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Accumulation of Heavy Metal in Chinese Waterchestnut (*Eleocharis dulcis* Burm.f.) Trin. Ex Hensch.) in Phytoremediation of Coal Acid Mine Water on Constructed Wetlands.

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Abstract

The coal open mining is an activity that has an impact on the environment, including acid mine drainage (AMD). The management of AMD can be done by phytoremediation using Chinese Waterchestnut (Eleocharis dulcis Burm.f.) Trin. ex Hensch.) on system of constructed wetlands (CWs). So the research was carried out with the aim of evaluation the accumulation of heavy metals iron (Fe) and Manganese (Mn) which were absorbed in E. dulcis in constructed wetlands system at WTP Air Laya PT. Bukit Asam. The accumulation of Fe in the roots of E. dulcis was 986.42 ppm (w/w) while the accumulation of Fe in the leaves was 392.22 ppm (w/w). The accumulation of Mn in the roots of E. dulcis was 24.49 ppm (w/w), while the accumulation of Mn in the shoots was 96.83 ppm (w/w). E. dulcis is known to have the potential to increase AMD pH and reduce levels of Fe, Mn and SO42- so that it can meet the quality standards of coal mining activity wastewater. The accumulation of Fe and Mn in the roots and shoots of E. dulcis and on AMD can be used as an effort to monitor the success of AMD phytoremediation on Constructed Wetlands system at WTP Air Laya.

Keywords : Acid mine drainage; constructed wetlands; Eleocharis dulcis Burm.f.Trin.ex Hensch; Phytoremediation.

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1. Introduction

Coal mining in Indonesia is generally carried out by open pit mining. Open-pit coal mining encourages the oxidation of sulfide minerals and releases sulfuric acid which will drastically lower the pH then produce waste in the form of acid mine drainage (AMD) which results in high accumulation of heavy metals in soil and water.

Acid mining water is water formed as a result of the reaction between oxygen, water and rocks containing sulfides to form AMD. The oxidation of pyrite (FeS_2) will form ferrous ions (Fe^{2+}), sulfate, and some acid-forming protons, so that environmental conditions become acidic. AMD has a low pH. The low pH value causes metals such as Fe to dissolve easily in water [1], [2]. Also stated that besides Fe, other metals are also found, such as Mn, Zn, Cu, Ni, Pb, Cd and others [2], [3].

Reducing the heavy metal content of AMD can be done with phytoremediation using plants hyperaccumulator [4]. According to [5], [6], plants *hyperaccumulator* is able to accumulate metals with a concentration of more than 100 times that of normal plants, where normal plants will be poisoned metal. This occurs due to differences in a series of physiological and biochemical processes and the expression of genes that control the absorption, accumulation and tolerance of plants to metals.

One of the plants that can be used for heavy metal phytoremediation is the Chinese Waterchestnut, or Purun Tikus (Ina) (*Eleocharis dulcis* Burm.f.) Trin. ex Hensch.) which belongs to the Cyperaceae family [5]. Chinese Waterchestnut a hyperaccumulator plant which has the ability to accumulation heavy metals, fast growth, and high resistance [7], [8].

Information regarding the of heavy metals Fe and Mn that are absorbed in the plant *E. dulcis* is important, because the data on the accumulation of heavy metals in *E. dulcis* can be used as monitoring the success of phytoremediation of acid mine drainage. This research was conducted with the aim of evaluating the accumulation heavy metal in *E. dulcis* as a monitoring of the success of phytoremediation of in constructed wetlands WTP 02 Air Laya.

2. Materials and Methods

This research was conducted from Mei to November 2021. Located at Laboratory Physiology and Development, Department of Biology, Faculty of Mathematics and Natural Sciences, University of Sriwijaya Indralaya. Sample analysis was carried out at the Palembang Industrial Research and Standardization Center. Samples of AMD and *E. dulcis* were taken at Air Laya Mine, PT Bukit Asam, Tanjung Enim.

The tools used are Atomic Absorption Spectroscopy (AAS), oven, and digital pH meter. The materials needed are AMD, roots and leaves (*E. dulcis*), $BaCl_2$, buffer A, concentrated HNO_3, and sodium chloride.

