Removal of Copper (II) Ions in Aqueous Solutions by Sorption onto Fly Ash

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Abstract. The ability of fly ash to adsorp Cu(II) ions from two different coal combustion systems was studied. Optimum removal was found at pH 5, contact time 30 minutes and 60 minutes for Fly Ash 1 and Fly Ash 2, respectively, and dosage 10 g/l. The difference in adsorption capacity between both fly ashes may be due to their carbon fraction and CaO content. The removal of Cu (II) ions was caused by both adsorption and/or precipitation. Precipitation is enhanced by lowering the carbon fraction and increasing the CaO content. The adsorption isotherm showed that the Langmuir model fitted well to the experimental data of both fly ashes. A thermodynamic study was conducted at three different temperatures: 25 °C, 45 °C, and 60 °C. The adsorption processes were spontaneous and endothermic and were more favorable at higher temperature.

Keywords: *adsorption; aqueous solutions; Cu ions; fly ash; Langmuir model.*

1   Introduction

Human activities release heavy metals into the hydrosphere in many different ways, such as effluent of industries, transportation, municipal sewage, land filling, mining, etc. Heavy metals can pollute the environment and cause public health problems. It is important to eliminate heavy metals from water because these elements are not biodegradable and tend to accumulate in living organisms, inducing various diseases and disorders. Some metals, like Hg, Pb and Cr, are very toxic to organisms, while others, like Fe, Mn, Cu, Zn, Ni and Co, even though essential for living beings, when present in excess of certain limits can be very harmful. Copper is highly toxic because it is bio-accumulative and persistent. It does not break down in the environment and is carcinogenic [1-3].

There are many processes suitable for the removal of metals from water, such as chemical precipitation, coagulation, biological systems, oxidation with ozone/hydrogen peroxide, ion exchange, photocatalytic degradation, and

adsorption [4]. Adsorption is the most extensively used method for the removal of heavy metals [5]. There are many low-cost materials that have been investigated for the removal of heavy metals from water, such as hardwood and corn straw [6], oil shale ash [7], carrot residues [8], *Lonicera japonica* flower biomass [9], and lignin [10,11].

Coal has been used as fuel for power generation on a wide scale since the 1920s. Over this period, coal combustion has increased significantly and is estimated to keep growing. Coal combustion produces fly ash at about 5-20 wt.% and is typically discovered in the form of fine fly ash (85-95 wt.%) and coarse bottom ash (5-15 wt. %). In 2015, Indonesia produced 461 million tons of coal, of which it consumed 87 million tons while it exported the remainder (*Kementerian ESDM*, Indonesia).

Fly ash, a particulate material generated from coal-fired power plants, is a very complex and abundant material that requires ultimate disposal. Fly ash has potential applications in wastewater treatment since its chemical composition, low cost and good adsorbent properties, such as porosity, surface area, and particle size distribution [12]. Removal of significant amounts of heavy metals from solutions by adsorption onto fly ash has been reported. The removal of chromium from aqueous solutions and wastewaters was examined by Sharma, *et al.* in [13]. They reported that the adsorption followed a first-order rate kinetics and the removal process of Cr(VI) is dependent on the pH of the solution. Polowczyk, *et al.* [14] used fly ash agglomerates (particles size 1.0-1.6 mm) for the removal of boron from aqueous solutions. The removal efficiency of boron depends on the pH of the solution. The kinetics data fitted well with a pseudo second-order model, while the Freundlich isotherm model was more appropriate than the Langmuir isotherm. Soco, *et al.* [15] investigated the adsorption of copper and nickel from aqueous solutions by fly ash. The adsorption fitted both the Langmuir and the Freundlich model. The removal of copper and nickel takes place by a particle diffusion mechanism.

The removal efficiencies of heavy metals using fly ash as adsorbent vary depending on the properties of the fly ash and the conditions used in the adsorption study. The specific properties of fly ash depend on the type of coal used, the system of combustion, collector setup, etc. Coal combustion systems are generally classified into fluidized bed systems and fixed bed systems. Fluidized bed systems have higher efficiency in producing energy than fixed bed systems. Fixed bed systems are commonly used in textile industries. The objective of this work is to compare the ability of removing Cu (II) ions from aqueous solutions using fly ashes from these two different coal combustion systems without pretreatment. Since fly ash is an alkaline material that contains large quantities of CaO and MgO, the hydroxide ion (OH$^-$) is liberated raising

pH during adsorption. In this case, Cu may form an insoluble product of $Cu(OH)_2$ and is removed through precipitation. Therefore, this work also evaluates the removal of Cu(II) ions because of precipitation.

