ABSTRACT

Indonesian government regulation No 85 year 1999 regarding management of hazardous material states that in order to identify and to define coal ash as hazardous material or non hazardous material, the coal ash should be evaluated by characteristic and toxicity tests. In this study, the properties of coal ash sample from Bukit Asam power plant were evaluated using chemical analyses and bioassay of Lethal Concentration (LC50-96 hour) and Lethal Dose (LD50-96 hour). The chemical analyses shows that the main chemical compositions of Bukit Asam coal ash were SiO2 (60.6 %) and Al2O3 (22.8%). Bukit Asam coal ash was categorized as non toxic criteria as its LC50-96 hour value exceeded 100,000 ppm. Meanwhile, the result of LD50-96 hour shows that mortality of mice was not found in every dose given (500; 5,000; 15,000; 30,000; 50,000 mg/kg BW) for 0-96 hours of observation so it can be classified as a non hazardous material based on the Indonesian government regulation. The results of TCLP test reveal that the concentrations of all the heavy metals were invariably well below the permissible limits for discharge of effluents according to Indonesia regulation and US. EPA standard. Thus, it was also categorized as non hazardous material. Radiation dose of Bukit Asam coal ash was 0.41 mSv/year and it was under standard limits for human being (1 mSv/year). The mean heavy metal contents in Brassica chinensis tissues with three times cultivation were above the WHO limits level. However, the addition of 17.5% coal ash in growth media drastically decreased heavy metals content (Cu: 25.6; Pb: 66.6; Cd: 48.8 dan Cr: 8.29 %) into the lowest content. The results generated from this study indicated that Bukit Asam coal ash has a vast potential for reclamation of degraded coal mining land.

Keywords: coal ash, chemical content, characteristic test, toxicity test, radioactive element, heavy metal

SARI

PP No 85 Tahun 1999 merupakan Perubahan atas PP No 18 Tahun 1999 tentang Pengelolaan Bahan Berbahaya dan Beracun (B3) menyatakan bahwa identifikasi dan penentuan abu batubara PLTU sebagai limbah B3 atau bukan limbah B3 dilakukan dengan cara uji karakteristik dan uji toksikologi. Uji karakteristik dilakukan melalui analisis kandungan kimia abu batubara. Uji toksikologi secara biologi dilakukan melalui uji LC50-96 jam dan LD50-96 jam. Abu batubara PLTU Bukit Asam mayoritas tersusun atas SiO2 (60.6 %) dan Al2O3 (22.8 %). Dari uji LC50-96 jam diketahui nilai LC50-96 jam sebesar 337.100 ppm sehingga dikategorikan sebagai bahan bukan beracun (non-toxic). Hasil uji LD50-96 jam diketahui bahwa kematian mencit (Mus musculus) tidak ditemukan dalam setiap dosis perlakuan (500; 5,000; 15,000; 30,000; 50,000 mg/kg BW) sehingga dikategorikan sebagai bahan bukan beracun dan berbahaya (non hazardous material). Dari hasil uji TCLP diketahui konsentrasi logam berat pada abu batubara bervariasi, semuanya berada di bawah ambang batas sehingga dikategorikan sebagai bahan yang bukan beracun dan berbahaya (non-hazardous material). Dosis radiasi yang dihasilkan abu batubara PLTU Bukit Asam sebesar 0.41 mSv/tahun, maka abu batubara PLTU Bukit Asam masih aman untuk dimanfaatkan karena berada di bawah nilai ambang dosis untuk masyarakat umum sebesar 1 mSv/tahun. Rata-rata kandungan logam berat (Cu, Pb, Cd dan Cr) yang berada pada seluruh jaringan caisin (Bras-
INTRODUCTION

In 2006, Indonesian government announced the first stage of a “fast track” program to accelerate the development of 10,000 MW of electric generating capacity. This program has been dominated by the development of coal power plant. Based on the Statistics Book of Electricity No 25/2011, total installed capacity of coal power plant is about 16,318 MW or 40 % from total national electric capacity (39,898.37 MW). This number would increase drastically in terms of the development of 3x10,000 MW of national electric programs. In 2020, utilization of coal ash would increase dramatically from 50 TWhour to become 320 TWhour. In the same year, supply of coal is predicted to be 108.3 million tons. A coal power plant generally produces about 8-10% of coal ash. Hence, Indonesia would produce approximately 21.66 million tons of coal ash per year. The huge amount of coal ash will potentially be serious problem in the future owing to its requirements for its storage.

