

The Effect of Coal Fly Ash Treatment with NaOH on the Characters and Adsorption Mechanism toward Methyl Violet in The Solution

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Abstract. The Coal fly ash (CFA) generated by coal-based thermal power plants is mainly composed of some oxides having high crystallinity including quartz, mullite and unburned carbon. In this study, the effect of CFA crystallinity toward its adsorption capacity and adsorption mechanism for methyl violet in the solution was investigated. CFA having various crystallinity was obtained by refluxing it with sodium hydroxide (NaOH) solution at various concentrations, temperature and reflux time. To evaluate the effect of crystallinity of treated CFA on the adsorption capacity and adsorption mechanism, adsorption of MV solution with treated CFA was carried out. The research shows that the reflux of CFA with NaOH solution leads to the crystallinity of quartz and mullite in CFA decreased. The decrease is proportional with the concentration increasing, the temperature elevation, and the longer time. The reflux using NaOH solution with high concentration (> 3 M) in addition causes a decrease in the crystallinity of quartz and mullite, also results in the formation of hydroxysodalite. The decrease of the CFA crystallinity gives an increase MV adsorbed. Adsorption of MV on treated CFA is a chemisorption.

Keywords: Coal fly ash, NaOH, Methyl violet, Chemisorption

1. Introduction

Large quantities of fly ash are produced during the combustion of coal in the production of electricity. In Indonesia, more than 1 million tons of coal fly ash (CFA) is being generated annually [1]. Most of this ash is only for landfilling. The improvement of CFA utilization has been carried out by applying it as adsorbent [1].

CFA is mainly composed of some oxides such as Al_2O_3 , SiO_2 , and unburned carbon that enables it to act as an adsorbent. The capacity of such CFA is relatively low [2], that may be caused by high crystallinity of Al_2O_3 and SiO_2 as well as the presence of the unburned carbon. The effect of CFA crystallinity toward Pb(II) adsorption has been reported [3]. In the present paper, the crystallinity effect towards methyl violet (MV) adsorption and its adsorption mechanism is reported.

The presence of dyes in liquid effluents generated by textile, paper, printing and plastic industries is undesired and harmful, and must be reduced before discharge to the environment. Adsorption process is one of the effective techniques that have been successfully employed for dyes removal from wastewater. Many adsorbent have been tested to reduce dyes concentration from aqueous solutions, like activated carbon [4] and some agricultural waste [5]. In order to improve efficiency of adsorption process, it is necessary to develop an adsorbent that is cheaper but has high adsorption capacity.

2. Experiment

2.1. Materials and Samples

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Sodium hydroxide (NaOH) in extra pure grade were purchased through Merck, CFA was obtained from Tanjungjati power plant, Jepara, Indonesia and methyl violet.

2.2. Instruments

X-ray diffractometer (Schimadzu XRD-6000), x-ray fluorescence spectrometer (Shimadzu), SEM (JEOL, Japan), NOVA 1200 microanalyzer (quantachrome), spectrophotometer (spectronic 20 Genesis), fourier transform infra red (FTIR) spectrometer (Shimadzu).

2.3. Procedures

2.3.1. Sample Preparation and Characterization

CFA sample that has been washed, dried, and sieved into 100-mesh in particle size was refluxed with NaOH having various concentrations (1, 3, 5 and 7 M), at lower and higher temperatures (60°C and 90°C) for 1, 2 and 6 hours. In the reflux, 1 gram of CFA and 6 mL NaOH solution were employed. The refluxed mixture was filtered and washed several times with deionized water until pH of the filtrate was around 7, and then it was dried at 120°C. The dried treated CFA was ready to be characterized and used as an adsorbent [3].

The chemical compositions of original CFA were analyzed using x-ray fluorescence (XRF). The crystallinities of original and treated CFA were characterized by means of x-ray diffraction (XRD) using Cu K α radiation [3]. Specific surface area and pore size distribution were characterized by N₂ physisorption at 77 K (NOVA 1200 microanalyzer) using Brunauer Emmet Teller (BET) and Barret-Joyner-Halenda (BJH) method, respectively while SEM micrograph was obtained from scanning electron microscope (SEM) [3]. Functional groups were characterized by fourier transform infra red (FTIR) spectrometer.

