Effectiveness of *Typha latifolia* for phytoremediation of cadmium in acid mine drainage

Maharani Permata Putri¹, Setyo Sarwanto Moersidik¹

¹Environmental Engineering Study Program, University of Indonesia, Depok 16424, Indonesia

Correspondent author: ssarwanto@eng.ui.ac.id

Abstract. One evidence of environmental pollution is the formation of acid mine drainage. In passive processing systems, the technique that is often used is phytoremediation because the costs incurred for this method are affordable and take advantage of natural ecosystems. In this study, the effectiveness of *Typha latifolia* in neutralizing acidity and removing heavy metal such as cadmium (Cd) is determined. Cadmium is one of the heavy metals that can be found in nickel, gold, and copper mining area. The acid mine drainage used in this study was artificially made with a concentration of 5 and 10 mg/L with a pH of 4. pH testing was carried out using a pH meter and the accumulation concentration of Cd was analyzed using Atomic Absorption Spectrophotometer (AAS). The results revealed that *Typha latifolia* planted on soil without fertilizer could increase the pH of acid mine drainage containing heavy metal Cd from 4 to ± 7 within 28 days. *Typha latifolia* can reduce the concentration of Cd in artificial acid mine drainage with the removal efficiency of 95 - 96%. The value of the Bioconcentration Factor in *Typha latifolia* exposed to acid mine drainage with concentrations of Cd 5 and 10 mg/L are > 1000, which means that this plant has the potential to be a heavy metal hyperaccumulator in phytoremediation.

1. Introduction

Indonesia is one of those top 10 in terms of volume of mining products, in 2019 the mining sector is still the government's mainstay in state of revenue for the state budget these days. However, it is unfortunate that mineral and coal mining has negative impacts that cannot be avoided. This negative impact is in the form of changes that occur in the landscape which results in damage to the environment around the mining area.

Acid mine drainage is water that comes from mines or rocks that contain certain sulfide minerals that are exposed and in an oxidized state [1]. It is tailings waste containing heavy metals which are toxic to both living things and the surrounding environment. Acid mine drainage can have a devastating impact on water quality. When large amounts of reduced sulfide minerals are exposed to water and air, large amounts of H⁺ are released which causes the pH of the water to be very low. Generally, conditions of extreme acidity mobilize metals released from oxidizing sulfide minerals and associated minerals. This mobilization occurs because several of metals become more soluble in water due to lower pH and is said to be "acid-soluble" [2].

Cadmium (Cd) is a heavy metal that is toxic to living things and one of the elements that can be found in nickel, gold, and copper mining area. A treatment for acid mine drainage should be done to maintain the heavy metal concentration into a desirable amount. Passive treatment phytoremediation is
the use of plants to remove, move, stabilize, or destroy pollutants, both organic and inorganic compounds (Nur, 2013). *Typha latifolia* is an emergent plant that can survive at pH 4 – 10. Several studies have proven the ability of these plants to accumulate heavy metals Pb, Cd, Cr, Mn, and Fe. Research conducted in Kenya showed the ability of *Typha latifolia* to accumulate Cd in industrial wastewater reaches 97.19% [3]. Therefore, this research will conduct trials using acid mine drainage which has an acidic pH and contains a high heavy metals level. The bioaccumulation ability of *Typha latifolia* plants was also proven by research on several plants such as *Typha latifolia*, *Pistia stratoites*, *Salvinia molesta*, and *Eichornia crassipes* in accumulating Cadmium (Cd), the results showed *Typha latifolia* has the largest Bioconcentration Factor (BCF) compared with other plants [4]. The use of *Typha latifolia* plant as a phytoremediation agent can be considered as an alternative in managing heavy metals, especially Cadmium (Cd) found in acid mine drainage.

2. Material and Method

2.1. Preparation of Artificial Acid Mine Drainage

The research approach used in this research is quantitative. This research was conducted on a small scale using *Typha latifolia* plants aged 2 - 3 months with a height of 100 - 150 cm. The artificial acid mine drainage contains a heavy metal concentration of Cadmium (Cd) of 5 mg/L and 10 mg/L with a pH of 4. The manufacture of artificial acid mine drainage with a concentration of 5 mg/L and 10 mg/L is carried out using solid Cadmium (II) sulfate octahydrate or 3CdSO₄·8H₂O dissolved in groundwater. The metal is dissolved until the desired concentration is obtained. To get the specified pH value of 4, the artificial acid mine drainage is added with HNO₃ solution and NaOH solution.