2   Experimental Section

2.1   Fly Ash

Fly ashes were collected from the coal-fired power plant of PT Indonesia Power, Cilegon Indonesia that uses a fluidized bed combustion system (called Fly Ash 1) and from PT Trisula Textile, Bandung, Indonesia that uses a fixed bed combustion system (called Fly Ash 2). The fly ashes were sieved to separate coarser particles from particles finer than 0.075 mm (ASTM No. 200 sieve). Fly ash 1 had a very small particle size with more than 80 wt. % passing the number 200 sieve while only 40 wt. % of Fly Ash 2 particles were smaller than 0.075 mm. The pH values of the fly ashes were determined by soaking 2 g of fly ash with 100 ml of distilled water and pH was recorded at 1 h intervals for a period of 24 h. The elemental composition of the fly ashes was obtained by X-ray fluorescence (XRF) analysis using a PANalytical Epsilon3 instrument. The loss on ignition (LOI) was determined by heating a dry sample (left at 105 °C in an oven and then cooled in a desiccator) to 600 °C over a period of 2 h. XRD patterns of fly ash samples were measured using a Bruker D8 Advance instrument (Cu Kα radiation, 30 kV, 40 mA) over a range of 2θ values from 3° to 50°. A scanning electron micrograph (SEM) JEOL JSM 6510 LV was utilized to characterize the morphology of the fly ashes.

2.2   Chemicals

Appropriate amounts of analytical grade $CuSO_4.5H_2O$ (Merck Co.) were dissolved in distilled water and transferred in to a 1-liter volumetric flask for preparing stock solution (1000 mg/L) of Cu^{2+} ions. A certain concentration range of Cu^{2+} standard solution was obtained by diluting the stock solution with distilled water. Solutions of 0.1 M HNO_3 and 0.1 M NaOH were used for pH adjustment.

2.3   Adsorption Experiments

Adsorption of Cu from aqueous solutions was studied in batch experiments. A series of bottles containing 100 ml of 100 mg/l Cu(II) shaken at a temperature of 25 °C with a constant amount of fly ash (1 g) and at different pH values (3.0-8.0). The pH was adjusted with the addition of sodium hydroxide (NaOH) or nitric acid (HNO_3). After shaking at 250 rpm for 180 minutes, the solutions were filtered using Whatman filter paper of grade 40 and the concentration of

Cu(II) was determined by atomic absorption spectrometer. In order to examine the effect of contact time on the adsorption of Cu(II) ions, 1 g fly ash was added to 100 ml of 100 mg/l solutions at pH 5. The solution was shaken at 250 rpm for different periods of time (5-180 minutes) at a temperature of 25 °C. After shaking, the samples were taken and filtered and the Cu(II) concentrations of the filtrates were measured. All experiments were done in duplicate. The data were discarded when the relative error exceeded 5% and the experiment was repeated until the relative error was less than that value.

2.4 Precipitation Experiments

Leachate from fly ash was used to examine the effect of pH increase on Cu(II) removal by fly ash. The leachate was prepared as follows: 1 g of fly ash was soaked in 100 ml of distilled water for one hour, after which the fly ash was separated from the solution. To determine the precipitation, Cu(II) was introduced into the leachate. After one hour, the concentration of Cu(II) residue in the filtrate of leachate was measured.

3 Result and Discussion

3.1 Characteristics of Fly Ashes

The difference in characteristics of fly ashes can be caused by different sources of coal or coal combustion systems. Table 1 shows the chemical composition of the fly ashes used in this work. Both fly ashes contained SiO_2 and Al_2O_3 at about 80%. CaO contents comprised about 6.4% (Fly Ash 1) and 2.7% (Fly Ash 2) respectively. Therefore, both of these fly ashes can be classified as low calcium class F according to ASTM C618.