Result of several research from different countries shows that application of coal ash combining with other materials for reclamation of abandoned mine area could improve soil fertility in preparing nutrient for plant (Mitra et al. 2003), acting as alternative ameliorant (Truter et al. 2009) and immobilizing heavy metals (Ciccu et al. 2001). Long-term monitoring (14 years) of plants, soil, and drainage water did not indicate any potential long-term negative impacts associated with utilization of Flue Gas Desulfurization (FGD) product. Also, heavy metals content in plant biomass tissue and soil water did not significantly increase (Chen et al. 2009).

However, in Indonesia, there is a limited research of coal ash from power plant on the effect and potentiality of coal ash as an amandment in agricultural application and utilization for reclamation abandoned mine area. In this study, toxicity level and radiation dose of coal ash were evaluated with the aim of helping opening up the usage of coal ash.

METHODOLOGY

The coal ash for this study was taken directly from coal ash storage facility at Bukit Asam power plant, South Sumatera Province. A total of 100 kg of coal ash samples was collected as a mixture of fly ash and bottom ash in equal proportion of volume. Scope works of this research involves physical, chemical and mineral composition of coal ash including environmental aspects by laboratory test and bioassay as needed by environmental regulation. Also, experimental study was conducted by implementation of coal ash utilization for agriculture at laboratory scale.

Toxicity analysis was conducted by biological and chemical test (BAPEDAL, 2001) including Lethal Concentration (LC50-96 hour) and Lethal Dose (LD50-96 hour). LD50-96 hour analysis was performed based on the procedures issued by US. EPA OPPTS 870.1100 and Standard Methods for the Examination of Water and Wastewater (Eaton et al. 2005) using mice (Mus musculus). The obtained data were calculated by probit analyses using MICRO-PROBIT program. Meanwhile, LC50-96 hour test was conducted based on ASTM: E 729-88a Guide for conducting acute toxicity with fishes, macro invertebrates and amphibians (ASTM, 1988). Goldfish (Cyprinus carpio Linn.) was used for this research as a sensitive testing organism. The acute toxicity test was conducted by storing 10 fishes into 4 liters of treated media. As a comparison, a control containing dilution liquid without treatment was provided. The test was carried out for 96 hours by examining the total dead fishes obtained every 24 hours. The total dead fishes were then calculated to determine LC50-96 hour value using probit analysis method.

The chemical analysis of coal ash was performed using Toxicity Characteristics Leaching Procedure (TCLP) according to the USEPA SW-846 Method 1311. The TCLP test involved the extraction of contaminants from a 100-g size-reduced sample of waste material with an appropriate extrac-
tion fluid. A 20:1 liquid to solid (L/S) ratio was employed, and the mixture was rotated for 18 ± 2 hours at 30 rpm using a rotary agitation apparatus. After rotation, the final pH was measured, and the mixture was filtered using a glass fiber filter. The filtrate was collected in an appropriate container, and preservative may be added if needed. The filtrate was analyzed for a number of constituents based on government regulation (BAPEDAL, 2001) and US. EPA standard to find out as to whether the coal ash can be classified as hazardous or toxic.

The concentration of uranium (U), radium (Ra), Thorium (Th) and Kalium (K) were measured based on National Council on Radiation Protection and Measurements (NCRP), Environmental Radiation Measurement, NCRP Report No 50, Washington (1977) using spectrometer gamma. Furthermore, to identify the impact of coal ash utilization on plant, Brassica chinensis was used because of its high ability on heavy metal absorption. The addition of coal ash in plant's growing media were 0; 5; 10; 12.5; and 17.5 % respectively. The cultivation of Brassica chinensis was repeated three times. The contents of metal elements (Cu, Pb, Cd, and Cr) in Brassica chinensis were analyzed and compared with WHO critical level standard of plant for human consumption.

RESULTS AND DISCUSSION

Chemical Content of Bukit Asam Coal Ash

The chemical composition of coal ash used in this research is shown in Table 1. Chemically, the coal ash contained silicon dioxide, aluminum oxide, ferric oxide, titanium dioxide, phosphorus pentoxide, calcium oxide, magnesium oxide, sodium oxide, and potassium oxide. Table 1. shows that the main constituent of Bukit Asam coal ash were SiO₂ (60.6 %) and Al₂O₃ (22.8 %), while other components Fe₂O₃; H₂O; CaO; MgO; TiO₂; MnO; P₂O₅; and total sulfur were less than 5 %. The major component of coal ash was silicates (SiO₂) with percentages of 60.6 %. Thus, this coal ash has been utilized as additive material for cement product and paving block.

