Palm Oil Fuel Ash [POFA]: innovative potential applications as heavy metal removal materials in gold mining wastewater

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Abstract. Gold mining wastewater contains heavy metals hazardous to the environment. The alternative solution to overcome the contamination problems was using adsorbent to reduce the amount of heavy metal content in the wastewater. Palm oil fuel ash [POFA] as a potential adsorbent to absorb the heavy metal content. This current study focused on the application of palm oil fuel ash [POFA] for the removal of heavy metal in the environment. The technology used in this study was the combination of adsorption and precipitation methods. Gold mining wastewater and supernatant were analyzed using Inductively Coupled Plasma [ICP] mass spectrometers. The result of this study showed that the level of heavy metals in the gold mining wastewater was successfully reduced at large amounts and that the POFA had a good adsorption capability.

1. Introduction

Toxic pollutants that derive from various anthropogenic activities are often contained in wastewaters. Activities that contribute to toxic pollutants are mining and non-environmentally friendly agriculture systems, also pollutants that came from earthquakes, volcanoes eruption, and storms. Three major groups of pollutants namely organic pollutants, inorganic pollutants, and biological particles. This study focused on inorganic pollutant groups, especially heavy metal ions. Heavy metals in wastewaters are necessary to be removed before the wastewater be discharged directly into the environment. If the wastewaters contain heavy metals ion directly discharged, it will damage the environment as a toxic and carcinogenic agent in nature. Heavy metal ions are elements from the fourth period of the periodic table, commonly chromium [Cr], cobalt [Co], nickel [Ni], copper [Cu], zinc [Zn], arsenic [As], and sometimes lead [Pb], mercury [Hg]. Heavy metals are available and can be found in nature but now the numbers are increasing due to industrial pollution which is also increasing [1].

The toxic ions enter the human body through the consumption of contaminated food [2]. The accumulation of heavy metals in the human body that exceeds the standard limits will be toxic and can cause various and serious health problems [3]. For example, a high concentration of Zn may cause skin irritations, vomiting, and stomach cramps, then too much accumulation of Ni in the human body causes cancer of the kidney and lungs [1]. Wastewater has a bad effect on the sustainability of the human population because it is a major source of disease and inhibits growth so wastewater treatment is needed so that contaminant levels can decrease [4]. Heavy metals will accumulate over a long period in the human body because of its very difficult nature and cannot even be degraded [5]. Various methods for removing heavy metal from wastewater have been studied, including the application of
electrochemical processing [electrocoagulation and electrodeposition], the process of physicochemical [ion exchange and chemical precipitation] and adsorption [using an organic material such as activated carbon, carbon nanotubes, rice husks, palm oil fuel ash [pofa], etc.] [6].

POFA is one of the by-product variants in the palm oil industry. POFA contains several chemical components such as SiO2, Al2O3, Fe2O3, CaO, and MgO. Solid waste from palm oil extraction combustion from various parts of the plant (fibers, kernels, husks, oil palm empty fruit bunches, and shells) can be used to make POFAs. To produce energy and large ash after combustion, the empty palm oil fruit shell usually burnt in the power plants. Some of the ash is being used as a fertilizer for the palm trees, but since its highly alkaline nature at a pH of around 11, the ash must be careful handling and disposal [7]. Previous studies have shown the chance of using POFA as a cement replacement material [8], escalation of soft soil conditions [8], and as an adsorbent for remove Zinc from aqueous solution [9]. However, a significant amount of POFA is still disposed to landfills requiring large hectares of land; because of limited applications [10] [11]. Based on these considerations, the use of POFA as organic material adsorbent is very important to develop, because this method is low cost and effective for the treatment of wastewater. Also, the use of POFA as adsorbent is effective to reduce the accumulation of POFA in landfills and also increase the economic value of the POFA.

2. Materials and Methods
Palm Oil Fuel Ash [POFA] as an adsorbent used in this study is the product of burning palm oil shells for power generation activities provided by the Rubber Industry in Jambi Province, Indonesia. The gold mining wastewater used for the experiment was taken from small-scale gold mining at Pangkalan Jambu, Merangin Regency, Indonesia. The laboratory-scale test was used and the adopted technique was adsorption using Palm Oil Fuel Ash [POFA] as an adsorbent for heavy metal and precipitation technique. An Inductively Coupled Plasma [ICP] as an atomic mass spectrometer was used for all chemical analyses of all heavy metal detection.

