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Decrease Levels of Mercury (Hg^{2+}) using Vetiver Plants *(Vetiveria zizanioides)* in Mining Waste at Mandailing Natal Regency

Riny Febriani Danur[1*], Rizal Irfandi[2]

[1]Program Studi Biologi, Fakultas Matematika dan Ilmu Pengetahuan Alam, Universitas Negeri Medan, Jalan William Iskandar Psr V Medan Estate
[2]Program Studi Pendidikan Biologi, Fakultas Keguruan dan Ilmu Pendidikan, Universitas Puangrimaggalatung, Sengkang, Indonesia. 90915

**Corresponding Author: rinyfebrianidanur@gmail.com*

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Abstract: *Phytoremediation is one method of handling polluted land due to mining industry. This study aims to examine the effect of planting vetiver (V. zizanioides) on phytoremediation of mining waste contaminated with mercury (Hg) in Mandailing Natal Regency to reduce the impact of enviromental pollution due to mining activities. This research was carried out for three months at the Greenhouse of FMIPA University of State Medan and at Research Center and Standardisation Industry (Baristand) of Medan City. This type of research is an experimental study with a completely randomized design. The number of treatment combinations consisted of 4 variations of exposure to waste with 2 repetitions of testing the mercury content in plants. Results was found that vetiver plants were able to absorb metallic mercury in the planting media contaminated with original mining waste up to 7.1045 mg/Kg and 15.68 mg/Kg on synthetic waste contamination for 12 days of exposure. These results also indicate that V. zizanioides is able to accumulate more heavy metal mercury (Hg) in the soil over the longer planting time.*

Keyword: *Phytoremediation, Vetiver, Vetiveria zizanioides, Mercury (Hg)*

INTRODUCTION

Several sub-districts in Mandailing Natal Regency are traversed by the Batang Natal river which has a length of 70.50 km and many illegal mining operations are found operated by local communities. Mining in the Mandailing Natal Regency area is one of the illegal gold mining locations that are commonly found in the North Sumatera. This community mining has been operating since 2009 and has become one of the main livelihoods of the people in this area. The changes in the environment around mining areas can occur at any time, so that effective waste management is an indicator of the sustainability of mineral mining operations. One of the impacts of environmental damage caused by mining activities is residual material or waste originating from the production process known as tailings (Halimah, 2003).

Waste products from gold mining activities generally contain heavy metals that can have adverse effects on the environment due to the presence of toxic elements such as mercury (Hg) which is applied in the extraction process of precious metals (gold). Waste from gold processing activities that have been mixed with mercury for the purification process is generally disposed of and channeled into ditches, ponds or rivers so that this toxic waste containing mercury will contaminate the surrounding environment. Mercury that comes from the waste is then turned into methyl mercury due to natural processes. If methyl mercury compounds enter the human body through the medium of water, it can cause poisoning as experienced by the victims of the Minamata Tragedy (Sipayung, 2012; Fashola et al., 2016).

Heavy metal mercury (Hg) is one type of pollutant that gets special attention from the public and the government because it has strong toxic properties compared to other heavy metals (Briffa, 2020; Balali-Mood, 2021). Mercury has a residence time of thousands of years which can settle in sediments and enter and accumulate in the bodies of living things through several ways, that is: through the respiratory, skin and digestive tract so that it can cause death (Perryman et al., 2020; Rodriguez et.al., 2018; Wardhana, 2004).

Based on Saturi's report in Mongabay (2014) the results of laboratory tests of gold processing wastewater in Mandailing Natal Regency contain chemical substances such as: mercury, lead, arsenic, cadmium, copper, nickel and zinc which are within the threshold of quality standards. Data from the ITM (Medan Institute Technology) Chemical Engineering Student Forum stated that the level of mercury discharged into the mining industry in Mandailing Natal Regency reached 1.22 mg/l where the threshold was set by the government based on the Decree of the Minister of State for the Environment Number 202 of 2004 concerning Quality Standards for Gold Wastewater and/or Copper Ore Mining Business and or Activities only 0.005s mg/L. Preliminary tests on mining liquid waste in Hutajulu Village, Hutabargot, Mandailing Natal Regency at Research Center and Standarization Industry (Baristand) Medan reveals that the mercury levels found in the samples reached 0.015 mg/L which has passed quality standards.

One technique for handling mercury waste pollution that is environmentally friendly is to apply bioremediation techniques using plants or known as phytoremediation. Phytoremediation is a remediation technique that uses plants to remove, stabilize, destroy or remove contaminants in the form of organic and inorganic compounds found in the environment (Meagher, 2000; Purakayastha and Chonkar, 2010; Rozzaq, 2017). Phytoremediation using vetiver *(V. zizanioides)* has been recognized to be very effective in reducing heavy metal waste pollution through its root system. This plant is able to withstand extreme soil conditions including areas contaminated by heavy metals.

