



Phytoremediation Study of Water Hyacinth (*Eichhornia Crassipes*) on Zinc Metal Ion (Zn^{2+})

Muhammad Nasir¹, Muhammad Nur^{1*}, Dingse Pandiangan², Susan Marlein Mambu², Siti Fauziah³, Indah Raya⁴, Ahmad Fudholi^{5,6}, Rizal Irfandi¹

¹ Department of Biology Education, Faculty of Teacher Training and Education, Universitas Puangrimaggalatung, Sengkang 90915, Indonesia

² Department of Biology, Faculty of Mathematics and Natural Science, Universitas Sam Ratulangi, Manado 95231, Indonesia

³ Department of Industrial Engineering, Universitas Muhammadiyah Luwuk, Banggai 94711, Indonesia

⁴ Department of Chemistry, Faculty of Mathematics and Natural Science, Hasanuddin University, Makassar 90245, Indonesia

⁵ Solar Energy Research Institute, Universiti Kebangsaan Malaysia, Bangi, Selangor 43600, Malaysia

⁶ Research Center for Energy Conversion and Conservation, National Research and Innovation Agency (BRIN), Serpong 15314, Indonesia

Corresponding Author Email: nurprima333@gmail.com

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ABSTRACT

The high level of community activity around the river has resulted in high levels of heavy metals contained in river water. Commonly found heavy metals such as zinc (Zn), mercury (Hg), and copper (Cu). To reduce or remove heavy metals in the waters, phytoremediation techniques are used. The purpose of this study was to determine the ability of water hyacinth plants (*E. crassipes*) in remediating Zn^{2+} metal in contaminated Lake Tempe water. The research method used includes the sampling process, acclimatization, physicochemical analysis, Zn analysis, Bio-Concentration Factor (BCF), and infrared (IR) analysis. The Zn concentration in Lake Tempe water decreased after 30 days of the phytoremediation process. And the highest adsorbed Zn (II) metal ions on water hyacinth plants was 77,257 ppm on the 30th day. It was found that there is a relationship between the BCF value and the phytoremediation time, the higher the phytoremediation time, the higher the BCF value obtained. IR data show the presence of Zn metal bonds in plants involving the functional groups C=S, C=N, and OH. This indicates that water hyacinth (*E. crassipes*) has the potential to be used as a phytoremediation agent in adsorbing Zn in Lake Tempe waters.

1. INTRODUCTION

Water hyacinth (*E. crassipes*) comes from the Pontedariaceae Family that grows in shallow ponds, wetlands, swamps, slow waterways, lakes, reservoirs, and rivers. The reproduction of this plant is classified as very fast especially in the rainy season, so many think that this plant is a weed or a disturbing plant [1-4]. *Eichhornia crassipes* (water hyacinth) is listed as one of the most productive plants on earth and is considered the world's worst aquatic weed. As a result, this plant is considered a plant that triggers environmental problems. This impacts the environment and economy in all other countries and regions of the world with subtropical or tropical climates. Apart from this, it is based on research that the worst aquatic plants in the world can be used as the best therapeutic pool. The chromatogram assessment developed in thin layer chromatography (TLC) shows a total of eleven amino acids in water hyacinth (shoots and rhizomes) [5], the presence of amino acids in water hyacinth makes water hyacinth a very potential as a phytopremediating agent for heavy metals. The population is very much floating in the water, it can result in increased evapotranspiration (evaporation and loss of water through plant leaves) and decreased oxygen levels in water due to a lack of received sunlight [6]. The presence of water hyacinth in the waters is

not completely detrimental, on the other hand, water hyacinth can absorb heavy metal pollutants [7]. The lack of research on this plant encourages research to review more of the benefits of the water hyacinth (*E. crassipes*).

