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Research Article

Mercury removal from gold mining wastewater using palm oil fuel ash (POFA)

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Abstract

Mercury is a harmful element that commonly accumulates in the environment through anthropogenic activities such as gold mining. This study aimed to examine the use of palm oil fuel ash (POFA) as an agricultural waste to remove mercury in gold mining wastewater. The technology applied in this study was adsorption and precipitation. POFA was first washed until neutral then mixed with gold mining effluent with time variation of 30, 60, 90 minutes. Next, precipitate it for 30 minutes. The adsorbent dose used in this study was 250 mg with 1 litre effluent. The maximum adsorption efficiency observed in this study was 96.77%. The utilization of POFA as an adsorbent reduced mercury levels in wastewater below the allowed released mercury level to the environment (0.0025 mg Hg/L). Results indicate that reducing mercury from gold mining wastewater by utilizing POFA was simple, effective, and low-cost to be implemented.

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Introduction

One of the most harmful metals is considered to be mercury, commonly released naturally in the aquatic ecosystem or by anthropogenic action (Kudo et al., 1998; Rahmi et al., 2019). Anthropogenic action is the origin of mercury mostly found in small-scale gold mining; mercury concentration found in these anthropogenic activities is also found to be increased (Marrugo-Negrete et al., 2017). Mercury has three forms in nature which are elemental mercury (Hg^0); inorganic mercury, mainly in the form of mercuric ($HgCl_2$, HgS) and mercurous (Hg_2Cl_2) salts; and organic forms, such as ethyl ($C_2H_5Hg^+$) and methylmercury [$(CH_3Hg)^+$] (Bjørklund et al., 2017). This element could potentially harm the healthiness of people, fish, and wildlife. Additionally, mercury could be accumulated by humans, which could be found in the widely known case of Minamata that indicated food contaminated with mercury poisoning had caused mercury poisoning illness (Kudo et al., 1998; Alijani et al., 2015). Disastrous consequences of accumulated mercury in the human body (chromosomal aberrations, nervous system disorders, intellectual deterioration, etc.) are already well-known (Rahmi et al., 2019). Considering the effect of mercury poisoning, mercury ions removal from water and wastewater is essential. Therefore, various research efforts by many researchers have focused on removing mercury compounds using various techniques.

Currently, new technologies are focused on the process of adsorption because they are economical, a very simple, most adaptable, and well-established technique for the removal of heavy metals as well as mercury (Alijani et al., 2015; Attari et al., 2017). Another technology for removing mercury from an aqueous solution such as physicochemical processes (ion exchange and chemical precipitation), reverse

osmosis and ultra-filtration usually involve costly materials and demanding operational costs (Samad et al., 2019); on the contrary, due to high-energy consumption, the application of electrodialysis method, membrane electrolysis and electrochemical precipitation has been limited (Alijani et al., 2015).

Heavy metal contaminants removal by utilizing agricultural waste adsorbents are mostly found in recent studies. There are several available adsorbents based on agricultural waste used for mercury removal from water. Most of these adsorbents are usually high cost and hard to prepare because they require many stages of pretreatment. POFA is a kind of agricultural waste, as a palm oil by-product in the industry. In any case, a significant amount of POFA is still disposed to landfills because of limited applications. POFA is generated from the combustion of palm oil solid waste extraction, which has effective adsorption capability for removing heavy metal from an aqueous solution. The utilization of POFA as mercury removal offers low-cost technology and also reduces the accumulation of POFA in the environment (Zainudin et al., 2015).

All adsorbents utilized in mercury removal technologies have at least one drawback and limitations. Activated Carbons (AC) have porous structure (large mesopores and micropore volumes) and have high specific surface area contributed to increased cost but demanding in preparation and regeneration processes (Attari et al., 2017). Chitosan is biodegradable, available and low-cost, but the physical and chemical properties are poor, for example, low mechanical properties and have high solubility in acid solution (Rahmi et al., 2019). Coal fly ash (CFA) is an effective, low-cost material to capture mercury; however, because it contains heavy metals when removing mercury from the effluent, the CFA may release other heavy metal toxic to the medium (Attari et al., 2017). Sugarcane bagasse has a high mercury adsorption capacity for aqueous ions removal; however, pH adjustment is required (Khoramzadeh et al., 2013). Treated sawdust (*Acacia arabica*) has nearly 100% heavy metal ions adsorptive removal but is difficult to prepare and require a high cost (Meena et al., 2008).

