Remediation of mine acid water using mangrove sediment

J Tandiarrang, K Mustari and N L Nafie
Hasanuddin University, Makassar, Indonesia

Email: jenitatandiarrang@gmail.com

Abstract. The handling of acid mine drainage has so far been carried out chemically and physically so it is inefficient because it can cause new pollutants. Therefore, biologically, AAT countermeasures can use bioremediation techniques by utilizing sulfate-reducing bacteria (BPS) which are abundant naturally in sediments. This study aims to analyze the ability of sediments of mangroves in neutralizing acid mine water, to analyze the optimum pH resulting from the sediments of mangroves in the neutralization of acid mine water, to analyze how reduced levels of sulfates, heavy metals mangan and iron produced, to analyze the type of mangrove sediments of the most good in the neutralization of acid mine drainage. Acid mine water samples were taken at PT. Walanae Sand, Lamuru Bone, mangrove sediments taken in the mangrove tourism area of Tongke-Tongke Sinjai. This type of research is an analysis using descriptive methods in the form of field data collection, sampling in the field and testing in the laboratory. The results showed that mangrove sediments are able to increase pH and reduce sulfate levels, can increase the pH value from 2.24 to 7.02, the optimum pH can be achieved by using sand mangrove sediments that are 7.02 on day 10. Reducing sulfate levels from 1,171 ppm to 0.625 ppm with using sand mangrove sediments on the 10th day, but can not reduce the content of manganese (Mn) and iron (Fe) by using sand or mud mangrove sediments because the metal content in these sediments is higher than acid mine water. The best mangrove sediments in the neutralization of acid mine drainage are sand sediments because the time needed is faster in neutralizing the pH and reducing sulfate levels.

1. Introduction

Environmental problems can be caused by a variety of activities both on a limited scale (narrow) and on a large scale. In general, environmental problems are caused by natural events, rapid population growth, excessive use of natural resources, industrialization, and transportation [1].

Mining activities will certainly have many impacts, both on the environment and are economically and socially. One of the elements causing the impact is the waste produced as a by-product or residual from the cultivation and treatment which is often large in volume and many types. The types of waste generated from various types of mining activities are mine water, overburden, the waste solution from the tailings process, residual ore, and sludge. From the US-EPA study (1995) the influence of mining activities producing waste can cause impacts on the environment such as surface water and groundwater pollution, disturbing human health, causing damage to flora and fauna and air pollution. Billions of tons of acidic waste rock piles are produced from mining activities. In addition to the acid nature that threatens the life of the acid mine waste, it also contains extremely high dangerous metals. Acid and heavy metal pollution in the environment affects the number and composition of biological species by biogeochemical cycles of a number of chemical elements. Acidic properties can trigger the formation of heavy metals which will cause metal pollution in the aquatic environment [2].

Management of mining waste is one aspect that is very important mining activities, including the disposal of tailings during the operating process should pay attention to the prevention of seepage of...
processing a liquid fraction of the tailings as waste sludge tailings generated from pyrite mining will be exposed, causing contact with oxygen or water. As a result, sulfuric acid will form which can cause acidity in the environment. The acidic environment will have an impact on organisms especially on plants or if entering into a river will kill fish and other organisms. Sulfuric acid formed from mining activities is known as acid mine drainage (AAT).

Mine acid water is acidic water and contains iron and sulfate, which is formed under natural conditions when geological strata containing pyrites are exposed to an oxidizing atmosphere or environment. Acid mine water can be formed from coal mines, both in surface mining and underground mining [3].

So far, the handling of AAT is chemically and physically so that it is inefficient because it can cause new pollutants, therefore we need a more environmentally friendly treatment that is biologically where the material used is material that is widely available in nature. Therefore biologically, AAT countermeasures can use bioremediation techniques by utilizing sulfate-reducing bacteria (BPS) which are abundant naturally in sediments [4].

