

Phytoremediation of Hexavalent Chromium Using Aquatic Plants in Nickel Mine Waste

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ABSTRACT

The abundant wealth that Indonesia has is very profitable. Wealth is not only from natural resources, but wealth or biodiversity is also able to make Indonesia an independent country in managing its environment. One of the varieties that can be utilized is the existence of aquatic plants that can be used in the restoration of polluted environments. The ability of plants to recover from pollutants is called phytoremediation. Hexavalent chromium/Cr(IV) is a hazardous waste originating from the washing of ore/open pit waste from rainwater washing. The quality standard allowed for Cr (IV), according to the Minister of Environment Regulation No. 9 of 2006, concerning the Quality Standard of Wastewater for Nickel Ore Mining Businesses and/or Activities is 0.1 mg/L. Besides being used to reduce pollutant loads, this aquatic plant can also provide aesthetic value because it has a very beautiful shape, type, color, and flowers. The purpose of this research is to find out which plants can be used to reduce hexavalent chromium levels. Variations of aquatic plants that can reduce levels of hexavalent chromium which are harmful to living things include water hyacinth/*Eichornia crassipes*; water hyacinth; *Kayambang/Salvinia Cucullata*; *Kiambang/ Apu Wood/ Pistia Stratiotes*; *Hydrilla verticillata*; *Water Bamboo/ Equisetum hyemale*; *Water spinach / Ipomoea Aquatica*; and *Sagittaria lancifolia*. This aquatic plant can reduce Cr (IV) up to 99.5%. The ability of these aquatic plants not only to reduce Cr (IV) but also to reduce TSS, BOD, and COD and to neutralize pH. The combination of several aquatic plants also provides a high effectiveness value.

Keywords: phytoremediation; hexavalent chromium; water mine waste; aquatic plants.

INTRODUCTION

Indonesia has enormous natural resources so that they can be optimally utilized to support national development. One of the resources that play a role in mineral/mining resources. Mining prospects will create growth and increase the national economy for the prosperity of the people by preserving and functioning the environment [1]. Mineral resource exploration activities depend on market demand, prices of mineral commodities and processed minerals,

geological conditions at the site, technological innovation (exploration, post-exploration, refining), capital, political conditions, and the existence of legal certainty in an area [2] and [3]. There was a Minerba law in 2009, but it came into force in 2014, namely the elimination of exports of mineral raw materials before processing [4]. With this regulation in place, the mining industry cannot be separated from the problems that arise both in land clearing but

also in the process of processing minerals into valuable metals, namely waste.

One of the environmental problems caused by open pit mining is being able to change the surface ecosystem of the land and result in reducing soil quality both in productivity and environmental quality. The open pit will also cause Cr to be exposed to the surface and result in the oxidation of Cr to Cr (IV). The open pit is carried out by open pit mining is carried out on a flat mining site with a sloping topography [5]. Rainwater that flows can leach heavy metals that are present and flow into the waters [6]. In the mining industry, it is expected to make ponds or open swamps that are used to treat polluted water. Ponds/ponds/swamps are designed to optimally purify polluted water through integrated physical, chemical, and biological processes [7]. According to Moore [8], in the earth's crust the chromium content is around 100 mg/L. Oxidation of chromium to Cr (IV) in mine water needs to be processed first because it is dangerous or classified as B3 and has an LC 50 and LD 50 according to PP 82 of 2001. Cr (IV) compounds are the most difficult to decompose than other chromium compounds and have a high level of danger when it enters the body through the food chain [9]; [10] and [11]. According to [12] and [13], high doses of hexavalent chromium can cause immune disorders, skin irritation, eye noses, and respiration. The worst conditions can cause carcinogenicity due to gene mutations [14]. The Cr (IV) measurement method can be carried out using the Indonesian National Standard/ SNI 6989.71: 2009 test method for water and wastewater [15].

To be able to find out what levels of pollution exist in the mining area, it is necessary to analyze the components: heavy metals (Cu, Cd, Zn, Pb, Ni, Cr IV, Fe, Mn,

and Co), pH, and the number of solids suspended [16]. This analysis was carried out at inlet points, settling ponds, outlets and then compared with quality standards [17]. According to [8], the safe level of chromium that is safe for abiotic life is around 0.05 mg/L.

