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The character of dual site adsorbent on coal fly ash toward Pb (II) adsorption

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Abstract: - Coal fly ash (CFA), generated during combustion of coal in the electricity production is recognized as an environmental pollutant. CFA is composed primarily of some oxides including SiO_2, Al_2O_3 having active site and unburned carbon that anables it to act as a dual site adsorbent. However, the existence of unburned carbon in coal fly ash can generate two possibilities. It can improve the adsorption capacity, or contradictionly hinder the adsorption.The aim of this paper is to study the contribution of unburned carbon on coal fly ash toward characters, adsorption capacity and adsorption mechanism. In this context, CFA with various unburned carbon content were employed as adsorbent of Pb(II) in aqueous solutions. The research shows that the existence of unburned carbon in CFA leads to the increase of specific surface area and pore size, but the adsorption capacity for Pb(II) decrease. Adsorption kinetics of Pb(II) onto CFA could be approximated with a pseudo second order kinetic model with the rate constant was $0.298\ g.mg^{-1}.min^{-1}$.

Keywords: - *coa fly ash, unburned carbon, dual site adsorben, Pb(II), adsorption*

I. INTRODUCTION

Coal fly ash, generated during the combustion of coal in power plant, is an industrial by-product which is recognized as an environmental pollutant. Increasing concern about the environmental consequences of such disposal have led to investigations into other possible utilization avenues, including as adsorbent. However, the adsorption capacity of CFA is not very high. Several authors have reported the conversion of coal fly ash into zeolite and used it to reduce heavy metal and dye concentrations from aqueous solutions [1,5,6,7,8]. Zeolite is regarded as an effective but expensive adsorbent due to its high cost of manufacturing. In order to improve the efficiency of adsorption processes, it is necessary to develop cheaper adsorbents with high adsorption capacities.

CFA contains mineral composed of SiO_2, Al_2O_3 having active site and unburned carbon that anables it to act as a dual site adsorbent. However, the existence of unburned carbon in coal fly ash can generate two possibilities. It can improve the adsorption capacity, or contradictionly hinder the adsorption. It has not been explored yet. The aim of this paper is to give a contribution for understanding the effect of unburned carbon on coal fly ash toward characters, adsorption capacity and adsorption mechanism. In this context, Pb(II) is choosen because it is one of the major pollutants which is primarily discharged from printing, paper, ammunition and electroplating industries to the water and environment.

II. MATERIALS AND METHODS

1.1. Sampel Preparation and Characterization

The effect of unburned carbon on coal fly ash toward characters, adsorption capacity and adsorption mechanism was evaluated by reducing and increasing unburned carbon content to obtained CFA having various unburned carbon content. CFA was collected from electrostatic precipitators of Tanjungjati power plant, Jepara, Indonesia. Before any treatment, it was washed with deionized water and dried. CFA was further treated with various sulfuric acid concentration (50 to 75 w/w), temperatures (60 to 90°C) for three to six hours to reduce unburned carbon content. The ratio of CFA weight to sulfuric acid volume was 1 g of CFA to 6 mL 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, characterized and then used as an adsorbent in the sorption experiments. The unburned carbon content on CFA was also reduced by heating at 400-800°C for 1 hour. In addition, the effect of unburned content were 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 composition of original CFA was 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). The Brunauer-Emmett-Teller (BET) surface area and pore size were characterized by

N_2 physisorption at 77 K using NOVA 1200 microanalyzer. While, the morphology of CFA surface was obtained from scanning electron microscope (SEM).

1.2. Batch Adsorption Experiment

Original or treated CFA (1 g) was put into an erlenmeyer filled 50 mL of Pb(II) solution. Pb(II) solution concentrations were varied from 10 to 1000 mg.dm^{-3}. The adsorption was carried out at pH of 5. The erlenmeyer contained the mixture was placed in a waterbath at 26^{o}C and shaken mechanically for 5 to 180 minutes. Subsequently, suspended solid was filtered and the filtrate was analyzed to determine Pb(II) concentration using atomic absorption spectrophotometer. To investigate the effect of pH on adsorption, 1 g of original or treated CFA was added to an erlenmeyer filled 50 mL of 10 ppm Pb(II) solution. The pH was adjusted with base/acid to an appropriate pH (pH range of 3 to 9). The erlenmeyer filled the mixture was placed in a waterbath at 26^{o}C and shaken mechanically for 180 minutes. The ash was separated from the solution and the filtrate was analyzed to determine Pb(II) concentration using atomic absorption spectrophotometer.