There are few recent studies that apply POFA as heavy metal removal. Despite the fact that POFA has similar characteristics to CFA, it does not contain heavy metals (Zainudin et al., 2015). The application of CFA as an adsorbent is economically and technically effective, but utilizing CFA could release other toxic elements into the environment (Attari et al., 2017). Due to this limitation, the utilization of POFA as mercury removal in an aqueous solution promises a low cost, safe and simple technology without the risk of releasing other toxic into the environment. From this research, POFA is expected to be an alternative solution for agriculture waste utilization to eliminate mercury in gold mining water waste.

Materials and Methods

The experiment used wastewater from gold mining that was taken from small-scale gold mining in Jambi Province, Indonesia, with the coordinate of 2°08'17.1"S 101°54'31.2"E. Experiment was conducted on a laboratory-scale by adopting organic material adsorption and precipitation processes. Palm Oil Fuel Ash (POFA) that was used as an adsorbent in this study was obtained from Rubber Industry in Jambi Province, Indonesia. POFA was prepared by washing it to neutral then was heated to 100 ^{0}C for 30 minutes to be activated. This method was more simple compared to that had been conducted by Attari et al. (2017) that added sodium hydroxide and sodium aluminate to the adsorbent preparation stage.

The adsorption technique used in this research was adapted from the method of Attari et al. (2017) by differentiating the use of equipment, amount of waste, adsorbent dose and time variation. Phase for mercury removal process was one litre of gold mining wastewater samples mixed with 250 mg POFA adsorbent by maintaining slow agitation with the variation of 30, 60, and 90 minutes then switched off, then rest it (precipitation) to enable the solution to rest for as long as 30 minutes precipitation. The precipitate was filtered, using Whatman filter no 42 with 42.5 mm diameter and 2.5 µm pore, and separated the obtained POFA residue. The step was repeated three times with the difference of agitation time.

The POFA residue was collected then analyzed by utilizing Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Diffraction (XRD). The supernatant was sent to Inductive chemical analysis-Coupled Plasma Mass Spectrometry (ICP-MS) as an atomic mass spectrometer for all chemical analyses of all heavy metal detection.

The simplified process flowchart in this study is summarized in Figure 1. ICP-MS result data were then analyzed to compare the obtained sample result whether it had fulfill the required value that had been set by the government in Ministry of Environment and Forestry Decree No. 202 of 2004. Next, conduct mercury removal efficiency (%) calculation using the following equation (Meena et al., 2008; Gusain et al., 2020).

$$\text{Mercury Removal Efficiency (\%)} = \frac{(c_o - c_e)}{c_o} \text{ x } 100 \quad \text{.....(1)}$$

where :

C_o (mg/L) is the initial concentration of mercury in gold mining wastewater
C_e (mg/L) is the final concentration of mercury in gold mining wastewater

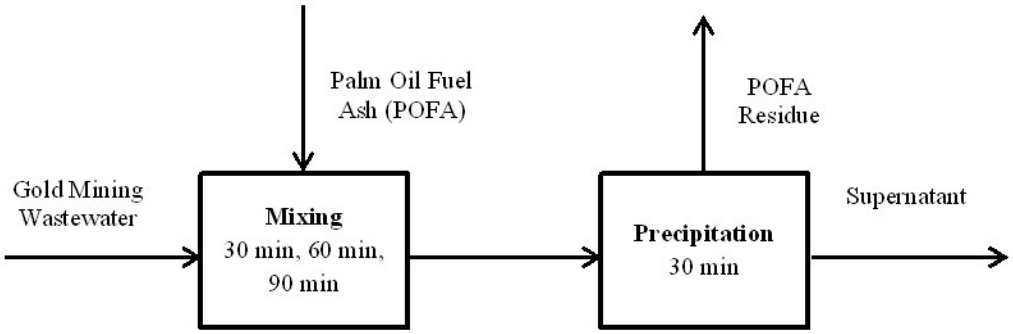


Figure 1. Simplified process flowchart.

Result and Discussion

POFA characteristics

POFA was analyzed by utilizing Scanning Electron Microscopy - Energy Dispersive X-Ray (SEM-EDX) to see its morphological surface prior to and after the mercury removal treatment. As shown in Figures 2 and 4, prior to the mercury removal process, there were many active sides that probably could bind Hg ion to pores adsorbent. After the process was done, it was shown that the pore's adsorbent was closed because heavy metal was bound to adsorbent pores. FTIR analysis result is shown in Figure 3 and interpreted in Table 1 based on the spectroscopy method (Harwood and Claridge, 1996; Bienz et al., 2021).

