Palm Oil Fuel Ash (POFA) as an Innovative Material for Arsenic Removal from Mining Effluent

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ABSTRACT
Arsenic is toxic element, accumulate in the environment as main contaminant in aqueous waste stream. This study aimed to analyze the capability of raw palm oil fuel ash (pofa) as a potential adsorbent to remove arsenic contamination in the wastewater of mining effluent. Technology applied in this study was adsorption followed by precipitation. The maximum arsenic removal percentage of 100 % and a maximum adsorption capacity up to 0.224 mg/g was discovered. The results indicate that the method for arsenic removal from wastewater using raw pofa was effective, simple and low-cost to apply.

Keywords: adsorption, agricultural waste, mercury removal, palm oil fuel ash (pofa).

1. INTRODUCTION
Polluted water has become an urgent environmental concern nowadays mainly originated from industrial activities along with geogenic factors that lower water quality [1]. Arsenic is one of water pollutant which is relevant due to its dangerous effects on the human body because this metalloid leads to acute and chronic damage depend on the associated factors with the route of exposure (eg, water concentration, time of exposure) [2]. Arsenic toxicity depends on the oxidation state and health issues in consequence of living organisms vulnerable to these metalloids included melanosis, cancer, brain damage, keratosis and cardiac disorders [3], [4].

Some anthropogenic activities; such as ignition of fossil fuel, mining, smelting, semiconductors processing, production of fertilizer, chemotherapeutic drug; produce effluent with toxic metals or oxygen anions, including arsenic, selenium, mercury, molybdenum, barium, lead, cadmium, and chromium [5], [6]. Arsenic is also generated in huge quantities as a result of mining activities, such as ore transportation, mineral extraction, refining, smelting and disposal of waste and wastewater effluent around the mine, both during active operation and long after mine shutdown [5].

Recently, various methods to remove Arsenic out of wastewater have been studied, such as coagulation-precipitation, physical separation, filtration, reverse osmosis, adsorption, ion exchange, and other techniques [7]. Surface adsorption and anion exchange predominate as effective physicochemical processes for harmful oxyanions removal, such as Arsenic, from wastewater even low concentrations [8], [9].

Regarding arsenic removal from wastewater [10], low cost adsorbent that could remove heavy metals from wastewater was reviewed. These review discuss arsenic adsorption in a wastewater by utilizing coal fly ash as its adsorbent. Swami, 2006 [11] has reviewed various non-conventional technologies to remove industrial wastewater contaminants that also includes the discussion of arsenic adsorption from water by coal fly ash. Chiban, 2012 [12] reviewed concisely about chemistry of arsenic and the low-cost adsorbents utilization for arsenic removal from water. Despite utilization of coal fly ash as adsorbent economically and technically effective, in the other hand using Coal Fly Ash can let go another toxic element to environment [13]. Due to these limitations, some researchers have innovated to find adsorbents to absorb heavy metals without having a negative impact on the environment. One kind of this type of adsorbent was palm oil fuel ash (pofa). POFA is one of agricultural waste type, as by-product in palm oil industry. Application Palm Oil Fuel Ash as heavy metal removal propose low cost technology and also lower accumulation of Palm Oil Fuel Ash (POFA) in the environment [14].
2. MATERIALS AND METHOD

2.1. Adsorbent Preparation

Adsorbent used as primary matter for arsenic removal was palm oil fuel ash as residual combustion from industrial boilers. Obtained palm oil fuel ash would be kept in a closed bottle and preserved with an 30°C temperature prior performing the process of adsorption with a sample of mining effluent.

2.2. Sampling

This study obtained its effluent to be examined from three gold mine effluent located at Pangkalan Jambu, Merangin Regency, Indonesia. The gold mine coordinate is 1°44′04″S 101°34′35″E. Samples were kept in a closed bottle with a preserved room temperature. To distinguish the sampling location, code with letter A, B, C were given to each sample and then numbered 1, 2, 3 to distinguish the adsorption time of each sample. Table 1 showed the research matrix of arsenic removal on gold mining effluent using palm oil fuel ash and Figure 1 indicate the coordinate of the gold mine.

2.3. Method of Adsorption

By contacting palm oil fuel ash with gold mine wastewater, the mercury adsorption process will be performed. Room temperature with atmospheric condition is used in the process of stirring palm oil fuel ash with gold mine wastewater. Gold mine wastewater to palm oil fuel ash adsorbent ratio was 1 : 4. Stirring time performed are as follows 15 minutes, 30 minutes to 45 minutes. Figure 2 shows the process diagram of mercury adsorption.

| Sample | Adsorption time (minutes) |
|--------|---------------------------|
| A₁     | 15                        |
| A₂     | 30                        |
| A₃     | 45                        |
| B₁     | 15                        |
| B₂     | 30                        |
| B₃     | 45                        |
| C₁     | 15                        |
| C₂     | 30                        |
| C₃     | 45                        |

Table 1. Research Matrix

Figure 1 Coordinate of sampling location in Merangin Regency, Jambi Province.

