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Regional Case Study

Identification of Fe and Mn Heavy Metal in Stream Sedimentation at Putri Cempo Landfill

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Abstract

The Putri Cempo landfill serves as the final disposal site for organic and inorganic waste. Waste from the landfill can dissolve and settle in river sediments, potentially accumulating heavy metals, such as iron (Fe) and manganese (Mn), which easily bind to organic matter. This study aims to determine the content of Iron (Fe) and Manganese (Mn) in rivers around the Putri Cempo landfill. The concentrations of Fe and Mn weres analyzed using atomic absorption spectrometry (AAS) according to SNI 6989.84:2019, with sediment sampling conducted in rivers around the Putri Cempo landfill. Sediment sampling in these rivers revealed Fe levels of 1519.414245 mg/L and Mn levels of 130.033 mg/L. The analysis indicated that Fe concentrations exceeded the established quality threshold, whereas Mn levels remained below it. Heavy metals like Fe and Mn negatively impact abiotic and biotic environments, including human health and agricultural productivity. Elevated heavy metal levels disrupt ecosystem balance and pose health risks, making their management crucial. Reducing heavy metals in river sediments near the landfill is essential. Remediation efforts using bioremediation and phytoremediation technologies can help mitigate these impacts. Ongoing efforts are necessary to control heavy metal contamination in river sediments, ensuring ecosystem stability and public health.

Keywords: Heavy metal; identification; iron; manganese; Putri Cempo Landfill

1. Introduction

Putri Cempo is one of the landfills located in Jebres District, Surakarta City, Central Java. This landfill plays an important role in managing the waste generated by the surrounding communities. Therefore, it is important to understand the role and impact of the Putri Cempo landfill on the environment and surrounding communities. Waste disposed of at the Putri Cempo landfill can come from various sources, such as households, industries, and commercial entities. It can also be organic waste, which is biologically degradable material derived from plants, animals, and food waste, and can be decomposed (Atelge et al., 2020). There is also non-organic waste, which is waste that is difficult to decompose, including paper plastics, metals, and others (Hakiki, 2023).

Waste, especially inorganic waste, contains various components, one of which is heavy metals (Krishnan et al., 2021). Waste contains metal compounds that decompose and dissolve, resulting in the formation of liquid waste called leachate (Karamina et al., 2020). Heavy metals themselves are metals that are included in the group of metal elements that have a specific gravity ≥ 5gr / cm³ (Al-Khuzaie et al., 2020). These metals have detrimental effects on the environment at certain levels (Groffen et al., 2021). Heavy metals easily bind and settle at the bottom of water, collecting into sediments (Yanti and Afdal, 2021). Heavy metals cannot be degraded or destroyed (Rosita, 2023). Various types of waste are collected in the Putri Cempo landfill, such as utensils, plastic, glass, and other waste. Items such as tools and used tires can produce iron (Fe). Waste such as batteries, glass, and used fireworks can produce manganese (Mn) (Dey et al., 2023). Fe and Mn enter the river sediments around the Putri Cempo landfill mainly due to human activities and natural processes. The open dumping process at the landfill allows heavy metals from waste to be leached and carried into the river, especially during rainfall or through surface runoff. Poorly managed waste disposal also causes heavy metal accumulation in river sediments (Fathassabilla and Budianta, 2023). Geological and anthropogenic factors around the landfill contribute to the distribution of heavy metals in soil, which can reach the river and settle in sediments, potentially causing pollution (Darmansyah et al., 2020). In addition, the weathering of rocks and soils contributes to the release of heavy metals into streams, adding to the complexity of interactions between the environment and human activities in the context of pollution (Aprilia, 2021).

Because the Putri Cempo landfill uses an open dumping system for waste management, hazardous substances, such as heavy metals contained in waste, can easily seep into the soil and groundwater, causing several problems, such as river and groundwater pollution (Khaira and Afdal, 2022). Water quality monitoring is important to determine the level of pollution. Sediment can be used as an indicator of heavy metal pollution in river water (Fuad and Pane, 2023). This is because heavy metals are toxic and persistent and easily accumulate in the water column and sediments (Milasari et al., 2023). Heavy metals can also easily bind to sediments (Kluska and Jabłońska, 2023).

