

ACID MINE TREATMENT METHOD BIOREMEDIATION COAL MINE USING BACTERIA AND THIOBACILLUS THIOBACILLUS FERROOXIDANS THIOOXIDANS

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ABSTRACT

Coal is a natural resource categories of non-renewable, so that its presence must be maintained. Formation of Acid Mine is characterized by one or more water quality characteristics as follows: a. Nilai pH is low (1.5-4); b. Konsentrasi high dissolved metals, such as ferrous metals, aluminum, manganese, cadmium, copper, lead, zinc, arsenic and mercury; c. Nilai high acidity (50-1500 mg / L CaC); d. Nilai high sulfate (500-10000 mg / L); E. The salinity (1-20 mS / cm); f. Konsentrasi low dissolved oxygen. The safest alternative and environmentally friendly for the desulfurization of coal is microbiologically using bacteria Thiobacillus ferrooxidans and Thiobacillus thiooxidans. The combined use of both bacteria is intended to further optimize desulfurization. Thiobacillus ferrooxidans has the ability to oxidize iron and sulfur, while the Thiobacillus thiooxidans not able to oxidize sulfur by itself, but it grows on sulfur that is released after the oxidized iron. Bacteria Thiobacillus chemolithotrophs thiooxidans is a bacteria that use S reduced as a source of energy. Sulfuric acid is the end product of the reaction and cause the pH of the surrounding environment 2 or less. Oxidizing bacteria are tolerant of acidity is Thiobacillus ferrooxidans, Thiobacillus thiooxidans at pH 2-3, and Thiobacillus acidophilus at pH 1.4.

Keyword: acid mine water, bioremediation, bacteria Thiobacillus ferrooxidans, Thiobacillus thiooxidans.

INTRODUCTION

East Kalimantan is one of the largest mines which have the potential of the rich natural resources in Indonesia, crude oil, gold, diamonds and coal are several large-scale mining products in each year. The coal mine is a flagship product that comes from East Kalimantan now. However, coal is a category of natural resources are non-renewable, so that its presence must be maintained. So that national development can scroll continuously by promoting natural resources are managed baik. Salah the national development goals is to improve the welfare of a just and humane society. Availability of natural resources in promoting development is very limited and uneven, while the demand for natural resources continues to increase, due to increased development to meet the needs of the population. However, in the stage of national development, some people are now considered to be minor particularly memorable indifference would be "rules of

the game" in response to the environment, it is feared will happen exploitation of business land that ultimately environmental equilibrium disorders can not be avoided. In an effort to control pollution and environmental damage caused by the construction, development planning needs to be done based on the principle of sustainable development. The principle of sustainable development is done by combining the ability of the environment, natural resources and technology into the development process to ensure this future generation and future generations. "acid mine drainage (AMD)" or "acid rock drainage (ARD)" is formed when mineral sulphides particular that of the rocks exposed to conditions where there is water and oxygen (as a major factor) which cause oxidation and produce water with acidic conditions. The result of this chemical reaction, along with the water that are acidic, can get out of their home if there penggelontor sufficient

water, usually rainwater on the rock pile can experience the infiltration / percolation. Water discharged from this source, commonly referred to as the Acid Mine.

Generally, the mining company uses top (topsoil) or compost to restore soil fertility. On average it takes 5,000 tons per hectare of compost or top soil. The conventional method is less appropriate in the vast former mining land. Utilization of industrial waste paper sludge could be an alternative choice. The paper industry produces 10 percent of the total pulp sludge containing N and P (Anonymous, 2006a).

Experiments showed dose of 50 percent paper sludge can improve soil properties is more effective than treatment of top soil. Paper sludge is a double role in the process of soil bioremediation former coal mining as a source of soil organic matter (BOT) and sulfate reducing bacteria inoculum source (BPS). Giving sludge in the former coal mine raises two processes namely improvement of the environment (soil amendment) and effective microbial inoculation.

Giving 50 percent of paper sludge into the soil a former coal mine land capable of decreasing the availability of 98.8 percent Fe, Mn 48 percent, 78 percent and Cu Zn 63 percent. CPM is able to reduce sulfate to sulfda-metal compounds are not available.