The high level of community activity around the river has resulted in high levels of heavy metals contained in river water. The increase in metal levels in the waters will be followed by an increase in the levels of these substances in aquatic organisms such as shellfish, seaweed, and other marine life. The use of these organisms as food ingredients will endanger human health [8]. When metals enter the human body, these metals will be accumulated in the body tissues and cannot be excreted any longer outside the body. At levels that are already high in the human body, it will cause serious negative impacts, namely; inhibits enzyme activity so that metabolic processes are disrupted, causing chromosomal abnormalities (genes), inhibiting fetal development, lowering female fertility, inhibiting spermatogenesis, reducing peripheral nerve conduction, inhibiting hemoglobin formation, causing kidney damage, causing blood deficiency or (anemia), swelling of the head (encephalopathy), and cause emotional and behavioral disorders [9].

Several attempts have been made to remove metals, such as nanofiltration [10, 11], ion exchange resins [12], electrocoagulation [13], and adsorption [14, 15]. However,

this method is relatively expensive, less effective and detrimental to health [16]. Another alternative that can be used to remediate metal pollutants is with certain plants that can absorb and accumulate high concentrations of metals known as phytoremediation. Phytoremediation is a remediation method that continues to be developed in the field of science and technology to clean polluted soil, water or air [17], relying on the role of plants to absorb, degrade, transform, and mobilize metal pollutants from the environment. Phytoremediation is also cost-effective, and durable for repair of contaminated sites. The most significant factor in phytoremediation is the selection of suitable plants, their absorption potential to absorb high levels of pollutants, and their ability to survive in polluted waters [18-20]. Water treatment with aquatic plants has been used in many parts of the world, and it has the following benefits: low cost, simple operation, and high pollution treatment rate [21-24]. Aquatic plants such as; Water hyacinth is suitable for phytoremediation because of its fast plant growth, high potential for metal accumulation, and high tolerance to toxic substances so it is potential to be used as a phytoremediation agent, and can tolerate a fairly large variation in nutrients, temperature and pH [20].

Water hyacinth also has the capacity as a bioaccumulator able to absorb anions or cations in waste and can grow quickly and can survive in poor conditions [25].

Several literature reviews related to this study have been conducted including on polluting metals such as cadmium (Cd), lead (Pb) and copper (Cu) metals. Water hyacinth (*E. crassipes*) can reduce cadmium metal (Cd) in polluted water and can reduce the concentration of liquid waste. The advantages of using plant samples are that they can reduce toxic properties faster without damaging the surrounding environment, are more durable, and have high levels of contaminants [26]. Hyacinth has the ability to absorb Pb metal quite high in polluted water [27]. Other studies showed that the absorption of Pb by water hyacinth on the basis of EAPR process was much lower than that in the phytoremediation due to high precipitation of lead metal in the aquatic plume during the electromigration process. While on the similar process, the absorption of Cu was very high in the plant root [28]. This study will evaluate the phytoremediation of water hyacinth on the absorption of Zn metal. In this study, samples were obtained from Lake Tempe, located in South Sulawesi Province, Indonesia. The purpose of this study was to determine the ability of water hyacinth plants (*E. crassipes*) in remediating Zn²⁺ metal in contaminated Lake Tempe water.

2. MATERIALS AND METHODS

2.1 Tempe and water hyacinth (*E. crassipes*) lake water sampling

The sample in this study was obtained from Lake Tempe which is located in Wajo Regency, South Sulawesi. Samples were taken randomly at different points.

2.2 Acclimatization phase of water hyacinth plants (*E. crassipes*)

At this stage, a sample of water hyacinth (*E. crassipes*) is grown in a container that is similar to its environment. It is expected that the sample can adapt and be able to survive until

the end of the study. Samples of water hyacinth (*E. crassipes*) were placed in a square container then added with Lake Tempe water. This acclimatization process was carried out for 7 days without any additional nutrition.

After the acclimatization process was completed, a sample of water hyacinth (*E. crassipes*) with good quality and of the same size (5 cm) was selected for the phytoremediation stage. While the Tempe Lake water sample obtained was added by adding ZnCl₂ with a concentration of 50 ppm.

