The Absorption of Iron (Fe) and Manganese (Mn) from Coal Mining Wastewater with Phytoremediation Technique Using Floating Fern (*Salvinia natans*), Water Lettuce (*Pistia stratiotes*) and Water Hyacinth (*Eichornia crassipes*)

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Abstract

Coal mining activities can cause environmental problems, especially mining with surface mining methods since it may produce acid mine drainage. In order to overcome these problems, efforts are needed to restore the output water conditions so that before flowing into public waters it can meet environmental quality standards which are in accordance to the laws and regulations. In this study, phytoremediation techniques were used to manage coal mining wastewater. Phytoremediation technique used aquatic plants to treat the wastewater. The plants used in this study were Floating Fern (Salvinia natans), Water Lettuce (Pistia stratatiotes) and Water Hyacinth (Eichhornia crassipes). To observe the effect of time on the absorption of iron (Fe) and manganese (Mn), the plant species were used as phytoremediation agents. Based on the results of the study, it was known that the highest absorption of metals in plants (phytoremediation agents) for 30 days for the Manganese (Mn) parameter was water hyacinth (Eichornia crassipes) and, the one that absorbed most iron (Fe) was Floating Fern (Salvinia natans). On the other hands, based on measurements of metal content, water hyacinth (Eichornia crassipes) was the most effective in absorbing Iron (Fe) and Floating Fern (Salvinia natans) was the most affective in absorbing Manganese (Mn).

Keywords: Coal, Acid mine drainage, Phytoremediation

1. Introduction

Industrial development is a necessity of every country to support its economy because it increase high economic growth, create jobs and can provide basic human needs. Increasing population and advancing industrial development increase energy needs. In order meet Indonesia's energy needs, both industrial and household sectors in Indonesia still rely on fossil energy sources from both oil and coal. Coal fuel is still used as fuel for steam power plants (PLTU).

During 2000 – 2011, Indonesia's energy consumption increased by 300 million Barrel of Oil Equivalent (BOE). The sector that dominates energy consumption experienced a shift from 38.8% for household sector and 35.6% for industry in 2000 to 37.2% and 30.7% for industrial and households sector respectively in the next ten years

(BPPT-Outlook Indonesia, 2013). Coal is widely used to fuel steam power plants (PLTU), so coal mining activities are increasing as well.

Enim Regency is one of the regions that have a very large coal resource of 13.563.210 tons from the South Sumatra's total resources of 22,240,470,000 tons; 60.98% of the province resource and 23, 57% of the national resources whose total is 57,857 .700 tons (Data from the Muara Enim Mining Service, 2013). The amount of coal reserves in Muara Enim Regency is 6.25 billion and coal mining activities have been carried out.

Coal mining in Muara Enim district all uses surface mining systems. Surface mining causes many open areas which then form giant holes and produce waste water. The waste water needs to be managed so that it does not become acid mine drainage. Mine acidic water has very high acidity (110-64,000 mg / l CaCO3) and high conductivity (600-30,000 µs / cm) which is capable of dissolving the heavy

metals it passes. Therefore, acid mine drainage is very dangerous for public water system. Heavy metals that can be dissolved by acid mine drainage are, for example, Arsenic, Cadmium, Copper, Silver and Zinc. Acid mine drainage increases the dissolution and releases of various heavy metals. Water contaminated with heavy metals is very dangerous for public healthiness. Consequently, many diseases may appear such as kidney and liver damage (Parulian, 2009 and Paul C Eck, et al, 1989).

With the impact that can be caused by acid mine drainage, the management of coal mining wastewater must be carried out. Waste water is managed by flowing them into mud settling ponds which are then treated so that all hazardous substances contained in the water meet the standard the quality of waste water which has been stipulated in the Decree of the State Minister of Environment Number 113 2003 before being transferred to public waters. There are four parameters that must be fulfilled by each coal mining company before coal waste water is flowed into public waters, namely: acidity (pH) between 6-9, suspended residue (TSS) 400 mg / l, Iron content (Fe) 7 mg / l and Manganese (Mn) content 4 mg / l. Management of mining wastewater can be carried out actively by adding limestone to normalize low pH and using alum to reduce total suspended solids (TSS) and passive management by utilizing phytoremediation techniques. Phytoremediation technique uses water plants to treat wastewater.