Table 1   Chemical analysis of the fly ashes.

Constituent	wt. (%)	
	FA 1	FA 2
SiO_2	52.5	48.2
Al_2O_3	27.8	35.4
MgO	4.5	0.8
CaO	6.3	2.7
Fe_2O_3	4.9	5.4
LOI*	1.2	6.5
Others	2.8	1.0
pH	10.9	8.8

* Loss on ignition

The morphology of the fly ashes is shown in Figure 1. In general, the particles of Fly Ash 1 were predominantly spherical in shape with a relatively smooth

surface. The spherical particles were generally hollow and empty (cenosphere). The particles of Fly Ash 2 were mainly composed of irregular and carbon particles. From Figure 2 it can be seen that both of the fly ashes mainly consisted of an amorphous phase that creates a broad hump between 15° and 30° 2θ in both fly ashes. There are some peaks that indicate quartz, mullite, and hematite.
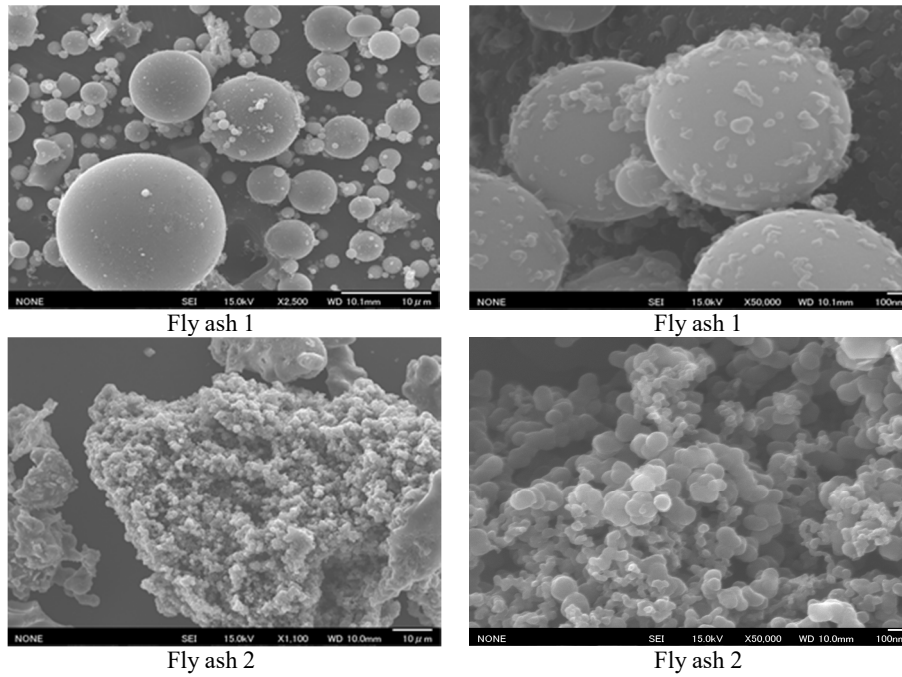

Fly ash 1 — Fly ash 1 — Fly ash 2 — Fly ash 2

Figure 1 SEM pictures of the fly ashes.
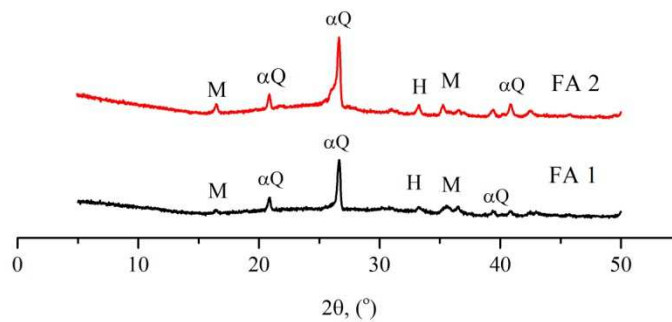

Figure 2 XRD patterns of the fly ashes. Mineral abbreviations: M, mullite; Q, quartz; H, hematite.