III. RESULTS AND DISCUSSION

1.3. Characterization of CFA

The original CFA employed in this research shows the presence of significant fractions of SiO_2 and Al_2O_3, as reported in Table 1. The silico-aluminous nature of the ashes is confirmed by XRD. Fig. 1 clearly shows the peaks of quartz and mullite which are crystalline phases of SiO_2 and $3Al_2O_3.2SiO_2$, respectively. Difractogram of treated CFA is reflected in Fig. 2. It shows several sharp diffraction peaks that were different with diffractogram of original CFA. At heating treatment, the intensity of quartz decreases. While, at H_2SO_4 treatment, hydroxysodalite ($Na_6(Si_6Al_6O_{24}).8H_2O$) can be identified. Similar observations were made by Woolard [2] who found hydroxysodalite at NaOH treated CFA.

Table 1. Chemical Composition of original 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
unburned carbon	19.11

Fig. 3 illustrated SEM micrograph of the original CFA. Most of CFA mineral have smooth surface, whereas others have rougher surface because the surface is covered by unburned carbon, as can be seen in Fig. 3b. Besides covers CFA mineral surface, unburned carbon is also randomly distributed as a mesopore material. Specific surface area (SSA) and pore diameter of CFA are presented in Fig. 4 and Table 2, respectively. The existence of unburned carbon in CFA leads to the increase of SSA and pore diameter. It is because unburned carbon is a porous material that contributes to the increase of SSA and pore size. Montagnaro and Santoro [3] also noted an increase in the SSA of CFA as a result of the existence of unburned carbon in CFA.

Table 2. Pore Size of CFA

	unburned carbon content (%)	
	19,11	46,15
pore size (nm)	3,055	3,384

1.4. Effect of sulfuric acid, heating and sieving treatment toward unburned carbon content

Fig. 5 demonstrates that sulfuric acid treatment causes a decrease of unburned carbon content in CFA. At constant sulfuric acid concentration and processing time, higher temperature causes unburned carbon content in CFA decrease. At constant temperature and processing time, higher sulfuric acid concentration causes unburned carbon content in CFA decrease. While, at constant temperature and sulfuric acid concentration, longer processing time also causes unburned carbon content in CFA decrease. Heating from 400^{o}C to 800^{o}C causes a decrease of unburned carbon content. Higher temperature gives lower unburned carbon content. The decreasing of unburned carbon content caused by heating is more than that of caused by sulfuric acid treatment. Otherwise, sieving treatment leads to an increase of unburned carbon content in CFA.

1.5. Pb (II) adsorption by CFA-unburned carbon as dual site adsorbent

Fig. 6 shows that an increase of unburned carbon content on CFA causes adsorption capacity decrease. Even though unburned carbon can give a contribution to the Pb(II) adsorption, but the contribution of active sites on CFA mineral is higher than that of unburned carbon pore. A great amount of unburned carbon can form agregates and cover the active site on CFA surface, so chemical binding between the active sites and Pb(II) can not happen. Consequently, Pb(II) adsorption decrease. Desorption test using aquadest also shows that most of adsorption occur at the active site, as can be seen in Table 3. If Pb(II) can be desorbed by aquadest, it indicates that Pb(II) adsorption occurs at unburned carbon with weak interaction (physisorption). Otherwise, If Pb(II) can not be desorbed by aquadest, it indicates that Pb(II) adsorption occurs at active site with stronger interaction (chemisorption). Table 3 shows that only 4.53 % of Pb(II) can be desorbed by aquadest. It indicates that most of adsorption occur at active site. The increase of unburned carbon content on CFA gives an increase of Pb(II) desorbed.

Table 3. Comparation of Pb(II) adsorbed and Pb(II) desorbed from CFA having various unburned carbon content

	unburned carbon content (%)	
	0,42	19,1
Pb(II) adsorbed, mmol/g	0,0599	0,0309
Pb(II) desorbed, mmol/g	0,0016	0,0014
Pb(II) desorbed, %	2,63	4,53

Fig. 7 illustrates the adsorption behavior of various CFA as a function of pH. It is apparent that in all cases, the amount of Pb(II) adsorbed increases as pH increases until pH = 5. However, at pH higher than 5, the amount of Pb(II) adsorbed decreases as pH increases. It is because, at high H^+ concentration, competition between H^+ ion and Pb(II) ion occurs so the adsorpstion capacity decreases. While, at lower H^+ concentrations, the active site becomes more negatively charge, so interaction between Pb(II) ion with active site occurs easily and the adsorption capacity increases. At pH higher than 6, metal precipitation occurs so Pb(II) adsorption decreases.

