ZEOLITIZATION OF COAL WASTE AS Cu(II) ION ADSORBENT

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Abstract

Zeolization of coal waste was carried out as an adsorbent for Cu(II) ions. Fly ash tailings were collected from Lati Steam Power Plant (SPP) Berau and tested using SEM instruments, X-ray diffraction and AAS. Synthetic zeolites are prepared by hydrothermal reaction under alkaline and alkaline conditions. Characterization of the synthetic zeolite using SEM has formed a zeolite material with a pore size >10 μ m and shows an increase in the amount of Na from 3.06% to 11.82%. XRD results show that Na-P1 zeolite is formed at the main top of 2016, 30, 33, 10 and 40, 80, and the relative intensities are 34, 31 and 36, respectively. In addition, elemental materials such as silica and mullite are continuously formed on the main top of 2026.50 and 26.10, the relative strength of silica is 100, and the relative strength of mullite is 57.9. The optimum adsorption capacity of zeolite for maximum copper ion was 80.330% at pH=4, 97.958% at 150 mg adsorbent weight, and 94.550% at 50 min contact time. The formation of these new materials significantly improved the adsorption capacity of fly ash under optimal conditions of pH = 4, sorbent weight of 150 mg, and contact time of 50 min.

Keywords: fly ash, synthetic zeolite, silica, mullite

Introduction

The rapid development of industries in various countries has also led to a significant increase in industrial pollution. Therefore, the problem of industrial waste is becoming a serious global problem. This makes industrial wastewater treatment a global problem, as waste from various sources can accumulate in soil or enter water bodies.

One type of industrial waste in East Kalimantan is fly ash obtained from burning coal at the Lati Steam Power Plant (SPP) in the Berau district. The fly ash produced accounts for 10% of the total weight of coal used in the combustion process of PLTU Lati. 300 tons of new coal is used every day. Therefore, the total fly ash produced is about 30 tons per day. This fly ash is often discarded in landfills or simply accumulated in industrial areas, thus causing environmental problems. Various studies have been conducted on the use of fly ash to increase its economic value and reduce its negative impact on the environment, one of which is its use as a cement substitute. The composition of fly ash includes silica (SiO₂), alumina (Al₂O₃), and iron oxide (Fe₂O₃), with the remainder being carbon, calcium, magnesium, and sulfur (Mazari 2009).

The aluminosilicate framework in fly ash is similar to that of zeolite, so it can be modified by converting fly ash into zeolite, which is expected to increase the potential of fly ash as a heavy metal adsorbent.

Heavy metals such as copper are examples of contaminants that, when exceeding tolerable levels, can damage human physiological systems and other biological systems. Copper is used in industries such as coatings, metal alloys,

steel, dyes, cables, pesticides, pipes and paints.

Therefore, by Kep-51/Menlh/10/1995, the Government has set the first quality standards for liquid industrial waste with a metal content of less than 2 mg/L for copper and less than 0.6 mg/L for the electroplating industry. established a set of the presence of Cu ions in industrial wastes is usually accompanied by other heavy metal ions. In the coatings industry, Cu ions are the fifth most concentrated metal ion after iron, Cromium, Tin and Zink metals. followed bv less concentrated metal ions i.e. Nickel, Manganese, lead, Cadmium and silver (Venkatiswaran 2007).

references Several (Gupta & Bhattacharayya, 2008) describe several treatment methods for heavy metal ions in industrial wastewater. These methods include neutralization, precipitation, ion exchange, biosporulation, and adsorption. Adsorption is the recommended method for removing these metal ions when metal ion concentrations are low. Adsorption intermolecular processes include attraction, ion exchange, and chemical bonding.

Fly ash can be modified into activated carbon because it usually has moderate crystallinity, very inhomogeneous pore size, low catalytic activity and contains many impurities. Therefore, it must be activated before use. Acid treatment, hydrothermal treatment, calcination, oxidation and impregnation increase the Si/Al ratio and fly ash range. (Pardoyo, dkk 2009). The purpose of fly ash activation is to remove impurities in fly absorption improve the ash and performance of compounds or ions in solution and air.

Activated carbon is widely used as an effective adsorbent in a variety of applications and is one of the most widely used adsorption processes for the treatment of liquid industrial waste. However, the adsorption of metal ions with commercially available activated carbon after the adsorption process is relatively expensive.