2.3.2. Batch Adsorption Experiment

CFA adsorbent was mixed with MV solution in an erlenmeyer. Then the mixture was placed in a waterbath that the temperature can be adjusted and shaken mechanically for a period of time. Subsequently, suspended solid was filtered and the filtrate was analyzed to determine MV concentration using spectrophotometer at $\lambda_{max} = 581$ nm.

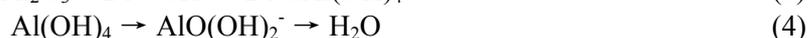
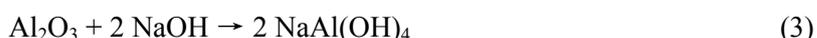
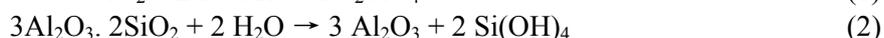
3. Results and Discussion

3.1. Chemical composition of CFA

The chemical composition of CFA analyzed using x-ray fluorescence spectrometer shows that the major components of CFA are SiO₂(36.47%), Al₂O₃(19.27%) and carbon (19.11%), while the XRD pattern of CFA shows that CFA contains crystalline phase including quartz (SiO₂), mullite (3Al₂O₃·2SiO₂) and amorphous components, as shown by Fig.1 [3].

3.2. Effect of NaOH Treatment toward CFA Characters

Generally, treatment using NaOH solution leads to a decrease in the intensities of quartz and mullite as shown in Fig. 2. An interesting data is observed that is appearance of new peaks at $2\theta = 13.9$, $2\theta = 24.2$, $2\theta = 42.7$, when the reaction was carried in high NaOH concentration, high temperature or long time [3]. The new peaks is indicated as hydroxysodalite (1.08Na₂O□Al₂O₃ 1.68SiO₂□18H₂O) [5]. The intensities are proportional with their crystallinity, and degrees of quartz, mullite, and hydroxysodalite crystallinity have been calculated by comparing the respective intensities to the standard intensities. Fig. 3 and 4 show that the degree of quartz and mullite crystallinities reduces, while the degree of hydroxysodalite improves in accordance with the extention of reaction time, elevating of temperature and increasing of NaOH concentration [3], as shown by reaction (1)-(5) [6].



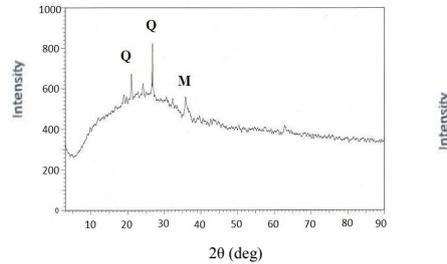
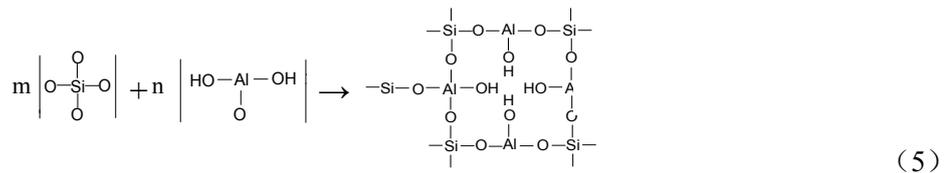