3.2   Effect of pH

The adsorption of metal ions from wastewater is dependent on pH. The pH affects the surface charge of the adsorbent, degree of ionization, and speciation of the adsorbate [16]. Figure 3 shows the removal percentage of Cu(II) ions as a function of pH at a concentration of 100 mg Cu/l and a fly ash dosage of 10 g/l. The adsorption of Cu(II) ions increased as pH increased and quickly reached over 90% removal at pH 5 for Fly Ash 1 and over 50% removal at pH 6 for Fly Ash 2.

The adsorption of metal ions at the solid-solution interface is not only controlled by the concentration of free metals but also by the more strongly adsorbed hydroxo, carbonato and other metal species [16]. Metal ions in aqueous solutions hydrolyze according to the generalized expression for divalent metals shown in Eq. (1):
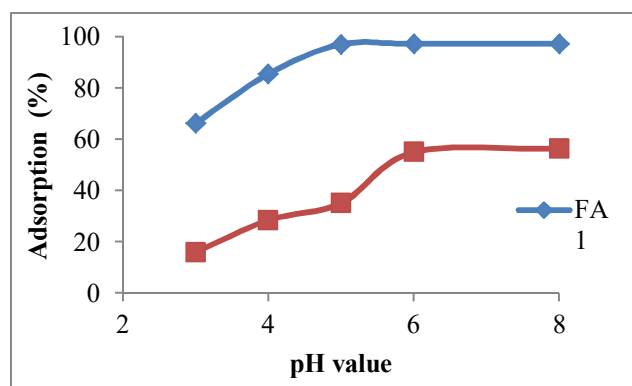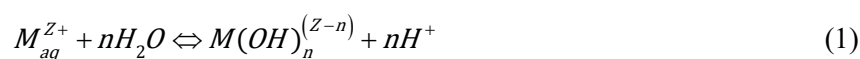
$$M_{aq}^{Z+} + nH_2O \Leftrightarrow M(OH)_n^{(Z-n)} + nH^+ \tag{1}$$

Figure 3 Effect of pH on the removal percentage of Cu(II) ions: initial concentration 100 mg/l, fly ash dosage 10 g/l, contact time 180 min.

The distribution of various hydroxo complexes depends on the pH of the solution and the stability constants. The stability constant (pK_1) for the hydrolysis reaction for $CuOH^+$ is 8 [16]. Complexes of hydroxyl-metals adsorb with higher affinity than completely hydrated metals. The requirement of free energy for adsorption diminishes due to the formation of an OH group on the metals [17].

Furthermore, the functional oxidized group (SiO_2, Al_2O_3, Fe_2O_3) present on the surface of the fly ash and the pH of the solution influence the adsorption of

Cu(II) ions. The surface of silica (SiO_2) indicates great affinity towards metal ions [18]. According to the experimental results, Fly Ash 1 with high CaO and SiO_2 content (Table 1) is more effective than Fly Ash 2 for removal of Cu ions because of the formation of Ca and Si complexes such as calcium silicates ($2CaO.SiO_2$).

The alkaline nature of fly ash makes the pH of the solution increase as the fly ash is added to the solution. When this occurs, the Cu(II) ions are expected to precipitate out of the solution under higher pH conditions. To elucidate the effect of a pH increase on Cu removal, a precipitation experiment was performed. Table 2 presents the removal owing to adsorption and precipitation of Cu(II) in the leachate. The Cu(II) removal by Fly Ash 1 with a low carbon fraction (represented as low LOI) was higher than by Fly Ash 2. The Cu(II) removal caused precipitation to increase with decreasing LOI and its contribution was 72.4% of the total Cu(II) removal. Precipitation is the dominant reaction of Cu(II) removal when the carbon fraction declines [19].

Table 2   Removal (mg/l) of Cu(II) by adsorption and precipitation.

	Fly Ash 1	Fly Ash 2
Adsorption at pH 5	97.39^a	60.07^a
Precipitation in the leachate (initial pH of leachate)	72.45^b (12,1)	44.27^b (8,2)
Precipitation contribution*	74.4*	32.5*

  * = b/a x 100%

3.3   Effect of Contact Time

The effect of contact time on the adsorption of Cu was measured by varying the equilibrium time between the adsorbent and adsorbate in the range of 5-180 min, while the concentration of Cu(II) ions was kept 100 mg/l at a fixed fly ash dosage (10 g/l) and a pH of 5. The results of these experiments are shown in Figure 4.