Environmental pollution of land recently received considerable attention, because of the globalization of trade apply strict rules ecolabel. Soil pollution sources generally are heavy metals and toxic aromatic compounds produced by mining and industrial activities. These compounds generally are mutagenic and carcinogenic that is harmful to health (Joner and Leyval, 2001 in Madjid, 2009).

Bioremediation of heavy metal contaminated soil has a lot to do with the use of heavy metal-reducing bacteria that can not be absorbed by plants. Research results indicate that the fungus has a larger

contribution of the bacteria, and increasing their contribution to rising levels of heavy metals (Fleibach, et al, 1994 in Madjid, 2009).

Ectomycorrhizal fungus may increase the tolerance of crops to the toxic metal through the accumulation of metals in ekstramatrik hyphae and "extrahyphae slime" (Aggangan et al, 1997 in Madjid, 2009). thereby reducing absorption into the host plant. However, not all mycorrhizae can improve the host plant tolerance to toxic metals, because each mycorrhizal have different influences. Utilization of mycorrhizal fungi in bioremediation contaminated soil, in addition to the accumulation of such materials in the hyphae, can also be through the mechanism of the metal pengkomplekan by external hyphae secretion.

Heavy metal pollution on forest ecosystems influence on the health of forest plants, especially the development and growth of forest seeds (Khan, 1993 in Madjid, 2009). This sort of thing very often occur around the mining area (tailings and vicinity). Soil contamination with heavy metals will increase seedling mortality and thwart prgram reforestation. Research Aggangan et al (1997) in Madjid (2009) on the stands of Eucalyptus showed that Ni more dangerous than Cr. Symptoms of poisoning Ni looked at a concentration of 80 $\mu\text{mol} / \text{l}$ on land not dinokulasi with mycorrhizal while the soil inoculated with *Pisolithus* sp., Symptoms of poisoning occurred at a concentration of 160 $\mu\text{mol} / \text{l}$. *Pisolithus* isolates taken from mining residues Ni is much more resistant to high Ni content than the *Pisolithus* taken from Eucalyptus stands are not contaminated heavy metals.

Bioremediation wetland polluted by industrial waste (organic pollutants, sediments high or low pH in the flow path and settling ponds) can also be done by utilizing the semi-aquatic plants such as *Phragmites australis*. Oliveira et al, 2001 at Madjid, 2009) showed that *Phragmites australis* can be associated with

mycorrhizal fungi through gradual drying in a short period of time. It can be used as a polluted land management strategies (phytostabilisation) by increasing the rate of development of mikotropik species. Research Joner and Leyval (2001) in Madjid (2009) showed that mycorrhiza in soil contaminated by polysiklik aromatic hydrocarbon (PAH) from industrial waste effect on the growth of clover, but not against growth reygrass. With mycorrhizal clover yield reduction rate for PAH can be suppressed. But if the addition of mycorrhizae coupled with the addition of surfactant, a substance that dissolves PAH, the rate of decrease in the yield increases clover.

Plants growing on a coal mining waste researched Rani et al (1991) in Madjid (2009) shows that of the 18 local plant species studied, 12 of them bermikoriza. Plants that thrive in the land coal waste, found their "oil droplets" in vesicle mycorrhizal roots. This shows that there is a filtration mechanism, so that the material is not toxic until it is absorbed by plants.

Mycorrhiza can also protect plants from the excesses of certain toxic elements such as heavy metals (Killham, 1994 in Madjid and Novriani: 2009). The mechanism of protection against heavy metals and toxic elements that can be given mycorrhizal through filtration effects, disabling chemical or accumulation of these elements in the fungal hyphae. Khan (1993) in Madjid and Novriani (2009) states that vesicles arbuscular mycorrhiza (VAM) can occur naturally in plants pioneer in industrial waste land, coal mine tailings, or other polluted land. Inoculation with suitable inoculants can accelerate reforestation effort contaminated soil toxic substances.