Activated carbon also loses 10-15% of its activity during regeneration. Also, activated carbon is a flammable material, so it is not suitable for use at high temperatures. Therefore, researchers need cheaper adsorbents as an alternative raw material for the production of activated carbon.

Modification by converting fly ash to zeolite is expected to increase the potential of fly ash as a heavy metal adsorbent, as the aluminosilicate framework in zeolite becomes more negatively charged and increases the cation exchange capacity of the adsorbent. The conversion of fly ash to zeolite is carried out by a hydrothermal reaction under alkaline or acidic conditions. (Koukouzas et al 2010; Musyoka et al 2009; PPPTM 1997).

In this case, it is necessary to investigate to determine whether fly ash can be used as a synthetic zeolite and can adsorb Cu(II) ions at optimal pH, weight and contact time to obtain the best shape to accept adsorption zeolite.

Research Methods

Materials

Materials used include test materials and chemicals. The test material used was fly ash or fly ash, which is the residue of the incineration of the Lati Steam Power Plant (SPP) in Berau, while the chemicals used included NaOH, HCl, H₂SO₄, CuSO₄ and CuCl₂, using ACS compliant reagents Grade (\geq 95%) are commonly used in food, drug or pharmaceutical applications and are suitable for many laboratory and analytical applications.

Instrumentation

The following instruments were used in this study: Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy (SEM-EDX) to analyze the zeolite morphology and concentration of elements contained in the fly ash, and AAS (Atomic Absorption Spectroscopy) to analyze the adsorbed Cu(II). FTIR to determine the crystallinity of the compound formed.

Procedure

The first stage is the production of synthetic zeolite from activated fly ash followed by a hydrothermal reaction under closed conditions. Ash weight 20g, then add 20g NaOH and 100ml distilled water. The mixture was then stirred with a stirrer at a speed of 800 rpm for 48 hours at a solution temperature of 47°C. After the mixing process was completed, the vessel was placed in an oven at 140°C for 48 hours for a hydrothermal process. After that, the samples were rinsed with distilled water until the pH of the filtrate was 9-10, then the samples were dried at 90 °C for 24 h and placed in airtight plastic containers readv for characterization and use as adsorbents.

Characterization was performed using scanning electron microscopy to observe surface morphology and sample composition.. X-ray diffraction was then performed to determine structure and crystallinity so that it could be seen whether the zeolite material had formed, followed by FTIR to determine the crystallinity of the compound formed. The characterization results demonstrate the feasibility of fly ash as a synthetic zeolite as a Cu(II) adsorbent.

The experiment was performed at room temperature using a shaker rotating at 150 rpm while varying 3 independent variables, namely pH, contact time, and adsorbent weight, to best understand the interaction between the variables. The pH range used was 2-6, the contact time was 5-90 minutes, and the adsorbent weight was 30 mg-150 mg. The optimal determined conditions were by considering the percent adsorption efficiency values under each experimental condition. The filtrate of the mixture was filtered and measured using AAS.

Results and Discussion

Preliminary test and characterization

Preliminary experiments were performed using scanning electron microscopy (SEM) on hydrothermally treated fly ash (synthetic zeolite) and fly ash from Berau's Lati Steam Power Plant (SPP) to observe the morphology or surface texture of the adsorbent crystals. Fly ash has a smooth surface texture and spherical crystal shape (floating beads) with particle sizes ranging from 0.1 µm to 10 µm (Figure 1). The composition of fly ash is mainly O atom, 51.87%, Si 15.80%, Al 12.35%, In 8.29%, Fe 5.66%, Na 3.06%, Mg 1.32%, S 1.17%, Cu 0.46%, K 0.03% and C not detected.



Figure 1. Surface morphology of fly ash, 2000x magnification

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The surface texture of synthetic zeolite is rough and irregular square. The crystals are relatively irregular in shape and tend to aggregate into larger particles > 10 μ m in size (Figure 2). According to the composition analysis, the ratio of Si and Al of the obtained synthetic zeolite is close to 1, and the composition is as follows: O atom 60.68%, Si 10.10%, Al 10.67%, Indium 3.46%, Fe 2.21%, Na 11.82%, Mg 0.54%, S 0.09 %, Cu 0.42%, K and C were not detected.