Besides this, the presence of heavy metals contained in coal can also cause severe pollution to the environment. The heavy metal is a natural element contained in the coal itself because the constituent elements of the coal itself are derived from the main elements (carbon, hydrogen, oxygen, N, S aluminum, and Si). Then the second element is (iron, manganese, Ca, K, Na, P, Ti), while for the heavy metal elements are (As, Ba, Cd, Cr, Pb, Cu, Hg, Zn, Ag) [5].

The creation of acidic properties is a conducive environment for the growth of *Thiobacillus Ferooxidans*. This bacterium is known to be able to increase the rate of pyrite oxide by one million times greater than without it. Therefore, the microorganism community influences the formation of sulfuric acid, so the presence of *Thiobacillus Ferooxidans* is the most important factor determining the formation of AAT. These bacteria are also able to adapt to mutations in the event of extreme habitat changes. In addition to *Thiobacillus Ferooxidans*, *Leptospirillium Ferrooxidans* was also found, but the number was lower [6].

Biological methods that can be used are bioremediation by using microorganisms in tackling pollutants for the recovery of polluted land and waters. One alternative bioremediation is to use sulfate-reducing bacteria (BPS) to reduce sulfate, besides that it is also able to reduce the concentration of heavy metals such as iron, zinc, copper, and others. Sulfate-reducing bacteria can be obtained from muddy substrates as in sediments. In the sediment biochemical activity occurs due to microbial activity in the environment, naturally can release contaminants such as metal sulfate. This method is carried out in bioreactors that are no longer inoculated by microbes from the outside because naturally there are microbes inside and settling on wetland sediments [7].

Species composition and mangrove growth depend on the physical composition of the sediment. The proportion of sand, dust and clay particle size affects sediment permeability, fertility, and salinity of sediments [8].

The existence of BPS originating from mangrove sediments can overcome acid mine drainage with an increase in pH indicator which indicates an increase in the population of sulfate-reducing bacteria and a decrease in sulfate levels accompanied by a decrease in heavy metal content in water [9].

This study aims to determine the ability of mangrove sediments in the neutralization of acid mine drainage, To find out the optimum pH produced from mangrove sediments in the neutralization of acid mine drainage, To find out how much the decrease in sulfate levels, heavy metals manganese and iron produced, To find out the types of mangrove sediments best in the neutralization of acid mine drainage.

2. Materials And Methods

2.1. Location, time and design of the study

The research location is in PT. Pasir Walanae, Lamuru, Bone South Sulawesi. This sample test is carried out in a laboratory. This research took place from April to May 2019.
2.2. Tools and materials

The tools used in this study are: glass tools such as Petri dishes (pyrex), Erlenmeyer (Pyrex), measuring cups (Pyrex), diluent bottles, Bunsen, spoilers, sample bottles, pH meters (Orion), atomic absorption spectrophotometers (SSA), incubator (Heraeus), Ohaus balance (Ohaus), oven (Heraeus), autoclave (All American), enkes and light microscopes.

The materials used in this study were acid mine drainage samples taken from the company, mangrove sediment samples from mangrove communities, aquades, alcohols, AgNO₃ solution, HCL, BaCl₂.

3. Sterilizer

All tools used are sterilized beforehand, glassware such as Erlenmeyer and diluent bottles as well as plastic tools that cannot stand heat are sterilized using an autoclave with a temperature of 121 °C with a pressure of 2 atm for 15 minutes. Petri dishes are sterilized using an oven with a temperature of 180 °C for 2 hours.

3.1. Mangrove Sediment Sampling

Mangrove sediments obtained in 5-10 cm dip then put into 5 kg plastic samples which are then taken and treated in the laboratory.

