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The Character of Dual Site Adsorbent on Coal Fly Ash Toward Benzene Adsorption

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ABSTRACT
Large quantities of coal fly ash (CFA) are produced during combustion of coal in the production of electricity. Most of this ash has not been widely used. CFA is mainly composed of some oxides including Al_2O_3 and SiO_2 having active site and unburned carbon as a mesopore that enables it to act as a dual site adsorbent. To get different characters of dual site, CFA was sieved using 150 mesh size, heated at 400^oC and reacted with sodium hydroxide solution. Furthermore, CFA was used as adsorbent of benzene in aqueous solutions. Equilibrium data were evaluated by single site and dual site isotherm models. It can be concluded that single site model yielded excellent fit with equilibrium data of benzene. The values of maximum concentration of adsorbate in solid surface ($C_{\mu m}$) and Langmuir constant (K_L) are affected by [Si+Al]/C ratio in CFA. The increase of [Si+Al]/C ratio causes a decrease of q_m and K_L values.

Keywords : coal fly ash, adsorption, benzene

1. Introduction

Large quantities of CFA are produced during the combustion of coal in the production of electricity. In Indonesia, more than 1 million tons of CFA is being generated annually [1]. 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 an adsorbent [2]. CFA is composed of some oxides including Al_2O_3, SiO_2 having active site and unburned carbon (C) as a mesopore material [3] that enables it to act as a dual site adsorbent.
On the other side, benzene is one of the toxic pollutant and carcinogenic compound [4] used as a raw material in the petrochemical industry [5]. Several methods have evolved over the years on the removal of it in industrial waste water. However, adsorption is an appropriate method to remove benzene at a low concentration level. Many adsorbents have been tested to remove it from aqueous solutions including activated carbon [5]. However, to improve the efficiency of adsorption process, it is necessary to develop an adsorbent that is cheaper but has high adsorption capacity including CFA. In this paper, the effect of dual site on CFA toward benzene adsorption is discussed.

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2. Material and methods

2.1. Sample Preparation and Characterization

Benzene in extra pure grade were purchased through Merck. While, CFA was obtained from Tanjungjati power plant, Jepara, Indonesia. Before any treatment, CFA was washed with distilled water and dried. To study dual site character of CFA toward benzene adsorption, it is used CFA having [Si+Al]/C ≈ 0.5, [Si + Al]/C ≈ 2 and [Si + Al]/C ≈ 90, obtained from sieving of CFA using 100 mesh size, reaction of CFA with sodium hydroxide 3M at temperature of 60^{o}C for 2 hours; and heating of CFA at 400^{o}C, respectively. Furthermore, the chemical compositions of CFA was analyzed using x-ray fluorescence (XRF). While crystallinity and morphology of CFA were analyzed using XRD (Schimadzu XRD-6000) and SEM (JEOL, Japan), respectively. Surface areas and pore structures of the prepared samples were established from nitrogen adsorption isotherm as measured at 77K by means of a NOVA 1200 microanalyzer (QUANTACHROME). The surface area was calculated using BET equation while the pore size distribution was established through the use of BJH method.

2.2. Batch Adsorption Experiment

Each of CFA (4g) was put into an erlenmeyer filled 230 mL of benzene solution. The erlenmeyer contained the mixture was placed in a waterbath at 28^{o}C and shaken mechanically for 72 hours. Subsequently, suspended solid was filtered and the filtrate was analyzed to determine benzene concentration using gas chromatography (GC).

2.3. Isotherm Models

Isotherm models used in this study are a single site and dual site which is modificated from langmuir and freundlich isotherm. Models used in this study are single-site langmuir (1st model), single site freundlich (2nd model), dual site langmuir-langmuir (3rd model), dual site freundlich-freundlich (4th model), dual site langmuir–freundlich (5th model) and dual site freundlich-langmuir (6th model).

2.3.1. 1st model : single site langmuir

In this model, contribution of active site in the benzene adsorption is assumed very small, so it can be ignore. Adsorption occurs on the unburned carbon having homogeneous energy. Other assumption, it is localized adsorption and each site only bind one atom or molecule. In addition, the interaction between the adsorbate molecules is ignored. The equation of 1st model is describes as :

$$C_{\mu} = C_{\mu m} \frac{K_L C_e}{1 + K_L C_e} \quad (1)$$

where $C_{\mu m}$ is maximum concentration of adsorbate in solid surface at equilibrium (mmol.g^{-1}), C_e is the concentration of adsorbate in solution at equilibrium (mmol.dm^{-3}), C_{μ} concentration of adsorbate in solid surface at equilibrium (mmol.g^{-1}) and K_L is the Langmuir constant related to the adsorption sites affinity (dm^3.mmol^{-1}).

