Remediation of lead-contaminated soil from artisanal mining site using natural zeolite

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Abstract. One of the impacts of artisanal gold mining (ASGM) activity is lead (Pb) contamination in soil. This research was conducted on the Pb contaminated soil at the ASGM sites in Banyumas and Wonogiri in Central Java and Kulon Progo in Yogyakarta. This research aims to conduct a study of Pb mobility in contaminated soil and laboratory experiment to carry out remediation of Pb contaminated soil using natural zeolite with the batch test. The results showed that the Banyumas soil sample had higher Pb mobility compared to the other two soil samples. The batch test results showed that zeolite application useful to reduce Pb in the contaminated soil samples, where the Banyumas soil sample results in optimum value results due to the highest Pb mobility. The batch test results also showed that pH was a significant factor in the remediation process. This study concluded that the zeolite application reduces the concentration and mobility of Pb in the soil and affect the sorption by plants.

1. Introduction

Artisanal gold mining (ASGM) activities are commonly found in Indonesia [1]. One of the impacts of this activity is the lead (Pb) contamination on the soil [2, 3]. This study investigated the Pb contaminated soil from three ASGM sites, namely in Gumelar (Banyumas District), Selogiri (Wonogiri District), and Kokap (Kulon Progo District) in Java, Indonesia. In natural conditions, Pb is present in minerals such as galena (PbS) [4, 5]. Several studies demonstrated that Pb concentration in ASGM in the study area was detected in elevated concentrations such as in mineral vein, tailings, soils, waters, and river sediments [6, 7, 8, 9]. The lead in the soil can be a source of pollutants and are exposed to humans in several ways such as distributed by hand to mouth, inhaled through breathing, also entering the digestive system, and entering the bloodstream [10]. The other exposure exists through the plants consumed by humans [11]. This research aims to conduct a study of the Pb mobility in the contaminated soil samples obtained in several ASGM locations aforementioned and to conduct a batch test to carry out the remediation experiment using natural zeolites.

2. Material and methods

2.1 Natural zeolite sample

The natural zeolite sample was obtained from Tegalrejo, Gunungkidul District, Yogyakarta, Indonesia. The mineralogical composition of the natural zeolite sample was analyzed using the X-ray diffraction (XRD) analysis and composed of clinoptilolite and mordenite and also other minerals present such as...
quartz, plagioclase, illite, and smectite (Fig. 1) [12]. Other properties of the natural zeolite sample can be seen in Table 1.

**Figure 1.** Mineralogical composition of natural zeolite sample by X-ray diffraction.

**Table 1.** Natural zeolite properties.

| Component     | (%) |
|---------------|-----|
| Mordenite     | 22  |
| Clinoptilolite| 6   |
| Illite        | 18  |
| Smectite      | 15  |
| Quartz        | 13  |
| CEC (meq/100 gram)\(^1\) | 102.8 |
| Specific surface area (m\(^2\))\(^2\) | 35 |

\(^1\) analyzed by BaCl\(_2\) method  
\(^2\) analyzed by a BET method

### 2.2 Pb contaminated soil samples

The Pb contaminated soils were obtained from ASGM sites in Gumelar Banyumas (sample B), in Selogiri Wonogiri (sample W), and Kokap Kulon Progo (sample K). The soil samples were taken at 5 cm depth by using a hand auger in order obtaining a soil sample not disturbed by humus and plant roots. A sample of 3 kg was taken and cleaned from roots, gravel, and then crushed and sieved on a 2 mm sieving. The Pb concentration in the soil samples was analyzed using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP AES) after aqua regia digestion.

**Table 2.** Some physical and chemical characteristics of soil samples.

| Soil Samples | Particle size fraction | pH | CEC\(^1\) (meq/100 gram) | Organic\(^2\) (%) | Pb (mg/kg) |
|--------------|------------------------|----|--------------------------|------------------|------------|
| B            | sand 68.2  silt 17.3  clay 6.4 | 5.9 | 34 | 1.2 | 540 |
| W            | sand 60.3  silt 16.5  clay 10.1 | 6.3 | 39 | 0.9 | 405 |
| K            | sand 66  silt 12  clay 13.7 | 6.7 | 40 | 1 | 289 |

\(^1\) analyzed by BaCl\(_2\) method  
\(^2\) analyzed by TOC analyzer
Table 2 shows the properties of the soil samples. The soil samples generally were sandy soils, with minor silt and clay. The soil samples have different Pb concentrations of 540 mg/kg, 400 mg/kg, and 289 mg/kg, for sample B, W, and K, respectively. The cation exchange capacity (CEC), organic content, and pH values in the three soil samples were not showed significant differences.

2.3 Experimental procedure
The mobility of Pb in the contaminated soil samples was analyzed by conducting a sequential extraction analysis, based on the method described by another researcher [13], where the partitioned fractions were divided into five fractions included: Fraction 1 (F-I): exchangeable; Fraction 2 (F-II): metal bound to carbonate; Fraction 3 (F-III): metal bound to iron and manganese oxides; Fraction 4 (F-IV): metal bound to organic matter; and Fraction 5 (F-V): residual fraction. For the remediation study, a batch test was carried out by adding different zeolite applications with 50 mesh sizes, from 1 to 15 grams/100 grams of soil samples B, W, and K (1, 3, 5, 7, 9, 15 grams/100 gram soil). The soil samples then were mixed with the natural zeolite and placed inside in the 150 ml flask, and then 100 ml of 0.01 M CaCl2 was added, and the pH was conditioned at 6. The mixture was then stirred for three hours at 25°C and precipitated with a centrifuge machine at 200 rpm. The solution was then filtered with a 0.45 um filter, and the filtrate then was measured for Pb and pH. All Pb concentration in the solution was measured using the ICP AES.