2.2. Preparation of Plant and Growing Media

*Typha latifolia* plants were placed on the soil planting medium without fertilizer. The soil is homogenized first by mixing it by hand in the ground. The water system that used in this experiment is a batch system, thus in day zero exactly 3 L of water poured in the container of *Typha latifolia* plants. Before the research is carried out, the plants will be acclimatized for 14 days to adapt to their new environment. Changes in pH and Cadmium (Cd) content in stagnant water will be observed on days 0, 3, 7, 14, 21, and 28. pH testing was carried out using a pH meter and the accumulation concentration of Cd was analyzed using Atomic Absorption Spectrophotometer (AAS). While the concentration of Cadmium (Cd) metal that accumulates in plants will be tested on days 0, 14, and 28.

2.3. Removal Efficiency

Cadmium (Cd) heavy metal removal efficiency is measured by calculating the number of contaminants in the artificial acid mine drainage that were removed. The efficiency of this removal is determined in the form of the percentage removal of the heavy metal content of Cd by the *Typha latifolia* plant, the calculation shown in equation (1) [5].

\[
Removal\ efficiency\ (%) = \left(\frac{initial\ metal\ concentration - final\ metal\ concentration}{initial\ metal\ concentration}\right) \times 100
\]

(1)

2.4. Bioconcentration Factor (BCF)

Bioconcentration factor or what is often called the bioaccumulation factor is the ability of plants to accumulate heavy metals that have been absorbed in plant organs. The calculation of the bioconcentration factor is explained in the equation below [4].

\[
BCF = \frac{metal\ concentration\ in\ plant\ (ppm)}{metal\ concentration\ in\ solution\ (ppm)} \times 100
\]

(2)
3. Results and Discussion

3.1. pH analysis

Table 1. pH Results in Artificial Acid Mine Drainage After 28 Days

| Day  | 5 mg/L | 10 mg/L | Control |
|------|--------|---------|---------|
| 0    | 4      | 4.05    | 6.4     |
| 3    | 5.79   | 5.72    | 6.5     |
| 7    | 6.25   | 5.94    | 6.7     |
| 14   | 6.67   | 6.13    | 7       |
| 21   | 7      | 6.54    | 7.2     |
| 28   | 7.25   | 7       | 7.4     |

Table 1 presents the final pH results from duplo data in artificial acid mine drainage after contacted with Typha latifolia plant for 28 days. The increase in pH that occurs in artificial acid mine drainage with a concentration of 5 mg/L within 28 days reaches 81% with a final pH result of 7.25. In a study conducted by Dufresne et al. (2015) [6] obtained the same results showing that the Typha latifolia plant was able to change the pH of an acidic solution to a neutral condition. At a concentration of 10 mg/L the highest increase occurred on the third day (amounting to 1.67). The increase in pH that occurred in artificial acid mine drainage with a concentration of Cadmium 10 mg/L within 28 days reached 73% with a final pH result of 7. The increase in pH in acid mine drainage is caused by the photosynthesis process which produces \( \text{O}_2 \) and releases \( \text{OH}^- \) ions in water and takes up \( \text{H}^+ \) ions present in water[7]. It is the content of the hydroxyl ions in the water that causes an increase in the pH of the artificial acid mine drainage. In the process of photosynthesis, free \( \text{CO}_2 \) will be used to form carbohydrates and oxygen for plant survival, which at that time will cause the pH of the water to increase.