2.3.2. 2nd model : single site freundlich

In this model, contribution of active site in the adsorption is assumed very small, so it can be ignored. Adsorption occurs on unburned carbon having heterogeneous energy.

Other assumption, it is localized adsorption and no interaction between adsorbate molecules. The equation of 2nd model is described as:

$$C_\mu = K_F\, C_e^{1/n} \quad (2)$$

where K_L (mmol.g^{-1}) is Freundlich constant, and 1/n (dm^3.g^{-1}) is heterogeneity factor.

2.3.3. 3rd model : dual site langmuir – langmuir isotherm

In this model, active sites and unburned carbon contribute to the adsorption. Active sites and unburned carbon are considered to the different patch having different energy levels. Each patch is independent and there is no interaction between patches. While, at the same patch, site has homogeneous energy distribution. Adsorbate molecules is adsorbed only by one site and there is no interaction between adsorbate molecules. 3rd model is described as :

$$C_\mu = C_{\mu m1}\, \frac{K_{L1}\, C_e}{1+ K_{L1}\, C_e} + C_{\mu m2}\, \frac{K_{L2}\, C_e}{1+ K_{L2}\, C_e} \quad (3)$$

where '1' indicates site 1 (unburned carbon) and '2' indicates site 2 (active sites). K_{L1}, K_{L2}, $C_{\mu m1}$, $C_{\mu m2}$ can be determined by trial and error method which gives a minimum Sum of Square Error (SSE).

2.3.4. 4th model : dual site freundlich – freundlich isotherm

In this model, active sites and unburned carbon contribute to the adsorption. Active sites and unburned carbon are considered to the different patch having different energy levels. Each patch is independent and there is no interaction between the patches. While, the same patch has heterogeneous energy distribution. Adsorbate molecules is adsorbed only by one site and there is no interaction between adsorbate molecules. The model is described as :

$$C_\mu = K_{F1}.C_e^{1/n1} + K_{F2}.C_e^{1/n2} \quad (4)$$

where '1' indicates the site 1 (unburned carbon) and '2' indicates the site 2 (active sites). K_{F1}, K_{F2}, n_1, n_2 can be determined by trial and error method which gives a minimum SSE.

2.3.5. 5th model: dual site langmuir – freundlich isotherm

In this model, active sites and unburned carbon contribute to the adsorption. Active sites and unburned carbon are considered to the different patch having different energy levels. Each patch is independent and there is no interaction between the patches. Unburned carbon patch has a homogeneous distribution energy, while active sites patch has heterogeneous distribution energy. The 5th model is described as

$$C_\mu = C_{\mu m1}\, \frac{K_{L1}\, C_e}{1+ K_{L1}\, C_e} + K_{F2}.C_e^{1/n2} \quad (5)$$

where '1' indicates the site 1 (unburned carbon) and '2' indicates the site 2 (active sites). K_{L1}, $C_{\mu m1}$, K_{F2}, n_2 can be determined by trial and error method which gives a minimum SSE.

2.3.6. 6th model: dual site freundlich isotherm – langmuir

In this model, active sites and unburned carbon contribute to the adsorption. Active sites and unburned carbon are considered to the different patch having different energy levels. Each patch is independent and there is no interaction between the patches. Unburned carbon patch has a heterogeneous distribution energy, while active sites patch has homogeneous distribution energy. 6th model is described as :

$$C_\mu = K_{F1}.C_e^{1/n1} + C_{\mu m2}\frac{K_{L2}\,C_e}{1+K_{L2}\,C_e} \quad (6)$$

where '1' indicates the site 1 (unburned carbon) and '2' indicates the site 2 (active sites). K_{F1}, n_1, K_{L2}, $C_{\mu m2}$ can be determined by trial and error method which gives a minimum SSE.

3. Results and Discussion

3.1. Characters of CFA

The chemical compositions of original CFA obtained from x-ray fluorescence (XRF) analysis is presented in Table 1 [6]. It shows that the major component of CFA are silica (SiO_2), alumina (Al_2O_3) and carbon. While, the comparation of [Si+Al]/C ratio of CFA used in this study is described in Table 2. To confirm the existence of silica and alumina, CFA was also analyzed using x-ray diffraction (XRD). The XRD pattern of original CFA can be seen in Figure 1 [6].