The results indicate that the adsorption of Cu(II) ions by fly ash increased with increase of contact time and reached maximum value after 30 min for Fly Ash 1 and 60 min for Fly Ash 2, and thereafter remained constant. Soco [15] found that the equilibrium contact time for Cu is 60 min. The same result was obtained by Lingamdinne [9], where the equilibrium contact time for the removal of Cu ions by *Lonicera japonica* biomass was achieved after 1 h.

It can be concluded that the removal of Cu ions occurs quickly. Therefore, a contact time of 30 min and 60 min for Fly Ash 1 and Fly Ash 2, respectively, was used in all subsequent experiments.
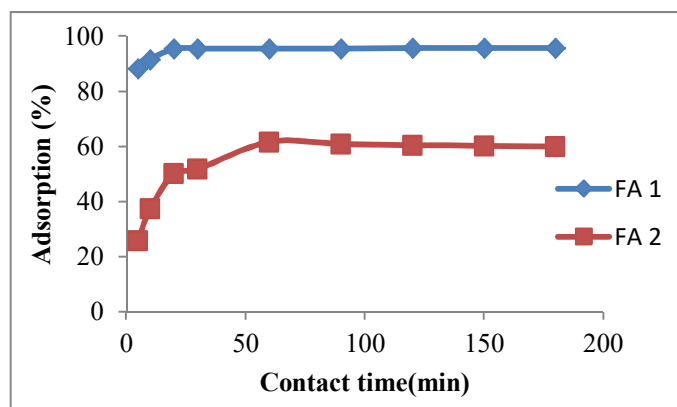
Figure 4 Effect of contact time on the removal percentage of Cu(II) ions: initial concentration 100 mg/l, fly ash dosage 10 g/l, pH 5.

3.4   Effect of Adsorbent Dosage

Figure 5 illustrates the effect of adsorbent dosage on the removal of Cu(II). The adsorbent dosage is an important parameter because it determines the capacity of an adsorbent for a given initial concentration of the adsorbed materials. The results show that the adsorption efficiency increased from 24.9 to 93.9% and from 29.3 to 56.7% as the dosage increased from 1 to 10 g/l for Fly Ash 1 and Fly Ash 2, respectively. This increase is explained by the increase in surface area and the available adsorption sites of the fly ash. With increasing fly ash, the available sites for binding Cu(II) ions increases and thereby enhances the adsorption.
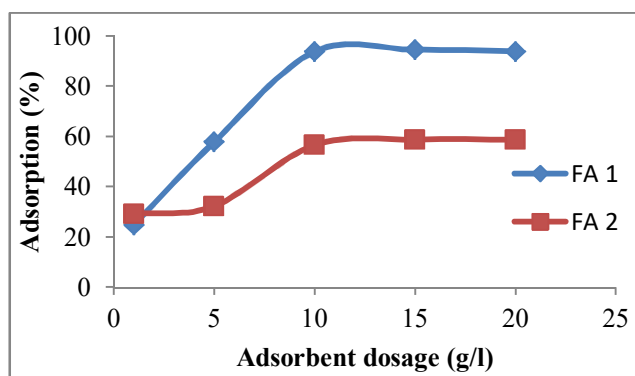

Figure 5 Effect of adsorbent dosage on the removal percentage of Cu(II) ions: initial concentration 100 mg/l, pH 5.

3.5   Adsorption Isotherm

Langmuir and Freundlich isotherms were used to model the adsorption tests at equilibrium. The adsorption isotherms were determined at different temperatures (25, 45, and 60 °C) in a concentration range from 25-175 mg Cu/l for Fly Ash 1 and from 20-70 mg Cu/l for Fly Ash 2. The Langmuir isotherm is expressed by Eq. (2) as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{2}$$

where Ce is the equilibrium concentration of Cu(II) in solution (mg/l); q_e is the amount of Cu(II) adsorbed onto the adsorbent at equilibrium (mg/g); K_L is the Langmuir equilibrium constant; and q_m is the maximum sorption capacity (mg/g). q_e was calculated according to the following formula in Eq. (3):

$$q = \frac{(C_0 - C_e) \times V}{m} \tag{3}$$

Plotting of C_e/q_e against C_e gives a straight line with a slope of $1/qm$ and an intercept of $1/q_m K_L$. The values of K_L and q_m can be calculated. The maximum adsorption capacities of the fly ashes for Cu(II) are shown in Table 3. As can be seen in Table 3, the maximum adsorption capacity (q_m) increased as the temperature increased from 25 to 60 °C for both fly ashes. Similarly, the K_L values increased with increasing temperature.