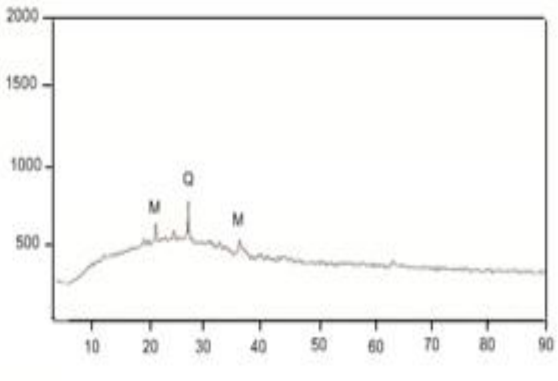
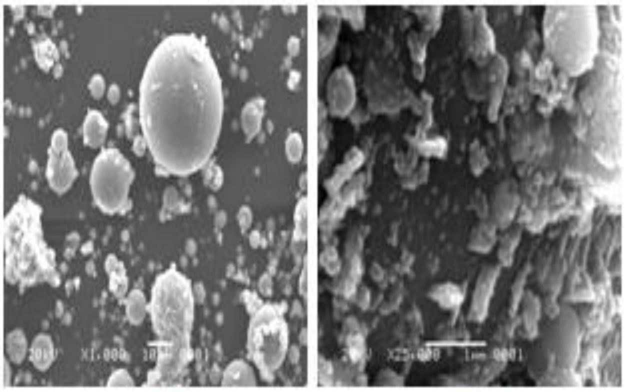


Fig. 1 : XRD patterns of original CFA



(a) (b)

Fig. 3: SEM micrograph of CFA magnification: (a) 1000 x (b) 25.000 x

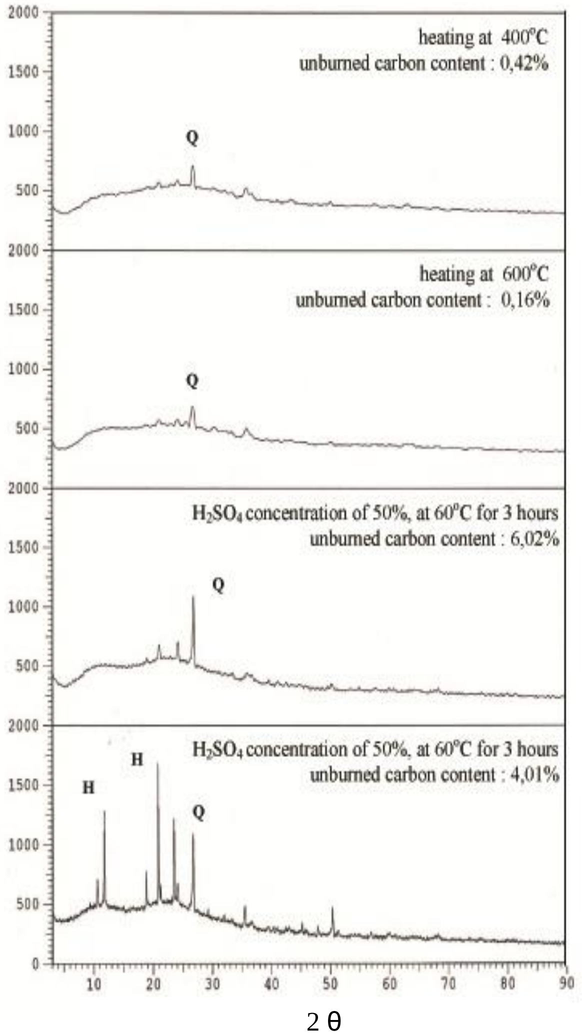


Fig. 2 : XRD patterns of treated CFA

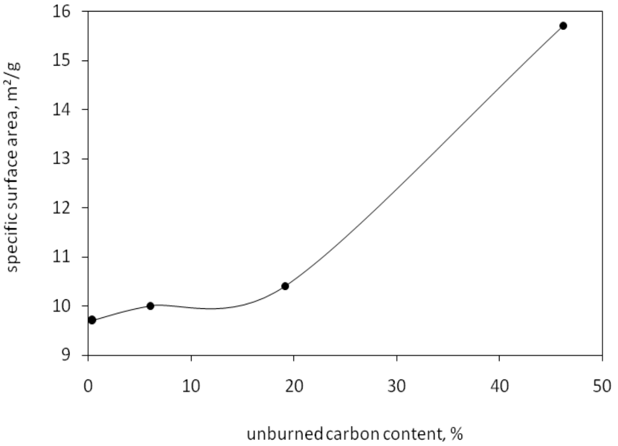


Fig. 4 : Specific surface area of treated CFA having various unburned carbon content