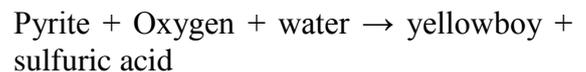
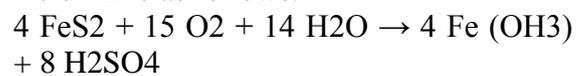
RESEARCH METHODS

This research was conducted at the coal mines along the Mahakam River Samarinda. Formation of Acid Mine is

characterized by one or more water quality characteristics as follows:

- a. Low pH values (1.5 - 4)
- b. A high concentration of dissolved metals, such as ferrous metals, aluminum, manganese, cadmium, copper, lead, zinc, arsenic and mercury
- c. Value acidity is high (50-1500 mg / L CaC)
- d. The value of high sulfate (500-10000 mg / L)
- e. Value salinity (1-20 mS / cm)
- f. Low dissolved oxygen concentration

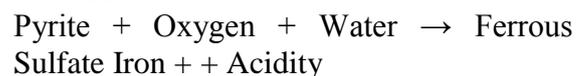
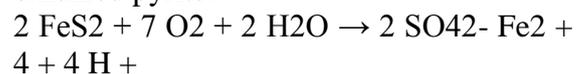
The general reaction formation of Acid Mine as follows:



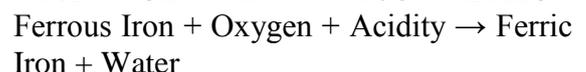
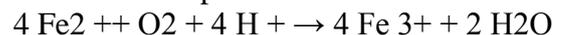
The reaction can be broken down into four stages of the reaction:

1. The first reaction is a reaction accompanied weathering of pyrite oxidation process.

Sulfur is oxidized to sulfate and ferrous iron is released. From this reaction yielded two moles of acidity from each mole of oxidized pyrite.



2. The second reaction, the conversion of the ferrous iron into ferric iron that consumes one mole of acidity. The reaction rate is slow at pH <5 and abiotic conditions. Bacteria thiobacillus will accelerate the oxidation process.



3. The third reaction is the hydrolysis of iron. Hydrolysis is a reaction that separates water molecules. Three moles of acidity resulting from this reaction. The formation of ferric hydroxide precipitates depending on the pH, the more at a pH above 3.5.

$4 \text{ Fe}^{3+} + 12 \text{ H}_2\text{O} \rightarrow 4 \text{ Fe}(\text{OH})_3 + 12 \text{ H}^+$
 Ferric Iron + Water → Ferric Hydroxide (yellowboy) + Acidity

4. The fourth reaction is an advanced oxidation of pyrite by ferric iron. This is the propagation reaction is going very fast and will stop if ferric iron pyrite or depleted.

Oxidising agent in this reaction is a ferric iron.

$\text{FeS}_2 + 14 \text{ Fe}^{3+} + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 15 \text{ SO}_4^{2-} + 16 \text{ H}^+$
 Pyrite + Ferric Iron + Water → Ferrous Sulfate Iron + Acidity

RESULTS AND DISCUSSION

Acid Mine is a term used to refer to the acidic water arising from mining activities. This is to differentiate in acid arising by other activities, such as excavation for the construction of building foundations, creation of ponds, and so on. On mining activities, some mineral sulphides commonly found are:

FeS ₂	Pyrite
Cu ₂ S	Chalcocite
CuS	Cuvelite
CuFeS ₂	Chalcopyrite
MoS ₂	Molybdenite
NiS	Millerite
PbS	Galena
ZnS	Sphalerite
FeAsS	Arsenopyrite

Pyrite is a mineral sulphides commonly found in mining, especially coal. Pyrite oxidation reaction is as shown by the following chemical reaction, with water and oxygen as an important factor. AAT is characterized by the formation of one or more water quality characteristics as follows:

low pH values (1.5 - 4)

- a. high concentrations of dissolved metals, such as ferrous metals, aluminum, manganese, cadmium, copper, lead, zinc, arsenic and mercury.
- b. high acidity values (50-1500 mg / L CaCO₃)
- c. value high sulphate (500-10000 mg / L
- d. value of salinity (1-20 mS / cm)

e. Low dissolved oxygen concentration

Based on chemical equations can be known process of formation of acid mine water is as follows:

♣ Equation 1: $\text{FeS}_2 + 7/2 \text{ O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2 \text{ H}^+ + \text{SO}_4^{2-}$
 (Iron sulfide is oxidized releasing ferrous iron, sulfate and acid.)

♣ Equation 2: $\text{Fe}^{2+} + 1/4 \text{ O}_2 + \text{H}^+ \rightarrow \text{Fe}^{3+} + 1/2 \text{ H}_2\text{O}$
 (Ferrous iron into ferric iron oxidizes.)

