

Heavy Metals Release from Polluted Soil of a Traditional Gold Mining Area at Java Island-Indonesia

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Abstract

From thousand years ago, gold mining were established for human desires. The development of technology for the gold exploration can't stop the existence of traditional ways in gold mining. Unfortunately, traditional mining activity generally has a bad waste management level that makes some heavy metals release to the environment. Heavy metal substances like Cd, Pb, Zn, Co, and Hg can be found easily from the traditional gold mining area. Those metal substances are very toxic, moreover they have possibility to introduce into food chain and accumulate in human body. Thus, creates numerous of health problems. The investigation of heavy metals release from polluted soil surrounding gold mining area demands physico-chemical properties of soil were characterized including water content, pH, conductivity, metals content, total organic carbon (TOC), and cation exchange capacity. Afterwards, the adsorption-desorption of heavy metal (Pb) was studied to estimate the mobility of the metals in the environment. From the experiments, sample 1 (nearest the gold mining source) was found containing higher metals concentration than sample 2 (a bit far from the gold mining source). In addition, it was found that higher TOC content of sample 1 was correlated to the higher cation exchange capacity. In the kinetics study, the adsorption of Pb follows the Langmuir adsorption isotherm model with the r^2 at 0.9691. While, maximum adsorption of Pb was 2500 mg/kg and adsorption energy at 32.8 kJ mol⁻¹. For the study of Pb desorption, tartaric acid concentration of 1 mol/L produced maximum desorption ability at 3512.4 mg/kg. From these results, it could figure out that the soil around the traditional gold mining area was polluted with heavy metals with high possibility to enter the food chain due to their high mobility.

Keywords: heavy metals, traditional gold mining, physico-chemical properties, adsorption-desorption.

1. Introduction

Soil contamination caused by heavy metals released is commonly happens. This case is most important environment problem because the ability of heavy metals to accumulate and cause toxicity in biological systems - humans, animals, microorganisms and plants has been reported [1,2]. One of the most discussed activities causing heavy metals released is gold mining. Modern and

traditional gold minings destroy landscapes and create huge amounts of toxic waste. Many gold mining activities dump their toxic waste directly into soil and water bodies. The waste, usually a gray liquid sludge, is laden with deadly cyanide and toxic heavy metals. The heavy metal pollution has the characteristic of the high toxicity, and difficult to degrade, and its mobility brings a severe range of hazards [3]. As chemical hazards, heavy metals are non-biodegradable and can remain almost indefinitely in the soil environment. However, their availability to biota can change considerably depending on their chemical speciation in the soil. The adequate protection and restoration of the soil ecosystems, therefore, require the characterization and remediation of soils that are contaminated with heavy metals [4, 5]. Commitment and compliance of industries in following of the government regulations related to the activity in handling of industrial wastes are immemorial problems that must be faced up to now. Many cases and findings of industry that still produces wastewater which contents not comply with the law are constantly to be found. Another matter which is endangering is secret disposal from industries to environment where people live, grow crops, and raise livestock. In fact, the government has made regulations and policies of responsibility to the industry in wastewater treatments, which are be found in the Law of the Republic of Indonesia Number 32 of year 2009 on the Protection and Management of the Environment and the Indonesian Government Regulation Number 101 of year 2014 on the Management of Hazardous and Poisonous Wastes. Previous report regarding mining activities affected on high level of heavy metals in soils, streams, and plant which can pose serious health problem in animal and human [6-8]. Soil has the ability to exchange the heavy metals with human and animal via ground water and food chain [6]. The evidence of specific impacts caused by heavy metals released from industry wastes is could influence the process of mitosis and reduce the germination of seeds of plants [9]. Meanwhile, the characteristics of the soil such as organic content and cation exchange capacity determine the mobility of heavy metals to the environment [10]. In addition, the presence of low molecular weight organic acid (LMWOA) in the soil structure as a natural product of the root exudates, secretion of microbial, and decomposition of plant and animal residues could controlling mobility and transport of

heavy metals [11]. LMWOA is involved in many interactions in soil solution and capable of forming complexes with metal compounds [12-15]. Therefore, the characterization contaminated soil samples around traditional gold mining area will be investigated in this study in relation with heavy metals content and mobility to the environment. The presence of tartaric acid as LMWOA will be evaluate in the desorption of heavy metal. Characterization and remediation of heavy metals-contaminated soil are required for application of soil ecosystems protection and restoration.

2. Materials and Methods

Materials

Soil samples were taken from Kulonprogo, Yogyakarta (Java island Indonesia). Each of soil samples was taken at 0-30 cm of depth and named as sample 1 (about 10m from the mining source), and sample 2 (about 30m from the mining source) . Locations of the sampling site is shown in Figure. 1. All chemicals used in this research were analytical grade (p.a.) from Merck (Germany) and Sigma-Aldrich (USA).