3.2. Removal Efficiency Analysis

Typha latifolia plants are able to survive in extreme conditions, have a good survival percentage, and good adaptability. In addition, this plant also has a high yield of biomass[8]. Figures 1 and 2 showed the removal of Cadmium (Cd) metal content in artificial acid mine drainage using Typha latifolia plant for 28 days. The highest decrease occurred on the 3rd day, namely 4.2 mg L with a percentage of removal of 84%. These results are consistent with research conducted by Githuku et al. (2018) [3] which proved that the Typha latifolia plant was able to accumulate Cr, Cd, and Pb metals. In addition, the highest percentage of Cadmium removal occurred on the 3rd day, which is 79%. Removal of Cadmium metal with water hyacinth plants resulted in the initial absorption of Cadmium metal which was quickly obtained within 48 hours [9]. This high accumulation can be caused by the nature of the heavy metal Cadmium (Cd) which settles easily, allowing the metal to settle in the soil and begin to accumulate in the Typha latifolia plant. The removal efficiency that occurred on the last day (day 28) was 95%. Increasing the performance of removal efficiencies is usually influenced by the plant's ability to survive. As we can see from the equation in figure 1 and figure 2 the optimum removal of Cd in artificial acid mine drainage happened at day 18. Typha latifolia plants have a good survival percentage and good adaptability. In addition, the growth stage of plants in constructed wetlands is also an important factor to increase absorption or removal of heavy metals, because adult plants have a better ability to modify the environment and accumulate metals in the rhizosphere [10]. Adult plants have better aerenchymatous tissue to transport higher oxygen. It also increases microbial respiration in the rhizosphere which promotes removal mechanisms by bacteria.
The coefficient of determination ($R^2$) on the graph in figure 1 is 0.9995 or 99.95% and in figure 2 is 0.9982 or 99.82% using double exponential, which means that there are 2 factors in the removal factor which are quick and slow removal. Quick removal occurred on days 0 to 3 because the Typha latifolia plant was still in good condition and acid mine drainage was just concentrated in the reactor. Meanwhile, slow removal occurred on days 3 to 28 where the plants began to experience absorption deficiency because the heavy metal Cadmium was a non-essential element for the Typha latifolia plant which could damage the plant. The presence of Cd in plants causes necrosis, leaf chlorosis, reduced plant growth, and damage during the photosynthetic process, especially the PS-I and PS-II photosystems, which lead to the reduction of chlorophyll synthesis[11]. If photosynthesis is not optimal, the carbohydrate compounds produced for cell wall formation cannot be maximized [12]. Therefore, if the higher the concentration of the heavy metal Cadmium, the carbohydrate synthesis process will be more inhibited which will affect the efficiency of removal in plants. In the phytoremediation mechanism, plants will absorb nutrients and heavy metals in the soil from acid mine drainage, then these substances will be transported from the roots to the leaves so that the plant's wet weight will increase, which means an increase in the concentration of the heavy metal Cadmium (Cd) in plants [13].
Figures 3 and 4 present the relationship between pH and removal percentage of acid mine drainage with various concentrations of Cd 5 mg/L and 10 mg/L. For the concentration of Cd 5 mg/L the increase in the optimum pH was 4.1 to 5.79 on the third day. This also happened to the removal efficiency which changed from a concentration of 4.9 mg/L to 0.8 mg/L on the third day with a percentage of 84%. The same results were obtained from research conducted by Githuku et al. (2018) [3] where the removal efficiency of Typha latifolia plants on the third day was more than 50%, which is 75%. For the concentration of Cd 10 mg/L, similar to the optimum change in the pH of artificial acid mine drainage on the third day (4 to 5.72), the removal of artificial acid mine drainage containing heavy metal Cadmium (Cd) with a concentration of 10 mg/L also changed from 9.8 mg/L to 1.68 mg/L with a percentage of 83%. On the seventh day, the percentage had reached 91% and on the following days, the percentage of removal increased insignificantly only by 0.5 - 2%. The results of this study are following the analysis conducted by Kumari and Tripathi (2015) [14] which states that there is a positive relationship because along with the increase in contact time there is a change in pH and changes in removal efficiency increase. Thus, it can be concluded that the increase in the pH of artificial acid mine drainage occurs in line with the increasing efficiency of removal of artificial acid mine drainage containing the heavy metal Cadmium (Cd).

