The adsorption of hg$^{2+}$ ions from the illegal gold mining wastewater using fly ash from palm shells

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Abstract. Mercury has a significant negative effect on the health of humans and living things, and is a dangerous element that is widely known. Mercury is commonly found in gold mining wastewater. One way to remove mercury from waste water is to use the adsorption process. One of the adsorbents used in the absorption of mercury is palm shell fly ash. Palm shell fly ash is solid waste from the result of burning palm shells on the boiler. The use of fly ash from palm shells as an adsorbent is preferred because it is cheap, environmentally friendly and available in large quantities. The adsorption process is carried out by contacting the adsorbent directly with waste water. Addition of adsorbents to wastewater can increase the pH of wastewater to 4 levels. The best adsorption results are indicated by the efficiency of mercury ion absorption up to 100%. The adsorption capacity of the adsorbent increases with increasing time of stirring the adsorbent in wastewater.

1. Introduction

Illegal Gold Mining is a mining business carried out by individuals, groups of people, or companies with legal entities that do not have permits and government agencies in accordance with applicable laws and regulations. Illegal gold mining was started by the existence of traditional miners, which later developed because of the factors of poverty, limited employment and business opportunities, involvement of other parties acting as brokers, disharmony between the company and the local community, and a prolonged economic crisis followed by misinterpretation about reform. On the other hand, weaknesses in law enforcement and statutory regulations that eliminate community mining also contribute to the rise of unlicensed gold mining [1]. Illegal gold mining activities, which do not follow the principle of proper mining, have caused damage to the environment, waste of mineral resources, and cause mining accidents. This can create a disaster if it is not managed properly [2]. Mining activities are carried out through extracting metals from metal ore, these rocks are crushed with water and given a small amount of chemicals that help release metal from mercury [3].

Heavy metals, especially mercury ions and their species, is a serious global environmental threat. Mercury, due to the nature of volatility, chemical and its bioaccumulation, regarded as one of the most toxic elements that affect humans and the environment [4]. There are two sources of heavy metal ions in wastewater, namely natural sources (such as volcanic activity, soil erosion, and weathering of rocks and minerals) and sources derived from anthropogenic activities (such as combustion of fuels, mineral processing, landfills, urban runoff, effluent mining industry, agricultural activities, metal finishing and coating, printing boards, textile dyes, semiconductor manufacturing, etc.) [5].
There are many small-scale gold mines scattered in Merangin District, Jambi Province, Indonesia. This gold mine is one source of anthropogenic activity that does not have permits so that there is a lack of supervision in environmental treatment after the completion of mining activities. As a result of this gold mining, there is the presence of wastewater basins containing heavy metals which are hazardous to the environment including mercury metal as mining waste. The water in the basin is used by the surrounding community for daily activities even though the water is not suitable for consumption because the heavy metal content is above the threshold value [6,7].

According to current regulations of the Standard Nasional Indonesia (SNI 01-3553 2006), maximum concentration of mercury in drinking water is 0.01 mg/L and 0.001 mg/L, respectively [8]. Various methods for removing mercury from wastewater have been studied, including the application of electrochemical processing (electroplation, electrocoagulation and electrodeposition), the process of physicochemical (ion exchange and chemical precipitation) and adsorption (using organic material such as activated carbon, carbon nanotubes, rice husks, fly ash etc.) [9]. Of all these methods of adsorption, the use of solid waste as an adsorbent is very important to develop, because this method is low cost and effective for the treatment of wastewater and gas. There are many publications about the elimination of elemental mercury from exhaust gases [10-14], but limited research has been carried out on Hg^{2+} ion removal from water, especially with the use of fly ash, synthetic zeolite and composites. In Indonesia fly ash can be obtained from burning palm shells on the boiler [15]. In this study, research will be conducted on the adsorption of mercury using fly ash from palm kernel shells. The purpose of this study was to determine the adsorption capacity, adsorption efficiency and the effect of pH on mercury adsorption processes.

2. Materials and method

2.1. Preparation of adsorbent
The main raw material as mercury (II) adsorbent media is fly ash from palm shells combustion in the boiler of PT Aneka Bumi Pratama. Flying ash is then stored in a closed container and maintained at atmospheric temperature before the adsorption process is carried out with wastewater from the gold mine effluent.

2.2. Sampling
The wastewater examined in this study is the residual of gold mining wastewater taken from 3 location points in Pangkalan Jambu, Merangin Regency, Indonesia. Gold mining location coordinates was 1°44'04"S 101°34'35"E. Samples are stored in a closed container and kept at room temperature. Samples were then coded A, B and C to differentiate taking points and then numbered 1,2 and 3 to distinguish the amount of fly ash added during the adsorption process. Research matrix of mercury adsorption on wastewater of gold mining using fly ash from palm kernel shell’s fly ash was shown in table 1 and gold mining location coordinates shown at Fig 1.

| Sample | Fly Ash (gram) | Wastewater (mL) | Time (minutes) |
|--------|----------------|-----------------|----------------|
| A₁     | 250            | 1000            | 15             |
| A₂     | 250            | 1000            | 30             |
| A₃     | 250            | 1000            | 45             |
| B₁     | 250            | 1000            | 15             |
| B₂     | 250            | 1000            | 30             |
| B₃     | 250            | 1000            | 45             |
| C₁     | 250            | 1000            | 15             |
| C₂     | 250            | 1000            | 30             |
| C₃     | 250            | 1000            | 150            |

Note: A = Sample from location A; B = Sample from location B; C = Sample from location C
Figure 1. Gold mining location coordinates in Pangkalan Jambu, Merangin Regency, Jambi Province.

