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Phytoremediation of Mine Acid Water Using Aquatic Plants

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Abstract: One of the impacts resulting from mining process is the occurrence of AMD (Acid Mine Drainage), which is rainwater or groundwater mixed with rock. AMD contains specific sulfides in coal, leading to highly acidic water with elevated concentrations of iron and manganese. Furthermore, phytoremediation offers a method to enhance specific contaminant levels in various environmental mediums, including soil, sediment, dirt or sludge, groundwater, and surface water. This waste treatment approach employs readily applicable, efficient, and effective plant species, such as burhead or Amazon sword, Melati air (*Echinodorus palaefolius*), Water hyacinth or eceng gondok (*Eichhornia crassipes*), and globe fimbry or Mendong (*Fimbritylis globulosa*) which are aquatic plants in South Sumatra with the capacity to absorb heavy metals. Therefore, this study aims to measure the growth response of each aquatic plant (*Echinodorus palaefolius*, *Eichhornia crassipes*, and *Fimbritylis globulosa*) in each treatment. It also analyzes the amount of heavy metal uptake in the form of Fe and Mn by each aquatic plant (*Eichhornia crassipes*, *Echinodorus palaefolius*, and *Fimbritylis globulosa*) used. Additionally, it investigates the ability of these plants to facilitate the phytoremediation of AMD using compost derived from OPEFB (Oil Palm Empty Fruit Bunches) to reduce the presence of Fe and Mn elements. The study employs a bioreactor and encompasses two treatment factors, namely the type of aquatic plants (*Echinodorus palaefolius*, *Eichhornia crassipes*, and *Fimbritylis globulosa*) and the composition comparison between OPEFB compost and limestone. The result shows that the combination of treatments in terms of plant types and media composition yields the highest growth, with a weight of 286.25 g in T2K1 treatment. This involves Eceng gondok and a media composition of compost to limestone in a ratio of 50% to 50%. Moreover, Mendong exhibits the highest absorption of Fe metal, with a value of 0.82 g, followed by Eceng gondok with 0.55 g, while Melati displays the lowest at 0.38 g. Regarding the absorption of Mn, Eceng gondok demonstrates the highest uptake, measuring 0.36 g, followed by Melati and Mendong at 0.11 g and 0.06 g, respectively.

Key words: AMD, phytoremediation, OPEFB, constructed wetland.

1. Introduction

Coal mining is a mineral extraction activity that involves excavating the surface of the earth using heavy equipment or the blasting method. The open pit mining system employed in the process can result in significant alterations to the natural topography, leading to a reduction in environmental quality. Additionally, one of the adverse consequences of mining is the emergence of AMD [1]. The formation of AMD is influenced by three main factors, namely water, air, and materials containing sulfide minerals. Dissolved pyrite compounds cause the pH of the water to decrease and also have high Fe and Mn elements [2].

AMD occurs in coal mining activities as rainwater or groundwater mixed with rocks containing certain sulfides in coal, which causes water to be very acidic and contains high concentrations of iron and manganese [3].

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One method for dealing with pollution due to AMD is phytoremediation. This biotechnology is used to repair certain contaminants in soil, sediment, dirt or silt, groundwater, surface water, and wastewater. Plants with the potential as phytoremediation agents include *Eichornia crassipes*, *Eleocharis dulcis*, *Typha latifolia*, *Salvinia* sp., *Fimbritylis globulosa*, and *Chrysopogon zizanioides* [4].