3.3. Bioconcentration Factor Analysis
Bioconcentration Factor (BCF), which is the ability of plants to accumulate heavy metals that have been absorbed in plant organs. If a plant has a Bioconcentration Factor (BCF) value of more than 1000, it is generally considered a plant that has the potential to be positive for phytoremediation. If a plant has a Bioconcentration Factor (BCF) between 250 - 1000 then the plant is a medium accumulator and if it is less than 250 then the plant is classified as a low-level accumulator which is not considered a phytoremediation agent [15]. Several studies have mentioned the ability of the Typha latifolia plant as an accumulator of heavy metals such as Zn, Mn, Ni, Fe, Pb, Cu. For the concentration of Cd 5 mg/L the Bioconcentration Factor (BCF) on the roots, stems, and leaves of Typha latifolia plants are 11781; 47469; 490 each. According to Sukumaran (2013) [4] plants that have a Bioconcentration Factor (BCF) value of more than 1000 are generally considered to be plants that have positive potential for phytoremediation. So, it can be said that the Typha latifolia plant can be a hyperaccumulator plant of the heavy metal Cadmium (Cd). For the concentration of Cd 10 mg/L the amount of the Bioconcentration Factor (BCF) on each part of the roots, stems and leaves are 44222; 49174; 1033. From this calculation, the value of the Bioconcentration Factor (BCF) in all parts exceeds the value of 1000 which means that the Typha latifolia plant is a good heavy metal hyperaccumulator plant.
Plants have a defense mechanism to neutralize heavy metal exposure by forming chelating agents such as phytocelatins and metallothioneins. Phytocelatins in plants are produced in the roots and aerial organs. Cadmium ion (Cd$^{2+}$) was found to be the most effective stimulator for phytocelatins synthesis. Therefore, when under pressure, the heavy metal Cd phytocelatins can be a good defense mechanism so that plants are able to tolerate the level of metal toxicity. In a study conducted by Postrigan, et al. (2012) [16] transgenic tobacco plant, phytocelatins increase its resistance to various levels of Cadmium. Metallothioneins also have a role in detoxifying heavy metals in plants. Metallothioneins are produced in the roots, stems, leaves, and are mostly found in developing shoots [11]. When chelating agents are unable to withstand metal toxicity, plants will produce a byproduct of essential aerobic metabolism called Reactive Oxygen Species (ROS) [17]. ROS includes hydroxyl radicals, oxygen, and hydrogen peroxide which influence changes in physiological, biochemical, and molecular mechanisms in cell metabolism [18]. High levels of ROS will cause damage to cell proteins, lipids, and nucleic acids. The presence of metals will cause membrane lipid peroxidation, DNA damage, protein denaturation, iteration in cell enzyme activity, oxidation of carbohydrates, breakdown of cell pigments, and oxidative damage of lipids and proteins that cause cell death or apoptosis [19]. Plants have a natural defense mechanism by producing enzymatic and non-enzymatic antioxidants. Plants exposed to excessive amounts of metals were observed to experience oxidative stress which was minimized by plants through antioxidant enzymes such as catalase, peroxidase, ascorbate peroxidase, and others. This enzyme will work if the defense mechanism with a chelating agent is unable to withstand metal toxicity. Macrophytes such as Alternanthera sp., Eclipta sp., Marselia sp., Typha sp., And Ipomea sp. which are exposed to heavy metals, will show a correlation of metal accumulation and hyperactivity of antioxidants such as catalase and peroxidase [10]. This mechanism has been shown to recover heavy metals through a phytoremediation process.

Basically, the plants used in phytoremediation are plants that have a high growth rate and have a mechanism that can tolerate metal toxicity. From the journal written by [20] the phytoremediation mechanisms that occur in *Typha latifolia* plants are phytostabilization, rhizofiltration, phytoextraction, and phytovolatilization. However, rhizofiltration is the best mechanism to explain the phytoremediation capability of *Typha latifolia* plants. Beginning with rhizofiltration, the process of absorbing contaminants into the root system of the *Typha latifolia* plant. Then the phytostabilization process is the process of attaching substances which are contaminants to the roots of the *Typha latifolia* plant. Roots play a very important role in rhizofiltration. Factors such as changes in pH in the rhizosphere and root exudates help the deposition of heavy metals on the root [21]. Rhizofiltration can be used to accumulate Pb, Cd, Cu, Ni, Zn, and Cr metals which are normally retained in the root system. After being absorbed by the root system, a phytoextraction process occurs in which the absorption of heavy metals in the roots of the *Typha latifolia* plant will be translocated to the top of the plant such as stems and leaves. In the process of absorbing water, the stems have capillary power, where the reeds on the xylem will be an intermediary for the rise of water to the plant parts. Metals such as Ag, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, and Zn are the best candidates for phytoextraction removal. After the phytoextraction process is followed by a phytovolatilization process where there is the absorption of heavy metal contaminants Cadmium (Cd) and release of contaminants into the atmosphere by the process of transpiration by the *Typha latifolia* plant either in its original form or after metabolic modification. Contaminants can also be stored in the parts of the *Typha latifolia* plant which are then converted into harmless substances with a natural defense system. Macrophyte plants such as *Typha latifolia* adapt by developing efficient cell structures with spaces between cells to collect carbondioxide.