2.3 Physicochemical analysis of Tempe Lake water samples

The physicochemical analysis includes pH test, total nitrogen, total phosphate as P, TDS test, and TSS test. Analyses were performed before and after the phytoremediation process. Values at zero (0) days are recorded as initial values, while values recorded after phytoremediation are indicated as final values.

2.4 Analysis of Zn levels of water hyacinth plants (*E. crassipes*) and lake Tempe water

The phytoremediation process of water hyacinth plants (*E. crassipes*) which came into contact with Lake Tempe water contaminated with Zn (II) 50 ppm was carried out for 30 days. Testing of zinc content contained in the sample was measured 4 times with 10-day intervals using Atomic Absorption Spectrophotometer (AAS).

2.5 Bio-concentration factor (BCF)

The BCF value shows the magnitude of the ability of a plant to absorb heavy metals contaminated by an area. BCF calculates the amount of metal concentration in plants is directly proportional to the concentration of metals in water [29].

2.6 Infrared (IR) analysis

IR is used to identify functional groups of compounds contained in water hyacinth (*E. crassipes*). Weigh the dry powder of water hyacinth (*E. crassipes*) weighed as much as ± 1 mg to make pellets using KBr. The dried pellets were then analyzed using infrared spectroscopy.

3. RESULTS AND DISCUSSION

3.1 Physicochemical analysis of lake Tempe water

The physicochemical properties of Lake Tempe contaminated with Zn (II) were tested before and after the phytoremediation process with water hyacinth (*E. crassipes*) including pH, TDS, TSS, Total N, total P and Zn for 30 days as parameters for viewing Zn metal contamination in lake Tempe. The phytochemical analysis of Lake Tempe water is in Table 1.

The degree of acidity (pH) is a logarithmic scale to indicate the acidity or alkalinity of a solution. pH affects the toxicity of pollutants and the solubility of some gases and determines the form of the substance in water. The pH of a liquid is determined by the concentration of hydrogen ions or the percentage of hydrogen ions in the solution. The normal pH

value of water is around neutral, which is between pH 6 and 8, while the pH of polluted water varies depending on the pollutant. Table 1 showed that the pH value before phytoremediation was 7.53 to 7.04 after phytoremediation. The pH analysis results showed a decrease in pH in the Tempe Lake wastewater sample. This is because parts of the plant have fallen off and the oxidation process of sulfate formation affects the pH value [30]. The absorption of heavy metals by plants also affects the decrease in pH value. The pH value in Lake Tempe water is still classified as neutral, meaning that pollution is still within the minimum limit so that it will be easier to minimize with the phytoremediation process.

Total Dissolved Solids (TDS) is a measure of the combined content of all inorganic and organic substances in the form of small solids found in water. Excessive solids can increase turbidity so that it will inhibit the entry of sunlight into the water and ultimately affect the photosynthetic process in the water. Table 1 showed an increase in the TDS value from before phytoremediation of 124 mg/L to 129 mg/L after phytoremediation. The increase in TDS value is due to a large amount of deposition of several organic compounds in the growing media, so that plant parts will gradually die over the length of the phytoremediation process. The increase in TDS content is also directly proportional to the level of turbidity in the water, namely the higher the TDS concentration, the higher the turbidity level, and vice versa.

Total Suspended Solid (TSS) is the amount of weight of material suspended in a certain volume of water expressed in mg per liter or ppm. TSS is used as one of the parameters for

measuring the quality of liquid waste that measures organic and inorganic floating solids. The suspended solids in the water causes turbidity so that it blocks the entry of sunlight into aquatic plants. Table 1 shows the results of TSS testing in Lake Tempe water where before phytoremediation the TSS value was 110 mg/L and increased after the phytoremediation process, namely 433 mg/L. The increase in the TSS value is linear with the TDS value. This shows that the levels of dissolved organic or inorganic compounds in the Tempe Lake water increased, which is thought to have originated from the water hyacinth plant (*E. crassipes*).