Sampling Method of Collection

Acid Mine Drainage samples taken from the open channel AMD, WTP 02 Barat PT. Bukit Asam, Tanjung Enim, South Sumatra and carried out measurements of the AMD pH *in situ*.

Samples of root and leaf *E. dulcis* taken from the constructed wetland location of WTP 02 Air Laya, PT. Bukit Asam, Tanjung Enim, South Sumatra. The samples of *E. dulcis* roots that were taken were the roots that entered the sediment and the shoot were green leaves [4]. The sample was put into plastic and stored in a cool box filled with dry ice for preparation in the Physiology and Development laboratory, Biology Department, Sriwijaya University and then analyzed at the Palembang Industrial Research and Standardization Center.

Sediment Preparation

The sediment preparation procedure is based on research conducted [4]. The sediment samples were taken 0-10 cm vertically. After that, enter a cool box filled with ice. The sediment sample was mashed first. Furthermore, the refined sediment sample was dried in an oven for approximately 5 hours at a temperature of 105°C until the water content was lost and a constant weight was obtained. The sediment is then ground until smooth and 3 g are taken to be dissolved by adding 20 ml of concentrated HNO_3. Then let stand for 24 hours. According to, the addition of HNO_3 is to break the bonds of organometallic complex compounds so that they can bind heavy metals properly [2], [9].

The sediment samples were then heated with a hotplate for 5-10 minutes at a temperature of 150°C-200°C. HNO_3 as a strong oxidizing agent when the solution is heated can accelerate the breaking process of organometallic to organic. The next step is to add distilled water until the volume reaches 50 ml, then it is deposited. The sediment sample that has been deposited is then filtered with filter paper to filter the water phase. The solution obtained is ready to be analyzed using AAS.

Root and shoot E. dulcis preparation

Preparation is done by cutting the roots and shoots into small pieces to facilitate drying of the sample. Then put it in the oven for about 5 hours at a temperature of 105°C until the water content is lost and a constant weight is obtained. After that, the root and leaf samples were pounded until smooth. Furthermore, samples of roots and shoots that have been refined are weighed as much as 3 g to be dissolved in 10 ml of concentrated HNO_3, and let stand for 24 hours. Root and leaf samples that have been left for 24 hours are heated with a hotplate for 5 to 10 minutes at a temperature of 105°C-200°C. Then add distilled water until the volume reaches 50 ml, and precipitated. The sample was then filtered with filter paper for solution and the solution obtained was ready to be analyzed using AAS [4], [9].

Observation Variable Acid Mine Water (AMD) Parameters

The value of the degree of acidity (pH) in acid mine water AMD pH measurement is carried out using a pH meter by entering AMD into the pH meter then viewing the pH measurement results.

Content of Iron (Fe) in AMD

Measurement of Fe content was carried out by taking a sample of AMD which was then analyzed based on SNI 6989.4 of 2009, concerning the method of testing for Fe by using its AAS [10]. The water sample was taken and then put 50 ml of the shaken test sample until it was homogeneous into the Beaker glass. Add 2.5 ml of nitric acid. Then heat it in an electric heater until the solution becomes 25 ml. Added 25 ml of distilled water, put it in a 50 ml volumetric flask through filter paper and set 50 ml with distilled water. The test sample is ready to measure its absorption with AAS. Fe content is calculated by the formula:

Contents of Fe (ppm) = C x df

Notes :
C: Contents obtained from measurement results
df: Dilution Factor

Content of Manganese (Mn) in AMD

Calculation of Mn is done by taking a sample of acid mine drainage which is then analyzed based on SNI 06-6989.5 of 2009 using the AAS method [11]. Enter 50ml of the shaken test sample until it is homogeneous into the beaker. Add 2.5 ml of nitric acid. Then heat it in an electric heater until the solution becomes 2 ml. And 25 ml of distilled water was added, put in a 50 ml volumetric flask through filter paper and adjusted for 50 ml with distilled water. The test sample is ready to measure its absorption with an atomic absorption spectrophotometer (AAS). The manganese content (Mn) is calculated by the formula:

Content of Mn (ppm) = C x df

Notes:
C: Content obtained from measurement results
df: Dilution Factor

Content of Sulfate (SO_4^{2-}) in AMD

Calculation of Sulfate content (SO_4^{2-}) is done by taking a sample of acid mine drain which is then analyzed based on SNI 6989.20 of 2019 with the turbidimetric method [12]. First, buffer solution A is made, 50 ml of water sample is taken and then put into a beaker glass. The sample was added with 20 ml of buffer A, then added a measuring spoon of $BaCl_2$ crystals and stirred constantly using a magnetic stirrer for 1 minute, after that it was inserted into the cuvette found on the Spectrophotometer, then pressed read. The sulfate level will appear on the screen.