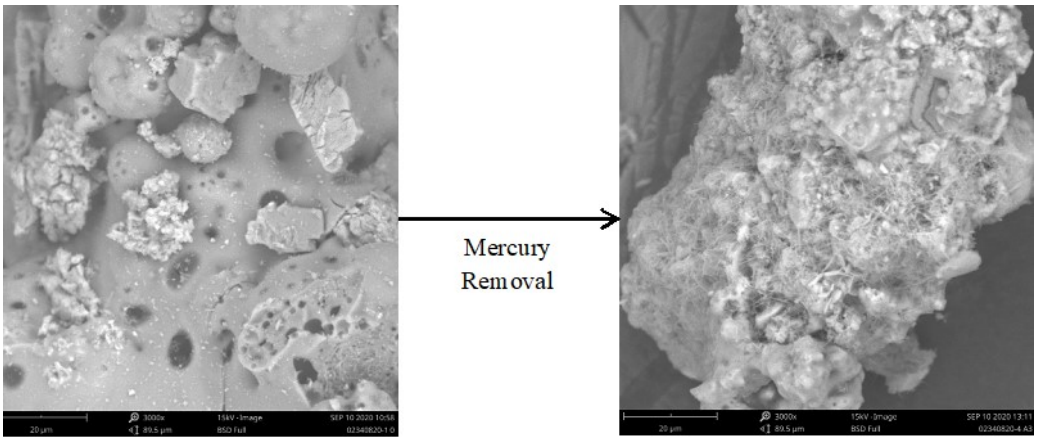


Figure 2. SEM Image of POFA before and after mercury removal.

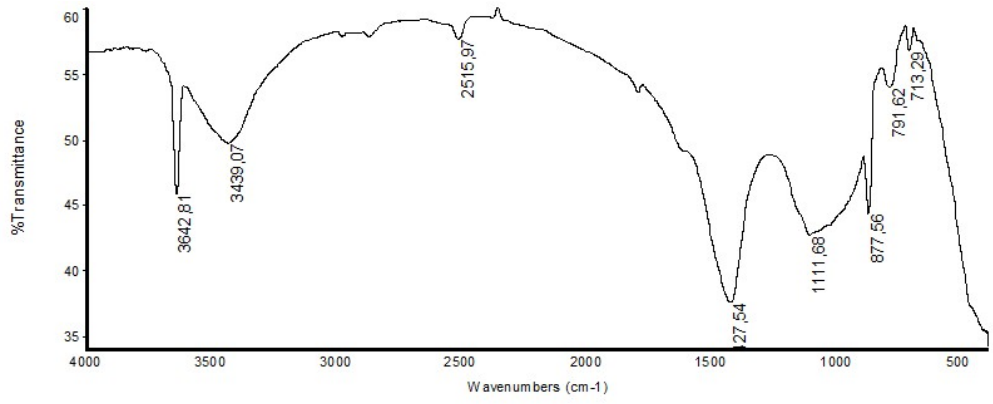
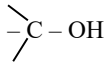
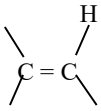
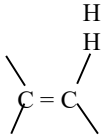
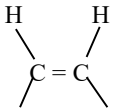


Figure 3. FTIR image of POFA.

Table 1. Band Interpretation from FTIR of POFA graph.

Band Range (cm^{-1})	Band (cm^{-1})	Group	Remarks
3650–3590	3642.81	Free O – H	Sharp
3600–3200	3439.07	Intermolecularly H-bonded O—H	Often broad but may be sharp for some intramolecular single-bridge H-bonds; the stronger the H-bond the lower the frequency
3200–2500	2515.97	Intramolecularly H-bonded O–H of the chelate type and as found in carboxylic acids	Broad; the stronger the H-bond the lower the frequency; sometimes so broad as to be overlooked
1450–1410	1427.54	CO_3^{2-}	
1150–1040	1111.68		C–O stretching
895–885	877.56		
840–790	791.62		C–H out-of-plane deformation; conjugation shifts the band towards 990 cm−1
730–675	713.29		

This FTIR interpretation result is backed with the result shown in EDX reading that shows raw POFA contained 33.9 % O, 23.67 C, 22.41 Si, 12.62 K dan 7.40 Ca. This existence of a free O-H bond allows ion exchange between the H atom and mercury to happen on the active side of the adsorbent. A double bond of C atom followed with negative ion on several sides allows POFA to be bonded with 2 positive ions given by mercury. XRD analysis result shown in figure 5 shows that POFA contains 53% Quartz (SiO_2) and 47% Calcite ($CaCO_3$).