2.3. Adsorption method
The mercury adsorption process is carried out by contacting fly ash with wastewater from gold mining. The temperature used in the stirring process is room temperature at atmospheric condition. The ratio of wastewater to adsorbent was 1: 4. Stirring time varies from 15 minutes, 30 minutes to 45 minutes. Process diagram of mercury adsorption showed in Fig 2.

Figure 2. Process diagram of mercury adsorption with fly ash at gold mining wastewater.

2.4. Sample analysis
The analysis of mercury in sample using Inductively Coupled Plasma (ICP) conducted at Water laboratory of Universitas Andalas, Sumatera Barat, Indonesia. Water samples were destroyed using concentrated nitric acid (HNO₃) in a beaker glass and heated using hotplate. After the extraction process, the sample is cooled, and then filtered and stored in a clean sample bottle before analysis. Determination of metal elements in solution can be achieved by using spectroscopic inductively coupled plasma (ICP) techniques. This method measures the specific light of the element emitted by the metal in the sample. Hg²⁺ adsorption amount per unit mass of adsorbent and Hg²⁺ absorption percentage was calculated using the following equation [14].
\[ q_e = \frac{(c_o - c_e)V}{m} \]  
\[ \% \text{ Adsorption} = \frac{(c_o - c_e)}{c_o} \times 100 \]

where:

- \( q_e \) (mg/g) was adsorption capacity,
- \( c_o \) (mg/L) was the initial concentration of Hg\(^{2+}\) in solution
- \( c_e \) (mg/L) was final concentration of Hg\(^{2+}\) in solution,
- \( V \) (L) was the volume of wastewater
- \( m \) (g) was the mass of palm shell’s fly ash

3. Result and Discussion

3.1. Adsorption capacity and percentage of Hg\(^{2+}\) removal

Values of Hg\(^{2+}\) before and after adsorption have been tabulated. Based on these data, the calculations of the adsorption capacities value have been calculated using equation (1) and the calculations of the adsorption percentages of Hg\(^{2+}\) has been calculated using equation (2). The results of this calculation are shown in Table 2.

| Sample Code | Hg (mg/L) | Adsorption Capacity (mg/g) | % Adsorption |
|-------------|-----------|----------------------------|-------------|
| A1          | 0.066     | 0.104                      | 28.26       |
| A2          | 0.023     | 0.276                      | 75.00       |
| A3          | 0.005     | 0.348                      | 94.57       |
| B1          | 0.033     | 0.208                      | 61.18       |
| B2          | 0.008     | 0.308                      | 90.59       |
| B3          | 0         | 0.34                       | 100.00      |
| C1          | 0.02      | 0.144                      | 64.29       |
| C2          | 0.01      | 0.184                      | 82.14       |
| C3          | 0         | 0.224                      | 100.00      |

Note:
- A = Sample from location A
- B = Sample from location B
- C = Sample from location C

Based on Table 3, graphs are arranged to show the relationship between adsorption capacity over time and also graph that indicates the relationship of Hg\(^{2+}\):adsorption (%) against time. The adsorption capacity versus time shown in Figure 3, based on this figure shows that with the longer its stirring time the adsorption capacity is also increasing. The same trend is also shown in Figure 4 which shows the relationship between percentage of Hg\(^{2+}\):adsorption over time. The longer the stirring time indicates that the adsorption efficiency is getting better.
Comparisons have been made between fly ash from palm shells used in this study and the adsorbent used in several previous studies to see the \( \text{Hg}^{2+} \) absorption value (Table 3). The results of this study indicate that palm shell fly ash has a higher adsorption yield compared to some of the adsorbents studied from previous studies. An additional advantage of using fly ash from palm kernel shells as an adsorbent is the low cost and available in large quantities. Because of these properties, palm shell fly ash has great potential to adsorb \( \text{Hg}^{2+} \) ions from gold mining wastewater.

\textbf{Table 3.} Comparison of adsorption yields of various adsorbents for Hg (II) ion.

| Adsorbent                                      | \( C_0 \) (mg/L) | Adsorption Capacity (mg/g) | % Mercury removal | Reference |
|------------------------------------------------|------------------|----------------------------|-------------------|-----------|
| Treated sawdust (Acacia Arabica)              | 3                | -                          | 99.4              | [16]      |
| Ostrich bone waste                            | 30               | -                          | 87.7              | [17]      |
| Mercapto modified with alkali lignin          | 200              | 112                        | 94                | [18]      |
| Sugarcane bagasse                             | 76               | 14.7                       | 97.584            | [19]      |
| Mesoporous carbon                             | 10               | 35.27                      | 99                | [20]      |
| Tridax procumbens                             | 100              | 6.06                       | 96.5              | [21]      |
| 4-aminoantipyrine immobilized bentonite       | 1                | 52.9                       | >98               | [22]      |
| Mercapto-modified bentonite (B-SH)            | 36.95            | 19.3                       | 99.23             | [23]      |
| Fly Ash From Palm Kernel Shell                | 0.085            | 0.348                      | 100               | This Study |

\[\text{Figure 3.} \] The effect of adsorption capacity (mg/g) over time.

\[\text{Figure 4.} \] The effect of time against percentage of mercury (II) removal.
4. Conclusion

Unlicensed gold mining is one type of anthropogenic activity which in practice produces effluents containing heavy metals that are harmful to the environment. One solution to absorb heavy metals that exist in wastewater is by adsorption using palm shell’s fly ash. Fly ash of palm kernel shells has the potential to be developed as an inexpensive adsorbent and has a large adsorption efficiency. The best value of adsorption capacity was 0.348 mg/g. From this study it is known that the longer the adsorbent interaction with wastewater through the adsorption process, the heavier metal absorbed. Therefore, it can be concluded that the use of fly ash from palm kernel shell as an adsorbent is an alternative solution to overcome the problem of wastewater as a result of illegal gold mining.

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