Eichhornia crassipes has a fast growth rate, hence the plant is considered a weed that can damage the aquatic environment. *Eichhornia crassipes* floats in water and takes root in the ground. The ability to adapt and grow quickly makes water hyacinth a good phytoremediator. *Eichhornia crassipes* has been proven to reduce pollution caused by AMD (Acid Mine Drainage) [5]. Meanwhile, *Echinodorus palaefolius* can absorb and decompose pollutants which can reduce the pollutant content. It also absorbs oxygen and air through the leaves, stems, and roots released back into the area around its roots (rhizosphere). This happens because the plant has spaces between cells or air passages as a transport medium from the atmosphere to the roots. The oxygen released by this water jasmine is used by microorganisms in decomposing organic matter [6]. *Fimbritylis globulosa* is a hyperaccumulator plant that can extract heavy metals due to its fast growth, and high resistance. Mendong is also used for phytoremediation to reduce iron, manganese, and mercury levels in mine wastewater. It is reported that the plant can reduce mercury levels in the wastewater of people's gold mines. The concentration of mercury in the gold mine before treatment with *Echinodorus palaefolius* was 4.019 mg/L. Subsequently, the concentration of mercury dropped to 0.170-0.340 mg/L. The highest absorption at 96% was found in the treatment using 2 kg of *Echinodorus palaefolius* [7].

Constructed wetlands are wastewater treatment systems that use vegetation, soil, and microorganisms to replicate natural wetland processes. There are two main types of waste treatment systems, namely: surface (Surface Flow Constructed Wetland or FWS) and sub-surface flow systems (Sub-Surface Flow Constructed Wetland or SSF-Wetlands). Surface-flow artificial wetlands offer a range of advantages over sub-surface artificial wetlands, including lower construction and operating costs, simpler design, improved flow control, and other benefits [8].

OPEFB (Oil Palm Empty Fruit Bunches) can improve the physical, chemical, and biological properties of the soil when administered in large quantities. The waste can be used as a source of organic fertilizer needed by soil and plants. OPEFB has a fairly high nutrient content such as N, P, and K, and a pH of 10.9 [9]. The availability of empty fruit bunches as a source of organic matter in South Sumatra is very abundant, considering there are 73 oil palm processing factories operating in the area. The availability and abundance of palm bunches must be considered when considering their use as a material for AMD. The quality of the organic matter contained within the palm bunches must also be evaluated before their use in AMD treatment. Recent studies have demonstrated that OPEFB possesses the ability to reduce turbidity and metal content in water, particularly iron (Fe) and manganese (Mn). The presence of functional groups, including hydroxyl and carboxylic acids, is thought to be the primary mechanism behind the adsorption of dyes and metal ions through chelation. Metal ions, such as iron (Fe), manganese (Mn), and lead (Pb) experience strong adsorption to increase the stability of the bonds [9].

2. Materials and Methods

2.1 Materials and Methods

This study was conducted at the Greenhouse of the Department of Biology, Faculty of Mathematics and Natural Sciences (MIPA) of Sriwijaya University from August to September 2022. AMD samples were taken from void PIT 2 PT. Baturona Adimulya, Musi Banyuasin Regency. Furthermore, measurement of the parameters of acid mine water under South Sumatra Governor Regulation No. 8 of 2021 was carried out at the Environmental Laboratory, South Sumatra Province.

Eichhornia crassipes, *Echinodorus palaefolius*, and *Fimbritylis globulosa* were taken from wetlands in Ogan Ilir Regency while the Organic Material of Empty Oil Palm Bunches was obtained from the Palm Oil Plantation of PT. Guthrie Pecconina Indonesia III, Musi Banyuasin Regency.

2.2 Experimental Design

This study used a CRD (Completely Randomized Design) with two treatment factors. The first factor was the type of aquatic plants, namely Water Hyacinth (*Eichhornia crassipes*), Water Jasmine (*Echinodorus palaefolius*), and Mendong (*Fimbritylis globulosa*). The second factor was the ratio of empty palm fruit bunches compost to limestone at 25%:75%, 50%:50%, and 75%:25%, respectively. The experiment involved treating each type of aquatic plant with varying ratios of empty palm fruit bunch compost to limestone, with each treatment being repeated three times. The control treatment consisted of a comparison of empty palm fruit bunch compost without any aquatic plants.

2.3 Data Analysis

Data obtained from observations were analyzed using ANOVA (Analysis of Variance) to test the effect of concentration on the parameters. The LSD (Least Significant Difference) test with a level of 5% was performed when the ANOVA results had a significant effect.