3. Instruments

Atomic Absorption Spectrometer (Perkin-Elmer 3110), pH meter (Hanna), and conductivity meter (OHAUS ST 10C-B).

4. Methods

4.1 Characterization of soil samples

25 g of field-moist soil samples were weighed into a porcelain dish and dried in an oven at 105 oC for 24 h according to ISO 11465. The determination of the ash content were done using muffle furnace at 550 oC according to DIN CEN/TS 14775 and pH according to ISO 10390. The effective cation exchange capacity of soil samples was determined using BaCl₂ and MgSO₄ solutions according to DIN ISO 11260. The electrical conductivity of soil samples was measured after extracted with water at certain ratio according to DIN CEN/ TS

15937. The metal contents were determined after HF and aqua regia digestion based on BS EN 13656.

4.2 Adsorption-desorption study of Pb from polluted soil sample

A series of batch desorption experiments were conducted with tartaric acid as an extractant to examine the effect of concentration, pH, contact time, and volume of tartaric acid on chromium removals. In determining optimum concentration for soil treatment, 1 g of soil samples were put into a series of centrifuge tubes and 30 mL of tartaric acid solutions with different concentrations was added to each centrifuge tube. The pH of the system was adjusted at the value of 3.5. The suspensions were shaken for 24 h. Afterwards the soil suspensions were centrifuged and the supernatants were filtered through a Whatman no. 42 paper. The filtrates were analyzed for chromium content. The pH effect of tartaric acid solutions was studied in the different pH values of 3.5, 5.0, 8.0, and 10 with concentration of 0.5 mol L⁻¹. As a control, deionized water was prepared in the same way as the tartaric acid treatment and compared with the results of tartaric acid treatments. Thereafter the same procedure above mentioned was used. Mass of soil samples and volume of tartaric acid solutions were same with previous method. Tartaric acid was used at pH 3.5 and 0.5 mol L⁻¹ of concentration. Thereafter the same procedure above mentioned was used. Mass of soil samples and volume of tartaric acid solutions at same amount as mentioned above. The effect of tartaric acid solution volumes was investigated by addition of different amount of volumes those are 10, 30, 60, and 100 mL with 1 g of soil samples. Concentration of tartaric acid were 0.2, 0.5, 0.8 and 1.0 mol L⁻¹ and pH of the systems were 3,5 and shaken through optimum contact time. Thereafter the same procedure above mentioned was used. All of the methods above were conducted at temperature of ± 25 °C and ± 1 atm of pressure.



Figure 1. Soil sampling site in Yogyakarta-Indonesia

5. Results and Discussion

5.1 Characterization of the soil samples

The results of physical-chemical characterization of the soil samples (1 and 2) from traditional gold mining area in Kulonprogo-Yogyakarta (Java island-Indonesia) were summarized in Table 1. In general, the soil samples at every point had a lower water content whether at air dried or 105 °C. These results were due to soil samples located in the high area (hill) in the middle part of Java island. The pH values of the soil samples were determined by the addition of H₂O, KCl, and CaCl₂ solutions so that pH values were obtained compatible with the natural conditions or as a yield of exchange with other cations. Both salt solutions were used due to existence of K⁺ and Ca²⁺ in soil at high concentration. The pH values were in the area of neutral (pH = 7). Soil's ability to bind heavy metals is also influenced by organic matter in the soil [16, 17]. The organic matter consists of organic carbon (C-organic) as the main constituent component that is as much as 58% [18]. These organic matters can be decomposed through humification process into humus, which is one blackish brown soil fraction [19]. In Table 1, the higher TOC of sample 1 is related with lower ash content. In the soil structure, the presence of organic matters will limit the inorganic substance such as silica oxide and other mineral oxides. Determination of ash content was done by heating soil samples using gradually increased temperature up to 550 °C for oxidizing the entire organic materials. The electrical conductivity of the soil can be directly linked to the amount of ions in it. The higher electrical conductivity at sample 1 possibly related to the higher metals ion especially for Pb. In other hand, the UK and US standard limits for Cd and Pb were 3.0 and 300.0 mg/kg soil. It means that soils in the area of traditional mining in Yogyakarta-Java Island were highly contaminated with heavy metals. While for FTIR spectral data, it was mentioned existence of -OH group of carboxylic acid structure of soils in 3626 cm⁻¹, also Si-O and Si-O-Al groups at the regions of around 1600 cm⁻¹ and 790 cm⁻¹, respectively.