TOPICS

This research was conducted based on a literature review where the samples used were samples taken from Cr (IV) waste in open pit mines. In open pit mining, rainwater will leach Cr (IV) metal and will flow into the waters. The industry will collect Cr (IV) waste in pools or ponds so that sampling can be done in ponds, and phytoremediation will be carried out in these ponds using controlled aquatic plants. In the research, the aquatic plants used to remediate Cr (IV) were Water Hyacinth/*Eichornia crassipes*; water hyacinth; Kayambang/ *Salvinia Cucullata*; Kiambang/ Apu Wood/ *Pistia Stratiotes*; Hydrilla *verticillata*; Water Bamboo/*Equisetum hyemale*; Watercress/*Ipomoea Aquatica*; and *Sagittaria lancifolia*.

RESULTS AND DISCUSSION

Phytoremediation

Phytoremediation is one way that can be done for waste treatment by using plant media as an agent to remove pollutants so that the pollutants become harmless and environmentally friendly [18], [19], [20]. Cleaning the environment from heavy metals using phytoremediation techniques uses methods that are simple, inexpensive, and do not have a negative impact on the environment [21]. According to Raskin [22] and [23], the plants selected for phytoremediation activities use plants that have high biomass productivity, capacity to accumulate high concentrations of

contaminants, short life cycles, can grow relatively fast, minimal nutrient requirements, resistant to sunlight, easy to reproduce, inexpensive, easy to manage and maintain and acts as a catalyst for other wastes.

Plants used for phytoremediation in processing can be plants that live in soil or water. Plants that are often used in efficient wastewater treatment are plants that live in water [24]. The aquatic plants used also usually have good aesthetic value for the aquatic environment. The plants used to decompose Cr (IV) waste are water plants. This is because Cr (IV) waste is accommodated in ponds or ponds so that plants that can live in water are suitable for the application of this method.

To support plant growth as a medium in phytoremediation techniques, nutrients such as nitrogen, phosphorus, and potassium are needed. Nitrogen can stimulate plant growth (roots, stems, branches, and leaves) and increase chlorophyll, protein, and fat, as well as other organic compounds. Phosphorus is used to stimulate the growth of roots, flowers, fruit, and seeds, and potassium functions to strengthen plants so that they do not collapse easily and do not drop flowers and fruit [25].

Phytoremediation Mechanism

The effectiveness of the phytoremediation method is influenced by several factors, namely plant weight, bush roots, and plant growth phase. Plants will work to process contaminants in both solid and liquid form by absorbing, accumulating, and degrading waste [26]. The mechanism that occurs when phytoremediation works with several basic concepts, namely (Kelly1997 dalam [24]):

- a. Phytoextraction is the absorption of pollutants by plants and then stored

and accumulated in the stems, leaves, or roots. This plant can be called a hyperaccumulator.

- b. Rhizofiltration is the ability of roots to absorb, precipitate and collect heavy metals in waste.
- c. Phytodegradation is the ability of plants to absorb pollutants, then the pollutants will be metabolized by involving enzymes such as nitroreductase, laccase, dehalogenase, and nitrase.
- d. Phytostabilization is a plant process of converting waste into non-toxic compounds without first being absorbed by plants.
- e. Phytovolatilization is a process by which plants absorb heavy metals and then convert them into volatile substances so that plants can transpire them.

Phytoremediation Aquatic Plants

Phytoremediation in artificial swamps in the treatment of waters from liquid waste pollution usually uses aquatic plants. Aquatic plants have various benefits besides being used as ornamental plants as well as producing energy in ecosystems, handicrafts, food, medicine, and also as oil producers [27]. Aquatic plants are classified into three categories namely:

- a. Floating where all parts of the plant (leaves) float on the surface of the water
- b. Emerging plants appear above the surface, but their roots are in the sediment
- c. Submerged plants as a whole are in the water [28].

According to Beardshow [29], the grouping of aquatic plants is based on the natural position of aquatic plants when they are in the waters (Figure 1).