4. Conclusion
Passive treatment is generally preferred in acid mine drainage treatment compared to active treatment because passive methods have more advantages, especially in terms of environmental sustainability, maintenance, and lower costs. Based on the results in this research, *Typha latifolia* planted on soil without fertilizer could increase the pH of acid mine drainage containing heavy metal Cd from 4 to ± 7.
within 28 days. The increase in pH in acid mine drainage is caused by the photosynthesis process which produces O$_2$ and releases OH$^-$ ions in water and takes up H$^+$ ions present in water. *Typha latifolia* also can reduce the concentration of Cd in artificial acid mine drainage with the removal efficiency of 95 - 96% because this plant has a good survival percentage and good adaptability. The value of the Bioconcentration Factor in *Typha latifolia* exposed to acid mine drainage with concentrations of Cd 5 and 10 mg/L are > 1000, which means that this plant has the potential to be a heavy metal Cadmium (Cd) hyperaccumulator in phytoremediation.

References

[1] N. I. Said, "Teknologi Pengolahan Air Asam Tambang Batubara "Alternatif Pemilihan Teknologi!"," Jurnal Air Indonesia, vol. 7, 2014.
[2] C. Zipper, J. Skousen and C. Jage, "Passive Treatment of Acid-Mine Drainage," in Virginia Cooperative Extension, Petersburg, 2011.
[3] C. Gituku, J. Ndambuki, R. Salim and A. Nadejo, "Treatment potential of Typha latifolia in removal of heavy metals from wastewater using constructed wetlands," in the 41st WEDC International Conference, Nakuru, 2018.
[4] D. Sukumaran, "Phytoremediation of Heavy Metals from Industrial Effluent Using Constructed Wetland Technology," Applied Ecology and Environmental Sciences, vol. 1, p. 6, 2013.
[5] A. Anning and R. Akoto, "Assisted phytoremediation of heavy metal contaminated soil from a mined site with Typha latifolia and Chrysopogon zizanioides," Ecotoxicology and Environmental Safety, vol. 148, pp. 97-104, 2018.
[6] K. Dufresne, C. Neculita, B. Jacques and T. Genty, "Metal Retention Mechanisms in Pilot-Scale Constructed Wetlands Receiving Acid Mine Drainage," in 10th ICARD IMWA 2015, 2015.
[7] M. Ciria, M. Solano and P. Soriano, "Role of Macrophyte Typha latifolia in a Constructed Wetland for Wastewater Treatment and Assessment of Its Potential as a Biomass Fuel," BioSystems Engineering, vol. 92, no. 4, pp. 534-544, 2005.
[8] S. Mukhopadhyay, N. Manna and S. Mukherjee, "A laboratory scale study of phytoremediation of arsenic by aquatic plant (water lettuce)," in International Conference on Cleaner Technologies and Environmental Management, Pondicherry, 2007.
[9] A. Espadas, R. Portales, L. Sosa, G. Gomes and G. Vidal, "Review of Constructed Wetlands for Acid Mine Drainage Treatment," Water, no. 10, 2018.
[10] P. Mahajan and J. Kaushal, "Role of Phytoremediation in Reducing Cadmium Toxicity in Soil and Water," Journal of Toxicology 2018, vol. 2018, p. 16 pages, 2018.
[11] A. Pratama and A. Laily, "Analisis Kandungan Klorofil Gandasuli (Hedychium gardnerianum Shephard ex Ker-Gawl) pada Tiga Daerah Perkebunan Daun yang Berbeda," in Seminar Nasional Konservasi dan Pemanfaatan Sumber Daya Alam 2015, Malang, 2015.
[12] M. Kumari and B. Tripathi, "Efficiency of Phragmites australis and Typha latifolia for heavy metal removal from wastewater," Ecotoxicology and Environmental Safety, vol. 112, pp. 80-86, 2015.
[13] M. Amoroso, C. Benimeli and S. Cuozzo, Actinobacteria: Application in Bioremediation and Production of Industrial Enzymes, Boca Raton: CRC Press, 2013.
[14] B. Postrigan, A. Knyazev, R. Kuluev, O. Yakhin and A. Chemeris, "The activity of synthetic
Acknowledgement

This study was financially supported by Research Grant University of Indonesia with the contract number NKB-2482/UN2.RST/HKP.05.00/2020.