This result differed from POFA analysis from Malaysia, in which most of its mineral content is Al_2O_3 and only 20% of Quartz (Chandara et al., 2011). High silica content in POFA makes POFA a really good adsorbent because of its photophysical inertness, chemistry stability and easiness of modifying its surface (Robles-Jimarez et al., 2022).

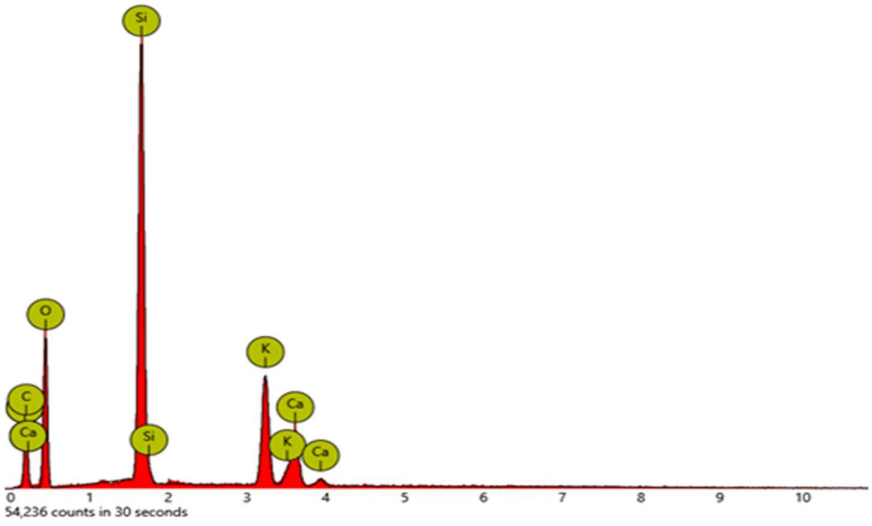


Figure 4. SEM-EDX image of POFA.

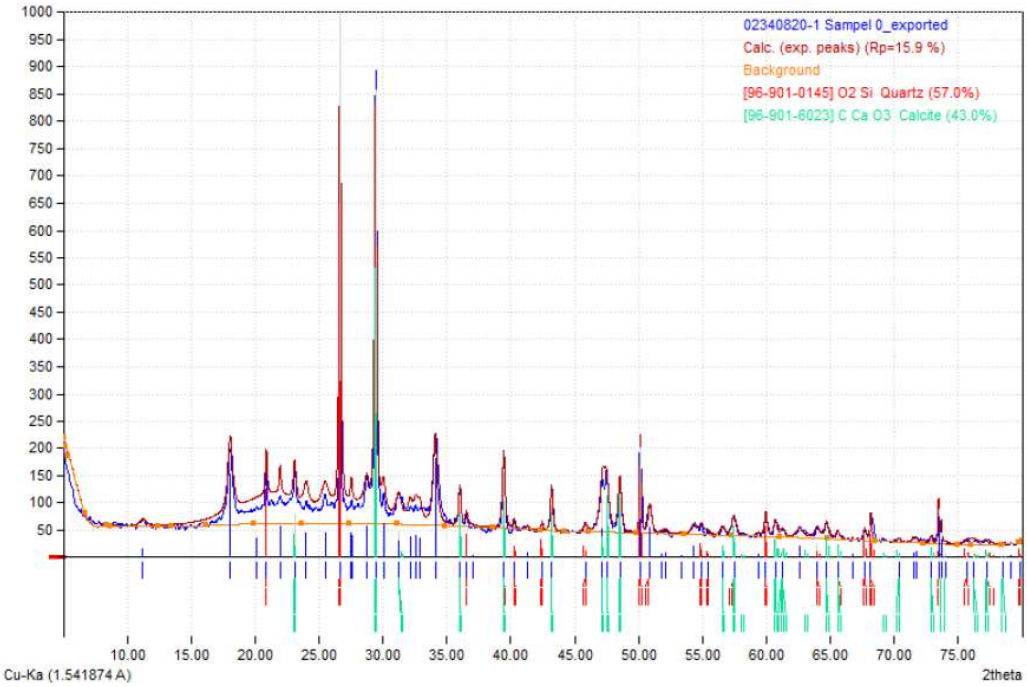


Figure 5. XRD image of POFA.