The content of nitrogen (N) and phosphate (P) in Lake Tempe is considered as an important factor to review the effectiveness of the phytoremediation process. Along with the process of photosynthesis and decomposition in plants, there is also a decrease in total nitrogen and total phosphate concentrations. Table 1 shows that the total nitrogen and phosphate content has increased, where the total nitrogen content is 1.2105 mg/L to 5.6488 mg/L and the total phosphate content is 0.0452 mg/L to 0.0516 mg/L. The increase in nitrogen and phosphate content is due to the presence of fine roots, stems, or leaves on the fallen planting media which then rot in the Tempe Lake water.

Measurement of Zn concentration in Lake Tempe water showed good results at Table 1, where the Zn metal concentration decreased significantly by 1.2258 mg/L to <0.022 mg/L. This shows the ability of water hyacinth (*E. crassipes*) as a phytoremediation agent in reducing Zn²⁺ levels in Lake Tempe water.

Table 1. Physicochemical properties of Lake Tempe water contaminated with Zn (II) metal in phytoremediation experiments with water hyacinth plants (*E. crassipes*)

Parameters	Before	After	Unit	Test Method
pH	7.53	7.04	-	SNI 06-6989.11-2004
TDS	124	129	mg/L	SNI 06-6989.27-2005
TSS	110	433	mg/L	SNI 06-6989.3-2004
Total N	1.2105	5.6488	mg/L	AOAC Official Method 973.48.18 th Ed, 2005
Total Phosphate as P	0.0452	0.0516	mg/L	SNI 06-6989.31-2005
Zn	1.2258	<0.022	mg/L	SNI 06-6989.8-2004

3.2 Test the levels of Zn²⁺ water hyacinth plants (*E. crassipes*) and water using AAS

The concentration of Zn absorbed by water hyacinth (*E. crassipes*) and the concentration of Zn in Lake Tempe water was measured using the Atomic Absorption Spectrophotometer (AAS) method for 30 days which is presented in Table 2.

Table 2. Zn levels in water hyacinth (*E. crassipes*) and Lake Tempe contaminated with Zn

Time (Days)	Levels of Zn in Plants (mg/kg)	Water Levels of Zn (mg/L)	BCF
0	1.9041	1.2258	1.5533
10	46.1808	0.0955	483,5685
20	32.6027	0.3399	95.9185
30	77.2537	<0.022	3862,6850

Measurement of Zn concentration in plants was 1.9041 ppm, while in lake water Tempe was 1.2258 ppm with a BCF value of 1.5533. Zn levels increased in plants with the length of time

of the phytoremediation process, while the Zn concentration in Lake Tempe water decreased after 30 days of the phytoremediation process. And obtained Zn(II) metal ions which were adsorbed the most in water hyacinth plants, namely on the 30th day of 77.2537 ppm. In Table 2, it can be seen that on the 20th day there has been a decrease in the adsorption ability of water hyacinth plants against Zn(II) metal ions, this can be due to water hyacinth poisoning, which is indicated by the occurrence of chlorosis (yellowing of the leaves) in plants water hyacinth.

Chlorosis in this plant is caused by the inhibition of cell metabolism caused by the presence of metal ions that are absorbed by the water hyacinth plant. Excess metal can be toxic to plants and inhibit the work process of nutrients that play a role in plants. The Zn(II) metal ion absorbed by water hyacinth plants has increased again on the 30th day, this can be due to the detoxification process through phytocellin synthesis by water hyacinth plants in greater numbers, so that the water hyacinth can survive, and continue to absorb until the optimum absorption. In this study, the optimum absorption time of Zn(II) metal ions from water hyacinth plants has not been seen.