Another isotherm developed by Freundlich describes the equilibrium on a heterogeneous surface and does not assume monolayer capacity. The equilibrium data were correlated with the Freundlich isotherm in Eq. (4) as follows:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{4}$$

where q_e is the amount of Cu(II) ions adsorbed at equilibrium per unit weight of adsorbent (mg/g); C_e is the equilibrium concentration of Cu(II) ions in solution (mg/l); and K_F and n are Freundlich constants corresponding to adsorption capacity and intensity, respectively. A linear plot is gained when log q_e is plotted against log C_e and the values of K_F and n can be calculated from the intercept and the slope of the straight line respectively. The isotherm parameters are summarized in Table 3.

From Table 3, the Langmuir model can effectively and significantly describe the sorption data with regression coefficient $R^2 \geq 0{,}993$ for both fly ashes,

except Fly Ash 1 at 25 °C. This implies that uptake of Cu(II) ions occurs on a homogeneous surface by monolayer adsorption without interaction between adsorbed ions. The maximum adsorption capacity for Cu(II) at temperature 25-60 °C was calculated to be 8.54-11.43 mg/g and 5.09-5.84 mg/g for Fly Ash 1 and Fly Ash 2 respectively.

Table 3   Parameters for Langmuir and Freundlich isotherms.

Adsorbent	Isotherm	T (°C)	Parameters			
			q_m (mg/g)	K_L (l/mg)	R^2	R_L
		25	8.54	0.133	0.922	0.15
Fly Ash 1	Langmuir	45	10.05	1.374	0.993	0.21
		60	11.43	1.632	0.999	0.24
		25	5.09	0.144	0.996	0.38
Fly Ash 2	Langmuir	45	5.31	0.209	0.997	0.36
		60	5.84	0.285	0.998	0.37
			K_F (mg/g)	1/n	R^2	
		25	3.52	0.175	0.783	
Fly Ash 1	Freundlich	45	5.85	0.146	0.751	
		60	6.45	0.166	0.747	
		25	1.07	0.421	0.932	
Fly Ash 2	Freundlich	45	1.35	0.396	0.931	
		60	1.68	0.393	0.963	

To determine if Cu(II) adsorption onto the fly ashes is favorable or unfavorable for the Langmuir model, the isotherm can be classified by R_L, a dimensionless separation factor that was calculated using Eq. (5) as follows:

$$R_L = \frac{1}{1 + K_L C_e} \tag{5}$$

The value of R_L obtained in this work was found to lie between 0 and 1, indicating a high and favorable adsorption process (Table 3).

3.6   Thermodynamic Studies

Thermodynamic studies were conducted under the following conditions: adsorbent dose 10 g/l; Cu(II) concentration 50 mg/l; shaking at varying temperatures (25 °C, 45 °C, and 60 °C). The thermodynamic parameters can be assessed using changes in the equilibrium constants with temperature. Thermodynamic parameters such as standard Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) can be calculated with Eqs. (6) to (9):

$$K_C = \frac{q_e}{C_e} \tag{6}$$

$$\Delta G^0 = -RT \ln K_C \tag{7}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{8}$$

$$\ln K_C = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{9}$$

where R is the universal gas constant (8.314 J/mol °K) and T is absolute temperature (°K). The K_C, q_e, and C_e are the equilibrium constant, equilibrium concentration of Cu(II) and the amount of Cu(II) adsorbed onto the fly ash at equilibrium, respectively. The results of the calculation are shown in Table 4.