3.2. Characterization of Mangrove Sediments

Sediment measurements using the Soil Jar Test (FAO) method to determine the sediment used in the treatment with the Wentworth scale is to use a 500 ml measuring cup instead of an empty jar with a lid. The measuring cup is filled with half full of sediment then given almost full water. The measuring cup is closed using a plastic press, then shaken a few minutes until mixed. Leave the measuring cup until the precipitate is visible for a day, draw a sample of ± 5 grams into a cup then add a 10% sodium carbonate solution as much as 5 ml. Dry in the oven for 1 night, but at 550 °C for 2 hours, then cool, after chilling add Concentrated HCL as much as 5 ml, pour into 100 ml measuring flask and squeeze with aquadest, strain and take the liquid as much as 25 ml, heat for 30 minutes at 200 °C for 1 hour, add BaCl₂ 10% as much as 15 ml, continue heating for 1 hour, filter using whatman filter paper No.42, the filter results (solids and filter paper) are put in a porcelain cup that has been known to weigh, put for 2 hours at a temperature of 550 °C, cool and weigh, and then measure the pH, content-heavy metals manganese (Mn), iron (Fe), sulfate. Every wetland sediment used in the treatment was carried out with characterization intended to determine the initial conditions for the AAT sulfate reduction process.

3.3. Sampling of Acid Mine Water

Technique for extracting acid mine water in the field is based on SNI 6989-59-2006 about the method of sampling wastewater for pH by determining the point of acid water sampling in compartment 1 for 3 sample points, to represent the current pond conditions, then the volume of water samples acid mine taken for each point as much as 5 liters. Samples of water that have been taken are taken to the Water Quality Laboratory to determine the initial conditions of water quality prior to the titration test.

3.4. Making treatment

Further processing of AAT and sediment is made by the following treatments: AAT + mangrove sand (sand) sediment (60% + 40%), AAT + mangrove sand (sand) sediment (70% + 30%), AAT + mangrove sand (sand) sediment (80% + 20%), AAT + mangrove silt sediment (dust / mud) (60% + 40%), AAT + mangrove silt sediment (dust / mud) (70% + 30%) and AAT + mangrove silt sediment (dust / mud) (80% + 20%).

Sediment is put into the treatment container and put AAT 600 ml slowly on the wall of the bottle, then the container is tightly closed, observation every 2 days, observation starts on day 0, day 2, day 4
8, day 10, day 12, day 14 and day 16, the parameters measured were as follows: Reduction of Sulfate using gravimetric, observation increase in pH with a pH meter, measurements metal concentrations heavy iron (Fe) and manganese (Mn) using the Atomic Absorption Spectrophotometry (AAS) method.

3.5. Measurement of Sulfate Levels
Measurement of sulfuric acid levels in acid mine drainage samples was carried out by the gravimetric method. Mine acid water solution was added 0.3 mL concentrated HCL and BaCl\(_2\) drop by drop until the BaCl\(_2\) drop did not produce a precipitate, the solution was then heated, then added BaCl\(_2\), the addition was stopped if the solution does not form another precipitate, the precipitate from the previous result is filtered using waltman paper, the precipitate formed is washed using hot water until it can be stated that all the sulfates have settled. To ensure that the sludge is clean, an AgNO\(_3\) 0.1 M solution is added to the filtrate until no white (clear) color is formed, the filtered precipitate is added to the cup then flattened from 130 to 150 °C and then weighed, then the weight of the sediment is calculated = (cup weight + deposits) - empty cup weight [9].

3.6. PH measurement
The steps for measuring pH, in general, are as follows: carried out on a calibrated pH meter. The pH meter is turned on first until it's stable (15-30 minutes). The electrodes are then rinsed with aquadest and dried with tissue paper. Furthermore, the electrode is dipped for a while until a stable reading is obtained then the pH sample results are deformed [10].

3.7. Analysis of heavy metals Iron (Fe) and Manganese (Mn)
Analysis of heavy metals can be done with atomic absorption spectrophotometric (AAS). The determination of metal content in the sample is done by analyzing the atomic absorption spectrophotometric tool (AAS). Calibrated tools and sample determination. Then the solution is measured during sample setting, periodically checking whether the standard value is constant. Standard curves are made for each metal (absorbance / emission value X metal concentration m / mL).