Table 1 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
Carbon	19.11

Table 2 Si, Al and C content of CFA

[Si+Al]/C ratio of CFA	Component
0.5	Si
	Al
	C
2.0	Si
	Al
	C
90	Si
	Al
	C

Table 3 Characters of the coal fly ash

[Si+Al]/C ratio of CFA	Characters	Value
0.5	Total crystallinity, %	100.0
	Specific surface area, $m^2.g^{-1}$	15.7
2.0	Total crystallinity, %	65.0
	Specific surface area, $m^2.g^{-1}$	80.3
90	Total crystallinity, %	88.2
	Specific surface area, $m^2.g^{-1}$	9.7

It shows that CFA contains crystalline phases including quartz (SiO_2), mullite ($3Al_2O_3.2SiO_2$) and amorphous components.

Quantitatively, crystallinity of quartz and mullite are calculated using comparation between intensity of quartz or mullite peaks in treated CFA with standard quartz or mullite peaks as can be written [6] :

$$crystallinity = \frac{I_A}{I_o}\, x\, 100\% \quad (7)$$

where I_A is intensity of quartz or mullite peaks in treated CFA and I_o is intensity of standard quartz or mullite peaks. Total cystallinity is the summation of quartz, mullite and hydroxysodalite that may be composed during the treatment. Total crystallinity of CFA used in this study is described in Table 3. CFA having [Si+Al]/C ratio of 2.0 obtained from reaction of CFA with sodium hydroxide has the lowest total crystallinity and the highest specific surface area. It indicates formation of amorphous material caused by the damages of quartz and mullite after reaction of CFA with sodium hydroxide forms holes in CFA surface, as can be seen in Figure 2. CFA having [Si+Al]/C ratio of 0.5 comprises smooth spherical particles as can be seen in Figure 2a, while CFA having [Si+Al]/C ratio of 2.0 has rougher surface and full of holes, as can be seen in Figure 2b.

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

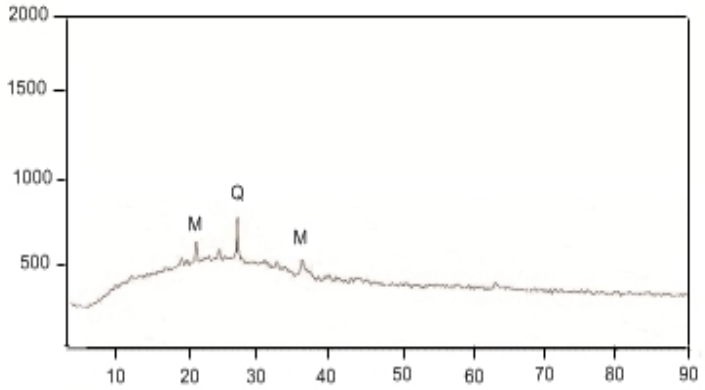
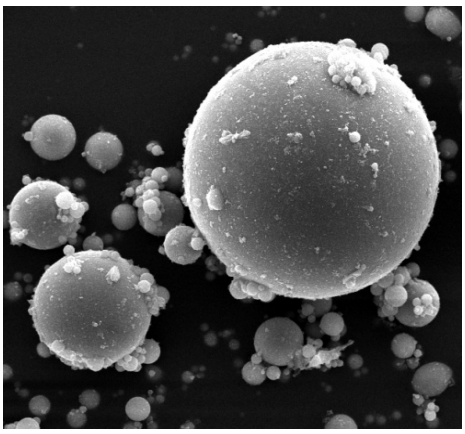


Fig. 2 *SEM micrograph of CFA having (a) [Si+Al]/C ratio ≈ 0.5 (b) [Si+Al]/C ratio ≈ 2.0*



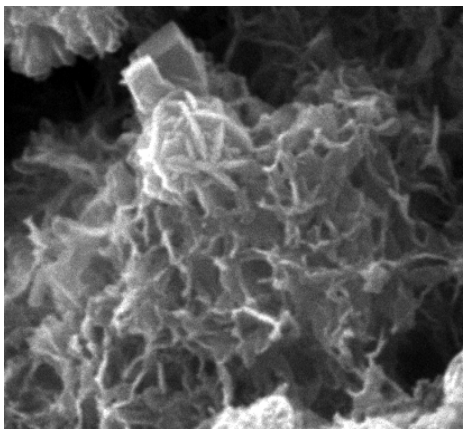


Table 5 Average deviation of C_μ model toward C_μ data

	Average deviation of C_μ model toward C_μ data (%)		
	[Si+Al]/C ≈ 0.5	[Si+Al]/ C ≈ 2	[Si+Al]/C ≈ 90
1st model	4.2	5.9	9.2
2nd model	33.8	22.6	30.1
3rd model	5.0	7.0	15.5
4th model	29.9	25.2	13.7
5th model	4.8	6.3	9.7
6th model	8.3	8.9	13.9