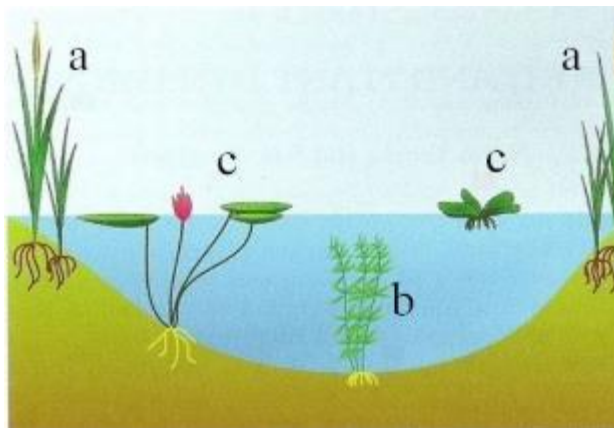


Figure 1. Grouping of aquatic plants (a. Emerged; b. Submerged; c. Floating)

The ability of aquatic plants to reduce Cr (IV) waste from several previous studies can be seen in the following explanation:

a. Water hyacinth/*Eichornia crassipes*

Water hyacinth (Figure 2) is a plant that is easy to adapt and reproduce quickly. Environmental factors that support the growth of water hyacinths are nutrients, water depth, salinity, pH, and light intensity [30]. The ability of *Eichornia crassipes* to carry out phytoremediation on Cr (IV) up to a limit of 8 mg/L is characterized by its slow growth [31]. Exposure to research conducted at PT Vale Indonesia by [32], research conducted with three treatments, namely water hyacinth in the young growth phase with a plant height of <35 cm, medium growing phase water hyacinth with a height of 35 – 60 cm and water hyacinth goiter old growth phase with a plant height of 60-80 cm. It can be shown that reducing the concentration of Cr (IV) from 0.56

mg/L to 0.2050 mg/L for seven days with an effectiveness rate of 63.39% was carried out in the young growth phase. The study also explained that there was a decrease in the initial pH of 7.75 to 6.74 (young phase); 6.84 (moderate phase), and 6.92 (old phase). Another study conducted [33] was able to reduce Cr (IV) waste in the batik industry from 0.0546 mg/L to 0.0378 mg/L within five days. Phytoremediation of water hyacinth in the research conducted [34] showed that the concentration of Cr (IV) in the batik industrial wastewater before treatment was 0.0761 ± 0.0070 mg/L, which could decrease to 0.0384 ± 0.0079 mg/L on nine days of study with the effectiveness of this reduction is $49.56 \pm 10.41\%$.

Water hyacinth plants can bind organic matter from mud particles so that they can purify the waters. Through the roots, chromium waste can be absorbed and then used in metabolic processes so that it absorbs contaminants in the water. This is evidenced by research [35], which stated that in his research on water hyacinth, it was able to reduce TSS by 37% on the 2nd day; 61% on the 4th day, and the largest percentage on the 6th day is 79%. TSS is a solid substance or particles suspended in water in the form of biotic (living) or abiotic (dead) components, for example, sand, silt, and clay [36]. The decrease in COD and TSS with water hyacinth phytoremediation was also carried out by [37] and can decrease by 85.85% and 92.47%, respectively.



Figure 2. Water hyacinth/ *Eichhornia crassipes*.

According to [38], breaking off the roots of a water hyacinth due to a physiological response to defend itself in a polluted environment will cause instability in the removal of Cr (IV). The breaking of water hyacinth roots only affects the level of Cr (IV) removal, while the concentration of Cr (IV) continues to decrease every day.

b. Hyacinth

Hyacinth is an aquatic plant of the species *Eichhornia crassipes*, which can live in water areas. Based on research conducted at PT Vale Indonesia Tbk. by [39], Hyacinth plants within seven days were able to reduce the initial Cr(IV) concentration of 0.88 mg/L to 0.028 mg/L. The ideal plant weight that can be used to achieve quality standards is 77.3 gr/L. In addition, research [40] regarding phytoremediation of industrial mining wastewater using Hyacinth can reduce the concentration of Cr (IV), TDS, and pH in 15 days. Cr (IV) drops to 99.5%. Another study conducted [41] on mine wastewater treatment ponds in 1 ha can reduce BOD (Biological Oxygen Demand) and COD (Chemical Oxygen Demand) by 89% and 71%, respectively.

c. Kayambang/*Salvinia cucullata*

Salvinia cucullata (Figure 3) is a plant that lives optimally with sufficient light, is rich in nutrients [42] and grows at an optimum temperature of 20 -30 C with a pH of 6.0 -7.5 with the ability to remediate Cr (IV) up to 8 mg/L [31]. This plant was able to reduce the concentration of Cr (IV) from 0.0488 mg/L to 0.0315 mg/L during a five-day experiment [33].