4. Results
4.1. Results of Initial Analysis of Semple
Initial analysis results from acid mine drainage samples showed a very low pH value of 2.24 which is acidic and sediment pH with a value of 6.9 which is neutral. This value can be seen that this mangrove sediment has the ability to neutralize the mine acidic water because its value is almost close to neutral pH which is 7. The content of manganese metal (Mn), iron (Fe) in acid mine drainage is 1,401 ppm and 2,564 ppm, sulfate content namely 1,171 ppm while in mangrove sediments the metal content of manganese was 3,273 ppm, iron was 4,361 ppm, sulfate content was 0.048 ppm.

4.2. Determination of pH Value
Data analysis results can be viewed on the tabs el 1, wherein the sediment used was divided into two samples, namely sediment p Asir and sediment sludge to the treatment of acid mine drainage 60% and 40% of sediment with time of observation until day 16. Each pH changes are seen on the day today.

Figure 1 shows a sample of 60% + 40% the average pH value on day 0 is 6.45 where this value is almost close to neutral pH and continues to increase the next day until the 12th day shows the number 7.02. An increase in pH in the treatment of mangrove sediments by a ratio of 60% + 40% due to the activity of sulfate-reducing bacteria (BPS) which reduces sulfate to sulfide, but on the 14th day to the 16th day decreased in value to 6.67. Sampel 70% + 30% The average pH value on day 1 was 6.07 and continued to increase until the 4th day with a value of 6.26 but on the 6th day to the 16th day it decreased with a value of 5.49. Samples with a ratio of 70% + 30% in sand on day 0 the pH was 5.95 which is lower than the previous sample. The increase in pH continued until the 4th day of 6.15, but
on the 6th day of the 16th day it decreased to 5.55. A sample of 80% + 20% pH value on day 0 is lower than the other samples which are 5.53 and on day 2 it has an increase of 5.72 but on day 4 to day 16 continues to decrease values up to 4.84. 80% solution + 20% sand on day 0 the pH value is 5.47, this value is lower than the three samples made. On day 2 it increased to 5.69, but on day 4 to day 16 that there were microbes that we're able to raise the pH of the sediment. continued to decrease up to 4.47.

4.3. *Determination of Sulfate Levels*

The results of the analysis of sulfate levels in threshold acid water are 1,171 ppm and sediment with sand and mud is 0.048 ppm, so it can be seen that mangrove sediments with sand and mud are able to reduce sulfate levels in acid mine water. Decrease in sulfate levels after treatment until the 10th day with sand sediment dropped to 0.625 ppm, this decrease occurs faster than using mud sediments.

In picture 2 shows decrease sulfate in the treatment with mangrove sediments is caused by the activity of sulfate-reducing bacteria originating from these sediments. BPS can use sulfate as an electron acceptor for its metabolic activity. Because the sulfate accepts electrons, this compound will be reduced to sulfide so that the sulfate concentration decreases. Decrease in sulfate levels with increasing pH and increasing the number of microbes. The increasing number of microbes causes sulfate reduction which will cause the pH to increase.

4.4. *Determination of Heavy Metal Content of Manganese (Mn), Iron (Fe)*

In figure 3, measurements heavy metals showed that contents heavy metal manganese (Mn) in the acid mine water is 1,401 ppm, while the sediment is 3.273 ppm. At the figure 4 heavy metal iron (Fe) in the acid mine water is 1,401 ppm, while in the sand and mud sediment is 3.273 ppm.

| Table 1. Data Analysis Results of pH in a solution of 60% + 40%. |
|-----------------|-----------------|-----------------|
| days to-        | mud sediment    | sand sediment   |
| 0               | 6.45            | 6.35            |
| 2               | 6.53            | 6.43            |
| 4               | 6.62            | 6.54            |
| 6               | 6.71            | 6.65            |
| 8               | 6.84            | 6.76            |
| 10              | 6.95            | 7               |
| 12              | 7.02            | 6.88            |
| 14              | 6.87            | 6.8             |
| 16              | 6.67            | 6.74            |
Figure 1. Analysis of pH in a 60% + 40 % solution.