3.2. Adsorption of Benzene

Adsorption of benzene is presented in Fig. 3. CFA having higher unburned carbon content ([Si+Al]/C ratio ≈ 0.5) has higher adsorption capacity. It shows that the unburned carbon contributes to the benzene adsorption. Unburned carbon is a non-polar material so it can adsorb benzene which is also a non-polar compounds. While, active site is a polar material so it is difficult to adsorb benzene. Interaction between unburned carbon and benzene involves Van der Waals forces.

To ensure adsorption properties of benzene, benzene is desorbed from CFA that had adsorbed benzene using distilled water [7]. If benzene can be desorbed by distilled water, it indicates that the adsorption force is weak. The desorption results is presented in Table 4. Data in Table 4 shows that almost all benzene can be desorbed by distilled water. It confirms that the adsorption properties is weak. Adsorption occurs at pore of unburned carbon through Van der Waals interaction and no involves chemical binding as has already been explained earlier.

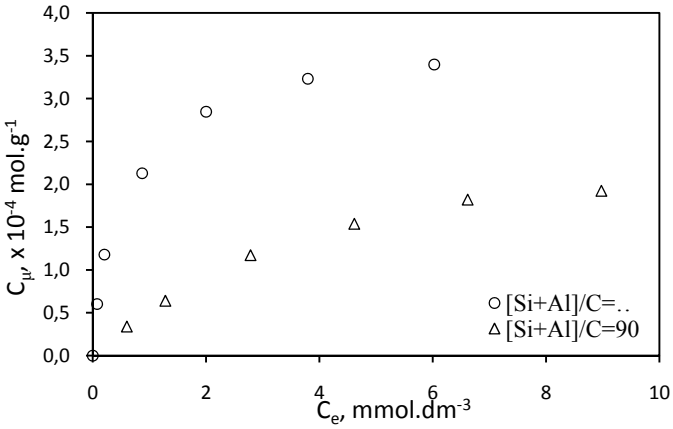


Fig. 3 *Adsorption of benzene (dose = 4 gram/230 cm^3, pH = 7, temperature = 28°C, time = 72 hours)*

Table 4 The amount of benzene adsorbed and desorbed by CFA having varied unburned carbon content

	[Si+Al]/C ratio of CFA	
	90	0.5
benzena adsorbed, mmol.g^{-1}	0.1821	0.3231
benzena desorbed, mmol.g^{-1}	0.1773	0.3156
benzena desorbed, %	97.4	97.7

Note : initial concentration of adsoption process = 800 mg.dm^3

3.3. Isotherm Models

The average deviation between C_μ model and C_μ data is described in Table 5. Data in Table 5 shows that 1st model is seen in accordance with experimental data for all CFA because it has the lowest average deviation. Benzene can only be adsorbed by unburned carbon through Van der Waals interaction as has already been explained earlier. Thus, there is suitability between experimental data with the 1st model assumption. Comparation between 1st, 2nd, 3rd and 4th models with experimental data is described in Figure 4, while the value of maximum concentration of adsorbate in solid surface at equilibrium ($C_{\mu m}$) and Langmuir constant (K_L) is described in Table 6.

Fig. 4 *Isotherm models for benzene : (a) 1st model (b) 2nd model (c) 3rd model (d) 4th model*