Figure 2. Surface morphology of synthetic zeolite, 200x magnification

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with

Compared with fly ash, the sodium content in the synthetic zeolite increased nearly fourfold, while no potassium was detected, so it can be concluded that the sodium ion is the charge balancer in the zeolite framework. The crystal structure of zeolite is inhomogeneous and prone to aggregation, believed to be due to the relatively large content of impurity ions

$$NaOH + xAl_2O_3.ySiO_2 \rightarrow Na_p[(AlO_2)_p(SiO_2)_q].h.H_2O$$
 (1)

The compound formed is called zeolite Na-P1. The p and q values are variations of the resulting synthetic zeolite. To date, more than 50 synthetic zeolites have been identified.

In addition, the two adsorbents were characterized by XRD under the following measurement conditions: target Cu atom, wavelength 1.5406, voltage 40 kV, current 30 mA. The characterization process was performed at a 2θ angle of 10-60. Basic information based on XRD process data and research by Musyoka et al. (2009) 6 main peaks with relative intensities exceeding 20%. From these

data, it can be seen that fly ash is a compound mainly composed of aluminum and silicon, that is, it has been confirmed that there are several compounds of Al₆Si₂O₃ and quartz SiO₂. The presence of silica minerals in fly ash is known by the formation of 1 main peak with cubic crystals at a 2θ angle around 26.468°.

Fe, In, Cu, Cr and Mg. These elements are

thought to be involved in the formation of

hydrothermal reaction (Wang et al. 2009).

The presence of this element is due to the

fact that the fly ash used is not pretreated

unwanted metals. The reactions that occur

in this process are written in equation (1).

acidic compounds

zeolite framework during the

to desorb

There are also peaks at 16.3496; 20.7041; 33.1060; 35.1315; and 40.6961 indicated the presence of silicon oxide in the form of hexagonal crystals. In NaOH 5 M activated fly ash there is a peak of 26.5539 with a relative intensity of 100% which indicates the presence of chromium

aluminum silicate oxide which indicates the presence of impurities that are also bound to the activation process when the Na ion activation process comes from NaOH. For XRD results on synthetic zeolite, 8 main peaks have a relative intensity of more than 20% which indicates that the quartz peak is in the form of silicon oxide in the form of hexagonal crystals.

In addition, there are 5 peaks with relative intensity > 30%, namely at an angle of 16.3367; 26.1473; 33.1537; 35.1484; and 40.8267. These five peaks indicate that there are differences between peaks and fly ash, where there is only one peak with a relative intensity of > 30%, namely at an angle of 40.6961. The difference in relative intensity indicates a change in fly ash after activation to form synthetic zeolite with a sharp diffractogram graph showing the formation of synthetic zeolite.

The difference in the peaks can be seen from the combination of the two diffractograms, more of the peaks in the synthetic zeolite are corundum (α-Al₂O₃) peaks, where the spectrum of alumina is sharper than those peaks, not activated, which Indicates an increase in crystallinity. The crystal structure affects the strength of the adsorbent's surface walls, thereby increasing the stability of the synthetic zeolite adsorbent in the presence of external physical pressures, such as pressure during agitation.

Combining the diffractograms also gives different main peaks, so it can be confirmed that new minerals different from the base material, namely zeolite Na-P1 and hydroxysodalite, were formed. This can be seen from the elongated shape of the synthetic zeolite curve. So it can be said that in synthetic zeolite a compound with the structural formula $Na_p[(AlO_2)_p(SiO_2)_q].h.H_2O$ is formed.



Figure 3. Combining the diffractograms (Red : Fly ash + Hidrotermal, Blue : Fly ash)

According to the characterization of the XRD database (Figure 4), the presence of $Na_6(AlSiO_4)_6.4H_2O$ compound was formation detected. The of these compounds is due to the addition of NaOH solution during the synthesis, making Na ions the charge-balancing ions in the zeolite framework. According to the test results, there are 7 main peaks at the 2θ angle, which are different from the peaks of the fly ash diffractogram. It can

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therefore be said that a new mineral different from the starting material, Na-P1 zeolite, is formed. The formation of this new material was found to increase crystallinity compared to the fly ash substrate. The increase in the crystallinity of the synthetic zeolite is considerable, indicating that the new mineral structure is more regular than that of fly ash, as evidenced by the more slender shape of the synthetic zeolite curve.