Aquatic plants used in this study were Floating Fern (Salvinia natans), Water Lettuce (Pistia stratatiotes) and Water Hyacinth (Eichhornia crassipes) which were planted in plastic jars with 10 liters of water. Then, what would be observed was the effect of time on the absorption of iron (Fe) and manganese (Mn) and plant species utilized as phytoremediation agents.
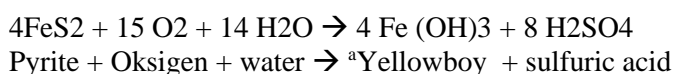
PT. Bukit Asam (Persero) Tbk was one of the mining companies located in Muara Enim Regency with very large production whose total production was approximately 15.260.619 tons in 2014 and mining area of 2.461.358 hectare divided into several Mining Business Permit Areas such as Air Laya, Banko Barat, Muaro Tigo Besar and Banko Tengah. With such large production, the mining activities required an ample land opening and consequently produced a tremendous wastewater. Therefore, the writers were determined to conduct this research at PT. Bukit Asam (Persero) Tbk.

2. Materials and Methods

Acid Mine Drainage Formation

Acid mine drainage is water formed in the mining area as a result of the reaction of sulfide minerals contained in the soil or rocks with the oxygen and water. Acid mine drainage is acidic with a low pH (<6). Sulfide minerals (pyrite, chalcopyrite, calcosite, spalerite, millerite and galena) contained in the soil are oxidized because of the overburden excavation activity causes the oxidation process with oxygen and water to produce acid mine drainage. Acid mine drainage is brownish red, yellow and even colorless. The water can be acidic or basic depending on the level of sulfate concentration (SO_4^{2-}), iron (Fe), manganese (Mn) and is also influenced by other minerals such as calcium sodium, potassium and magnesium. (Enggal Nurisman, et al., 2012). In general, the formation of acid mine drainage reactions are as follows:

$$4FeS_2 + 15 O_2 + 14 H_2O \rightarrow 4 Fe(OH)_3 + 8 H_2SO_4$$
Pyrite + Oksigen + water $\rightarrow$ [a]Yellowboy + sulfuric acid

Phytoremediation

Phytoremediation is composed of two words, phyto which comes from Greek meaning plant and remediation which means healing. Phytoremediation can be interpreted as solving problems or deficiencies (Anonimous, 1999). Phytoremediation is a bioremediation process that uses various plants to eliminate, move and/or destroy contaminants in soil and underground water (Sumarsih, 2008). Therefore, phytoremediation can be defined as the use of plants to remove, move, stabilize or destroy pollutants, both organic and inorganic compounds. In other words, Phytoremediation can be applied to organic and inorganic wastes as well as metal elements (As, Cd, Cr, Hg, Pb, Zn, Ni and Cu) in the form of solid, liquid or gas (Salt et al, 1998).

Instruments

The tools used in this research were jars with a volume of 10 liters as a reactor, drum, analytical scales and laboratory test equipment. The research materials used were aquatic plants such as Floating Fern (*Salvinia natans*), Water Hyacinth (*Eichornia crassipes*), Water Lettuce (*Pistia stratatiotes*) and laboratory test materials.

Variables
1. Independent Variables

Three types of plants used were: Floating Fern (*Salvinia natans*), Water Hyacinth (*Eichornia crassipes*), Water Lettuce (*Pistia stratiotes*), As control, the writers did not use any plants. Each treatment was repeated three times. Observation time consisted of three phases : 10 days, 20 days and 30 days

2. Dependent Variables

Iron Concentration (Fe) and Manganese Concentration (Mn)

Stages of Data Collection
Wastewater Sampling

Sampling was carried out in the coal mining area of PT. Bukit Asam (Persero) Tbk. Sampling began with preliminary sampling in all mud settling ponds in the PT. Bukit Asam (Persero) Tbk in the Air Laya mining area. Sampling began by taking a preliminary sample to get an initial picture of the wastewater conditions. The parameters measured included: the measurements of pH, TSS, Iron (Fe) and Manganese (Mn). Then, samples were examined at the Muara Enim Environmental Agency laboratory.

