be seen from Fig 3b, a CFA amorphous increase which is indicated by rougher surface and full of holes. Fig 3c exhibits the increasing of

hydroxysodalite crystal formation and decreasing of amorphous content.

Methyl violet adsorption

Effect of crystallinity, initial dye concentration and CFA dose

MV adsorbed by original CFA is lower than that of treated CFA (See Fig 5). The higher amorphous and specific surface area of CFA was the higher MV was adsorbed. An average pores diameter of original CFA is 1.52 nm, whereas MV molecule has diameter of 11 nm. Incompatibility of this size complicates MV molecule into the pore of CFA. CFA treated with 3M NaOH, reflux temperature and time of 60°C and 2 hours respectively increases pore diameter to an average of 14 nm, which is higher than that of MV diameter. As a consequence, the amount of MV adsorbed increases. On the other hand, for CFA treated with 7 M NaOH, reflux temperature of 90°C and time 6 hours, a lot of hydroxysodalite was formed and an average pore diameter become 1.35 nm. As a result, the MV adsorbed decrease.

Fig 5 exhibits that the percentage removal of MV decreases with the increasing initial MV concentration. This is because of equilibrium has been attained.

The percentage removal of MV increases with the CFA dose up to a certain limit and then it reaches nearly a constant value (See Fig 6). It was due to the availability of more surface area of CFA and active sites for adsorption. Fig 6 reveals that for the CFA dose which is higher than 1 g/50 mL does not have any effects on MV removal from the solution.

Effect of pH

pH of solution affect surface charge of the adsorbent as well as the degree of ionization of different pollutants. Fig 7 demonstrates that MV adsorbed increases with increasing of the pH solution. At high pH of solution, silica has more negative charge so that chemical binding of dye cation with active site of silica can easily happen. As consequence, the removal of MV from solution also increases.

Effect of contact time

In the first few minutes, the adsorbate uptake is very fast and then it becomes slow and finally level off (See Fig 8). 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 (Dogan et al. 2006).

Adsorption kinetics

In order to clarify the adsorption kinetics of MV 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 (Hefne, 2008):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

Where q_e and q_t are amounts of the MV adsorbed at equilibrium (mol g^{-1}) and at time t (mol g^{-1}), respectively, k_1 is the rate constant (min^{-1}), t is time (min). The adsorption rate constants (k_i) can be determined experimentally by plotting of $\ln(q_e - q_t)$ versus t . Experimental data were also fitted for the pseudo second order (Wen et al., 2006):

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

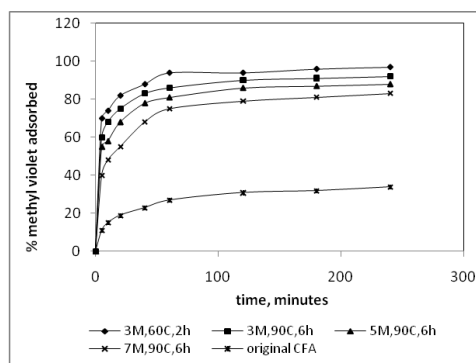
Where k_2 ($\text{g.mol}^{-1} \text{min}^{-1}$) is the rate constant. Equation (2) is solved graphically by plotting $\frac{t}{q_t}$ versus t . The value of q_e can be calculated from the slope of the straight line and k_2 from its intercept. Fig 9 shows that the experimental data fit with the pseudo second order model. Table 2 illustrates the k_1 and k_2 for pseudo first and second order rate constants as well as q_e for both of them.

Comparison with previous studies

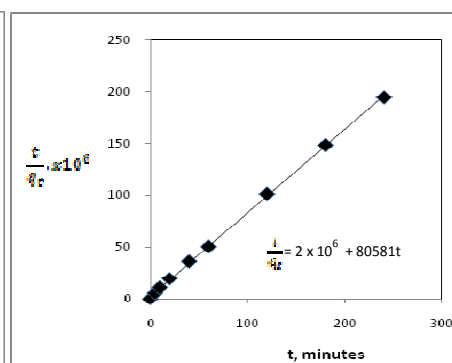
Some researchers have performed experiments related to adsorption for different fluid-adsorbent systems. Mall et al. (2006) conducted adsorption experiments using a system of MV-bagasse fly ash (BFA), Eren and Acer (2006) studied a reactive black 5-powder activated carbon (PAC) system, Yamada et al. (2003) evaluated a system of methylene blue-Columbian fly ash and this paper describes MV-NaOH-treated CFA system. NaOH-treated CFA can reduce the MV concentration up to 97%, whereas BFA can reduce MV concentration up to 95% (Mall et al., 2006). Using PAC as an adsorbent to adsorb reactive black 5 dye can reduce its concentration up to 90% (Eren and

Table 2. Parameters for adsorption kinetics of methyl violet

Pseudo first order			Pseudo second order		
q_e (mol g ⁻¹)	k_1 (min ⁻¹)	R^2	q_e (mol g ⁻¹)	k_2 (g mol ⁻¹ min ⁻¹)	R^2
3.8×10^{-7}	0.02	0.795	1.24×10^{-5}	3.2×10^3	0.999

**Figure 8.** Effect of contact time on MV removal

(CFA dose = 1g/50 mL MV solution, initial concentration of Mv solution = 10 ppm, pH = 9)

**Figure 9.** Pseudo second order adsorption kinetics of MV on treated CFA

treated CFA with 3M NaOH, 60°C, 2 hour adsorption : CFA dose = 1g/50 mL, initial MV concentration = 10 ppm, pH = 9

Acer, 2006). So it can be said that between those adsorbents, the quality of NaOH-treated CFA is the highest.

Adsorption capacity of NaOH-treated CFA of this study is 12.4×10^{-6} mol g⁻¹, while capacity of columbian fly ash is 1.6×10^{-6} mol g⁻¹ (Yamada et al., 2003). It means that NaOH-treated CFA has a good prospect for adsorbent. In addition the huge availability of CFA makes it as one of the low cost adsorbents.

CONCLUSION

The present study shows that NaOH-treated CFA is an effective adsorbent for remove MV from aqueous solution. CFA treated with low NaOH (1-3M), temperature of 60°C, time of 2 hours can decrease crystallinity of quartz and mullite, while with higher NaOH concentration, the decreasing of quartz and mullite are followed by formation of hydroxysodalite which can reduce its adsorption capacity. The amount of MV adsorbed depends on the initial concentration of MV, pH of solution, adsorbent dose and contact time. The effective conditions for MV adsorption are follows : the initial concentration, pH, and adsorbent dose are 10 ppm, 9, and 1 g/50 mL, respectively. Its equilibrium condition was practically achieved in 1 hour. Adsorption kinetics of MV onto CFA could be approximated with pseudo second

order kinetic model which the value of rate constant is 3.2×10^3 g mol min⁻¹.

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