The coal ash contains important nutrients for plant, particularly Ca; S; Mg. Also, CaO can increase the soil pH extensively because of high reactivity. Therefore, coal ash has a potential for use in reclamation of degraded mine land as stated by Singh et. al. (2011). The coal ash also consisted of minor percentage of oxide acid in the form of P₂O₅ (0.66 %).

LD₅₀-96 Hours

The test result shows that the mortality of mice was not found in every dose given (500; 5,000; 15,000; 30,000; and 50,000 mg/kg BW) for 96 hours of observation. Figure. 1 shows the mean daily weight of mice between control and treated mice. Each control and treated mice consisted of 5 mices. It can be seen that the mean weight of mice generally inclined between 0.04–1.00 gram every 24 hours during 96 hours of observation. After 96 hours of observation, control treatment of mice reached the highest mean daily weight than other treatments (22.72 gram). While, the lowest mean daily weight was gained by mice with treatment dose of 15,000 mg/kg BW.

Even though the weight of mice was affected by coal ash, but mice mortality was not found in every dose of coal ash given after 96 hours of observation. Based on this mortality result, it could be concluded that the Bukit Asam power plant coal ash is classified as a non hazardous material based on the Indonesia government regulation No. 85 year 1999.

LC₅₀-96 Hour

Table 2 shows the result of the acute toxicity against goldfish. The probit analysis results show that the elutriate percentage of Bukit Asam coal ash was as much as 33.71 (337,110 ppm). Elutriate reflected the coal ash fraction moving into the water.

<table>
<thead>
<tr>
<th>Component</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>CaO</th>
<th>MgO</th>
<th>TiO₂</th>
<th>MnO</th>
<th>P₂O₅</th>
<th>LOI</th>
<th>H₂O</th>
<th>S Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (%)</td>
<td>60.6</td>
<td>22.8</td>
<td>4.21</td>
<td>0.46</td>
<td>1.33</td>
<td>2.92</td>
<td>1.38</td>
<td>0.75</td>
<td>0.05</td>
<td>0.66</td>
<td>0.7</td>
<td>2.2</td>
<td>0.32</td>
</tr>
</tbody>
</table>
Toxicity criteria of LC50-96 hour test is based on the Australia Petroleum Energy Association (APEA) and the Energy Research and Development Corporation (ERDC) standards. Generally, there are 6 levels of toxicity criteria from non toxic (>100,000 ppm) until very toxic (<1 ppm) as shown in Table 4. Based on those criteria, Bukit Asam coal ash is categorized as non toxic against goldfish which LC50 96 hours exceeded 100,000 ppm.

Table 4. Toxicity criteria

<table>
<thead>
<tr>
<th>Toxicity criteria</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very Toxic</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Toxic</td>
<td>1 – 100</td>
</tr>
<tr>
<td>Moderately Toxic</td>
<td>100 – 1,000</td>
</tr>
<tr>
<td>Slightly Toxic</td>
<td>1,000 – 10,000</td>
</tr>
<tr>
<td>Almost Non Toxic</td>
<td>10,000 – 100,000</td>
</tr>
<tr>
<td>Non Toxic</td>
<td>&gt; 100,000</td>
</tr>
</tbody>
</table>

The major concern is potential hazard of trace element (Ag, As, B, Cd, Cr, Cu, Hg, Se, Zn) contamination into water and plants. Serious potential trace element hazards for plants and human being are B, As, Se, and Mo. Although some elements may pose concerns under some conditions, Boron, Cu, Ni, and Zn are essential for growth of many plants and Se is essential for animals, while As, Cd, Cr, and Pb are not essential to either plants or animals (Clark et al. 1999). Because of these concerns, the limit values for trace elements have been determined in leachates (TCLP). Based on Table 5, it can be concluded that the concentrations of all heavy metals under study in the leachates were invariably well below the permissible limits for discharge of effluents according to Indonesia regulation or US. EPA standard.
Table 5. Comparison of TCLP value standard between Indonesia regulation and US.EPA standard