Plants are also able to produce chelate molecules that function to bind metals, namely phytochelatin-glutathione, where Zn(II) is a borderline acid which will bind to the R-SH group found in water hyacinth phytocellin [31]. When the process of absorption of heavy metals, plants form a reductase enzyme in the root membrane which functions to reduce metals, which are then translocated to other parts of the plant through transport networks, namely xylem and phloem. To increase transport efficiency, the metal is bound by chelate molecules (binding molecules) which are then accumulated to all parts of the plant, namely roots, stems and leaves. Plants carry out an important inductive tolerance mechanism to heavy metals by synthesizing metal binding polypeptides, namely phytokhelatin. Phytokhelatin is formed together with the synthesis of the enzyme glutathione synthetase. Phytokhelatin is synthesized enzymatically by phytochelatin synthase (γ -glutamylcysteine dipeptidyl transpeptidase) from glutathione. The mechanism of metal detoxification by phytokhelatin occurs by means of phytochelatin binding to metals which will then be transported into plant vacuoles for storage. The environment that contains a lot of Zn metal makes the regulatory proteins in these plants to form binding compounds called phytokhelatin. Phytochelatin contains a peptide with 2-8 amino acid cysteine at the center of the molecule as well as a glutamic acid and a glycine at the opposite end. Phytochelatin is formed in the nucleus which then passes through the endoplasmic reticulum (RE), golgi apparatus, and secretory vesicles to reach the cell surface. When it meets metals, phytochelatins will form sulfide bonds at the sulfur end of cysteine and form complex compounds so that Zn and other metals will be carried to plant tissues. Metals can enter cells and bind to enzymes as a catalyst, so that chemical reactions in plant cells will be disrupted. Disorders can occur in the epidermal tissue, spongy and palisade. This damage can be characterized by necrosis and chlorosis in plants [32, 33].

The binding of metals by chelating occurs through root hairs and into the absorption system of water and nutrients. The chelating of the Zn metal can form complex compounds. Phytokhelatin is also an enzyme so that when the binding process occurs, the metal binds to the S (sulfur) group on the amino acid phytochelatin. The complex compounds and salts formed are subsequently absorbed. After absorption occurs in the roots, it will then be translocated to other parts of the plant organs through the transport network apoplastically. The reaction of cysteine (an amino acid that makes up phytochelatin) with metal ions of Zn (II) with metals that form complex compounds can be seen in Figure 1. The high absorption of Zn metal concentrations in water hyacinth plants can be caused because these aquatic plants contain a lot of protein compared to plants another. With the presence of proteins consisting of amino acid groups containing amines and side groups such as carbamides and amines, which have the potential as ligands in accumulating heavy metals. One of the amino acids found in water hyacinth aquatic plants is cysteine which is an amino acid that has a sulfhydryl (SH) group [34].

Bioconcentration measurement (BCF) as a parameter to assess the tendency of a chemical to be absorbed by aquatic plants. BCF is obtained from the ratio between the concentration of chemicals in plants and the concentration of chemicals in water [35, 36]. The higher the BCF value in a plant, the higher its ability to accumulate heavy metals. From Table 2 shows the value of BCF from day one (day 0) to day

30 has increased along with the length of time the phytoremediation process. This shows the ability of water hyacinth as an effective phytoremediation medium in absorbing metals.

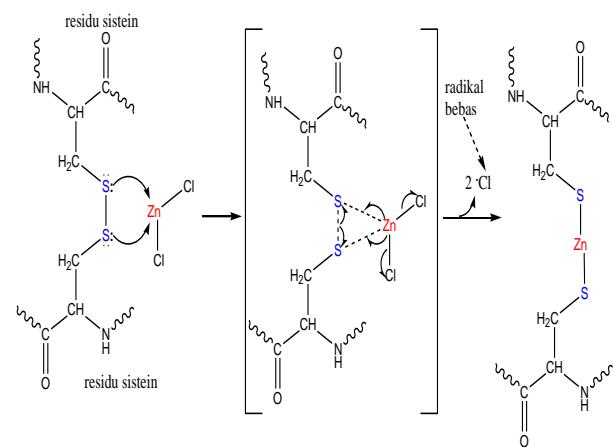


Figure 1. Reaction of cysteine (the constituent amino acids of phytochelatin) with the metal ion Zn(II)

3.3 Identification functional groups of water hyacinth plant

To determine the existence of the biosorption process between water hyacinth plants and Zn metal ions, an IR instrument was used to detect the occurrence of the Zn metal interaction process by comparing the spectrum of water hyacinth plants before and after the phytoremediation process. Figure 2 shows the results of the IR spectrum of water hyacinth plants before exposure to Zn metal (before the phytoremediation process) and Figure 3 shows the results of the IR spectrum of water hyacinth plants after exposure to Zn metal (after the phytoremediation process for 30 days).