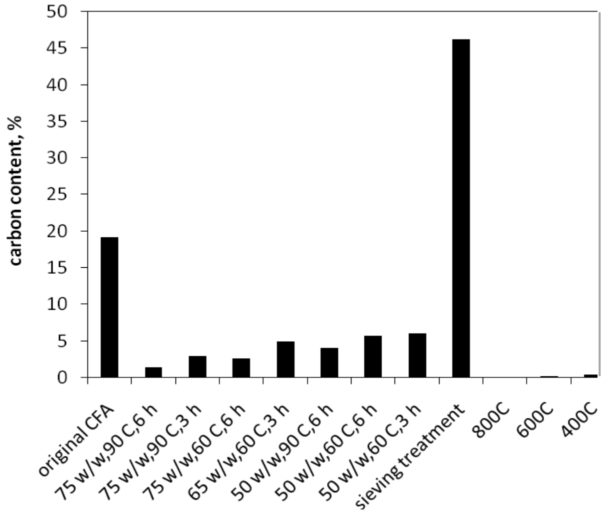


Fig. 5 : Carbon content of original and treated CFA
Note : x w/w, y C, z h means sulfuric acid concentration (w/w), temperature (^{o}C) and reflux time (hours)

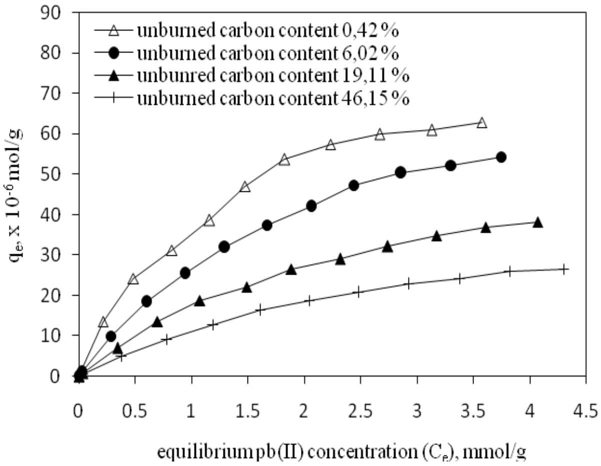


Fig. 6 : adsorption isotherm of Pb(II) in aqueous solution by CFA

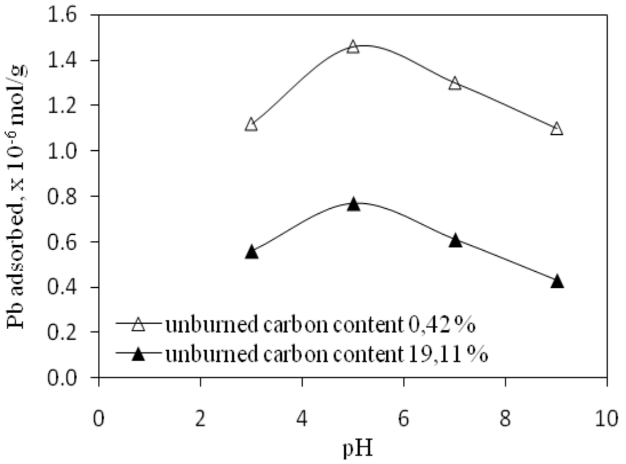


Fig. 7. Effect pH toward Pb(II) adsorbed

1.6. Adsorption kinetics

In order to clarify the adsorption kinetics of Pb(II) onto CFA, Lagergren's pseudo-first order and pseudo 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 [4] :

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

where q_e and q_t are amounts of Pb(II) adsorbed on CFA surface at equilibrium (mg.g^{-1}) and at time t (mg.g^{-1}), respectively, k_1 is the rate constant of pseudo first order model (min^{-1}) and 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 [4] :

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

where k_2 (g.mg^{-1}.min^{-1}) is the rate constant of the second order model. The adsorption rate constants (k_2) can be determined experimentally by plotting between t/q_t versus t where q_e can be calculated from the slope of the straight line and k_2 from its intercept. Tabel 4 illustrates the k_1 and k_2 for first and second order rate constants as well as q_e for both of them. It shows that the experimental data fit with the second order model.

Table 4. Parameters for adsorption of Pb(II) onto CFA derived from the pseudo first and second order kinetic models

Pseudo first order			Pseudo second order		
q_e (mg.g^{-1})	k_1 (min)	R^2	q_e (mg.g^{-1})	k_2 (g.mg^{-1}. min^{-1})	R^2
0.293	0.029	0.949	0.481	0.298	0.997

IV. CONCLUSION

It is concluded that unburned carbon hinder Pb(II) adsorption. The increase of unburned carbon content on CFA leads to a decrease of adsorption capacity. The amount of Pb(II) adsorbed also depends on pH of solution. Adsorption kinetics of Pb(II) onto CFA could be approximated with pseudo second order kinetic model with the rate constant is 0.298 g mol^{-1} min^{-1}.

V. ACKNOWLEDMENT

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