Figure 3. Kayambang/ *Salvinia Cucullata*

d. Kiambang/Apu wood/*Pistia stratiotes*

Kiambang (Figure 4) can live in low water quality, so it can be used to improve the environment by absorbing heavy metals in the waters [43]. Based on nutrient requirements, this plant can survive low nutrient conditions but can also survive high nutrient conditions. Exposure due to the presence of Cr (IV) is characterized by brown spots on the edges and tips of the leaves, causing dryness and slow growth. For this reason, the ability of *Pistia stratiotes* to reduce Cr (IV) to 4 mg/L [31]. According to [33], Cr (IV) in the batik industry also decreased from 0.0464 mg/L to 0.0240 mg/L during the five days of the study. In a study conducted [34] at an initial Cr (IV)

concentration of 0.0761 ± 0.0070 mg/L, it was able to reduce Cr (IV) to 0.0505 ± 0.0074 mg/L with an effectiveness value of 33.61 % within nine days.

Watermelon can not only reduce Cr (IV) levels but can also reduce COD in wastewater by 32.94% for 15 days, the greater the length of stay and the number of plants, the lower the COD level [44]. The ability to reduce COD was also explained by [45] a decrease in COD from a concentration of 38.1 mg/L to 18.50 mg/L on day 9 of 51%. The longer the roots and the greater the amount of apu wood used, the smaller the COD and TSS values that can be reduced [46]. Provision for BOD can also be done using kiambang plants to achieve an efficiency of 86.35% [47].



Figure 4. Kiambang/ Apu Wood/ *Pistia stratiotes*.

e. *Hydrilla verticillata*

Hydrilla verticillata (Figure 5) is a plant that grows below the surface of the water. This plant is not included in the category of hyperaccumulator plants [48]. Research conducted [34] on batik industrial waste (pH 7) with initial conditions Cr (IV) of 0.0761 ± 0.0070 mg/L decreased to 0.0678 ± 0.0043 mg/L with effectiveness of $10.84 \pm 5.61\%$ for nine days. *Hydrilla*

verticillata was also able to reduce COD by 79% [49].



Figure 5. *Hydrilla verticillata*.

f. Water bamboo/ *Equisetum hyemale*

Water bamboo, or the Latin term *Equisetum hyemale* (Figure 6), is a plant that is easy to grow anywhere, strong, easy to care for, and resistant to environmental influences. Water bamboo plants have an average height of 70 cm with a stem diameter of 0.4 – 0.6 cm and an average plant mass of 5.1 grams. This plant also has a high silicate content, which can absorb metals in plant roots [26]. Research conducted on Pb and Cr leachate samples [50] showed that there was a decrease in Pb levels (SNI 06-2516-1991 method) from 2.2923 mg/L to 0.40933 mg/L with an effectiveness value of 67.87%, while a decrease in chromium content (SNI 25611 100 1 method) from 0.3892 mg/L to 0.1510 mg/L or with an effectiveness value of 61.2%.



Figure 6. Water bamboo/ *Equisetum hyemale*.

g. Water spinach/ *Ipomoea aquatica*

Water spinach (Figure 7), which is commonly used as human and animal food, can be used in phytoremediation. The plants were chosen because they can utilize the nutrients present in organic matter to grow and develop so that they can adapt well [51]. In a study conducted [52] that water spinach (100-gram wet weight) can reduce 1.5 mg/L chromium to 1,345 mg/L within 3 days with an effective value of 10.3% then on the 12th day it decreases concentrations up to 0.421 mg/L or 72%, whereas 2 mg/L chromium in 3 days of treatment with water spinach reduced the chromium concentration to 1.267 with an accumulation efficiency of 11.7% and on the 12th day to 0.250 mg/L with an accumulation efficiency of 83%. This reduction process occurs using rhizofilter and phytoextraction where the chromium waste is absorbed by water spinach through the roots and then flows to the leaves and through the stomata is released into the air.