This study was conducted because no research has been conducted to examine the content of heavy metals iron (Fe) and manganese (Mn) in the sediments of the Putri Cempo landfill river, even though this landfill has the potential to be polluted with heavy metals due to the open dumping system used. In addition, sediments contaminated with heavy metals can spread or move to other ecosystems through water and the food chain, causing widespread pollution (Liu et al., 2024). Based on the background described above, the objectives of this study are to identify the content of heavy metals in the form of iron (Fe) and manganese (Mn) in the sediments of the Putri Cempo landfill river, analyze the suitability of the content with quality standards, determine the impact of the presence of these heavy metals on environmental components, and formulate strategies to reduce heavy metal levels in river sediments around the Putri Cempo landfill.

2. Methods

2.1. Research Time and Location

This study was conducted at the Putri Cempo landfill in Surakarta (Figure 1). River sedimentation sampling was conducted in the Putri Cempo landfill area, with coordinates of 7°32'0.91" N and 110°51'29.9" E. This location was chosen because the Putri Cempo landfill is in the vicinity of residential areas; therefore, it is important to determine whether the environment is contaminated and whether it can endanger the people who live nearby. The wet destruction process was conducted in the Laboratory of the Soil Science Study Program at Sebelas Maret University, Surakarta. Fe and Mn heavy metal testing using atomic absorption spectrometry (AAS) was conducted after obtaining the required mother liquor at the chemistry sub-lab of UPT Laboratorium, Sebelas Maret University, Surakarta.

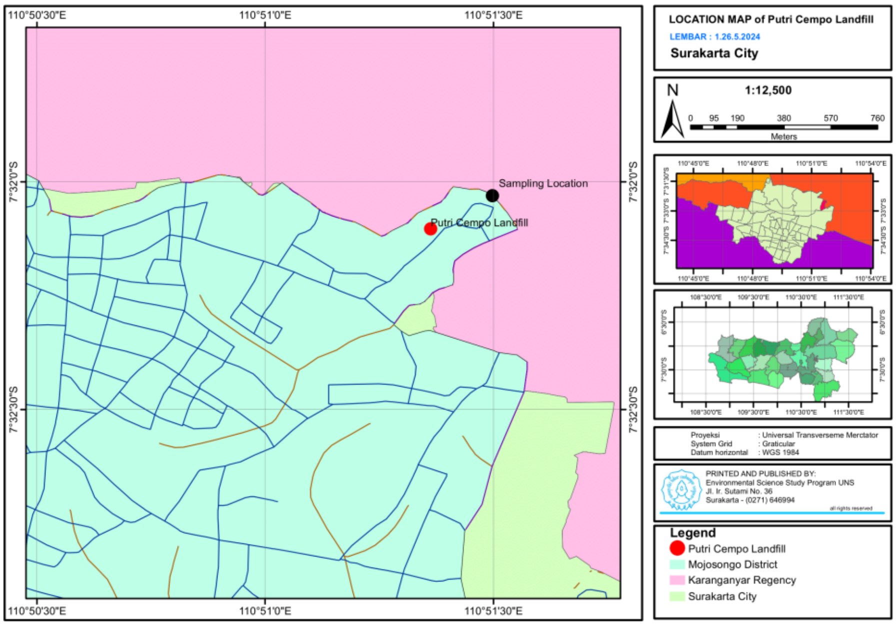

Figure 1. Map of the research location

2.2. Tools and Materials

The equipment used in this study comprised shovels or spoons, plastic bottles, plastic containers, a 250 mL glass beaker, a 50 mL volumetric flask, a 1 mL measuring pipette, Whatman filter paper, and an atomic absorption spectrometer (Husna, 2022). The materials used in this study were soil sedimentation from the river around the Putri Cempo landfill, $HClO_4$, aquabides, 1000 ppm Fe mother liquor, and 1000 ppm Mn mother liquor.

2.3. Data Collection

Sampling locations were determined based on the SNI 6989.57:2008 guidelines using a global positioning system (GPS) device. The river sediment sampling method in the Putri Cempo landfill area used simple random sampling (SRS), in which each point in the population had the same opportunity to be selected as a sampling location (Amalia et al., 2020). In this case, the selected river sediment sampling point was one that was close to a residential area or precisely behind the Putri Cempo landfill. Sediment was collected using a shovel and placed in a polyethylene bottle and labeled. Subsequently, the river sediment samples were dried in the sun and then sieved. After becoming a fine sand sample, the sample was immediately taken to the laboratory for testing.

