Bottom ash treatment by using seawater with Citrus aurantifolia

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Abstract. The combustion process of coal from a coal-burning power station in TNB Janamanjung Sdn. Bhd. for production of energy was produced a primary by-product called coal ash. The huge amount of bottom ash was considered harmful to the environment and typically disposed of on-site disposal systems without any further use. The environment can be polluted since the toxic elements such as heavy metals that exist in the ash could pose a danger to public health. To overcome these problems, an effective treatment needs to be done to overcome the problems. The purpose of this research is to study the possibility of developing a new technique to reduce heavy metal elements by using seawater as a washing method and Citrus aurantifolia as leaching methods. A good alternative from the use of citric acid from the Citrus aurantifolia was discovered to be substitute strong acids such as HCl in the leaching process since citric acid can react as an organic acid which fewer negative effects compared to the stronger acid to humans and the environment. The bottom ash was rinsed and soaked in the seawater for 24 hr before the leaching process by using Citrus aurantifolia. The result showed that the heavy metals content such as copper (Cu), zinc (Zn), and arsenic (As) can be decreased after the removal process. In fact, the results show that the heavy metal removal up to 92% for As when the bottom ash was soaked until 72 hr but for Cu and Zn, the removal efficiency higher when the bottom ash was soaked at 20 hr. In conclusion, the optimum time to remove heavy metal from bottom ash by using Citrus aurantifolia was determined but the efficiency differs with the time taken to soak the bottom ash in the acid solution.

1. Introduction
Coal ash is a combustion by-product obtained from a coal-fired power plant station. This ash contains several by-products that are produced from the burning of coal including fly ash and bottom ash. The physical and chemical properties of bottom ash produced were influenced by the type, source, quality of the parent fuel, and the operating conditions of the power plant influenced. Bottom ash is the coarser part collected at bottom of the furnace. In a developed country, it was reported that about 50 % of coal bottom ash had been utilized in the civil engineering industry such as road constructions, structural fills also as an aggregate replacement for embankments, and cement-bared composites [1]. The metallic element such as copper (Cu), nickel (Ni), chromium (Cr), zinc (Zn), and lead (Pb) resulting from the clarification of Coal Bottom Ash (CBA) in Malaysia was stated under the Schedule Waste (SW 104) Environment Quality Act 1974 [2]. In bottom ash, heavy metal oxide exists naturally with properties of high melting points, cannot volatilize and cause incomplete combustion in the furnace. Unlike organic wastes heavy metal is non-biodegradable and able to accumulate in living tissues, causing various
diseases and disorders; therefore, removal process or treatment process needed before discharge to the river. For instance, a possible human carcinogen from lead for instance, lead is a possible human carcinogen because it is a commutative poison [3]. While arsenic (As) remains the most toxic element to humans even at a low exposure dosage [4]. The major problem of Tenaga National Berhad (TNB) plant is producing a huge amount of bottom ash with high content of the heavy metal and cannot be disposed into the landfill, but it had to be transferred to the Kualiti Alam and should be disposed of in accordance with the regulations. There are several methods of extraction that can be used to recover heavy metals from coal ash but requires high energy and cost [5]. In the present study, a hydrometallurgical process (chemical leaching) has been discussed to recover some economically important metals. In other words, metal oxides bound in coal bottom ash are turned into metal ions that are released into the acid solution.

The acidic reagents have been used to compare the recovery of metal values from the pre-treated bottom ash samples at varying concentrations. The acid is used in the chemical leaching process to dissolve heavy metals contained in coal bottom ash. Process parameters such as acid/alkali concentration, working volume, and temperature have been optimized and the recoveries of metal values under optimum conditions were recorded. However, the chemical leaching method is considered uneconomical since this method requires the usage of strong acids and expensive acid proof equipment [6]. Many strong acids can be chosen for the extraction of heavy metals from the bottom ash as reported in the literature, such as inorganic mineral acids like sulfuric acid, hydrochloric acid, and nitric acid. The extraction process of heavy metals from the bottom ash in the hydrochloric acid consists of two steps, first pre-washing with water and second leaching in hydrochloric acid. It was confirmed that this process is quite effective to extract the valuable metals from the bottom ash. But considering procedures for safe handling of concentrated acids involved a high risk, the strong acid was replaced by using environmentally safe organic acid from key lime (Citrus aurantifolia). In this project, the selection solvent for the reduction of heavy metal in the bottom ash was investigated. This study was conducted to investigate the excessive seawater with Citrus aurantifolia and its capability to reduce the heavy metal from the bottom ash in various power stations. Besides, the heavy metal in bottom ash can be dangerous to the environment, aquatic life, and human and the leaching method by using Citrus aurantifolia can reduce the heavy metal content from the bottom ash. Lime precipitation can be employed to effectively treat inorganic effluent with a metal concentration of higher than 1000 mg/L. In this study, using lime precipitation was used cause the benefits include inexpensive equipment requirement, the simplicity of the process, and convenient and safe operations [7].