Figure 7. Water spinach/ *Ipomoea aquatica*.

h. *Sagittaria lancifolia*

Sagittaria lancifolia (Figure 8) is an aquatic plant that has aesthetic and beauty values, grows upright and stiff,

and has a height of ± 1 meter with oval leaves like spears, shiny leaf color, and flowers arranged in a swirl, there are 3 white-crowned flowers and greenish petals [53]. Based on research conducted [54] *Sagittaria lancifolia* plants were able to reduce chromium concentrations from a concentration of 5 mg/L to 4,379 mg/L or 87.59%. The ability of *Sagittaria lancifolia* based on the results of the Range Finding Test (RFT) at a chromium concentration of 5 mg/L leaves showed a yellow color (73% percentage of survival). At a concentration of 10 mg/L, the leaves turned yellow and looked wilted (50% percentage of survival).



Figure 8. *Sagittaria lancifolia* [55].

Phytoremediation can be done by combining several types of plants to produce optimal effectiveness. The combination of two types of plants (water hyacinth and watercress) or 3 types of plants (water hyacinth, watercress, and watercress) is effective in phytoremediation in increasing pH and decreasing COD (Chemical Oxygen Demand), BOD (Biological Oxygen Demand), TSS (Total Suspended Solid), ammonia, and water-oil/fat on days 4 and 8 [56].

Advantages and Disadvantages of Phytoremediation

Currently, phytoremediation is an innovative solution because it is considered capable of economically reducing heavy metal concentrations and is safe for the environment without causing negative impacts. Apart from being relatively inexpensive, this technique is also easy to monitor growth, maintenance, and maintenance so that the reduction in heavy metal concentrations can be ensured. The main advantage of the phytoremediation technique over other remediation techniques is its ability to produce secondary waste, which is less toxic, environmentally friendly, non-food plants. It multiplies quickly and can restore the natural state of the environment [57] and [58]. Several plant families have tolerant and hyperaccumulator properties of heavy metals. Various types of plants to break down pollutants, the ability to photosynthesize so that they can produce energy used for the detoxification process, the association of plants with microbes will generate a lot of added value in improving soil [59].

Harvesting of phytoremediation of aquatic plants

The costs incurred in phytoremediation are generally for plowing/building ponds, fertilizing, cultivating plants, plantations, disinfection, weeding, harvesting, and waste disposal [62]. In Hidayati's exposure [63] the success in phytoremediation is strongly influenced by the treatment of plant species. These plants are suitable for accumulating Cr (IV) waste at different pollution levels and varying amounts. Hyperaccumulator plants can absorb heavy metals around 1% of their dry weight. Harvesting is done periodically according to the age of the plant. Post-harvest

is carried out on phytoremediation plants, namely after contamination and accumulation of heavy metals in the next biomass harvesting biomass containing metals, as an effort to reduce volume, the plants will be burned, and the residual fuel will be stored in a particular location [64].

CONCLUSION

Phytoremediation is a technique for waste treatment, one of which is to reduce Cr (VI) levels in mine-made pond/swamp areas. Many aquatic plants can be used for this technique, including Water Hyacinth/ *Eichornia crassipes*; Hyacinth; Kayambang/ *Salvinia Cucullata*; Kiambang/ Apu Wood/ *Pistia Stratiotes*; Hydrilla *verticillata*; Water Bamboo/ *Equisetum hyemale*; Water spinach / *Ipomoea Aquatica*; and *Sagittaria lancifolia*. One of the critical factors that must be considered is the selection of the suitable species that can be used to reduce Cr (IV) concentrations or by combining one or two plants in the same Cr (IV) treatment. Phytoremediation is an easy technique and does not require a large amount of money. The utilization of plants in phytoremediation is expected to be a solution in waste treatment. Some of the literature reviews above can be used as a reference for research to reduce Cr (IV) levels in mine wastewater.

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