Figure 4. Characterization of the XRD database

Besides being tested with SEM and XRD, samples were also tested with FTIR to see the condensation reactions that occur in the hydrothermal process and the formation of synthetic zeolite crystals. FTIR results of fly ash (black graphic) and synthetic zeolite (red graphic) are presented in Figure 5.



Figure 5. FTIR Spectrum of Fly Ash and Synthetic Zeolite

Standard zeolites theoretically have characteristic infrared bands (Musyoka, 2009), namely asymmetric elongation of Si-Al-O bonds at frequencies of 1000-1500 cm⁻¹ and symmetrical elongation of Si-Al-O bonds at frequencies of 660 cm⁻¹. The bending vibration frequency of the Si-Al-O bond is 440 cm⁻¹. The main feature of crystallinity is in the D4R ring, which has a frequency of 740 cm⁻¹. The -

OH group at a frequency of 3400 cm^{-1} is the basis for NaOH absorption, while the anhydrous crystal is described by the bending of water molecules at a frequency of 1630 cm⁻¹.

As can be seen from Figure 5, both samples show asymmetric stretching of the Si-Al-O bond. The condensation reactions that take place allow for the cleavage and formation of new Si-Al-O-Si-Al (T-O-T) bonds catalyzed by hydroxide ions at frequencies of 3446.79 cm^{-1} and 3429.43 cm^{-1} , i.e. the bond components are extracted from the crystalline material. Both samples also show bending vibrations between Si-Al-O bonds. In addition, the synthetic zeolite formed bending of water molecules at a wavelength of 1637.56 cm⁻¹ which is an anhydrous molecule forming synthetic zeolite compounds.

To determine the crystallinity of the synthetic zeolite in the IR spectrum, the intensity of the D4R (double 4-ring) value, which is the bridge of oxygen atoms in the structure of the synthetic zeolite linked by crystal spheres, was measured. The larger the D4R value, the higher the crystallinity. The D4R value in this study was 744.52 cm⁻¹, a small

difference compared to the standard ring D4R zeolite of 4.52 cm⁻¹. This situation resulted in the formation of very weak crystalline properties, so the synthetic zeolite formed was detected as amorphous in XRD testing. This is due to suboptimal hydrothermal treatment.

Optimum experimental conditions

To determine optimal experimental conditions, the first step was to define a standard copper curve to determine the ability of fly ash and synthetic zeolite to bind copper ions. A copper standard curve was constructed by measuring standard solutions at concentrations of 0.5 ppm, 2 ppm, 4 ppm, 6 ppm, and 8 ppm using a wavelength of 324.8 nm. And use atomic absorption spectrophotometer (AAS) for analysis, and get the absorption data in Table 1.

Table 1. Cu standard curve data

Concentration (ppm)	Absorbance
0,5	0,069
2	0,27
4	0,533
6	0,786
8	1.059



The variables used in this experiment were the adsorbate pH with a range of 2-8, a contact time of 10–90 minutes, and an adsorbent weight of 30–150 mg. The optimum condition was determined by looking at the percentage value of the adsorption efficiency in each experimental condition. The adsorption data are reported in terms of adsorption capacity and efficiency, as shown in equations (2) and (3).

$$q = \frac{(Co - Ce)V}{m} \tag{2}$$

$$removal efficiency = \frac{(Co - Ce)}{Co} \times 100\%$$
(3)

Where Co is the initial concentration (mg/L), Ce is the equilibrium concentration (mg/L), V is the total volume (L) and m is the mass (mg).

Variations of synthetic zeolite are presented in Tables 2, 3, and 4.

pH Var.	Abs	Initial Cons.	Residu Cons.	Abs. Cons.	%Abs
2	2,298	50,000	17,385	32,615	65,230
3	2,267	50,000	17,155	32,845	65,690
4	1,301	50,000	9,835	40,165	80,330
5	1,403	50,000	10,605	39,395	78,790
6	1,728	50,000	13,065	36,935	73,870
7	1,881	50,000	14,225	35,775	71,550
8	2,285	50,000	17,285	32,715	65,430