2.4. Sample Analysis

Testing of heavy metals in this study was conducted using atomic absorption spectrometry (AAS) following SNI 6989.84:2019, based on the principle of energy absorption using the radiation of a wavelength by atoms, resulting in excited electronic energy (Hidayati et al., 2022). The parameters tested were iron (Fe) solution with concentrations of 0.5, 1, 2, 3, and 5 ppm. Before testing, the heavy metal samples were subjected to wet deconstruction. The manganese (Mn) levels were 0.1, 0.2, 0.5, 1, and 2 ppm.

2.5. Data Analysis

Data analysis in this heavy metal test research was conducted by calculating the value of metal content using a linear equation from the atomic absorption spectrometry (AAS) test results in iron (Fe) and manganese (Mn) standard solutions. Subsequently, the metal content results were compared with the heavy metal test results with river water quality standards in accordance with Appendix VI of

Government Regulation of the Republic of Indonesia Number 22 of 2021, concerning the Implementation of Environmental Protection and Management. The heavy metal content was calculated using the standard curve linear regression formula. The description of formula (1) is as follows:

$$y = mx + c \quad (1)$$

In this equation, y represents the sample uptake as the dependent variable, while x denotes the independent variable. The parameter m is the slope or coefficient of x, indicating the rate of change in sample uptake with respect to x. The constant c represents the intercept, corresponding to the value of y when x equals zero.

3. Result and Discussion

The final disposal site in Surakarta City is the Putri Cempo TPA. Waste at the Putri Cempo landfill includes domestic, market, and general waste (Prasenja et al., 2022). Waste accumulates together at final disposal sites. In the sediment compartment, heavy metal compounds tend to be higher than in the water compartment, similar to the Sukawinatan Palembang landfill, where Pb compounds in the sediment are higher than in the water (Warsinah et al., 2015). Heavy metal pollution affects the environment and the health of living organisms. Sedimentation occurs over an extended period for heavy metals (Karamina et al. 2021; Oktasari et al. 2018).

3.1. Fe Content of Sediment

Table 1 shows the relationship between absorbance and Fe concentration, in which the Beer–Lambert law describes the direct proportionality between the two variables (Delgado, 2022). Research published in the Microchemical Journal has shown that within a certain concentration range, the relationship between absorbance and Fe concentration is linear, with a correlation coefficient of 0.9997, indicating an excellent fit between the experimental data and the linear model (Henríquez et al., 2021). The linear equation y = 0.04507x – 0.0092 indicates that any increase in Fe concentration is followed by a proportional increase in absorbance.. As the absorbance depends directly on the concentration of the substance, any increase in the Fe concentration causes the absorbance to increase proportionally according to the gradient, indicating that the Beer–Lambert law applies within the measured Fe concentration range. The slope coefficient of this equation indicates the rate of change in absorbance per unit concentration, whereas a negative y-axis intersection point indicates measurement error or instrument background. A study published in the New Journal of Chemistry also supports these findings, showing that absorbance spectra can be used to calculate the concentration of iron in a solution using a similar linear regression approach (Mira et al., 2022). Although the R^2 value is not visible, this parameter is commonly used to assess how well the data fit the proposed regression model. In laboratory practice, these graphs are very useful for determining the concentration of an unknown solute by measuring its absorbance and utilizing a regression equation. This demonstrates the importance of graphs and equations in analytical chemical analysis, providing an efficient and accurate method for measuring concentrations based on the optical properties of solutions.

Table 1. Result of Fe testing on sediments

	y (abs)	m	x	c
Fe kel P 400x	0.162	0.04507	1519.41424	0.0092

The levels of Fe content in the sediments around the Putri Cempo River were very high (1519.414245 mg/L). This high level could be because that heavy metal content can be carried by rainwater which then dissolves materials from waste, potentially increasing the concentration of heavy metals in the river.. Water quality in the area is thought to be contaminated with heavy metals, which then settle at the bottom of the water as sediment (Triantoro et al., 2018). Liquid waste containing organic matter settles in the river, with the sedimentation process dominated by Fe. Sediments function as nutrient traps, which causes Fe to accumulate in the sediment. This phenomenon of heavy metal deposition in sediments occurs because of the higher density of metals compared to that of water (Astari et al., 2021).

3.2. Mn Content of Sediments

Table 2 shows the relationship between absorbance and Mn metal concentration, and illustrates the application of Beer–Lambert law, which indicates a direct proportionality between the two variables. The linear equation y= 0.07029 x – 0.0009 indicates that any increase in the Mn concentration will be followed by a proportional increase in the absorbance. The slope coefficient of this equation indicates the rate of change in absorbance per unit concentration, whereas a negative y-intercept may indicate a measurement error or instrument background (Dali et al., 2023). Although the R^2 value is not visible, this parameter is usually used to assess how well the data fit the proposed regression model.