3. Results and Discussion

3.1 Analysis Result of AMD

AMD used was obtained from the void of PIT 2 PT. Baturona Adimulya, located in Musi Banyuasin Regency, South Sumatra. The quality was determined by analyzing its Fe, Mn, TSS, and pH levels in PT. Binasawit Makmur. Samples of AMD were obtained using the grab method, in which the waste was collected in jerry cans at specific time intervals. Similarly, samples for testing the quality of AAT were obtained by collecting them from the voids.

The results of the AMD quality test can be seen in Table 1 and the pH value of the waste is very low at 4.0 causing acidity. The pH data show that AMD originating from voids is a "net acid" type acid mine water. This can be seen from the low pH, which is < 4.5, where at pH < 4.5 the alkalinity can reach zero [10]. Furthermore, the high acidity of AMD also causes metal to dissolve Fe and Mn. The Fe content of 1.87 mg/L and Totas Suspended Solid of < 13.5 mg/L met the quality standard while the Mn metal parameter of 10.88 mg/L still exceeded the quality standard. For 4 parameters analyzed, only Fe and TSS have met the quality standards, while pH and Mn exceeded the quality standards stipulated in the Minister of Environment and Forestry Regulation No. 5 of 2022 concerning Wastewater Treatment for Businesses and/or Activities Mining Using the Artificial Wetland Method.

3.2 Laboratory Analysis Result of Compost of OPEFB

The results of the content of N, P, K, Fe, and Mn on OPEFB are presented in Table 2.

Based on the analysis in Table 2 above (check the table), OPEFB compost has a relatively high Fe metal with a value of 2,830.62 mg/kg and Mn metal of 139.02 mg/kg. Meanwhile, the N, P, and K contained in OPEFB compost are very useful as a nutrient source for aquatic plants.

Table 1 Result of analysis AMD in laboratory.

Parameter	Analysis result	Standards*
pH (unit)	4	6-9
TSS (mg/L)	< 13.5	400
Fe (mg/L)	1.87	7
Mn (mg/L)	10.88	4

* PermenLHK No. 5 of 2022 concerning Wastewater Treatment for Mining Businesses and/or Activities Using the Artificial Wetland Method.

Table 2 Laboratory analysis result.

Result				
N (%)	P (%)	K (%)	Fe (mg/kg)	Mn (mg/kg)
2.02	0.190	0.21	2,830.62	139.02

Table 3 Aquatic plants biomass.

Treatment	Observation parameters after application				
	Biomass of aquatic plants (g)	Fe reduction (g)	Mn reduction (g)	pH enhancement (Unit)	TSS enhancement (mg/L)
T1K1	143.75[b]	8.03	8.46	2.00	1,006.75
T1K2	197.5[b]	6.98	9.30	2.25	540.00
T1K3	150.00[b]	4.98	9.92	2.50	1,134.00
T2K1	286.25[b]	2.17	9.55	2.00	308.00
T2K2	282.50[b]	2.76	10.04	1.75	568.50
T2K3	235.00[b]	2.76	10.39	2.00	537.50
T3K1	27.50[a]	2.95	9.51	2.50	377.50
T3K2	52.50[ab]	0.99	10.15	2.50	85.75
T3K3	27.50[a]	1.15	10.41	2.50	29.50

* T1: *Eichhornia crassipes*, T2: *Echinodorus palaefolius*, T3: *Fimbritylis globulosa*

K1: 25% compost: 75% limestone, K2: 50% compost: 50% limestone, K3: 75% compost: 75% limestone

3.3 Aquatic Plants Biomass

In this study, the effect of the treatment on the growth response of the three aquatic plants was measured based on the total growth weight in units of grams after treatment for 30 days. The total weight of growth was calculated by subtracting the weight after treatment from before.