IR data on water hyacinth powder shows that there is a shift in wavelength before and after the phytoremediation process in the C=S group from a wavelength of 1040.48 cm^{-1} to a wavelength of 1161.40 cm^{-1} . This causes a shift in the wavelength of about 120.92 cm^{-1} . This peak shift indicates the binding process of metal ions Zn to the C=S functional group found in water hyacinth. The C=N group before phytoremediation has a wavelength of 1635.77 cm^{-1} , whereas, after phytoremediation 1637.60 cm^{-1} , there is a shift in wavelength of 1.83 cm^{-1} , which indicates that there is a binding of metal ion Zn to the C=N group. There was also a shift in the wavelength from 3453.57 cm^{-1} to 3455.62 cm^{-1} , indicating that there was the binding of the metal ion Zn to the O-H group.

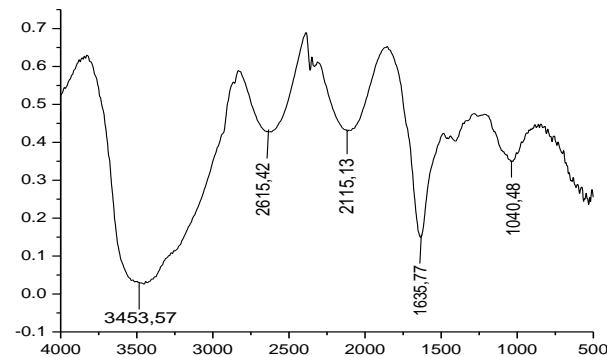


Figure 2. IR water hyacinth before the phytoremediation process

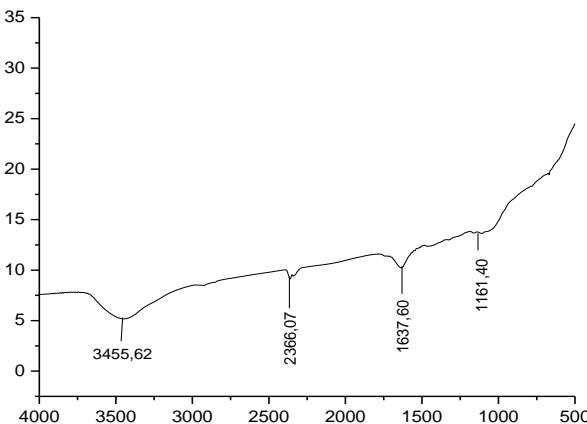


Figure 3. IR water hyacinth after phytoremediation process on planting media contaminated with Zn

4. CONCLUSIONS

The high absorption of Zn metal concentrations in water hyacinth plants can be caused because these aquatic plants contain a lot of protein compared to plants another. With the presence of proteins consisting of amino acid groups containing amines and side groups such as amines, which have the potential as ligands in accumulating heavy metals. One of the amino acids found in water hyacinth aquatic plants is cysteine which is an amino acid that has a sulfhydryl (SH) group. The Zn content in plants increased with the length of time of the phytoremediation process, while the Zn concentration in Lake Tempe water decreased after 30 days of the phytoremediation process. And the highest adsorbed Zn (II) metal ions on water hyacinth plants was 77.257 ppm on the 30th day. It was found that there is a relationship between the BCF value and the phytoremediation time, the higher the phytoremediation time, the higher the BCF value obtained. IR data show the presence of Zn metal bonds in plants involving the functional groups C=S, C=N, and OH. This indicates that water hyacinth (*E. crassipes*) has the potential to be used as a phytoremediation agent in adsorbing Zn in Lake Tempe waters.

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