The first objective of the study is to reduce the concentration of heavy metal in bottom ash by using seawater through the washing method and Citrus aurantifolia through the leaching method. Seawater was chosen because it is a natural water supply at power plant and showed a decreasing trend in heavy metal after washing by using seawater [8]. Then, the removal efficiency of heavy metal was calculated by using different contact times of bottom ash and Citrus aurantifolia.

2. Materials and Methods

2.1. Sample collection

The sample of bottom ash was collected at TNB Janamanjung Sdn Bhd, a thermal power plant at Perak, Malaysia. Then, the seawater was taken from Sungai Lang, Sabak Bernam beach which is located at Politeknik Sultan Idris Shah. The Citrus aurantifolia (key lime) peel is a by-product of the agricultural industry of juice making in Sabak Bernam. The material used to study the heavy metal removal by using seawater for washing technique and Citrus aurantifolia (key lime) as citric acid for the leaching method. Furthermore, for the leaching method, hydrochloric acid (HCl) with ACS Grade Acids concentration 12 M also used to make a comparison result between the use of lime (citric acid).
2.2. Washing process by using seawater
Before the seawater was taken, the bottle sample must be rinsed first with seawater before filling it into the bottle sample. Then, take the pH reading of seawater. The bottom ash was weighed in 50 grams. About 100 ml of seawater was measured and poured into the beaker. The bottom ash was filled into the beaker with 100 ml of seawater and stir it well. The bottom ash was allowed to soak in the seawater for 24 hr to allow maximum time contact between both materials. Lastly, the bottom ash was filtered to separate the bottom ash from the seawater [9].

2.3. Process of making acid solution
Juice production causes an enormous amount of citrus peels are produced every year. Citrus peels, the primary waste product of citrus juice production, are a good source of molasses, pectin, and limonene and are usually dried, mixed with dried pulps, and sold as cattle feed. In this study, the peel was used instead of lime juice as the main material. The lime peel was washed with deionized water to eliminate any impurities. Then, the process continued to change the lime peel into powder form. The lime peel was dry in the furnace and shredded until become powder. The lime powder was weighed in 25 grams and 200 mL of deionized water was added and stirred. This process to extract citric acid because the citric acids, after drying, the content is up to 8 % [10]. The advantages of using lime precipitation include the simplicity of the process, inexpensive equipment requirement, and convenient and safe operations. Using citric acid as the base metal cleaning formula can effectively remove the oxides formed on the surface of ferrous and non-ferrous metals, as a weak organic acid [11].

2.3.1. HCl solution. Meanwhile, the preparation of an HCl solution from 10 ml of HCl solution and 10 ml of deionized water (ratio required HCl: water 1) to ensure the pH less than 2. Many lixiviates can be chosen for the extraction of heavy metals from the bottom, such as inorganic mineral acids like sulfuric acid, hydrochloric acid, and nitric acid [12].

2.4. Leaching process with HCl solution and Citrus aurantifolia
The citric acid solution was heated up to 70°C the bottom ash was soaked into the solution within 60 minutes. Leaching process for HCl solution also applied the same method as citric acid solution. After the leaching process, the coal bottom ash was filtered and washed with distilled water at room temperature and dried the ash at 60 °C for 60 minutes in the furnace. Finally, the concentration of heavy metal was determined by using AAS (Atomic Absorption Spectrometer).