The test is carried out with one liter of gold mining wastewater sample mixed with Palm Oil Ash [POFA] adsorbent with slow stirring maintained for five minutes then turned off, the solution is allowed to stand for 45 minutes for the precipitation process. The precipitate was filtered, using a Whatman filter paper, then the obtained POFA residue was separated. At the final stage, the wastes were collected and the supernatant was sent for further test which is the chemical analysis on Inductively Coupled Plasma [ICP]. Scheme stages of this research summarized in Figure 1.

Figure 1. Schematic Diagram of Adsorption and Precipitation of Gold Mining Wastewater using Palm Oil Fuel Ash [POFA].
From the ICP Analysis, heavy metal adsorption percentage was calculated using the following equation [12].

\[
\% Adsorption = \left( \frac{C_0 - C_e}{C_0} \right) \times 100
\]  

where:
\( C_0 \) [mg/L] was the initial concentration of heavy metal in solution
\( C_e \) [mg/L] was the final concentration of heavy metal in the solution.

3. Result and Discussion

Representative values of this heavy removal treatment can be seen in Table 1. Each data point of the initial and final concentration of heavy metal content in solution represents the average of three equal tests; results of the chemical analyses were available in triplicate by ICP. Using the data presented in Table 1 and using equation [1] it is possible to plot Fig. 2, that shows a comparison of % adsorption of each heavy metal component.

| Type Of Heavy Metal | Initial Concentration [mg/L] | Final Concentration [mg/L] |
|--------------------|-------------------------------|-----------------------------|
| Arsenic [As]       | 0.044                         | 0.0066                      |
| Chromium [Cr]      | 0.154                         | 0.0103                      |
| Cobalt [Co]        | 0.078                         | 0.0086                      |
| Copper [Cu]        | 0.113                         | 0.0030                      |
| Lead [Pb]          | 0.160                         | 0.0170                      |
| Mercury [Hg]       | 0.077                         | 0.0166                      |
| Nickel [Ni]        | 0.095                         | 0.0130                      |
| Zinc [Zn]          | 0.399                         | 0.0240                      |

Figure 2. Comparison of adsorption percentage of each heavy metal component
Gold mining wastewater contains a high concentration of heavy metal as shown in Table 1. Heavy metal level minimum in clean water was 0.05 mg/L for Arsenic [As], 0.2 mg/L for Cobalt [Co], 0.05 mg/L for Zinc [Zn], 0.03 mg/L for Lead [Pb], 0.002 mg/L for mercury, 0.05 for Chromium [Cr], 0.2 mg/L for Nickel [Ni] and 0.02 mg/L for Copper [Cu]. Most of the value of heavy metal content in gold mining wastewater before treatment above the standard determined by the Indonesian Government except for Arsenic [As], Cobalt [Co] and Nickel [Ni]. Palm Oil Fuel Ash [POFA] showed very good results on adsorption heavy metal of gold mining wastewater, as final heavy metal concentration after the adsorption below the standard determined by the Indonesian Government.

The results of this study are consistent with research conducted by Samad et al in 2019 which shows mercury [II] ion removal value of 91.18% [13]. This is also in line with research conducted by Imla Syafiqah and Yusof in 2018 which states that mercury adsorption using modified POFA is an exothermic and spontaneous reaction to the use of POFA as an adsorbent is very promising because of the low cost and its good performance [14]. A research conducted by Yusof in 2019 reports the use of POFA as an adsorbent for the removal of As[III] and As[V] in water were able to successfully removed 48.7% and 50.2% of As[III] and As[V] [15]. There is still a few research conducted on the removal of heavy metal using POFA. The adsorption ability of some heavy metals from this research shows a better value than previous studies. As POFA was ashes from biomass, according to the European Community’s legislation, POFA categorized as nonhazardous waste. Concerning to improve soil quality, POFA can be used as a soil amendment to deactivate heavy metal in soil because of its adsorption ability and POFA also have the capability as fertilizer [16]. Based on the result, the adsorption process to remove heavy metal using POFA was very effective especially in mercury adsorption which had the highest adsorption percentage.

4. Conclusion
Effluent from gold mining contains a high amount of heavy metal hazardous for the environment. Palm Oil Fuel Ash is very potential to be developed as an adsorbent for the heavy metal content of gold mining wastewater. The results obtained indicate that the best adsorption value of heavy metals was in adsorption of mercury compounds which shows the adsorption percentage of 97.92%. Overall the use of POFA shows very good performance in terms of all metals.

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Acknowledgment
This work was supported by Lembaga Penelitian dan Pengabdian Masyarakat [LPPM] Universitas Jambi, Indonesia for senior lecturer’s research fund from PNBP of Jambi University.