Table 2. Variations in pH of synthetic zeolite



Figure 7. Influence Curve of Synthetic Zeolite pH on Cu²⁺. ion absorption

According to the Table 2 and Figure 7, it was found that the best absorbance was obtained at pH = 4. The adsorption efficiency of synthetic zeolite for Cu^{2+} is greatly affected by the pH value of the

adsorbate solution. This can be seen from the fact that the desorption process occurs at pH < 4 and the adsorption increases at pH = 4, and then the efficiency drops again at pH > 4. The decrease in Cu metal ion adsorption is due to the lower pH and larger oxide solubility of Cu^{2+} ions, allowing the metal adsorbed in the adsorbent pores to migrate back into the solution phase. Although the ability of the adsorbent to absorb copper metal ions decreases at pH values above 4, it can be said that in synthetic zeolites, the optimal pH conditions occur in an acidic environment. This situation differs from fly ash uptake conditions, which are more efficient at pH=7. Based on research by Musyoka (2009), Cu will be optimally adsorbed under acidic or alkaline

Table 3. Variation of fly ash pH

conditions, while the AAS results for fly ash show that at pH 5–6 shows a downward graph trend, then jumped up at pH = 7. Thus, it can be said that the data on the effect of pH on fly ash adsorption is invalid.

The ability of synthetic zeolite to absorb the largest Cu ion is 80.330%, while the percentage of fly ash absorption is 80.498%. This indicates that the synthetic zeolite is active in an acidic environment, and fly ash shows the optimum value in an alkaline environment.

pH Var.	Abs	Initial Cons.	Residu Cons.	Abs. Cons.	%Abs.
2	3,044	50	23,041	26,959	53,918
3	2,268	50	17,161	32,839	65,678
4	1,793	50	13,561	36,439	72,878
5	2,387	50	18,061	31,939	63,878
6	4,195	50	31,761	18,239	36,478
7	1,290	50	9,751	40,249	80,498
8	1,984	50	15,011	34,989	69,978
	70 60 50 40 30 20 10			•	
	0 () 2	4 6	8 10	
		1	pH Variation		

Figure 8. The curve of the effect of fly ash pH on the absorption of Cu^{2+} . ions

In general, the amount of adsorbed metal increases above pH 6. At low acidic pH conditions, the concentration of H^+ ions increase, and H^+ ions and metal ions compete with other cation exchange sites in the synthetic zeolite sorbent. The existence of competition between H^+ ions and metal ions will cause damage to the zeolite structure due to ion exchange competition, resulting in a decrease in the adsorption capacity of metal ions.

At the same time, high pH causes more metal hydroxides to precipitate out and reduce metal ions in the ocean. At such high pH, there is less competition for H^+ ions as metal ion competitors because the solution is alkaline and therefore metal ions are optimally absorbed. The second change is the contact time change shown in Tables 4 and 5. The experiment found that the maximum adsorption state of the synthetic zeolite gradually decreased with

the time change over 70 minutes and 90 minutes.

The adsorption of copper metal ions using synthetic zeolite as adsorbent was more stable when the stirring time was 50 minutes, because the copper metalcontaining solution was saturated at 70 minutes and 90 minutes stirring time, and the required separation does not last longer because the adsorption efficiency is close to 100%, which means that out of 50 ppm copper metal ions, only 2,725 ppm copper metal remains, 94.5% absorption occurs and is at the absorption saturation point. Along with that, the absorption capacity of synthetic zeolite decreased, but the range was not excessive, still in the range of 94%. Copper metal is readily absorbed by synthetic zeolites because copper metal is a reactive metal and this metal has the property of readily binding to organic materials and precipitation.

Table 4. The variation of synthetic zeolite contact time on the absorption of Cu^{2+} . ions

Time Var.	Abs	Initial Cons.	Residu Cons.	Abs. Cons.	%Abs.
10	1,221	50,000	9,225	40,775	81,550
20	1,151	50,000	8,695	41,305	82,610
30	1,003	50,000	7,575	42,425	84,850
40	0,743	50,000	5,605	44,395	88,790
50	0,363	50,000	2,725	47,275	94,550
70	0,392	50,000	2,945	47,055	94,110
90	0,376	50,000	2,825	47,175	94,350



Figure 9. The curve of synthetic zeolite contact time variation on Cu^{2+} . ion absorbance

In fly ash, the highest efficiency is 94,550%, which corresponds to a contact time of 50 minutes. As can be seen from the curve, the graph shows an increasing trend, which indicates that the contact time for fly ash to reach the optimum point is achieved by synthetic zeolite,

which is 94.5%, and the contact time greater than 90 requires a log. Therefore, it can be said that the activation of synthetic zeolite with fly ash can shorten the adsorption contact time and reach the optimum point.