Table 2. Result of Mn testing on sediments

	y (abs)	m	x	c
Mn kel P 100x	0.0905	0.0702 9	130.033	0.0009

Analysis of sediment samples from the Putri Cempo River, which is adjacent to the landfill, revealed a heavy metal Mn content of 1130.033 mg/L. Manganese was also detected; however, at lower levels. The presence of these metals may be due to the discharge of leachate from the landfill into nearby waterways. This leachate is rich in organic matter from domestic waste that is not dissolved and tends to settle in sediments (Siprana and Yenita, 2020). Research in the International Journal of Environmental Research and Public Health has shown that river sediments often accumulate heavy metals such as Mn, most of which are in an acid-soluble and oxidized state, suggesting the potential for significant ecological risks (Zhang et al., 2022). Heavy metals such as Mn tend to be bound to these organic materials and deposited on the riverbed. This is because oxidation–reduction occurs, which makes heavy metals react with organic matter. In addition, adsorption can affect the ability of heavy metals to bind to organic matter. Organic matter has a high adsorption ability for heavy metals, causing heavy metals to bind to organic matter and settle at the bottom of the river (Haynes and Zhou, 2022). The sediment composition in this area, which consists of wet sand and liquid mud, also plays a role in the elevated Mn content. It is thought that finer sediments have a greater capacity to bind heavy metals, thus increasing the detected Mn concentration. The distribution of heavy metals in sediments is influenced by their texture; muddy sediments with small particle sizes tend to have higher heavy metal content because of larger surface areas that allow more heavy metals to bind and settle (Rahmah et al., 2019). These findings emphasize the importance of understanding the interactions between sewage, sediments, and heavy metals in effective pollution mitigation and environmental management efforts.

3.3. Comparison of Fe and Mn Heavy Metal Results with Threshold Values

Based on the results of Fe metal analysis of sediment samples, the Fe content was found to be 1,519.4144 mg/L. These results show that Fe concentrations exceeded the threshold set by the Sediment Quality Guidelines for Metals and Associated Levels of Concern (2003) for the quality standard of heavy metal Fe in sediment, which is 20 mg/L (Table 3). It is known that the sediment at the sampling location has a muddy texture, where a smaller particle size corresponds with higher heavy metal content. High Fe content in the sediment can also be caused by weathering of the bedrock in the area (Sudarningsih, 2020). Thus, it can be concluded that the sediments at the research site were contaminated with Fe, which has the potential to negatively affect aquatic organisms and humans.

Table 3. Quality standards for Fe and Mn metals in sediment

Metal	Threshold
Fe	20[(a)]
Mn	248.77[(b)]

(a)*Sediment quality guideline for metals and associated levels of concern to be used in assessments of sediment quality (2003)*
(b)*National sediment quality survey US EPA (2004) (USEPA, 2004)*

Heavy metal testing for Mn in sediment samples revealed the presence of 130.033 mg/L of Mn. This indicates that the sedimentation at the sampling site is not affected by Mn because the concentration value obtained is lower than the threshold value of 248.77 mg/L set by the U.S. Based on the comparison results, it can be concluded that the Mn content in the sediment at the sampling location is safe for aquatic organisms and humans. Based on the comparison results, it can be concluded that the Mn content in the sediment at the sampling location is safe for aquatic organisms and humans. As demonstrated Sudarningsih (2020), have recently shown that the content of manganese (Mn) in sediments can come from weathering of rocks in water basins, volcanic activity, or can also come from active materials from used batteries that have been discharged into rivers and coasts. The persistent, non-biodegradable, and mutagenic nature of heavy metals in sediments can pose a serious threat to human health, living organisms, and ecosystems (Ling et al., 2023).

The presence of Fe and Mn in the study sediment is due to the sampling location near a pollutant source, namely, the Putri Cempo landfill. This indicates that the level of pollutants is directly correlated with the distance from the pollutant source, and the closer the source, the higher the pollutant level. It is also known that heavy metal content in river sediments can come from natural geological conditions or erosion, as well as from human activities such as agriculture, mining, and domestic waste disposal in the form of batteries, electronic equipment, textiles, and lubricants (Milasari et al., 2023). In addition, Fe and Mn in sediments can come from two main sources: minerals or biochemical sedimentation processes that occur in the river (He et al., 2023).