The values of $\Delta G°$ were negative at all temperatures and became more negative with an increasing temperature for both fly ashes. The negative values of $\Delta G°$ indicate that the adsorption process is spontaneous. A decrease in the negative value of $\Delta G°$ with an increase in temperature indicates that the adsorption process is more favorable at higher temperatures. It was obtained that the $\Delta G°$ values of Fly Ash 1 were more negative than those of Fly Ash 2. Adsorption onto Fly Ash 1 was more spontaneous than that onto Fly Ash 2.

Table 4   Thermodynamic parameters for Cu(II) adsorption onto fly ashes.

	T (°K)	$\Delta G°$ (J/mol)	$\Delta H°$ (J/mol)	$\Delta S°$ (J/mol°K)	R^2
	298	-9118.7			
Fly Ash 1	318	-13468.4	53834.1	211.4	0.999
	333	-16493.0			
	298	-1855.9			
Fly Ash 2	318	-3001.1	18200.6	67.1	0.985
	333	-4241.0			

A positive value of $\Delta H°$ implies that the adsorption process is endothermic. Adsorption in a solid-liquid system is a combination of two processes: (a) adsorption of adsorbate species, and (b) desorption of water molecules before being adsorbed. In endothermic adsorption, the adsorbate has to substitute more than one water molecule for their adsorption and this increases the endothermicity of the adsorption process. Hence, the value of $\Delta H°$ will be positive. The magnitude of $\Delta H°$ may also classify the type of sorption. The heat of physical adsorption is in the range of 2100-20900 J/mol, whereas the heat of chemisorption generally is in the range of 80000-200000 J/mol. Therefore, it

can be seen from Table 4 that the sorption of Cu(II) ions onto Fly Ash 1 can be attributed to physic-chemical sorption, while sorption of Cu(II) ions onto Fly Ash 2 is a physical adsorption process.

A positive value of $\Delta S°$ denotes an affinity of the adsorbent to the adsorbate. A positive $\Delta S°$ also implies an increased randomness at the solid/liquid interface during the adsorption process causing the adsorbate ions to not escape from the solid phase to the liquid phase. Hence, the amount of adsorbate that can be adsorbed will increase. The value of $\Delta S°$ of Fly Ash 1 was higher than that of Fly Ash 2 and therefore Fly Ash 1 could adsorb a larger amount of Cu(II) ions than Fly Ash 2.

3.7   Comparison of Adsorbents

A comparative evaluation of the adsorption capacities of the various fly ashes for the adsorption of Cu(II) ions is listed in Table 5. The adsorption capacities of the fly ashes used in this study indicate a relatively high uptake capacity of Cu(II) ions, which makes the fly ashes suitable for heavy metal removal from wastewater.

Table 5   Maximum adsorption capacity of Cu(II) ions by various fly ashes.

Adsorbent	Adsorption capacity (mg/g)	Temperature (°C)	Refs.
Fly ash	1.39	30	16
Fly ash + wollastonite	1.18	30	16
Fly ash	1.7-8.1	-	20
Fly ash (I)	0.34-1.35	20	18
Fly ash (II)	0.09-1.25	20	18
Fly ash	7.5	-	21
Fly ash	0.63-0.81	25	19
Fly ash	5.1	25	22
Fly ash	2.9-4.9	30	23
Fly ash	7	-	24
FA 1	8.54-11.43	25, 45, 60	This study
FA 2	5.09-5.84	25, 45, 60	This study

4   Conclusion

This study indicates that the fly ashes from two different coal combustion systems have potential to act as adsorbent for the removal of Cu(II) ions from aqueous solutions. The adsorption in these systems is highly dependent on the pH and chemical composition of the fly ash. The effects observed were: increase in metal removal with increasing solution pH, CaO content and carbon fraction (represented as LOI value). Fly ash with a high CaO content is more

effective for Cu(II) removal. The pH of fly ash increased when the LOI value declined. Furthermore, it was found that the contribution of precipitation becomes dominant when the fly ash has a low LOI value. The adsorption data correlated well with the Langmuir isotherm model. Thermodynamic parameters were evaluated and they revealed that the adsorption of Cu(II) ions is endothermic and that it is a spontaneous process. The positive value of $\Delta H°$ indicates that adsorption was more favorable at higher temperature and that possible chemisorption phenomena were present for Fly Ash 1 while sorption of Cu(II) ions onto Fly Ash 2 was a physical adsorption process.

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