Based on research conducted by Triastuti (2011), the use of vetiver plants on land contaminated with mercury in former landfill areas found the highest accumulation of mercury (Hg^{2+}) to be found in the roots of 0.698 mg/kg in the 100% polluted soil planting medium. According to Ristianingsih (2018), the use of vetiver plants *(V. zizanioides)* and bacteria can reduce oil and grease levels by 50-87% and oil content by 22-64% which pollute the aquatic environment. The results of research conducted by Wakano and Samson (2015) regarding the potential of vetiver plants in rehabilitating soil polluted with 0.1114 - 0.2882 ppm lead ranged from 71.08% - 73.71%.

Based on the explanation above, this study aims to examine the effect of planting vetiver plants (*V. zizanioides*) on the phytoremediation of mercury waste in Mandailing Natal Regency to reduce the impact of environmental pollution due to mining activities.

RESEARCH METHODS

Materials and Tools

The materials used in this study were *V. zizanioides*, aquabidest (H_2O), nitric acid (HNO_3), $HClO_4$ (perchloric acid), aluminum foil, filter paper, mining waste, synthetic mercury waste (Hg), and tissue were purchased from Merck, USA. The tools used in this study were AAS variant AA240ES, oven, electric bath, analytical balance, porcelain cup, desiccator and 3kg polybag.

Methods

The research procedure was carried out in 4 (four) stages: preparation of planting media, plant acclimatization, phytoremediation, and analysis of mercury content.

Planting Media Setup

The planting medium used is a mixture of 70% + 30% compost. The planting medium then put in a research polybag with a volume of 3 kilograms. The addition of compost to the phytoremediation process carried out in this study acts as a stimulant for the absorption of heavy metals Hg so that plants are able to stimulate microbial activity found in compost and soil to degrade metals. Plants play a role in releasing proteins, organic acids and other compounds needed by microbes in roots called exudates. This exudate then serves to attract microbes in the soil thus they approach plant roots, which is known as chemotaxis. The metals that are absorbed by the plant roots will then be passed on to other plant tissues such as plant stems and leaves.

Plant Acclimatization

Plant acclimatization is conducted by putting plants in polybags for 30 days and isolating them in a greenhouse to reduce pollution. Acclimatization allows the vetiver plant *(V. zizanioides)* to adapt to its new growing conditions.

Phytoremediation

After acclimatization was completed, the planting medium was contaminated using native waste and synthetic mercury (Hg) waste with a predetermined concentration variation of 10 mL in each polybag. Every day at 08.00 WIB watering is carried out. Waste contamination was carried out for 12 days and sampling was carried out on the 4^{th}, 8^{th} and 12^{th} days during exposure. The concentration of waste used in this study are:

- T : Original waste
- T_1 : Synthetic waste 0,5 ppm
- T_2 : Synthetic waste 1,5 ppm
- T_3 : Synthetic waste 5 ppm

Analysis of Mercury Content Analysis of the content (concentration) of plants after being given treatment was carried out on days 4, 8 and 12 using AAS

Each segment of the test plant consisting of roots, stems and leaves was cleaned and cut into small pieces. The sample was put in an oven at a temperature of 105°C for 2 hours until the weight was constant, then reweighed to ensure a constant weight. On the analytical balance, the dry sample was weighed up to 5 grams, then added 25 mL of aquabidest and 5 mL of HNO_3. A white precipitate is produced after heating the sample solution to a volume of 10 mL. After that, 1 mL of $HClO_4$ was added to the sample, which was then filtered into a 100 mL volumetric flask and pressed with aquabidest until the meniscus limit was reached. Sample measurements were carried out using *Atomic Absorpstion Spectrometer (AAS).*

RESULT AND DISCUSSION

The vetiver plant *(V. zizanioides)* is proven to be able to collect heavy metal mercury (Hg) produced from mining liquid waste sourced from mining liquid waste in Hutajulu Village, Hutabargot, Mandailing Natal Regency. The quantity of metal mercury (Hg) in mining waste in Hutajulu Village, Hutabargot, Mandailing Natal Regency which has been determined through a preliminary examination of mining waste samples is 0.15 mg/L. The concentration of mercury (Hg) that can be absorbed by vetiver plants *(V.*

zizanioides) which has been contaminated with original waste for 12 days of exposure can be observed in-Table 1.

Table 1. Concentration of Hg in vetiver *(V. zizanioides)* plants with original sewage contamination

Day	Average Absorbance	Average Concentration (mg/L)	Hg Concentration (mg/Kg)	Hg Absorbed (mg/Kg)
0	0,0084	0,0013	0,2555	
				0,5645
4	0,0095	0,0041	0,82	
				1,8445
8	0,0128	0,0105	2,1	
				7,1045
12	0,0155	0,0368	7,36	

Based on the results of the study on the concentration of mercury (Hg) in vetiver (*V. zizanioides*), it can be observed that the highest absorbed Hg concentration occurred on day 12 of 7.1045 mg/Kg. The concentration of mercury (Hg) that can be absorbed by vetiver plants (*V. zizanioides*) which is contaminated with natural and synthetic waste during 12 days of exposure can be seen in figure 1. below.