3. Result and Discussion

3.1. Effect of acid
In this study, the higher concentration of heavy metal was chosen to study removal efficiency by using washing and leaching method [13]. Table 1 shows the initial concentration of As is 5.3 mg/L, Cu is 13.3 mg/L, and Zn is 31.5 mg/L. All the samples that were washed with the seawater is made as initial concentration reading which is known as C_o and the samples that were treated known as a final concentration, which is C_f. When the bottom ash was treated with HCl solution for 12 hours period time, no significant reading for As but the results show reduction concentration for Cu and Zn with 8.0 mg/L and 23.8 mg/L. Meanwhile, for removal of heavy metal by using Citrus aurantifolia shows decrement in a concentration of Cu and Zn only at 5.5 mg/L and 22.1 mg/L. The heavy metal removal for HCl shows a higher efficiency for Cu and Zn in 12 hr contact time, but not for As because HCl was a strong acid to dissolve metal ions that are released into the acid solution.
Table 1. Experimental results for heavy metal removal from bottom ash.

| Solution          | Time (hr) | Concentration (mg/L) |   |   |   |
|-------------------|-----------|----------------------|---|---|---|
|                   |           | Copper, Cu           | Zinc, Zn | Arsenic, As |
| Seawater (Co)     | 24        | 13.3                 | 31.5     | 5.3   |
| HCl (Ci)          | 12        | 8.0                  | 23.8     | N/A   |
| Citrus aurantifolia (Ci) | 12 | 5.5                  | 22.1     | N/A   |

3.2. Effect of time taken
The results show in table 2, the efficiency of Citrus aurantifolia as desorption agent in bottom ash is higher when the bottom ash was soaked in the citric acid solution from 20 hr up until 72 hr and the removal efficiency increases up to 92% for As. However, for the other two metal (Cu and Zn) the optimum time for heavy metals removal needs to be discovered as the removal efficiency reduces with time.

Table 2. Experimental results for heavy metal removal from bottom ash.

| Solution          | Time (hr) | Concentration (mg/L) |   |   |   |
|-------------------|-----------|----------------------|---|---|---|
|                   |           | Copper (Cu)          | Zinc (Zn) | Arsenic (As) | Copper (Cu) | Zinc (Zn) | Arsenic (As) |
| Citrus aurantifolia (Ci) | 20 | 9.3                  | 23.5     | 0.6     | 30          | 25          | 89          |
|                   | 48        | 7.6                  | 26.1     | 0.5     | 43          | 17          | 91          |
|                   | 72        | 9.4                  | 28.3     | 0.4     | 29          | 10          | 92          |

3.3. Heavy metal removal efficiency
Figure 1 shown the result of bottom ash treat with Citrus aurantifolia (citric acid) and hydrochloric acid solution. Heavy metals removal for Cu and Zn by using HCl show a higher percentage compared with Citrus aurantifolia solution only 29% and 10%. However, by using Citrus aurantifolia solution with 72 hr soaked into the solution, the removal of As able to achieve up to 92%. From the experimental results, it was shown that only Cu and Zn can be removed from bottom ash by using HCl and Citrus aurantifolia, but for As only Citrus aurantifolia solution able to reduce the concentration of heavy metal and acted as a good desorption agent from bottom ash. Citric acid was behaved as a simple organic ligand and reacted with metal ion from As. The citric acid (CA) is one of the organic ligands commonly present in natural water systems. The speciation of metals in solution may enhance adsorption if the ligands themselves are adsorbed onto the mineral surface [14]. According to some research, under lower concentrations adsorption is an efficient method for some specified solutes, especially for heavy metals in wastewater.
3.4. Effect of removal efficiency with time

Meanwhile, figure 2 the most significant decrease concerning the concentration of heavy metal was noted in the care of As, with 92% as compared to Cu and Zn which after soaked in up to 17 hr. The removal efficiency of As was increased with time. Compared with the other two metals (Cu, Zn), the efficiency reduced over time. These results indicate that not all the heavy metals were reduced in a long time and reacted with *Citrus aurantifolia* solution. The original material of bottom ash contained numerous toxic elements that can be leach such as Cr, Cu, Mo, Sb, As, into the environment, but in this study only these three elements were tested before and after the leaching process due to higher amount compared to other elements. The results in table 1 also showed Cu and Zn only reducing concentration by using HCl but not *Citrus aurantifolia* solution. Only strong acid could remove the toxic elements (Cu, Zn) in bottom ash from TNB Janamanjung Sdn. Bhd over time.
4. Conclusion
In this study, the ideal time to remove heavy metal from bottom ash by using two types of acids were determined. The strong acid, HCl to remove heavy metal Cu and Zn were recorded in lower time but for As only by using organic acid (citric acid) the concentration can be reduced up to 92%. Besides, this research could help TNB Janamanjung Sdn Bhd to improve on green initiatives by not disposing of the by-product and sell to third parties such as cement industries.

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