Time Var.	Abs	Initial Cons.	Residu Cons.	Abs Cons.	%Abs.
10	1,763	50	13,331	36,669	73,338
20	1,738	50	13,141	36,859	73,718
30	1,631	50	12,331	37,669	75,338
40	1,464	50	11,071	38,929	77,858
50	1,323	50	10,001	39,999	79,998
70	1,262	50	9,541	40,459	80,918
90	1.221	50	9.231	40.769	81.538

Table 5. Variation of fly ash contact time on Cu²⁺. ion absorption



Figure 10. The curve of fly ash contact time variation on Cu^{2+} . ion absorbance

The third change was the weight of the adsorbent, which varied from 30 mg, 60 mg, 90 mg, and 150 mg. Among them, it can be seen from Table 6 that the more synthetic zeolite is used, the higher the absorption efficiency of Cu metal ions. The adsorption capacity of synthetic zeolite reached 98% when the adsorbent weight was 150 mg, while the adsorption capacity of fly ash was only 85% when the adsorbent weight was 90 mg, and the adsorption capacity decreased by 150 mg when using the adsorbent (Table 7).

0 2							
	Weight Var.	Abs	Initial Cons.	Residu Cons.	Abs. Cons.	%Abs.	
	30	0,391	50,000	2,936	47,064	94,128	
	60	0,332	50,000	2,494	47,506	95,012	
	90	0,200	50,000	1,490	48,510	97,020	
	150	0,138	50,000	1,021	48,979	97,958	

Table 6. Weight of synthetic zeolite on Cu^{2+} . ion adsorption



Figure 11. Synthetic zeolite weight curve for Cu²⁺. ion adsorption

Table 7. Weight of fly ash against Cu^{2+} . ion absorbance

Weight. Var.	Abs	Initial Cons.	Residu Cons.	Abs. Kons.	% Abs.
30	1,289	50	9,741	40,259	80,518
60	1,145	50	8,651	41,349	82,698
90	0,973	50	7,351	42,649	85,298
150	1,033	50	7,801	42,199	84,398



Figure 12. Fly ash weight curve against Cu²⁺ ion adsorption

Basically, the metal removal mechanism using zeolites involves ion exchange reactions. This synthetic zeolite can be used as an adsorbent to remove metals from solution because the zeolite is negatively charged due to the charge difference between Si⁴⁺ and Al³⁺. This negative charge arises because the trivalent aluminum atom must bind to the

other 4 electronegative oxygen atoms in the zeolite framework.

This negative charge allows synthetic zeolites to bind cations with weak bonds, such as Na and Ca cations. Because of this weak bond, synthetic zeolites act as cation exchangers. That is, Na cations are replaced by Cu (II) metal ions. The adsorption of metal cations occurs on the surface hydroxyl groups of the zeolites in combination with the positive charges of the metal cations and the negative charges on the surface of the synthetic zeolites.

The optimal conditions for adsorption of Cu (II) metal ions by synthetic zeolites were determined through a series of experiments. The optimal conditions were pH = 4, contact time 50 min, and sorbent weight 150 mg.

Conclusions

In summary, fly ash can be activated into synthetic zeolite by a hydrothermal process, thereby improving the adsorption capacity of Cu (II) metal ions. The optimum adsorption conditions were pH=4, the adsorption value was 80.330%, the weight of the adsorbent was 150 mg, the adsorption rate was 97.958%, the contact time was 50 min, and the adsorption rate was 94.550%. Advanced research is necessary to discover adsorption methods based on adsorption kinetics and adsorption isotherms.

Confession

The results of zeoliticization of coal waste in the form of fly ash as a Cu (II) ion adsorbent are presented in Coal Waste Treatment at Lati Steam Power Plant (SPP) Berau. Advising fly ash waste managers to treat fly ash waste as a sorbent can increase the saleable value of the waste. The results of this study were also submitted to the Department of Forestry of Mulawaman University to further investigate the uptake rate of other heavy metals by coal waste.

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