Table 1 Wastewater Sampling Standard

No.	National Standard Code	Sampling Method	Sample Type
1	6989.59.2008	Wastewater Sampling	-
2	6989.57.2008	Water and Waste - Section 57	Sampling surface water for its physical and chemical properties
3	6989.5.2009	Water and Waste – Section 4	Assessing iron (Fe) by Atomic Absorption Spectrophotometry (AAS) for testing dissolved iron in wastewater in the range of Fe 0.3 mg / l up to 10 mg / l with a wavelength of 248.3 nm
4	6989.5.2009	Water and Waste – Section 5	Testing Manganese (Mn) using Atomic Absorption Spectrophotometry (AAS)

Plant Sampling

Plants used as phytoremediation agents were Floating Fern (*Salvinia natans*), Water Lettuce (*Pistia stratiotes*) and Water Hyacinth *(Eichornia crassipes)*. These plants were taken from the company's Water Treatment which was analyzed before being planted in treatment media; coal mining wastewater and selected young plants with relatively the similar size.

Plant Planting in Waste

Floating Fern (*Salvinia natans*), Water Lettuce (*Pistia stratiotes*) and Water Hyacinth (*Eichornia crassipes*) taken from Water Treatment Process (WTP) Kramat of PT. Bukit Asam (Persero) Tbk would be planted in a plastic basin full of 10 liters of water. 300 grams of plants as phytoremediation agents consisting of Floating Fern (*Salvinia natans*), Water Hyacinth (*Eichornia crassipes*) and Water Lettuce (*Pistia stratiotes*) were included. In other words, there were 3 jars with 3 different plants and one jar without any plants as a control. Before wastewater planting, the content of Iron (Fe) and Manganese (Mn) would be analyzed as t0 and wastewater would be taken as samples to analyze the content of Iron (Fe) and Manganese (Mn) for 10, 20 and 30 days respectively. The plant planting was conducted as 3 different treatments below.

Plants were planted in 3 different treatments:
1. Treatment 1: plants were planted for 10 days
2. Treatment 2: plants were planted for 20 days
3. Treatment 3: plants were planted for 30 days

Every sample of the results examined would be noted to reduce the metal content in coal wastewater as t1, t2 and t3. Then, the metals absorbed by plants during the reduction of metal content in wastewater were calculated in mg / l.Measurements of iron and manganese levels were also carried out on plant samples by checking the levels of iron and manganese at the beginning of the study (0 days) and after the study (30 days).

3. Results And Discussion

The ability of Floating Fern (*Salvinia natans*), Water Lettuce (*Pistia stratiotes*) and Water Hyacinth (*Eichornia crassipes*)

The results of calculations and data processing obtained are in the table below:

Table 2 Levels of Iron (Fe) and Manganese (Mn) in Plants

Name	Metal Content in Plants After 30 Days (Mg / Kg)		% Increase in Metals after 30 days	
	Iron (Fe)	Manganese (Mn)	Iron (Fe)	Manganese (Mn)
Water Hyacinth	39,237	197,647	127,392	1227,619
Water Lettuce	47,183	105,793	200,780	714,820
Floating Fern	47,717	71,343	228,309	509.95

From the table, it can be seen that the plant with the greatest ability to absorb iron (Fe) is Floating Fern (*Salvinia natans*), 47.17 mg / kg and an increase precentage of 228.309%, while the plant which absorbes Mangan (Mn) most significantlyis Hyacinth Mumps (*Eichornia crassipes*) with an increase percentage of 1227,619%.
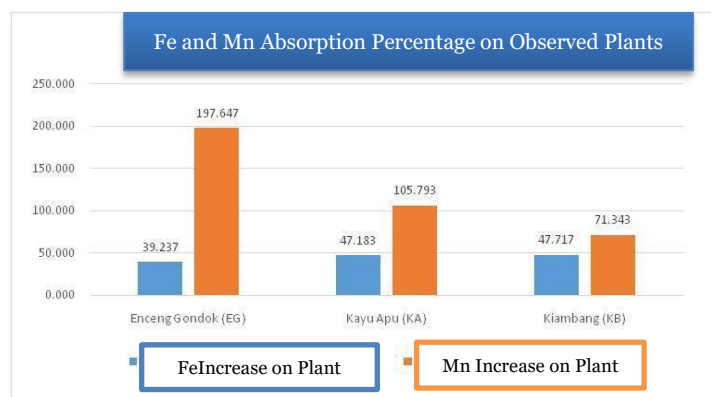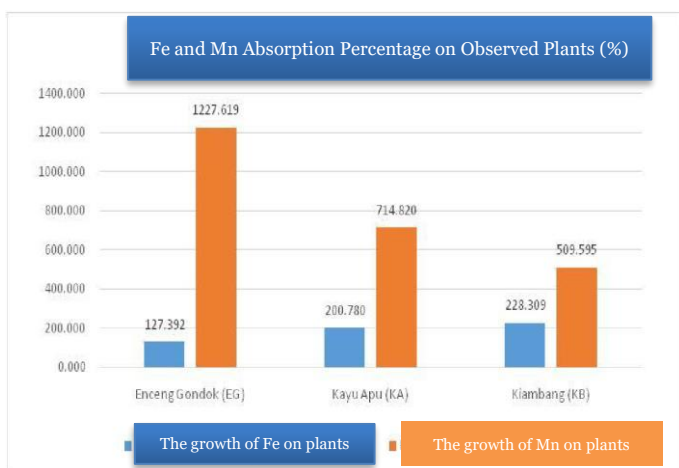