The concentration values of Fe and Mn metals obtained from river sediments around the Putri Cempo landfill were lower than those reported by Putri and Afdal (2017) for the sediments of the Batang Ombilin River. Based on the results of Putri and Afdal (2017), the sediments of the Batang Ombilin River have an average Fe metal concentration of 96,181 mg/L and Mn metal concentration of 1,897 mg/L. Both values exceed the threshold values based on the provisions of the Sediment Quality Guideline for Metals and Associated Levels of Concern to be used in Assessments of Sediment Quality (2003) for Fe metal and the US EPA National Sediment Quality Survey (USEPA, 2004) for Mn metal, as listed in Table 3. The high values of Fe and Mn in the sediment are due to the study location being close to an iron sand mining area and an illegal coal mining site (Putri and Afdal, 2017). The authors compared the results of the study with studies using river sediments because no previous studies have discussed the content of Fe and Mn metals in sedimentation around landfills.

3.4. The Impact of Heavy Metals on Abiotic, Biotic, and Cultural Elements

Heavy metals are hazardous and non-degradable elements. If waste containing heavy metals is disposed of carelessly, it can accumulate in soil and water, thereby posing a significant threat to environmental ecosystems (Widyasari, 2021). Heavy metals are also environmental pollutants that are most commonly found in water and can have negative impacts on humans who use water and organisms that live in these waters (Kamarati et al., 2018). The location of the Putri Cempo landfill, which is close to residential areas, is a problem. The types of heavy metals studied in this research were manganese (Mn) and iron (Fe). Manganese is a toxic heavy metal that can accumulate in biological stages. Manganese (Mn) is present in the soil in solid form. This is because if organisms, such as plants, animals, or microbes, absorb manganese from contaminated soil or water, the content can increase toxicity in higher-level organisms. In the environment, Mn is usually found in the form of solid compounds, such as oxides, hydroxides, or carbonates of Mn, which are part of the minerals in the soil. Particles in water and dust particles in the surrounding air with high manganese (Mn) content resulting from landfills can produce leachate, which causes environmental pollution (Afrianti, 2022).

Elevated levels of heavy metal manganese (Mn) in the environment can exert significant impacts on abiotic, biotic, and cultural elements. Abiotically, high Mn content in soil can alter the physical and chemical properties of the environment by clumping soil particles, thereby modifying soil aeration texture (Abuzahrah et al., 2023). Mn affects the availability of nutrients for plants and soil microorganisms, as it is an essential microelement required for photosynthesis, respiration, and plant metabolism. However, excessive Mn levels can inhibit the uptake of other nutrients, such as calcium, magnesium, and iron, which are crucial for plant growth. Excess Mn can form complexes with iron, reducing its bioavailability for plant assimilation. Elevated Mn levels can also impair water quality because dissolved Mn reduces water clarity, ultimately reducing biological productivity (Amoah et al., 2024). This reduces the availability of clean water for living organisms and society. Consumption of Mn-contaminated water or food by humans can cause health problems. Plants, animals, and microorganisms can also be exposed to Mn through food or water contaminated with heavy metals (Munir et al., 2021). This can lead to impaired growth and reproduction, organ damage, and oxidative stress in plants and animals. Elevated levels of Mn in agricultural soils can damage crop productivity, affect food security, and negatively impact the local economy.

Iron is the fourth most abundant metal in the Earth's crust (Gutteridge and Halliwell, 2024). Iron-mediated reactions support respiration in most aerobic organisms (Liu et al., 2024). If not properly protected, it can catalyze reactions that involve the formation of ratios that can damage cells, tissues, and organisms. The original form of iron is silver-white, which is strong and tough; however, pure iron is difficult to find today. Most iron contains carbides, silicides, foricides, and sulfides, while some have been found to contain contaminants. Iron (Fe) is an essential heavy metal whose presence is needed in certain amounts by every living organism; however, excessive amounts can be toxic to the ecosystem and its inhabitants (Supriyanti and Endrawati, 2015). Heavy metals, including iron (Fe), have high atomic weights and often accumulate in the environment, significantly impacting various aspects of life and ecosystems (Mitra et al., 2022). Excessive levels of iron can have direct and indirect impacts on abiotic, biotic, and human cultural elements. Degradation of soil and water quality and disruption of the balance of microbiota in soil and water are effects of iron metal contamination on abiotic elements. Decreased health of organisms in the ecosystem and bioaccumulation of heavy elements in species in the ecosystem are the effects on biotic elements. In the social environment, public health occurs, which can occur without the community realizing it. Increased iron levels in water and soil are caused by excessive industrial or agricultural activities. This has the potential to poison aquatic organisms and disrupt the food chain. Some plants may experience poisoning or impaired growth due to high iron (Fe) levels, but there are some other organisms that can utilize it for better growth. In the context of culture, iron (Fe) levels in agriculture and industry have significant economic and environmental implications. Thus, the treatment of iron (Fe) and manganese (Mn) levels in ecosystems and the environment is very important to maintain ecosystem balance, human health, and to minimize their negative impacts on abiotic, biotic, and cultural elements.