♣ Equation 3: $\text{Fe}^{3+} + 3 \text{ H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_3 + 3 \text{ H}^+$
 (Ferric iron can hydrolyze and form ferric hydroxide and acid.)

♣ Equation 4: $\text{FeS}_2 + 14 \text{ Fe}^{3+} + 8 \text{ H}_2\text{O} \rightarrow 15 \text{ Fe}^{2+} + 16 \text{ H}^+ + \text{SO}_4^{2-}$
 (Ferric iron directly react with pyrite and act as a catalyst that causes a very large ferrous iron, sulfate and acid.)

Based on the above, if the AAT out of the formation and into environmental systems public (excluding mining), then some environmental factors may be affected, such as water quality and allocation (as raw material for drinking water, as a habitat for aquatic biota, as a source of water for plants, etc.); soil quality and peruntukkanya (as habitat for flora and fauna of the land), and so on.

An important factor influencing the formation of Acid mine water somewhere is:

- a. concentration, distribution, mineralogy and physical form of the mineral sulphides
- b. the presence of oxygen, including in this case is the intake from the atmosphere through advection and diffusion mechanisms
- c. the amount and chemical composition of the water
- d. temperatures
- e. microbiology

By paying attention to these factors, it can be said that the formation of acid mine water is highly dependent on the conditions of formation. Differences among the factors mentioned above led to the formation and different results.

Associated with climatic factors in Indonesia, with temperatures and high rainfall in some locations where there are mining, the process of formation of AAT have different characteristics from other countries, because it has different climatic conditions.

Acid Mine Water Resources is of the open-pit mining, especially in coal mines, which have a risk of exposure to rain, so the potential is huge to be where the formation of Acid Mine.

Acid mine drainage can occur in both the mining open pit mines and underground mines. This situation generally occurs as elemental sulfur contained in the oxidized rock naturally also supported by high rainfall has been accelerating change becomes acidic sulfur oxides. Source - a source of acid mine drainage among others came from the activities - the following activities:

a. The water from the open pit

Rock layers will open as a result of terkupasnya overburden, so elemental sulfur contained in sulfide rock would easily oxidized and when it reacts with water and oxygen to form acid mine drainage.

b. Water from the waste rock processing unit

The material found in many mining waste is waste rock (waste rock). The amount of this waste rock will increase with the increase in mining activity. As a result, waste rock which contains sulfur will deal directly with the open air to form sulfur oxide compounds further the presence of water to form acid mine drainage.

c. The water from the landfill rock

Heaps of rocks from sulfide rock can produce acid mine drainage because of their direct contact with the air that ensued dissolution due to the presence of water.

d. Water from the tailings processing unit

The content of elemental sulfur in the tailings are known to have the potential to form acid mine water, the pH in the

tailings pond is usually quite high due to the addition of hydrated lime to neutralize acidic water discharged into it. The water that goes into the tailings pond that is acidic is expected to be caused when acid waste seeps from the tailings pond.

Acid water treatment must be done before the water is discharged into a body of water, so it will not pollute the waters around the mine site. Acid water treatment can be done by neutralizing. The neutralization of acidic water can use chemicals such as Limestone (calcium carbonate), Hydrate Lime (Calcium Hydroxide), Caustic Soda (Sodium Hydroxide), Briquettes Soda Ash (Sodium Carbonate), Anhydrous Ammonite.

a. Limestone (Calcium carbonate)

Limestone or commonly known as limestone has been used for decades to raise the pH and precipitate metals in acidic water. The use of limestone is handling the cheapest, safest and easiest of all chemicals. Disadvantages of this limestone is has limitations because of low solubility and limestone coat.

b. Hydrate Lime (Calcium Hydroxide)

Hydrated lime is a chemical that is commonly used to neutralize acidic water. Hydrated lime is very effective in terms of cost in a very large and high acidity state. Hydrated lime powder is hydrophobic, so long mixing hydrated lime is required to make water soluble. Hydrated lime has limitations in the effectiveness of the few places where a very high pH is required to convert the metals such as manganese.

c. Caustic Soda (Sodium Hydroxide)

Caustic Soda is a chemical commonly used and tested more frequently (do not have electrical properties), low flow conditions. Caustic raise the pH of the water very quickly, very easily soluble and is used where the manganese content is a problem. Its use is very simple, that is by dripping liquid caustic acid into the water, because it will spread its solubility in water. The major drawback of the use of caustic liquids for the treatment of acidic water is the high cost and danger in

handling. The use of solid caustic cheaper and easier than the caustic liquid.