6. Adsorption-desorption studies of Pb

From the adsorption isotherm processes as describe in Figure 3, it was found that highest adsorption concentration of the soil samples was achieved at the initial concentration of Pb solution at 200 mg L⁻¹. While, the optimum pH was obtained at pH 3.5. From the Pb speciation versus pH, the Pb²⁺ is existed at acid solution (PH 5). From the adsorption isotherm data achieved, the Langmuir and Freundlich isotherm model were used for the plotting analysis as described in Figure 4. By calculating the correlation coefficient (R²) of the two isotherm model, it was conclude that Pb adsorption to the soil samples from the traditional gold mining area. adopted Langmuir isotherm model than Freundlich isotherm model due to better R² at 0.9691. In addition, by using Langmuir equation as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_L q_m}$$

Table 1. Chemical properties of soil samples

Parameters	Sample point I	Sample point II
Water content (%)		
a. Open air drying	13.8 ± 1,1	15.7 ± 0.4
b. 105 °C	28.1 ± 0.7	31.9 ± 0.9
pH		
a. H ₂ O	7.3 ± 0.2	7.1 ± 0.1
b. KCl	7.1 ± 0.2	6.9 ± 0.1
c. CaCl ₂	7.1 ± 0.1	7.0 ± 0.1
Ash content (%)	24.5 ± 1.4	33.1 ± 3.0
Total organic carbon (TOC, mg C g ⁻¹ soil)	48.6 ± 1.1	39.0 ± 0.5
Electrical conductivity (μS cm ⁻¹)	1,192 ± 66	946 ± 83
Cation exchange capacity (cmol+ kg ⁻¹)	74.6 ± 3.9	34.9 ± 4.5
Metals content (mg kg ⁻¹)		
• Hg	15.5	16.4
• Cd	350.0	127.3
• Zn	389.3	361.8
• Pb	4193.8	1537.9

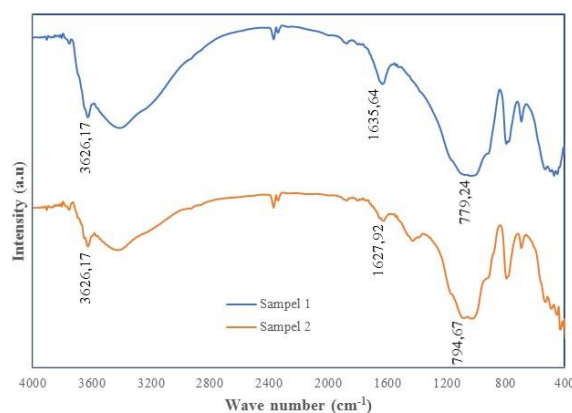


Figure 2. FTIR spectra of soil sample 1 and 2.

The maximum adsorption capacity of the polluted soil sample (q_m) was calculated at 2500 mg/kg. This small number of maximum adsorption capacity due to soil sample where already polluted with heavy metals. For the desorption process, the presence of tartaric acid was evaluated in the Figure 4 below. The desorption of pH from the polluted soil sample with the pH variation resulted the highest concentration of Pb desorbed from the soil matrix at pH 3.5. In the acid solution, Pb was existed as Pb²⁺, therefore easily release from the soil structure. By the presence of tartaric acid in the soil solution system, the concentration of Pb which desorbed from soil structure be increased significantly more than 40 times comparing with the desorption without tartaric acid (3512 mg/kg than 80 mg/kg) (Figure 5). The higher desorption result of Pb concentration due to the high presence of tartaric acid

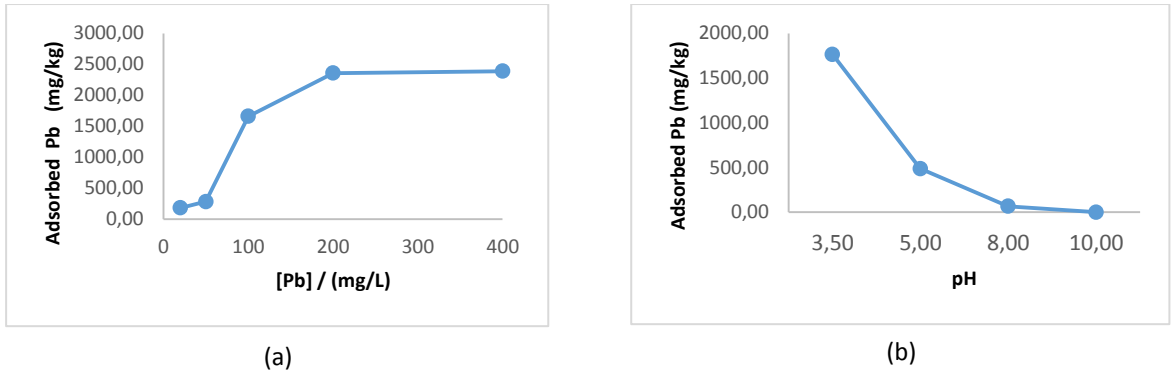


Figure 3. Pb adsorption processes with (a) initial concentration of Pb and (b) pH variations.