Mercury removal by POFA

Data of mercury amount in the solution and data of mercury removal efficiency can be seen in Table 1. According to the Ministry of Environment and Forestry Decree No. 202 of 2004, the upper threshold value of mercury in waste gold mining and copper is 0.005 mg/L. According to Table 2, the initial value of mercury waste in gold mining wastewater in this research was 0,0776 mg/L exceeding the upper threshold value set by the government.

Table 2. Experimental data.

Mixing Time	Hg in Solution (mg/L)	Mercury Removal Efficiencies (%)
0	0.0776	-
30	0.0396	48.96
60	0.0136	82.47
90	0.0025	96.77

The best contact time with 90 minutes was able to decrease mercury level below the government threshold, which was 0,0025 mg/L with 96.77 % mercury elimination efficiency. ICP-MS analysis results toward other heavy metal concentrations (Riduan et al., 2020) also shows that POFA utilization was able to reduce mercury contaminant in wastewater without the increase of any other heavy metal contaminant. This confirms that POFA utilization as mercury removal material is better than the utilization of CFA because it did not cause a negative effect on the environment. To obtain the best maximum contact time between POFA and gold mining wastewater, data presented in Table 2, which contains the mixing time of POFA with gold mining wastewater and adsorption efficiencies, were presented in Figure 6. The figure shows an exponential comparison trend curve Equation (2) with a correlation coefficient R^2 of 0.9489.

$$\% Hg = 0.7968 (T) + 28.257 \quad \text{.....(2)}$$

where % Hg = estimated adsorption efficiencies (%) of mercury and T = total time needed to mixing the solution.

Therefore, using the prediction Equation (2) to calculate how much time to be required to achieve 100 % adsorption efficiency of mercury removal in wastewater, a total of 90.04 minutes was obtained, which means only need less than 1 more minute for the perfection of the adsorption process.

Conclusion

Gold mining wastewater contains hazardous mercury for the environment. Adsorption utilizing agricultural waste was an innovative low-cost technology for mercury removal from gold mining wastewater because of the abundant amount in nature and free from dangerous materials. Most agricultural adsorbents require several stages of pretreatment prior to use as a removal agent of mercury. In this research POFA as one of the agriculture adsorbents could be used directly without any chemistry material in

addition to eliminating mercury in gold mining wastewater. It proved to be economical and properly effective in terms of mercury removal. This study yields the reduction of mercury levels to 0.0025 mg/L, which is below the 0.005 mg/L, upper threshold value allowed in water determined by the Indonesian government according to Ministry of Environment and Forestry Decree No. 202 of 2004 and the maximum adsorption efficiencies (%) achieved in this study is 96.77%.

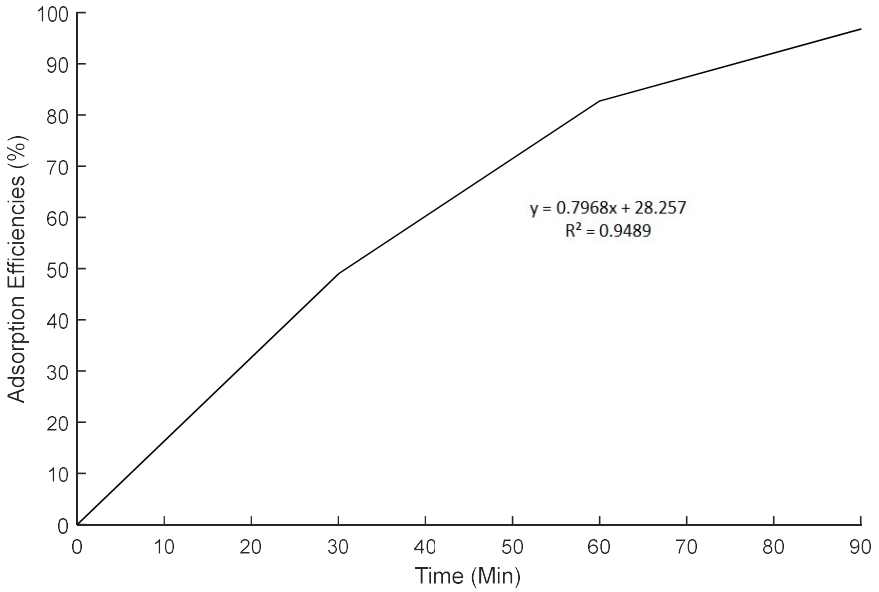


Figure 6. Adsorption efficiencies (%) vs mixing time.

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