Sulfate content SO_4^{2-} is calculated by the formula:

Contens of SO_4^{2-} (ppm) = C x df

Notes:
C: Content obtained from measurement results
df: Dilution Factor

3. Results and Discussion

Content of Fe and Mn in the roots and shoots of *E. dulcis* in constructed wetland WTP 02 Air Laya

Content of heavy metal accumulated in the roots and shoots of *E. dulcis* were used as an effort to monitor the success of AMD phytoremediation in Wetland WTP 02 Air Laya. Content of heavy metal in the roots and shoots of *E. dulcis* at constructed wetland WTP 02 Air Laya are presented in Table 1.

Table 1. Content of Fe and Mn in the roots and shoots of *E. dulcis* in constructed wetland WTP 02 Air Laya

Organs of *E. dulcis*	Fe (ppm)	Mn (ppm)
Root	986.42 ± 80.24	24.49 ± 3.24
Shoot	392.22 ± 79.40	96.83 ± 19.65

Note. ±: standard deviation

Table 1. indicates that content of Fe in the roots is higher than the shoots. The accumulation of Fe in the roots is higher because the roots are in direct contact with AMD and plants absorb water-soluble metals through the roots and carry out a detoxification mechanism. Table According to, Fe concentration tends to be the highest in the roots. This is because Fe tends to accumulate at the bottom of the water. Roots of plant will absorb Fe from sediments, so that Fe tends to accumulate in the roots [13]. Most of the Fe is accumulated more in the root than in the shoot. It is suspected that the detoxification process in plants has occurred while in the root zone [14]. Revealed that content of metal in the roots were greater because the roots localized metal elements by depositing them in the roots as a precautionary measure for metal element poisoning to plant cells. This detoxification mechanism aims to prevent plant metabolic processes [6].

Parameters Acid Mine Drainage

Fe and Mn metal content in *E. dulcis* is affected by AMD. Parameters for observing AMD quality characteristics are guided by Governor Regulation (Peraturan Gubernur No. 8, 2012) [15]. concerning the quality standards of liquid waste for coal mining activities (Table 2). AMD parameters in Wetland WTP 02 Air Laya can be seen in Table 2.

Table 2. Parameters in the constructed wetlands WTP 02 Air Laya

Parameters	Quality standars (ppm)	Inlet (ppm)	Wetland (ppm)	Outlet (ppm)
pH	6-9	4.0	4.51	6.0
Fe	7	0.54±0.01	0.06±0.01	0
Mn	4	6.28±0.09	4.64±0.04	5.29±0.06
SO_4^{2-}	-	3.62±0.02	3.78±0.15	3.13±0.03

Note. ±: standard deviation

Table 2. shows that AMD has a low pH at the inlet, low pH causes metals to be easily soluble in water. Then AMD showed an increase in pH in the wetland and outlet. This is because phytoremediation using E. dulcis has the potential to increase the pH of AMD. Plants change the chemical properties of the metals they absorb through oxidation-reduction reactions to avoid poisoning. Plants will absorb the metal so that the pH of AMD will be high. According to, pH in waters can be affected by the solubility of metals in water. The lower the metal content in the media, the higher the pH (alkaline). The increase in pH will decrease the solubility of metals in water, because it changes heavy metals from carbonate forms to hydroxy forms that form bonds in water bodies [16].

4. Conclusion

The accumulation of Fe in roots *E. dulcis* was 986.42 ppm and the accumulation of Fe in the leaves was 392.22 ppm. Furthermore, the accumulation of Mn in the roots of *E. dulcis* was 24.49 ppm while the accumulation of Mn in the shoots of 96.83ppm of *E. dulcis* is known to have the potential to increase the pH of acid mine drainage and reduce the levels of Fe, Mn and SO_4^{2-} so that it can meet water quality standards for coal mining activity waste.

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