Figure 1. Fe and Mn Absorption in Observed Plants

Fe and Mn Absorption Percentage on Observed Plants (%)

4.2 The Reduction of Iron (Fe) and Manganese (Mn) Levels in Coal Mining Wastewater after Phytoremediation Phase Calculation of Iron (Fe) and Manganese (Mn) levels by: Ho - Hn, where Ho = 0 days and Hn = n Days (10, 20 and 30). From the calculation, the results are obtained the following;

Table 3 Reduction of Iron (Fe) Levels in Coal Mining Wastewater

Name of Plants	The Reduction of Iron (Fe) Levels in Coal Mining Wastewater in the Day						
	0	10	%	20	%	30	%
Water Hyacinth	1,3	0,727	55,897	0,857	66,884	0,950	73,077
Water Lettuce	1,3	0,527	40,513	0,610	46,923	0,583	44,872
Floating Fern	1,3	0,453	34,872	0,827	63,590	0,740	56,923
No plant	1,3	0,600	4,615	0,160	12,308	0,14	10,769

Table 4 The Reduction of Manganese Levels (Mn) in Coal Mining Wastewater

Name of Plants	The Reduction of Mangan (Mn) Levels in Coal Mining Wastewater in the Day						
	0	10	%	20	%	30	%
Water Hyacinth	4,61	0,720	15,618	1,250	27,115	1,420	30,803
Water Lettuce	4,61	1,367	29,646	1,613	34,996	1,810	39,262
Floating Fern	4,61	1,660	36,009	1,973	42,805	3,203	69,487
No plant	4,61	0,030	0,651	0,080	1,735	0,050	1,085

Based on tables 3 and 4, it can be analyzed that the absorption of iron (Fe) and Manganese (Mn) by all plants continues to increase during the 30-day treatment period. The highest absorption of Iron (Fe) metal was found in the Water Hyacinth (*Eichornia crassipes*) plant with 73.077%. Water hyacinth (*Eichornia crassipes*) absorbs Iron (Fe) metal well and also absorbs Manganese (Mn) metal well by 69.487%.Floating Fern has been proven

from various previous studies to absorb heavy metals such as copper and nickel in concentrations of less than 0.3 mg / l (Jameel. M Dhabab 2010 in Ankhita Suhag et al., 2011). Besides, the metal that can be absorbed by Floating Fern from waste is with a concentration of 50 to 300 mg / l (Miranda, MG Ouiroz, A and M. Salazar, 2010 in Ankita Suhag, 2011).
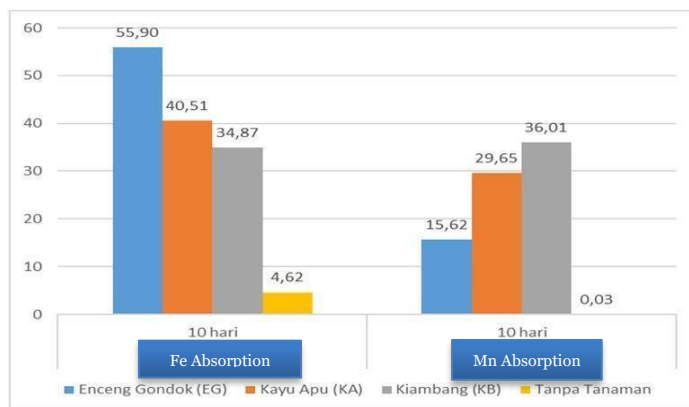