<table>
<thead>
<tr>
<th>Elements</th>
<th>Sample (mg/L)</th>
<th>TCLP Standard (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Indonesia regulation No 85/99</td>
<td>US. EPA</td>
</tr>
<tr>
<td>Arsenic (As)</td>
<td>0.001</td>
<td>5</td>
</tr>
<tr>
<td>Barium (Ba)</td>
<td>0.452</td>
<td>100</td>
</tr>
<tr>
<td>Boron (B)</td>
<td>2.891</td>
<td>500</td>
</tr>
<tr>
<td>Cadmium (Cd)</td>
<td>0.011</td>
<td>1</td>
</tr>
<tr>
<td>Chromium (Cr)</td>
<td>0.001</td>
<td>5</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>0.022</td>
<td>10</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>0.001</td>
<td>5</td>
</tr>
<tr>
<td>Mercury (Hg)</td>
<td>0.0001</td>
<td>0.2</td>
</tr>
<tr>
<td>Selenium (Se)</td>
<td>0.015</td>
<td>1</td>
</tr>
<tr>
<td>Silver (Ag)</td>
<td>0.001</td>
<td>5</td>
</tr>
<tr>
<td>Zinc (Zn)</td>
<td>0.142</td>
<td>50</td>
</tr>
</tbody>
</table>

**Radiation Exposure**

The assessment of radiation exposure from coal ash is critically dependent on the concentration of radioactive elements in coal ash that remains after combustion. Average adsorb dose \( D \) (nGy/jam) is gained by using equation:

\[
D = 0.461 \text{ARa} + 0.623 \text{RTh} + 0.0414 \text{AK}
\]

ARa equal with 226Ra, ATh equal with concentration of 232Th, and AK equal with concentration of 40K. Effective dose (HE) is obtained by using equation:

\[
H_E = D \times T \times F, \text{ (mSv/year)}
\]

T : time of exposure radiation (±7008 hours/year). It is assumed that coal ash is utilized for building material.
F : converted factor (0.7 Sv/Gy).

Radiation dose of coal ash after calculation is as much as 0.41 mSv/year. Based on regulation, this value is much lower than standard limit for human being (1 mSv/year).

**Heavy Metals Content of Brassica chinensis**

As mentioned before, the important consideration of coal ash utilization for agriculture or revegetation purposes is potential hazard of trace element (Cu, Pb, Cd, Cr) contamination into plants when toxic concentrations of these elements enter the food chain.

The result of heavy metals content in all parts of Brassica chinensis tissues for three times cultivation is shown in Table 6. Then, it was compared with WHO critical level standard of plant for human consumption. Heavy metals are known to be non-biodegradable and persistent environmental contaminants which may be deposited on the surfaces, and then absorbed into the tissues of plants.

Cu is an essential enzymatic element for normal plant growth and development but can be toxic at excessive level. The mean concentration of Cu was above WHO limits level, except 10% treatment (8.33 ± 0.577) ppm. The mean concentrations of Pb on sample were variably between (1.67 ± 1.528) and (6.00 ± 4.583) ppm. Those results reveal that all of mean Pb concentration were above WHO limits level. The mean concentrations of Cd were also found exceed the WHO limits level. Both of Pb and Cd are non-essential trace elements having no functions neither in human body nor in plants, but can induce various toxic effects in humans at low dose. The highest amount concentration of Cr was found at 10 % treatment (3.87 ± 4.456 ppm), whereas the lowest concentration was reached by 17.5% treatment (4.93 ± 3.690 ppm). Those Cr concentration results were above WHO limits level (1.3 ppm). Therefore it had potential risk for human health if they consume the plants. Heavy metals in all
samples mostly transcended WHO level limit, however this research revealed that the addition of coal ash to the soil had positive impact on decreasing all metals concentration.
CONCLUSION

The main constituents of Bukit Asam coal ash were SiO$_2$ and Al$_2$O$_3$. The biological toxicity test results of LC$_{50}$-96 hour and LD$_{50}$-96 hour show that the Bukit Asam coal ash can be considered as non-toxic material. The TCLP test result shows that the coal ash can be categorized as non-hazardous material. The radioactive elements in coal ash were not in alarming level of alarm. The mean concentration of all metals in mixture tissue of Brassica chinensis under study were above the WHO limit level, but the addition of a 17.15% volume of coal ash could reduce the concentration of heavy metals in this plant.

SUGGESTION

Combination of coal ash with another material such as farm yard manure has been known improving the growth and nutrients uptake of plants (Singh et al. 2011) because they change the soil structure and texture. Because of its chemical characteristics, coal ash has a vast potential for use in reclamation of degraded land such as at coal mining area.

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REFERENCES


