# Sediment Treatment for Increasing Ph and Reducing Heavy Metal Cadmium (Cd) In Acid Mine Drainage 

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#### Abstract

Acid mine drainage could be treated by using wetland sediment as the source of sulfate-reducing bacteria for increasing pH and reducing heavy metal. The purpose of this study is to compare between the abilities of mangrove and swamp sediments in increasing pH and reducing heavy metal cadmium in acid mine drainage. Acid mine drainage experiment was conducted in a reactor by adding sediment ( $20 \%$ ) and compost ( $10 \%$ ), then incubated for 30 days. The pH changes were measured using pH meter, while the cadmium content was analyzed using Atomic Absorption Spectrophotometry (AAS), both was measured on the fifth day. The result showed that swamp sediment increased pH to 6.8 , while mangrove sediment increased pH to 6.2 at the end of incubation. The results for cadmium reduction also indicated that swamp sediment ( P 2 ) could reduce cadmium from 1.88 to 0.17 ppm ( $90.96 \%$ ), while mangrove sediment (P1) reduced cadmium from 1.72 to $0.24 \mathrm{ppm}(86 \%)$. In addition, treatment only with compost (P3) and treatment without sediment and compost to control (P4) did not show any significant changes both for pH increase meant or cadmium reducement.


Keywords: Sediment; Acid mine drainage; Cadmium

## Introduction

The advancement of mining industries in Indonesia is accompanied by the increasing of environmental issues, especially on the aquatic environment as the consequences of acid mine drainage. Acid mine drainage pollution could affect the life of flora fauna, as well as human health $[1,2]$. Mainly, acid mine drainage is formed from the exposure of sulfite minerals in the form of metal sulfite, then oxidized into sulfate, and would form acid liquid if it exposed to water. Acid mine drainage has a low pH range (3-4), so it could dissolve heavy metals [3-5]. Therefore, it could be said that acid mine drainage is a hazardous waste from mining activities due to its acidic character that could dissolve heavy metal and is toxic to humans [6]. One of harmful heavy metal that commonly found in mining waste is cadmium, especially in lead or zinc mining. Cadmium usually found in a form of mineral sphalerite (ZnS) [7].

Acid mine drainage needs to be well managed in order to change it into the harmless material when entering water bodies, such as river or lake. Treatment of acid mine drainage is commonly conducted by applying chemical substances, such as limestone, or treated physically by immersing it into a big hole. However, both of those treatments are known to be inefficient, not eco-friendly, and expensive [3,8].

Due to some treatment problems, biological treatment or bioremediation that utilizing microorganism, such as sulfate-reducing bacteria, become a good alternative for treating acid mine drainage. The advantages of biological treatment are eco-friendly, efficient, and continuously developed to be better on treating mining liquid wasted [6].

Sulfate-reducing bacteria are capable of reducing sulfate and heavy metal ion concentration in acid mine drainage [4,5]. These bacteria are commonly found in the muddy substrates, such as wetland sediment. The condition of wetland sediment is anaerobic and rich with organic materials that supported many kinds of sulfate-reducing bacteria, so that wetland sediment naturally treats sulfite contaminants $[9,10]$.

The utilization of sediment as the inoculum sources for sulfatereducing bacteria could be applied in a bioreactor because bacteria naturally stay in the wetland sediment [11].
The experiments of $[10,12]$ found that the addition of swamp sediment in acid mine drainage could reduce the sulfate concentration and increase the pH . The activity of sulfate-reducing bacteria is in contrary with Thiobacillus ferrooxidant that triggers the formation of acid mine drainage. Therefore, according to the explanation above, we focused on comparing mangrove and swamp sediment as the inoculum sources for sulfate-reducing bacteria for elevating pH and reducing cadmium in acid mine drainage.

## Materials and Methods

## Samples

Materials used in this study were acid mine drainage, collected from mangrove and swamp sediments, and compost.