Figure 3. Percentage of Reduction of Iron and Manganese Levels in Wastewater Day
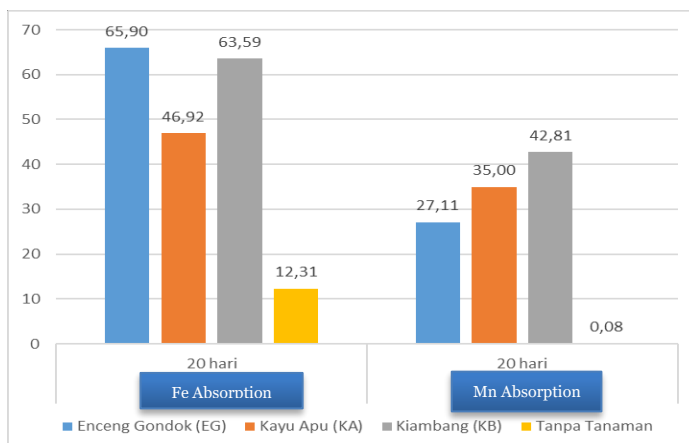

Figure 4. Percentage of Reduction of Iron and Manganese Levels in Wastewater Day – 20
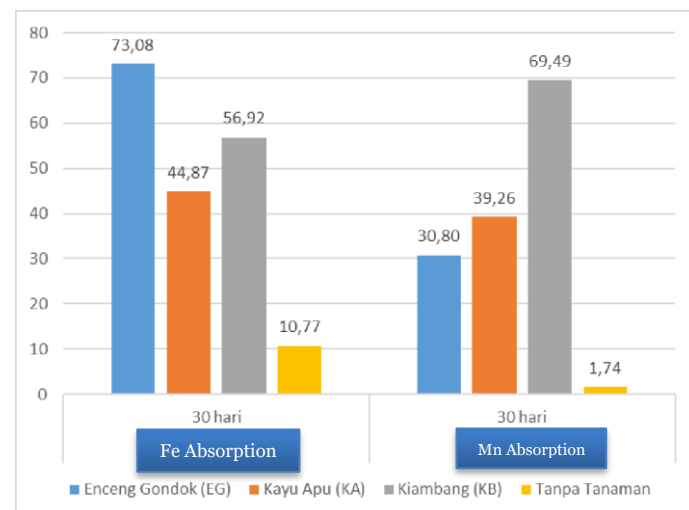
Figure 5. Reduction Levels Percentage Graph
Iron and Manganesein Wastewater Day - 30 From Figure 3 - 5 explain that absorption continues to increase for all metals by all plants. The highest absorption of iron (Fe) was found in water hyacinth (*Eichornia crassipes*) plants which accounted for 65.90%, while the highest absorption of Manganese metal (Mn) was found in Floating Fern plants (*Salvania natans*). Water hyacinth (*Eichornia crassipes*) absorbed Iron (Fe) well and simultaneously while had quite low absorption of Manganese (Mn). Floating Fern absorbed Manganese metal (Mn) well but was relatively higher in absorbing Iron (Fe) metal.
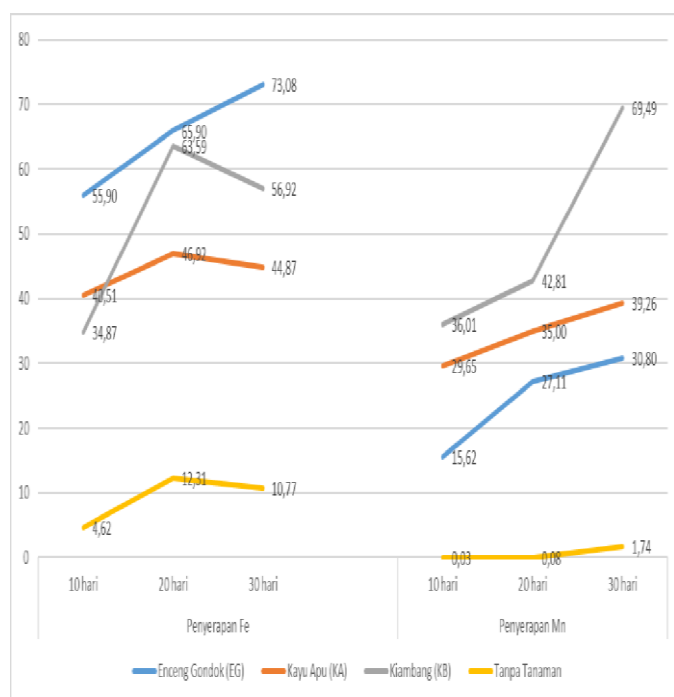