Figure 2. Analysis of sulfate content in acid mine drainage after treatment.

Figure 3. The content of heavy metal manganese (Mn) in acid mine drainage after treatment.
5. Discussion

The results of measurements of mangrove sediment analysis that have been carried out at a depth of 50 cm at the study site found that the content of sand (sand) is higher than the other 2 types of sediment and the content of silt (dust/mud) is higher than clay (clay). Existing sand sediments can be caused by waves from the sea which are quite high because of its location near the coast, while the existing mud sediments are usually caused by mangrove root systems. According to the Regulation of the Minister of Health of the Republic of Indonesia No. 416 / MENKES / IX / 1990 dated September 3, 1990 regarding Drinking Water Quality Requirements, the maximum permissible level of manganese is 0.1 ppm, iron is 0.3 ppm, sulfate content is 0.05 ppm. The results of the analysis of these two samples have exceeded the maximum level that has been set means that both samples have been contaminated by high metal and sulfate content.

Data from the analysis of pH on sand sediments was also carried out for 16 days wherein the sample treated with 60% + 40% on day 0 the pH was 6.35 where the value was quite high from the initial pH before treatment was given. Increasing the pH value continues from day 0 to day 10 pH reached 7 where this value has reached a neutral point for pH. However, on the 12th to 16th day the pH value decreased to 6.74. In this solution it can be seen that mangrove sediments are able to raise the pH in acidic mine water, mud sediments can raise the pH to 7.02 on the 12th day while the sand sediment pH raises to 7 on the 10th day.

An increase in pH in the AAT treatment with sediment treatment with sand texture shows a low AAT pH caused by the reaction of sulfide minerals with water so that the metal ions and hydrogen ions are released, while the sulfide ions will oxidize to dissolved sulfate ions, while H⁺ ions will cause a decrease in pH is an environment conducive to the growth of *Thiobacillus Ferrooxidans*.

The three samples above that are best for neutralizing acid mine drainage are treated with a ratio of 60% + 40% on the 12th day with a pH value of 7.02, which means that the value is a neutral number for pH. The pH value becomes neutral ie 7 occurs in samples with a ratio of 60% + 40% occurs on the 10th day so that the effective time is returned with the right ratio to neutralize acid mine drainage. The time required to raise the pH to 7 is 12 days with a neutral pH of 7. The time to neutralize acidic water is faster than the sample treated with mangrove sediment with mud because the pore size of the sand sediment is larger so that the process of sulfate absorption is faster than the mud.

In this treatment, an increase in sand and mud mangrove sediments increased due to the metal content in the sediment greater than the metal content in acid mine drainage to 2,411 ppm. It can be seen that this mangrove sediment can not reduce the amount of heavy metal iron in acid mine drainage but rather will increase. The content of heavy metal iron on the 10th day using sand sediment

![Figure 4](image-url)
increased to 2,813 ppm, this increase occurred because the content of heavy metals in the sediment itself is higher than that in acid mine drainage.

6. Conclusions And Suggestions

The results showed that mangrove sediments are able to neutralize acid mine drainage and can increase the pH value from 2.24 to 7.02, the optimum pH can be achieved by using sand mangrove sediments which are 7.02 on the 10th day. Reducing sulfate levels from 1,171 ppm to 0.625 ppm using sediments mangrove sand on the 10th day, but cannot reduce the content of manganese (Mn) and iron (Fe) by using sand or mud mangrove sediments because the metal content in the sediment is higher than acid mine drainage. The best mangrove method in neutralizing acid mine drainage is sand sediment because it takes faster time to neutralize pH and reduce sulfate levels. Future studies are expected to make a variety of sediment extraction sites and acid mine drainage so that the data is more varied, and additional processing of mangrove sediments is needed before it is used in the neutralization process of acid mine drainage.

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