Based on the results, it can be concluded that the growth response of aquatic plants in the constructed wetland system was significantly influenced by the type and ratio of the compost and limestone used. The treatments that used a higher ratio of limestone (superscript ‘a’ or T3K1 and T3K3) showed a lower growth response compared to others. On the other hand, the treatments that used a lower ratio of limestone (superscript ‘b’ or T1K1, T1K2, T1K3, T2K1, T2K2, and T2K3) showed no significant difference in growth response, with the T2K1 treatment showing the highest. And treatments that used same ratio of compost and limestone (superscript ‘ab’ or T3K2) showed no significant difference in growth response with (superscript ‘b’ or T1K1, T1K2, T1K3, T2K1, T2K2, and T2K3) and (superscript ‘a’ or T3K1 and T3K3). Therefore, a lower ratio of limestone is more suitable for the growth of aquatic plants in constructed wetland systems. The study also showed that Melati air and Eceng gondok are suitable aquatic plants for constructed wetland systems due to their fast growth rate and ability to use nutrients in the planting medium. The compost from OPEFB also proved to be a good source of nutrients for the plants, specifically nitrogen, phosphorus, and potassium. Overall, the study provides valuable insights for the development of effective and sustainable wastewater treatment systems using constructed wetlands [11].

3.4 Effect of Treatment Combinations on Reduction of Fe (Only One Table above Is Used)

In Table 3, the effect of the combined treatment factors on the reduction of Fe was significantly different between T1K1, T1K2, T1K3, T2K1, T2K2, and T2K3 to T3K1. Meanwhile, the T3K2 treatment was not significantly different from the T1K1, T1K2, T1K3, T2K1, T2K2, T2K3 and T3K1. The findings reveal that the optimal consecutive reduction of Fe was achieved through the combination of various treatments. Specifically, treatment T1K1 at 8.03 mg/L, T1K2 at 6.98 mg/L, T1K3 at 4.98 mg/L, T3K1 at 2.95 mg/L, TT2K1 at 2.17 mg/L, T3K2 at 0.99 mg/L, and T2K2 and T2K3 at 2.76 mg/L produced significant results. The variance in the decrease of Fe observed in each treatment was primarily attributed to the distinct plant types employed, which exhibited varying abilities in Fe absorption. Additionally, the media composition used also played a significant role in the outcome of the treatments.

The highest result of Fe reduction by the aquatic plants shown in Table 3 above was *Eceng gondok*, with a reduction of 8.03 mg/L. The utilization of this plant's capabilities in wastewater treatment, specifically in the context of AMD, is widely recognized due to its remarkable efficiency. *Eceng gondok* (water hyacinth) exhibits favorable properties, making it an excellent choice for such applications. This plant possesses the ability to effectively absorb heavy metals and sulfide compounds. Moreover, it boasts a protein content exceeding 11.5% and a significantly higher cellulose content of 64.51% compared to non-cellulosic components like lignin, ash, fat, and other substances [12]. *Eceng gondok* can be used to remove pollutants, because of its function as a biological filtration system, removing mineral nutrients, to remove heavy metals such as cuprum, aurum, cobalt, strontium, lead, and tin. In addition, water hyacinths can absorb heavy metals such as Fe and Mn [13].

For the T1K1 treatment, the final Fe content was 8.03 mg/L above the quality standard of 7 mg/L. This may be caused by the uncovering of the surface of the water in the treatment with plants, causing the re-oxidation of the metal sulfide formed and increasing the concentration of Fe metal. The increased concentrations of Fe and Mn were caused by biotic, abiotic, and photo-oxidation of metal sulfides on the surface of the wetlands [14].

3.5 The Effect of Treatment Combinations on the Reduction of Mn

From Table 3 above, the combined factors between treatments were not significantly different. The experiment resulted in the highest and lowest metal reduction in the T2K3 and T1K1 experimental combinations of 10.39 mg/L and 8.46 mg/L, respectively. Variations in the reduction of Mn metal occur because each type of aquatic plant has different abilities.