3 Result and discussion

3.1 Pb mobility
The sequential extraction analysis results showed that the samples of soil K and W were more dominated by the fractions III, IV, and V (Table 3). This result demonstrated that Pb in the samples of soil W and K were less mobile. This is because Pb in the soil sample W and K were produced by geogenic processes as enrichment due to the mineralization process.

| Soil Samples | Fraction I (Exchangeable) | Fraction II (Bound to Carbonates) | Fraction III (Bound to Iron and Manganese Oxides) | Fraction IV (Bound to Organic Matter) | Fraction V (Residual) |
|-------------|--------------------------|----------------------------------|-----------------------------------------------|-------------------------------------|---------------------|
| B           | 36,4                     | 39,3                             | 8,2                                           | 14,7                                | 1,4                 |
| W           | 8,3                      | 16,5                             | 32,1                                          | 30,1                                | 13                  |
| K           | 9,8                      | 20,1                             | 25,7                                          | 34,1                                | 10,3                |

The different result was presented for soil B, which showed more dominated the fraction I, II, and III (Table 3). This result demonstrated that Pb in the soil B sample was more mobile, and this was suspected due to the age of the mining site which relatively younger than the other two sites. Also, it is suspected that Pb in soil was possibly derived from vehicle emissions, considering this ASGM and gold processing site was located in a residential area. This situation was different from the other two ASGM sites. This result was confirmed by another study that mentioned the heavy metals fraction due to anthropogenic activities. Usually, the mobile fraction would be more dominant [14, 15].

3.2 Batch test
The results of the remediation experiment using the batch test generally showed that the natural zeolite used was adequate effective in reducing Pb concentration in contaminated soil samples. Several studies revealed the capacity of zeolite to reduce the concentration of metals in contaminated soils [16, 17]. In this experiment, several zeolite application were mixed with three Pb contaminated soils
obtained at different ASGM sites. The changes in the Pb concentration in the leachate solution indicated that the zeolite increased the sorption capacity of the soil, as shown in figure 2-4. Without the addition of zeolite, the concentration of Pb in the leachate solution was approximately 5, 0.35, and 0.4 mg/l, for the soil samples B, W, and K, respectively. This value was consistent with the results of sequential extraction which showed that the Pb mobility in the soil B sample had higher mobility, whereas the Pb would be more easily dissolved. The addition of zeolite showed a strong relationship with the concentration of Pb in the leachate solution (figure 2-4).

![Figure 2. Leachate Pb concentration v.s the zeolite application for soil B.](image)

![Figure 3. Leachate Pb concentration v.s the zeolite application for soil W.](image)
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Figure 4. Leachate Pb concentration v.s the zeolite application for soil K.

The Pb concentration in the leachate solution for all three soil samples dropped to less than 0.1 mg/l when 15-gram zeolite was added to the 100-gram soil samples. The addition of zeolite would increase the pH, and then it would effectively prevent the leaching of Pb in the soil that would be uptake by plants. For example, the pH value in the soil B sample increase from 5.9 to 7.9 when 15-gram zeolite was applied (table 4). Figure 2-4 shows the concentration of Pb reaching the minimum after the maximum amount of zeolite is applied. The optimum value of zeolite in the soil B sample was approximately 15 grams/100 gram soil, whereas the soils in W and K were approximately 9 gram/100-gram soil. This value might be due to the more mobile of Pb in the soil B. Therefore, and it required higher zeolite application to obtain the optimum value. The Pb concentration in the leachate solution before the zeolite applied was 5 mg/l for the soil B sample, and were 3.4 mg/l and 4.0 mg/l for the soil W and K samples, which was suspected that the Pb in the soil B sample was more mobile, confirmed by the result of the sequential extraction analysis.

Table 4. Effect of different zeolite application on pH levels of different soil sample.

| Zeolite application (gram) | Soil Sample |
|---------------------------|-------------|
|                           | B | W | K |
| 0                         | 5.9 | 6.3 | 6.7 |
| 1                         | 6.7 | 6.7 | 6.9 |
| 3                         | 6.9 | 6.9 | 7.3 |
| 5                         | 7.4 | 6.9 | 7.5 |
| 7                         | 7.8 | 7.3 | 7.9 |
| 9                         | 7.9 | 7.8 | 8.1 |
| 15                        | 7.9 | 7.8 | 8.2 |

The addition of 15% zeolite would reduce the concentration of Pb in the leachate by under 0.1 mg/l. Table 4 shows the effect of different zeolite application on pH levels and its show that the more zeolite is applied in the soil sample, the higher the pH is achieved.

4 Conclusion
The results of the research conclude the soil B sample has a higher Pb mobility compared to the other two samples, which are suspected because of additional sources of Pb in soil B. In remediation experiment, the addition of zeolite imply Pb concentration in leachate solution decreases as the increase of the surface area, pH, and CEC. In the batch experiment, the application of 15% zeolite was
effective to reduce the Pb leachate solution, up to 99%, 87%, and 88%, for samples B, K, and W, respectively. The optimum results were obtained in soil sample B as confirmed the Pb mobility was highest. The results showed the ability of zeolite to remediate the Pb in the soil, and as a significant factor, besides the CEC value, pH is a significant factor. An increase in pH, not only being a metal immobilization, but also contribute to the ion exchange, and making a stronger reaction in binding the metal, due to the lower proton competition because the pH of the soil sample increases thus the addition of zeolite can improve the Pb stabilization process [18].

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