## Methods

Sample collection: A sample of acid mine drainage was obtained from a mining in Camba, Bone Regency. Swamp sediment was collected around Makassar city, Indonesia, while mangrove sediment was collected from Tallo mangrove forest, Makassar. The sample was put in a tight head plastic drum and kept in a refrigerator at $2^{\circ} \mathrm{C}$.

Compost was obtained from the seller of decorative plants on Panaikang, the Makassar city.

Acid mine drainage and sediment characterization: Acid mine drainage sample was characterized by its pH using pH meter [13]. The sediment and compost were characterized based on total organic carbon using TOC meter [14] and nitrogen content using Micro Kjeldahl method [15].

Treatments: The treatments of acid mine drainage with sediments were conducted in a column of the anaerobic bioreactor. The processing column was equipped with wire frame at the bottom part that serves as a barrier between sediment and compost. Acid mine drainage was gradually poured into the column. The treatment was prepared using 3 liters of acid mine drainage with details of treatment: mangrove sediment $20 \%$ and compost $10 \%$ (P1); swamp sediment $20 \%$ and compost $10 \%$ ( P 2 ); compost $10 \% ~(\mathrm{P} 3)$; and control or without sediment and compost (P4). Each treatment with duplicate were used and incubated for 30 days at room temperature. During the incubation period, pH and cadmium content measurements were conducted every fifth day.
pH measurement: pH was measured using pH meter. pH meter was first calibrated in buffer solution pH 7 , then activated until stabilized for about $15-30 \mathrm{~min}$. The electrode was then rinsed with distilled water and dried. Next, the electrode was dipped into the acid mine drainage until resulting a stable output.

Cadmium (Cd) analysis: Two ml acid mine drainage sample were placed in a 100 ml chemical glass, to which 10 ml concentrated nitric acid were added, mixed and heated until dissolved. The acid residue was evaporated, rinsed with distilled water through the glass wall, filtered with whatman 42 filter paper in a volumetric flask 100 mL at pH 2 , while the excess acid was neutralized by adding NaOH 6 M and then, the absorbance was measured using AAS with A varian model AA-1275 flame and a deuterium background corrector was used for determination of Cd ions. The wavelength was set at 228.8 nm resonance line and the spectral band pass at 0.5 nm . A standard solution of Cd with gradual concentrations to aliquots of the $1: 10$ diluted sample solution. The cadmium concentration according to the linear equations. Results of cadmium analysis were reported in ppm units.

## Results and Discussion

The sediment of mangrove and swamp were used as the inoculum source of sulfate-reducing bacteria for treating acid mine drainage due to its species richness of sulfate-reducing bacteria [11,16]. On the other hand, compost that is rich with organic matter becomes the carbon sources for microorganism development. Before starting the acid mine drainage treatment, preliminary analyses for the content of organic carbon, total phosphorus, total nitrogen, and cadmium concentration were conducted in order to determine the initial condition of each sediment and compost. The preliminary analysis is presented in Table 1. The result showed that both mangrove and swamp sediments were already contained cadmium at its initial condition, approximately 0.001 ppm and 0.003 ppm respectively, while compost did not contain cadmium. The presence of cadmium was caused by the sampling location that located near the settlement area and household industry. In addition, [17] stated that cadmium could be presented through a natural process in a sediment.

| Sediment types | C Organic | N Total | P Total |
| :--- | :--- | :--- | :--- |
| Swamp sediment | $32.6 \%$ | $0.42 \%$ | $0.26 \%$ |
| Mangrove sediment | $29.7 \%$ | $0.51 \%$ | $0.33 \%$ |
| Compost | $22 \%$ | $13 \%$ | $6 \%$ |

Table 1. Content of carbon, phosphorus and nitrogen of sediments and compost samples.

The result of pH changes in acid mine drainage affected by sediment treatment is presented in Figure 1. The P1 treatment demonstrated a slow pH increase that started in day 10 to day 30 , from pH 3.5 to pH 6.2. Meanwhile, P 2 treatment demonstrated a rapid increase in pH value from pH 3.7 into pH 6.2 in day 20 , then pH 6.5 in day 25 , and finally pH 6.8 in day 30 . The P 3 treatment with pH 3.2 represented a slight increase of pH value into pH 3.8 from day 25 to 30 . The P 4 treatment showed no changes in its pH .