In Indonesia Minister of Environment Regulation No. 5 of 2022 concerning Wastewater Treatment for Mining Businesses and Activities Using the Construction Wetland Method, the quality standards for Fe and Mn metals are 7 mg/L and 4 mg/L. The Mn content at the end of the treatment (day 30) was above the quality standard due to the high Mn content in the OPEFB compost used. The results of laboratory analysis showed that the Mn content is 139.019 mg/L.

The combination of treatments (type of aquatic plants and media composition) resulted in almost the same decrease in Mn. This is because compost is mature organic material containing humus and can be used to minimize heavy metals. The substances in compost include humic and fulvic acids used to adsorb heavy metals due to the carboxyl or –COOH functional group. In decomposed compost, the functional groups are subjected to a deprotonization process to release the H^+ ions from the compounds and the functional groups will be negatively charged. This is the mechanism that occurs in the binding of the heavy metals Fe and Mn by organic matter. Furthermore, compost containing humic substances (fulvic acid, humic acid, and humin) can adsorb heavy metal complexes through cation exchange, chelation formation, and electrostatic bonding [15].

3.6 The Effect of Treatment Combinations on pH Enhancement

The combined treatment in the experiments carried out is presented in Table 3. In the table, changes in pH resulted in an increase that was not significantly different between treatments with each value increasing in T1K1, T1K2, T1K3, T2K1, T2K2, T2K3, T3K1, and T3K2 by 2, 2.25, 2.50, 2.0, 1.75, 2.0, 2.50 and 2.5, respectively.

Under stagnant conditions, a reduction process takes place whereby Fe^{3+} ions are transformed into Fe^{2+}. This process releases OH ions, which subsequently combine with H^+, resulting in a decrease in ion acidity and an increase in pH. Compost as an organic material subjected to maturation, is rich in organic acids. Sulfate-reducing bacteria use these organic acids as electron donors, thereby expediting the sulfate reduction process and facilitating a more pronounced pH increase. Furthermore, the pH of the water rises proportionally with an increased composition of compost in the mixture.

3.7 The Effect of Treatment Combinations on TSS Enhancement

The effect of plant factors in the experiment on Fe metal uptake was significantly different between the three types of plants used in the experiment. The highest absorption of Fe metal was 0.82 g using T3 (*Fimbritylis globulosa*), 0.55 g using T2 (*Eichhornia crassipes*) and the lowest was 0.38 g using T1 (*Echinodorus palaefolius*). From the treatment, plant species had a significant effect on metal uptake with different absorption between T1, T2, and T3.

For the effect of plant species on Mn metal uptake in the treatment, the table 3 shows significantly different results between the three media used. Plants T1, T2, and T3 differ significantly in absorbing Mn metal. Plant factors also have a significant effect on the reduction of Mn metal, where the Fcount is greater than Ftable. The highest Mn absorption by T2 (*Eichhornia crassipes*), T1 (*Echinodorus palaefolius*), and T3 plants (*Fimbritylis globulosa*) was 0.36 g, 0.11 g, and 0.06 g, respectively.

4. Conclusion

1. The study evaluated the effects of different combinations of aquatic plants and media composition on plant growth. Among the treatments, T2K1, which comprised *Eceng gondok* and compost-limestone mixture in a 50:50 ratio, yielded the highest growth, reaching a weight of 286.25 g. It can be inferred that the use of this combination can be a promising strategy for enhancing aquatic plant growth.

2. Among the aquatic plants evaluated, Mendong exhibited the highest absorption of Fe metal, with a recorded value of 0.82 g. *Eceng gondok* followed with an absorption of 0.55 g, while Melati air demonstrated the lowest at 0.38 g. These findings highlight the varying capacities of different aquatic plant species in absorbing Fe metal, with Mendong displaying the greatest potential for this function.

3. *Eceng gondok* exhibited the highest absorption of Mn, with a recorded value of 0.36 g. Melati air followed with an absorption of 0.11 g, while Mendong displayed the lowest at 0.06 g. Therefore, *Eceng gondok* may be a more effective option for Mn absorption compared to Melati air and Mendong.

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