Fig. 1 : XRD patterns of Tanjungjati fly ash

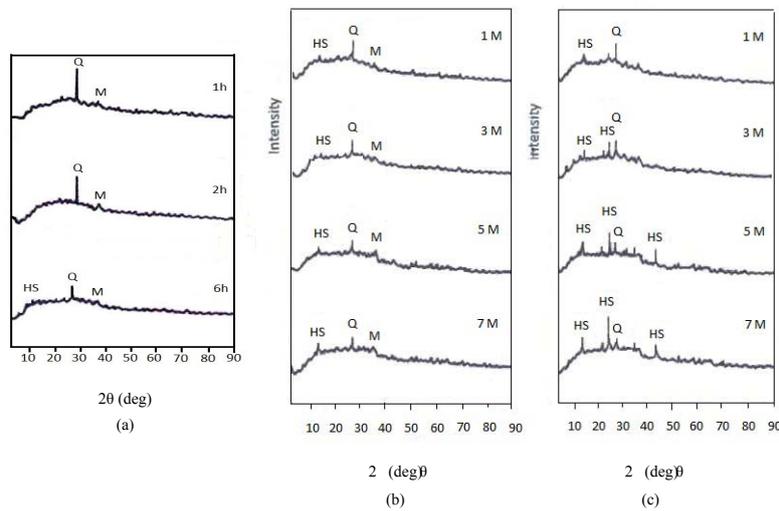


Fig. 2 : XRD patterns of treated CFA: (a) 60°C, 3M, 1,2 and 6 hours,; (b) 60°C, 6h, 1-7M; (c) 90°C, 6h, 1-7M

Further characterized samples are treated CFA possessing the highest degree of mullite and quartz crystallinity without hydroxysodalite formed (Q54M61HS0), medium degree of mullite, quartz, and hydroxysodalite crystallinity (Q44M51HS21), and the lowest degree of mullite and quartz crystallinity with the highest degree of hydroxysodalite crystallinity (Q36M41HS99) [3].

Specific surface area of the samples is illustrated in Fig. 5. It shows that the reflux enlarges specific surface area. Moreover, Q54M61HS0 gives the highest surface area, followed by Q44M51HS21, and that of Q36M41HS99. It is implied that the decrease of the surface area is strongly contributed by increasing crystallinity of hydroxysodalite. The relationship of pore diameter of CFA with the degree of crystallinity is shown in Fig. 6. It shows that the pore diameter of treated CFA is larger compared to untreated CFA. The largest pore diameter is found in Q54M61HS0 (14 nm), and the smallest pore diameter is found in Q36M41HS99 (1.35 nm). It is because hydroxysodalite is a crystall having small pore diameter (0.2 nm) and covers CFA surface partially, including amorphous component. Consequently, methyl violet having pore diameter of 11 nm can easily enter the Q54M61HS0 pore [3].

Fig. 7 illustrated SEM images of the untreated CFA and the treated CFA. When the 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. 7a), whereas Q54M61HS0 has rougher surface and full of

holes (Fig. 7b). Fig. 7c shows that some hydroxysodalite crystal covers Q44M51HS21 surface, whereas Fig. 7d shows that a lot of crystal in Q36M41HS99 surface and the holes reduce [3].

3.3. MV Adsorption

In general, MV adsorbed by original CFA is lower than that of treated CFA (See Fig.8). Increasing amorphous (A) and specific surface area of CFA gives an increase MV adsorbed. The effect of the adsorption time is shown in Fig.8. It is seen that the uptake of adsorbate is fast at initial stages of the contact period and it becomes slower near the equilibrium. 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 the adsorbate, the adsorption process becomes difficult due to repulsive forces between the solute molecules on solid and bulk phases. To confirm the mechanism adsorption, the existence of functional groups was analyzed using FT-IR spectrometer.

The FT-IR spectrum of original CFA is shown in Fig.9a. It shows the presence of an absorption band at $3425,58\text{ cm}^{-1}$ which may be attribute to intra-molecular H-bonded (-OH) groups while the peak at 2926 cm^{-1} and 2853 cm^{-1} are due to aliphatic C-H groups [7]. It shows that besides pores, there are active sites in carbon surface. The band at $478,35\text{ cm}^{-1}$ is assigned to the O-Si-O bending vibration while band at $788,98\text{ cm}^{-1}$ is due to symmetric vibration of Si-O-Si [7]. The band at 700 cm^{-1} to the presence of mullite [7] while band at $980-1100\text{ cm}^{-1}$ is assigned to the Al asymmetric stretching vibration in tetrahedral silica framework. After reaction with NaOH, the band at $3600-3200\text{ cm}^{-1}$ in the corresponding spectrum (trace A in Fig. 9b) shows a higher intensity. This may be associated with the stretching vibration of hydroxy groups involved in hydrogen bonding, probably with the participation of water adsorbed onto the carbon surface [8]. Bands in Si and Al region, specifically those near 1000 cm^{-1} become more intense. Trace B in Fig. 9b show that after the uptake of MV dye, intensities of some peaks mentioned above decrease. This provides a clear confirmation of the impact of such surface functional groups on the adsorption process and shows that the adsorption mechanism is chemisorption.