d. Briquettes Soda Ash (Sodium Carbonate)

Sodium Carbonate is usually used in small discharge with a low iron content. Selection of soda ash for acid water treatment is usually based on the use of a box or barrel with water inlet and discharge.

e. anhydrous Ammonite

Anhydrous Ammonia is used in some way to neutralize acidity and to precipitate metals in acidic water. Ammonia is injected into the pool or into the inlet such as water vapor, high solubility, the reaction is very fast and can raise the pH. Ammonia requires acid (H^+) and hydroxyl ions are formed (OH^-) that can react with metals to form a precipitate. Ammonia injection should be near the bottom of the pond or water inlet, because ammonia is lighter than air and rises to the surface. Ammonia effective for cleaning manganese occurs at pH 9.5.

f. Use of Alum as Material coagulant

Acidic water in mining operations also can be sure will have a very high turbidity, therefore, to reduce turbidity can use chemicals such as alum or alum or better known by the chemical formula $(Al_2SO_4)_3$. Coagulant alum are materials most widely used because these materials are the most economical, easy to obtain and easy storage market. Total use of alum depends on the turbidity (cloudiness) of water. The higher the turbidity of water, the greater the amount of alum required. The more doses of alum added, the pH will fall, because it was produced sulfuric acid so it is necessary to find an effective dose alum between pH 5.8 -7.4. If the natural alkalinity of the water is not balanced with alum dose needs to be added alkalinity.

One of the approaches made to the management of coal AAT is the method of bioremediation. Bioremediation is the use of microorganisms to reduce pollutants in the environment. When bioremediation occurs, enzymes produced by

microorganisms modify toxic pollutants by changing the chemical structure of these pollutants, an event called biotransformation. In many cases, biotransformation leads to biodegradation, where toxic pollutants degraded, its structure becomes complex, and ultimately into metabolites which are harmless and non-toxic.

Bioremediation is the process of cleaning the pollution of soil using microorganisms (fungi, bacteria). Bioremediation aims to break down or degrade contaminants into materials that are less toxic or non-toxic (carbon dioxide and water). Bioremediation of heavy metals in contaminated soil is defined as the process of cleaning (clean up) the land of contaminants (pollutants) in biology or using living organisms, either microorganisms (microfauna and microflora) and makroorganisme (plants). Bioremediation has grown on waste treatment hazardous waste (chemical compounds that are difficult to be degraded), which is usually associated with industrial activity. Included in pollutants include heavy metals, petroleum hydrocarbons, and halogenated organic compounds such as pesticides, herbicides, and others. Many new applications using microorganisms to reduce pollutants that are being tested. Bioremediation field is now supported by a better knowledge of how pollutants can be degraded by microorganisms, identifying the kinds of microbes that is new and useful, and the ability to improve bioremediation through genetic technology. Molecular genetic technology is very important to identify the genes that encode enzymes related to bioremediation. Characterization of the genes in question can increase our understanding of how microbes modify toxic pollutants into harmless. Or the type of recombinant microbial strains created in the lab can be more efficient in reducing pollutants. Recombinant microorganisms which were invented and first patented bacteria "oil-eating". These bacteria can

oxidize hydrocarbons commonly found in petroleum. The bacteria are growing faster than other types of bacteria that naturally or not created in a laboratory that has been tested. However, these findings have not been successfully commercialized because of this recombinant strain can only parse hazardous components in limited quantities. Strain too has not been able to degrade the molecular components heavier likely to persist in the environment.

The types of bioremediation are as follows:

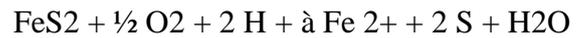
Biostimulasi: Nutrients and oxygen, in the form of a liquid or gas, is added to water or contaminated soil to reinforce the growth and activity of bacteria remediation that has been in the water or the land.

Bioaugmentasi: Microorganisms that can help clean up certain contaminants added to water or contaminated soil. This method is most often used in removing contamination somewhere. But there are several obstacles encountered when this method is used. Very difficult to control the condition of contaminated sites so that microorganisms can develop optimally. Scientists do not yet fully understand all of the mechanisms involved in bioremediation, and microorganisms are released into an unfamiliar environment may be difficult to adapt.