Figure 2 Process Diagram of arsenic removal using palm oil fuel ash.

2.4. Sample analysis

Inductively Coupled Plasma (ICP) analysis was carried out at Universitas Andalas’s Water laboratory, Sumatera Barat Province, Indonesia. Samples were mixed applying concentrated nitric acid (HNO₃) and heated. Subsequently to the extraction process, the sample was kept in a clean bottle after it was cooled down and filtered prior to its analysis. Inductively Coupled Plasma (ICP) techniques was used to determine metal elements in the solution. The ICP techniques would measure the specific element’s light emitted by the sample’s metal. The following is the equation to calculate Arsenic equilibrium adsorption capacity and arsenic removal percentage [15]–[17].

\[
q_e = \frac{(c_0 - c_e) \cdot V}{m} \quad (1)
\]

\[
Removal \ Percentage \ (%) = \frac{(c_0 - c_e)}{c_0} \times 100\% \quad (2)
\]

where \(q_e\) (mg/g) is adsorption capacity equilibrium, \(c_0\) (mg/L) is of Arsenic solution’s initial concentration, \(Ce\) (mg/L) is Arsenic solution’s final concentration, \(V\) (L) is effluent volume and \(m\) (g) is palm oil fuel ash mass.
3. RESULT AND DISCUSSION

3.1. Capacity of adsorption and removal percentage

Before and after data regarding arsenic concentration amount is presented in Table 2. Data presented in Table 2 are the calculation of equilibrium adsorption capacities values in equation (1) and the value of arsenic removal percentage in equation (2).

**Table 2. Arsenic Adsorption Percentage and Adsorption Capacity**

| Sample | As (mg/L) | Capacity of Adsorption (mg/g) | Removal Percentage (%) |
|--------|-----------|-------------------------------|------------------------|
| A1     | 0.034     | 0.136                         | 50.00                  |
| A2     | 0.022     | 0.184                         | 67.65                  |
| A3     | 0.012     | 0.224                         | 82.35                  |
| B1     | 0.022     | 0.084                         | 67.65                  |
| B2     | 0.017     | 0.104                         | 75.00                  |
| B3     | 0.008     | 0.14                          | 88.24                  |
| C1     | 0.006     | 0.064                         | 91.18                  |
| C2     | 0         | 0.088                         | 100.00                 |

Table 2 data is used to describe the relationship of adsorption capacity over time in Figure 3 and describe the relationship of removal percentage over time in Figure 4. The results of research by [16] about arsenic removal in wastewater using Fe$_3$O$_4$ nanocubes-impregnated graphene aerogel stated the longer the contact time, the greater the adsorption capacity and removal percentage achieved. That was in line with the result of this study as described in Figure 3 and Figure 4.

**Figure 3 Adsorption capacity (mg/g) to time effect.**

**Figure 4 Time to removal percentage (%) effect.**

Comparisons between palm oil fuel ash utilized in this study with adsorbent used in several previous study to observe the arsenic adsorption value have been made. The results of this study shown in Table 3 indicate that palm oil fuel ash (pofa) has better arsenic adsorption yield compare to previous adsorbents studies. Palm oil fuel ash also offer additional advantage as a economical adsorbent and are usable in large quantity. Palm oil fuel ash properties shows great potential in adsorption arsenic gold mine effluent.

**Table 3. Various adsorbents adsorption yield comparison for arsenic removal.**

| Adsorbent            | C$_0$ (mg/L) | Adsorption Capacity (mg/g) | Removal Percentage (%) | Reference |
|----------------------|--------------|-----------------------------|------------------------|-----------|
| Raw Coal Fly Ash     | 1            | 0.075                       | 38.4                   | [2]       |
| HCl- Fly Ash         | 3.5          | 0.35                        | -                      | [18]      |
| Fe-ASOH              | 1            | 0.20                        | 99.8                   | [2]       |
| HIOFAA               | 50           | 19.46                       | 99                     | [19]      |
| W Zeolite            | 25           | -                           | 99                     | [20]      |
| Palm Oil Fuel Ash (POFA) | 0.068      | 0.224                       | 82.35                  | This Study |

4. CONCLUSION

The emergence of wastewater effluent that contain arsenic are common problem found at a gold mine. One of the heavy metals contained in mining effluent were arsenic. Arsenic is a dangerous and toxic element to the human body. Therefore, it is necessary to remove arsenic from wastewater such as mining effluent. The use of palm oil fuel ash (pofa) to adsorp arsenic from wastewater effluent can reduce the amount of arsenic by 100% with a maximum adsorption capacity up to 0.224 mg/g. This study indicate that longer contact time between palm oil fuel ash and wastewater effluent will have a better arsenic removal efficiency. Thus this study
conclude that palm oil fuel ash could be an alternative adsorbent solution to resolve heavy metal (arsenic) problem in mining effluent.

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