3.5. Strategies to Reduce Heavy Metal Contamination in Sediments of the Putri Cempo Landfill River Flow

Heavy metals that pollute the environment are very dangerous for the health of the environment and society (Munir et al., 2021). High concentrations of heavy metals in the environment can cause environmental damage and increase metal toxicity. At the Putri Cempo landfill, there is a large amount of old waste that is not properly processed. Putra et al. (2016) recently demonstrated that the length of the waste pile in the landfill significantly affects the amount of heavy metals contained. An increase in heavy metal concentrations in old waste can be caused by prolonged degradation. When waste is not properly degraded, the metals contained in it will not be degraded; consequently, the existing heavy metals can be released, increasing the concentration of free heavy metals. In addition, the flow of water, such as during rainfall, can dissolve heavy metals, resulting in leaching. Along the sampling river, there was a large amount of waste that was washed away and eventually accumulated on the banks of the river. The waste appeared to be old, and much of it was destroyed.

Remediation using oats can be done to reduce heavy metal levels in river sediments in the Putri Cempo landfill. Remediation is a technology used to restore the environment, including land, water, and air, that has been polluted. With this method, heavy metals that have been degraded by microorganisms or absorbed by plants can be eliminated more effectively. The less-degraded environment provides better conditions for microbial and plant growth, and a lower cost is another reason this method is chosen. More specifically, bioremediation can be used to reduce heavy metals in sediments. Bioremediation involves cleaning soil pollution using microorganisms (Supriatna et al., 2021). One organism that can bind Fe and Mn heavy metals is Aspergillus. In addition, phytoremediation can also be performed. Phytoremediation involves converting pollutants with complex molecular chains into simple ones using plants (Irhamniet et al., 2018). Plants used in the phytoremediation process are hyperaccumulating plants, which have the ability to accumulate high concentrations (Christofer et al., 2022). Plants that can be used to reduce Fe and Mn levels include Fimbristylis globulosa Retz. Kunt mendong (Putri and Estuningsih, 2021). This plant is also easy to plant because it does not require special soil types

4. Conclusions

Studies have revealed that the Fe level in the river sediment around the Putri Cempo River is 1519.414245 mg/L, while the heavy metal Mn level is 130.033 mg/L. When viewed from the quality standards based on the US EPA, Fe metal has exceeded the quality standards and Mn has not exceeded the threshold. Elevated levels of Fe and Mn can exert significant impacts on abiotic, biotic, and cultural elements. If pollution levels continue to increase, it will be detrimental to vegetation and organisms living around the sediment. Therefore, efforts can be made to reduce heavy metal levels in the Putri Cempo TPA river sediment by remediation, especially bioremediation techniques using Aspergillus organisms and phytoremediation using Mendong plants.

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Ethics Statement

This study did not involve human participants, animals, or sensitive data; therefore no ethical approval was required.

CRediT Author Statement

Siti Rachmawati: Conceived and Designed Analysis, Collected Data, Performed Analysis, Wrote Paper. **Lia Kusumaningrum:** Conceived and Designed Analysis, Collected Data, Performed Analysis. **Sapta Ahmad Asfar Aulia:** Conceived and Designed Analysis, Collected Data, Wrote Paper. **Alifia Namira Utomo:** Collected Data, Performed Analysis, Wrote Paper. **Iffah Nabila:** Collected Data, Contributed and Analysis Tools, Wrote Paper. **Intan Dwi Kurniasari:** Conceived and Designed Analysis, Collected Data, Wrote Paper. **Anisa Eka Putri Aryanto:** Collected Data, Performed Analysis, Wrote Paper. **Siti Nurlita:** Conceived and Designed Analysis, Performed Analysis

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