Figure 6. Absorption Performance Trend Graph for Every Ten Days

The analysis of Figure 6, the absorption trends of plants every ten days are: The highest absorption for 30 days for the parameters of Iron (Fe) was by water hyacinth plants. The highest absorption for 30 days for Manganese (Mn) was by Floating Fern. The ability of absorption of Iron (Fe) and Manganese (Mn) was inversely proportional, if the plant: Tends to absorb Iron (Fe) well then the same plant and Did not absorb Manganese (Mn) well, and vice versa.

Table 5. The Growth of Absorption Performance Every Ten Days

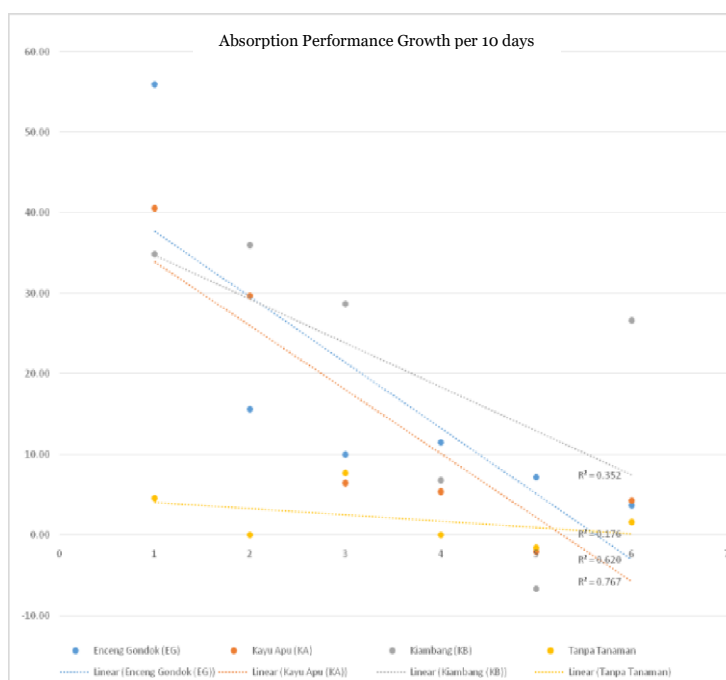| Name of Plants | % Absorption | | | | | |
| | 0 – 10 (day) | | 10 – 20 (day) | | 20 – 30 (day) | |
	Iron	Manganese	Iron	Manganese	Iron	Manganese
Water Hyacinth	4,61	0,720	15,618	1,250	27,115	1,420
Water Lettuce	4,61	1,367	29,646	1,613	34,996	1,810
Floating Fern	4,61	1,660	36,009	1,973	42,805	3,203
No plant	4,61	0,030	0,651	0,080	1,735	0,050

Figure 7. Graph of the Plant Absorption Performance Growth for Ten Days

Based on table 5 and figure 7, the treadline of absorption of all plants against Iron (Fe) and Manganese (Mn) every 10 days, the trend after the tenth day decreased the ability to absorb by all types of plants against Iron (Fe) and Manganese (Mn). Factors that affect the growth and performance of plants as phytoremediators are: temperature, pH, solar radiation and water salinity (Piyus Gupta, Surendra Roy, Amit B Mahindrakar, 2012).

4. Conclusion

From the results of the research conducted, it can be concluded that phytoremediation technique can be applied to improve the quality of coal mining wastewater with evidence of the addition of Iron (Fe) and Manganese (Mn) content in plants that become phytoremediation agents and reduction in Iron (Fe) content and Manganese (Mn) in coal mining wastewater. The highest absorption of metals in

plants (phytoremediation agents) for 30 days for Manganese (Mn) parameters is Water Hyacinth (*Eichornia crassipes*) and the most absorbing Iron is Floating Fern (*Salvinia natans*) whereas based on measurements of metal content in mining wastewater occur instead of Water Hyacinth (*Eichornia crassipes*) most effectively absorbing Iron (Fe) and Floating Fern (*Salvinia natans*) most absorbing Manganese (Mn). The effective absorption time for absorption of Iron (Fe) and Manganese (Mn) is on the tenth day, after the tenth day there is a decrease in the ability of absorption by plants.

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