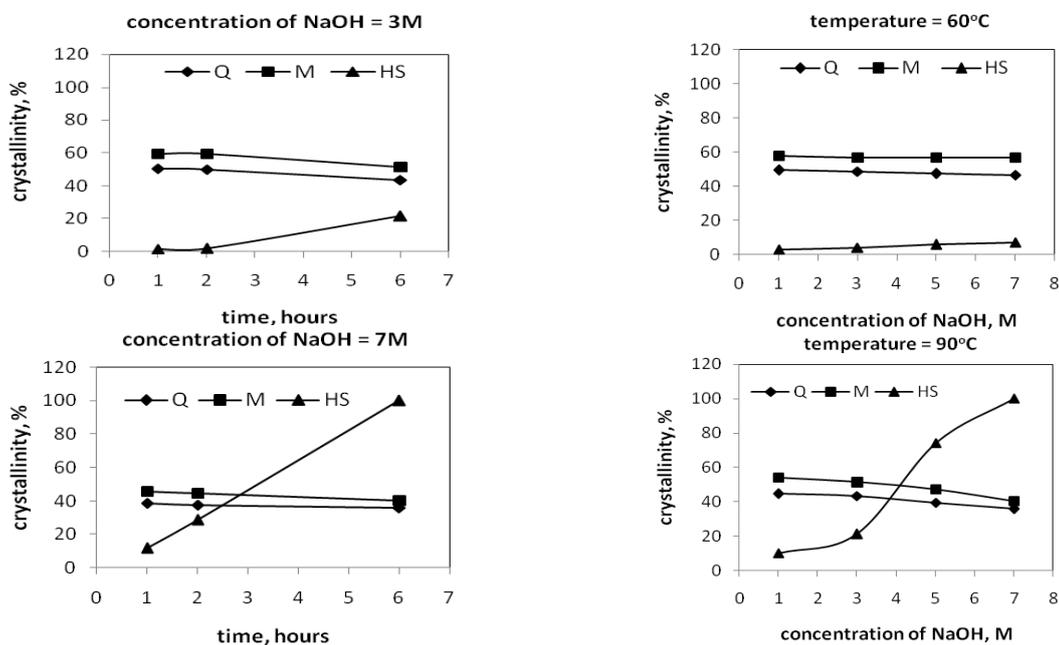


Fig. 3 : The effect of time toward crystallinity. Temperature: 60 °C. crystallinity untreated CFA Q = 88%, M = 71%, HS = 0% (noted as Q88M71HS0)

Fig. 4 : The effect of NaOH concentration toward crystallinity. Time: 6 hours.

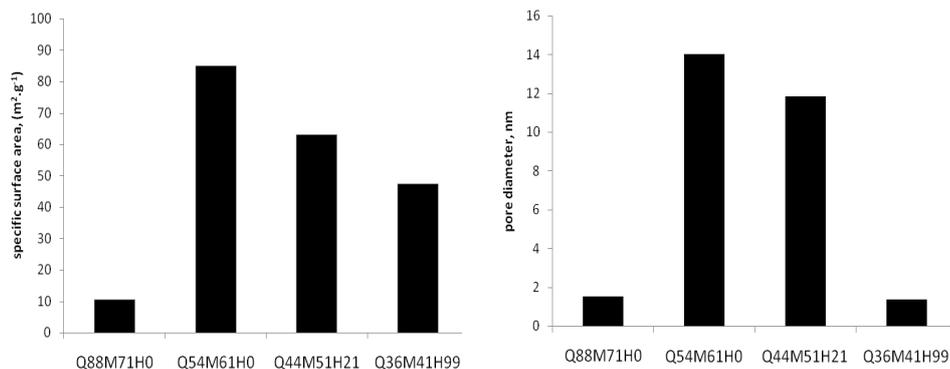


Fig. 5 : Specific surface area of untreated and treated CFA.