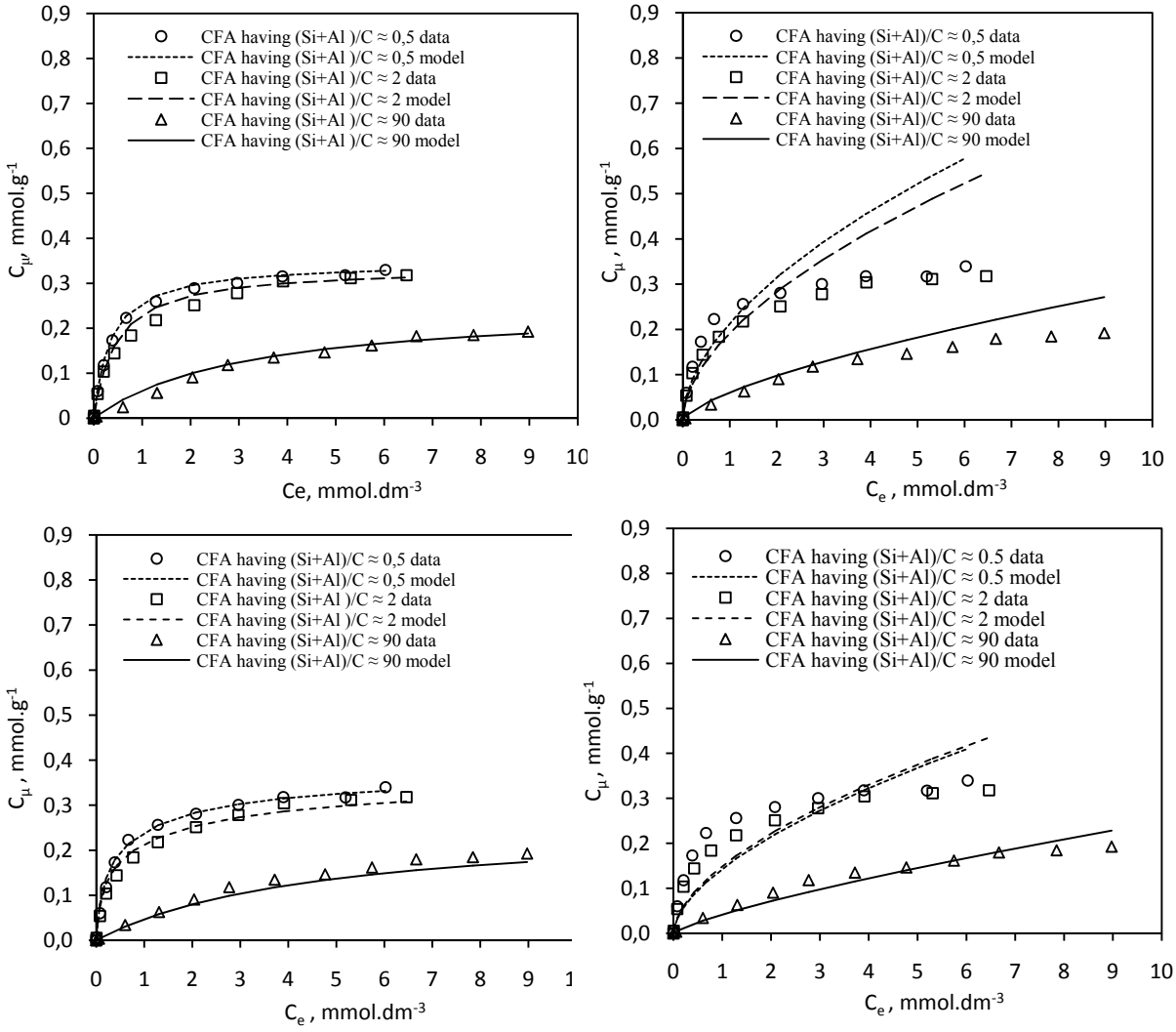


Table 5 Average deviation of C_μ model toward C_μ data

	Average deviation of C_μ model toward C_μ data (%)		
	[Si+Al]/C ≈ 0.5	[Si+Al]/ C ≈ 2	[Si+Al]/C ≈ 90
1st model	4.2	5.9	9.2
2nd model	33.8	22.6	30.1
3rd model	5.0	7.0	15.5
4th model	29.9	25.2	13.7
5th model	4.8	6.3	9.7
6th model	8.3	8.9	13.9

Data in Table 6 shows that the values of $C_{\mu m}$ and K_L are affected by [Si+Al]/C ratio in CFA. The increase of [Si+Al]/C ratio causes a decrease of the values of q_m and K_L values because the amount of unburned carbon in CFA decreases.

Table 6 The values of Cμm and KL for 1st model

[Si+Al]/C ratio of CFA	$C_{\mu m}$ (mmol.g^{-1})	K_L (dm^3.mmol^{-1})
0.5	0.3423	2.8860
2	0.3398	0.9259
90	0.2753	0.2588

Conclusion

It is concluded that CFA having high unburned carbon content has high adsorption capacity. The Langmuir model (1st model) yielded excellent fit with equilibrium data because the adsorption of benzene only occurs on unburned carbon. The values of $C_{\mu m}$ and K_L are affected by [Si+Al]/C ratio in CFA. The increase of [Si+Al]/C ratio causes a decrease of $C_{\mu m}$ and K_L values.

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