Intrinsic Bioremediation: Bioremediation of this type occurs naturally in water or contaminated soil.

The safest alternative and environmentally friendly for the desulfurization of coal is microbiologically using bacteria *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans*. The combined use of both bacteria is intended to further optimize desulfurization. *Thiobacillus ferrooxidans* has the ability to oxidize iron and sulfur, while the *Thiobacillus thiooxidans* not able to oxidize sulfur by itself, but it grows on sulfur that is released after the oxidized iron. The presence of pyrite oxidation is a major cause of acid sulfate soil problems. According to Dent (1986); Alloway and

Ayres (1997) the process of oxidation of pyrite in acid sulphate soils occur in several stages and involve chemical and microbiological processes. At first the dissolved oxygen in the ground water reacts slowly with pyrite, producing ferrous iron (Fe 2+) and sulfate or elemental sulfur. The reaction is as follows:



The oxidation of sulfur by oxygen occurs very slowly, but with the help of bacteria autotrop which acts as a catalyst, the reaction process runs as follows:



Bacteria *Thiobacillus* chemolithotrophs thiooxidans and bacteria that use S reduced as a source of energy. Sulfuric acid is the end product of the reaction and cause the pH of the surrounding environment 2 or less. By Anonymous (2002a) some oxidizing bacteria are tolerant of acidity is *Thiobacillus ferrooxidans*, *Thiobacillus thiooxidans* at pH 2-3, and *Thiobacillus acidophilus* at pH 1.4. Speed reduction in pH due to oxidation of pyrite is determined by the amount of pyrite, oxidation speed, the speed of change oxidation, and neutralization capacity. From the description of the process of oxidation of pyrite above shows that the microorganisms (bacteria oxidizing) a very important role in the process once the oxidation of pyrite, either as an oxidizer or iron sulfate. Without the bacteria as a catalyst for chemical oxidation process runs very slowly. Based on the calculations, oxidation caused by microbes several hundred times larger than chemical oxidation. The process of pyrite oxidation and reduction of the resulting ions or compounds occurring chemical and biological.

CONCLUSION

1. Formation of Acid Mine is characterized by one or more water quality characteristics as follows: a. Low pH values (1.5 - 4); b. A high

concentration of dissolved metals, such as ferrous metals, aluminum, manganese, cadmium, copper, lead, zinc, arsenic and mercury; c. Value acidity is high (50-1500 mg / L CaC); d. The value of high sulfate (500-10000 mg / L); e. Value salinity (1-20 mS / cm); f. The dissolved oxygen concentration is low.

2. Alternative safest and most environmentally friendly for the desulfurization of coal is microbiologically using bacteria *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans*. The combined use of both bacteria is intended to further optimize desulfurization. *Thiobacillus ferrooxidans* has the ability to oxidize iron and sulfur, while the *Thiobacillus thiooxidans* not able to oxidize sulfur by itself, but it grows on sulfur that is released after the oxidized iron.

Wikipedia. 2010. Bioremediasi – Wikipedia bahasa Indonesia, ensiklopedia bebas.

BIBLIOGRAPHY

- Anonim. 2010. Pemanfaatan Bakteri Pereduksi Sulfat untuk Bioremediasi Tanah Bekas Tambang Batubara.
- Anonim. 2008. Bakteri *Thiobacillus Ferrooxidans* Sebagai Penanganan Limbah Pertambangan (Batu Bara).
- Anonim. 2006a. Limbah Industri Kertas Perbaiki Lahan Tambang Batubara.
- Anonim. 2006. Rehabilitasi Lahan Bekas Tambang Menuju Pemanfaatan Lahan Yang Berkelanjutan : Leaflet Seminar Nasional.
- Arifin, H. 2007. Penambangan Batu Bara Dan Kesehatan Lingkungan.
- Astary, R. 2008. Pertambangan Batubara : Pro dan Kontra.
- Madjid, A dan Novriani. 2009. Peran dan prospek Mikoriza.
- Santosa, D.A., 2009. *Teknologi Bioremediasi Pulihkan Lingkungan Tercemar*.
- Sofyan, H. 2009. Dampak Lingkungan Eksploitasi Tambang Batubara.