Fig. 6 : Pore diameter of untreated and treated CFA. Q54M61HS0 means crystallinity of quartz 54%, mullite 61%, hydroxysodalite 0%

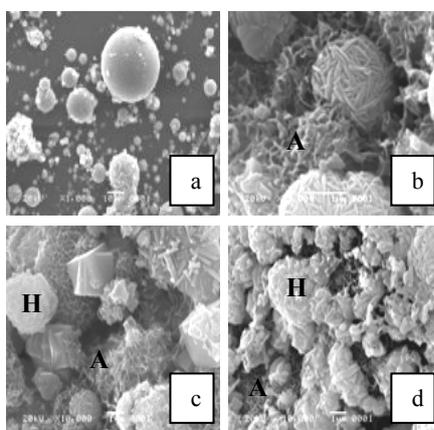


Fig. 7 : SEM micrograph of (a) Q88M71HS0 (b) Q54M61HS0 (c) Q44M51HS21 (d) Q36M41HS99

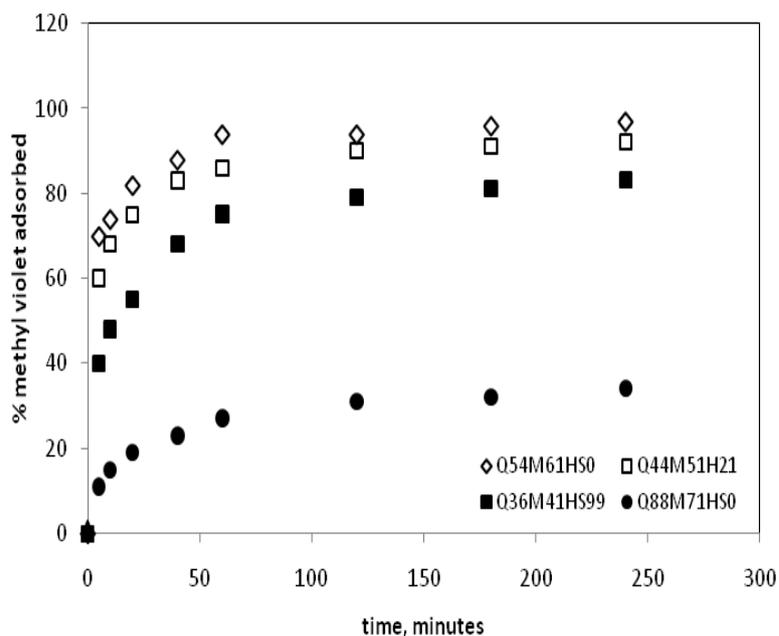


Fig. 8 : Effect of contact time on MV removal (CFA dosage = 1g/50 mL MV solution, initial concentration of MV solution = 10 ppm, pH = 9)

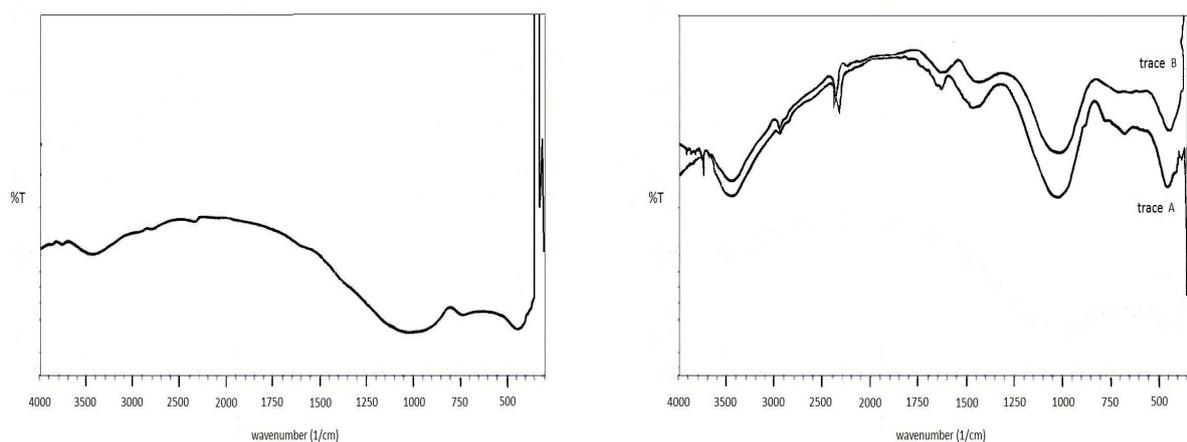


Fig. 9 : FT-IR spectrum of (a) untreated CFA (b) Q44M51W6

4. Acknowledgements

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