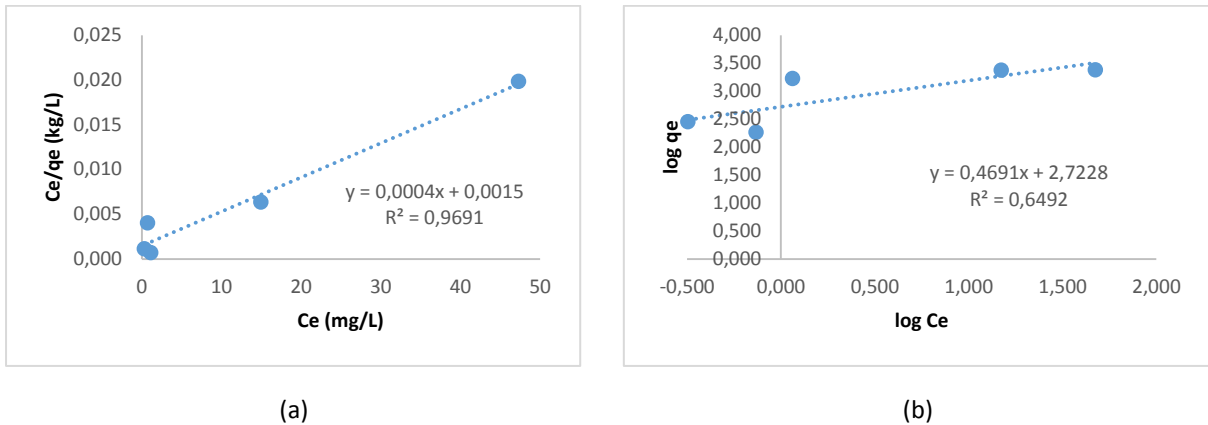


Figure 4. Adsorption isotherm model of Langmuir (a) and Freundlich (b) for Pb adsorption to the polluted soil sample.

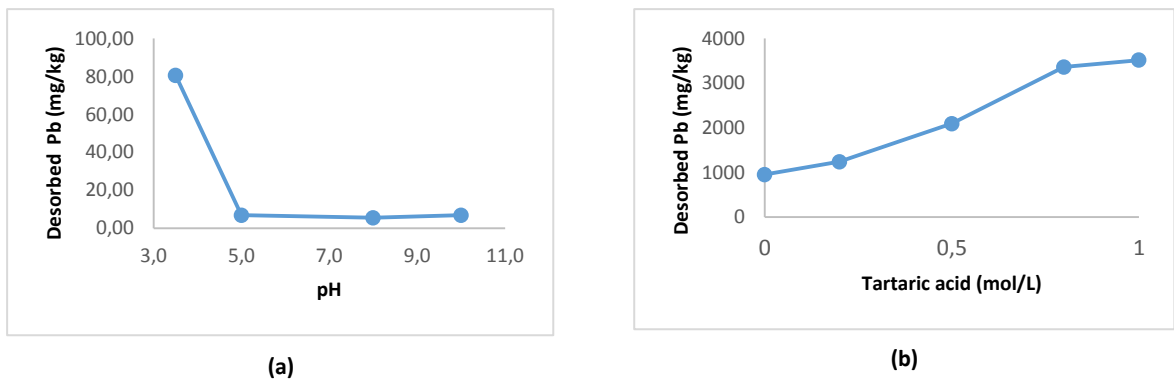


Figure 5. Desorption process of Pb with (a) pH variation, and (b) tartaric acid concentration effect.

active sites which were capable to form chelate complexes with Pb^{2+} in the soil-solution. Considering that traditional gold mining in Java island-Indonesia generally located at very close area to the agriculture region and shelter resident, so the serious actions in the environmental protection and remediation are urgently required

7. Conclusion

The traditional gold mining activities in Java island-Indonesia revealed environmental problems such as heavy metals pollution. The physico-chemical properties of

polluted soil samples affected not only in the concentration of heavy metals in soil structure, but also for their mobility to the environment. The higher TOC of the soil samples correlated with higher cation exchange capacity and lower ash content. While the metals content possibly affected on the conductivity properties of soil sample. From the adsorption-desorption studies, the Pb adsorption follows Langmuir isotherm model with the maximum adsorption capacity at 2500 mg/kg. Moreover, the presence of tartaric acid could increase the desorption process of Pb in the soil structure. The high polluted soil samples from the

traditional gold mining area should become environmental issues for the safety of human life in future.

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