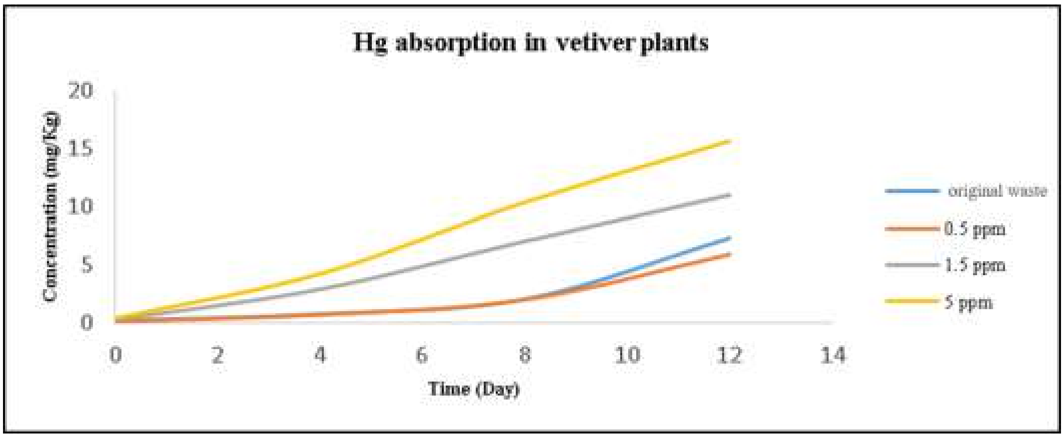

Figure 1. Graph of Hg metal uptake in vetiver plants (*V. zizanioides*)

The ability of vetiver to absorb soil contaminated with mining liquid waste and synthetic waste containing mercury is shown in Figure 1. The highest absorption of mercury (Hg) in plants contaminated with native waste occurred on the 12th day at 7.1045 mg/Kg. In the graph, it can be seen that both on contamination with liquid waste and synthetic waste, the absorption of mercury in plants seems to increase with the length of contact time.

Not all plants have the ability to adapt to an environment contaminated with heavy metals and accumulate these heavy metals. Plants that can accumulate heavy metals such as vetiver have various levels of sensitivity. Heavy metals such as mercury (Hg) are absorbed by plant roots as dissolved ions such as nutrients that enter with the flow of water. This plant then forms a reductase enzyme in its root membrane which functions to reduce metals. Mercury (Hg^{2+}) is transported from roots to various areas of the plant body via transport networks, mainly xylem and phloem, using metallic bonds by chelating molecules (binding molecules) which increase transport efficiency (Cristinaet.al., 2014; Triastuti, 2011). The mercury will then collect in the roots, stems, and leaves of the vetiver plant (*V. zizanioides*).

Heavy metals such as mercury (Hg^{2+}) are stored by vetiver plants when they form complex compounds with other elements and substances such as phytochelatins, which consist of several amino acids such as cysteine and glycine. Phytochelatins are formed together with the synthesis of the enzyme glutathione synthetase and in the plant body, phytochelatins make complex compounds with heavy metals and act as heavy metal detoxifiers. Metal detoxification by phytochelatins is carried out through a metal binding process, after which the metal is transferred to plant vacuoles for storage (Lenny, 2011).

Metal binding with chelating chemicals will then enter the water and nutrient absorption system through plant root hairs. The chelation of mercury with chelating chemicals can produce complex salts containing mercury bound to the S (sulfur) group of the amino acid phytocletain. Through the apoplastic transport network, the complex chemicals and the resulting salts will be absorbed and translocated to other plant organs with the heavy metal mercury being transported from the outside into the cell across the membrane. Since the mercury molecule is so large that it requires proteins or enzymes to pass through the membrane, this transport process cannot be carried out by conventional diffusion. Protons are then pumped out of the membrane into the apoplast area using ATP which results in a difference in proton concentration inside and outside the membrane. The energy from the proton gradient also transports mercury ions into the cell where this gradient enters the cytoplasm and eventually accumulates in the vacuole (Lenny, 2011; Anjum, 2015).

On the 12th day after exposure, the vetiver plant *(V. zizanioides)* revealed signs of poisoning including yellowing of the plant leaves and some curled and wrinkled leaves. This is because of the toxic impact of mercury (Hg) which inhibits plant metabolism. Because the plants used in the phytoremediation process have never been watered, one of the variables that limit plant metabolism is due to lack of water and other factors are lack of oxygen and temperature fluctuations.

CONCLUSION

Based on the research conducted, it can be concluded that the vetiver *plant (V. zizanioides)* has the ability to reduce mercury metal contamination (Hg^{2+}) in the original mining waste in Mandailing Natal Regency by 7.1045 mg/Kg and by 15.68 mg/Kg in waste contamination. synthetic for 12 days of exposure.

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