Koschorreck [18] explained that the pH increase in acid mine drainage treated with sediment is occurred because of the decrease in sulfate concentration as the result of sulfate-reducing bacteria activities. Basically, sulfate receives electron that resulted in sulfate reduction to sulfide and causes decreasing in sulfate concentration.


Figure 1: Changes of pH in acid mine drainage by treatment: mangrove sediment $20 \%$ and compost $10 \%$ (P1); swamp sediment $20 \%$ and compost $10 \%$ (P2); compost $10 \%$ (P3); and control or without sediment and compost (P4).

Church [19] suggested that the sulfate reduction process by the sulfate-reducing bacteria group produces sulfide and bicarbonate that affected the rise in pH . Therefore, sulfide would react with dissolved metal ions to form dissolved metal sulfide [20]. The result of this study demonstrated pH increase from acid into neutral in acid mine drainage treated with mangrove and swamp sediment. A low pH of acid mine drainage is caused by the reaction between sulfide minerals and water that resulted in the release of metal and hydrogen ions, meanwhile, sulfide ions were oxidized into dissolved sulfate ions and $\mathrm{H}^{+}$ions would lower the $\mathrm{pH}[21,22]$.

The analysis result of cadmium content in acid mine drainage that treated with sediment is presented in Figure 2. The cadmium concentration in P1 treatment started to reduce from day 10 to day 30, where the initial concentration was 1.72 ppm and was reduced to 0.24 ppm at $86 \%$ reduction. The P 2 treatment showed more rapid reduction that started from 1.88 ppm , went to 1.24 ppm on day 5 and finally reached to 0.17 ppm on day 30 , at $90.96 \%$ reduction.

The P3 treatment demonstrated lower cadmium reduction compared to P1 from 1.68 to 1.59 ppm or $5.36 \%$ reduction. On the other hand, the P4 treatment showed slight differences between the first day and the last day, being 1.62 ppm and 1.60 ppm , respectively, representing $1.23 \%$ reduction. The result showed that P1 treatment with addition of mangrove sediment resulted in more effective cadmium reduction compared to P 2 treatment with addition of swamp sediment. These results correspond to the vegetation that grows on the surface and influences the organic matter content, sediment texture, and a number of microbes [23].


Figure 2: Cadmium concentrations in acid mine drainage as a function of treatment: mangrove sediment $20 \%$ and compost $10 \%$ (P1); swamp sediment $20 \%$ and compost $10 \%$ (P2); compost $10 \%$ (P3); and control or without sediment and compost (P4).

According to the study result, the reduction of cadmium concentration in acid mine drainage treated with mangrove or swamp sediments demonstrated that the activity of sulfate-reducing bacteria in both sediments are capable of reducing heavy metal ions of cadmium and resulted in deposited cadmium metal ions [24].

The mechanism of cadmium metal ion reduction in acid mine drainage is started with the sulfate reduction $\left(\mathrm{SO}_{4}\right)$ into sulfide, then reacted with metal cation and formed metal sulfide that is deposited at the bottom of the bioreactor $[9,25]$. Therefore, the sulfate reduction process produces $\mathrm{H}_{2} \mathrm{~S}$ that has a role as an electron donor and reduce metal cation into metal sulfide. Low cadmium reduction presented in P3 and P4 treatments occurred because of evaporation and deposition process from loss abiotic factor process [1].

## Conclusion

According to the study results, it could be concluded that treatments with mangrove and swamp sediment could increase the pH value of acid mine drainage, reaching to 6.8 and 6.2 at the end of experiment period, respectively. Meanwhile, treatment without sediment showed no detectable change in pH during the incubation. On the other hand, swamp sediment could reduce the cadmium concentration in acid mine drainage by $90.96 \%$, while mangrove sediment reduced it by $86.05 \%$. Treatment without the addition of sediment showed almost no reduction in cadmium concentration.

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