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Remediation of Cu in the Contaminated Soil by Using *Equisetum debile* (Horsetail)[*]

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Abstract. Paddy fields in the Rancaekek area, Bandung Regency-Indonesia, has been contaminated by textile wastewater. The area needs to recover back to its normal condition and function. Several compounds were found in the soil, such as Cu, Zn, Pb, Cd, Co, Ni, and Cr. Phytoremediation was selected as a site remediation strategy, which employs plants to remove non-volatile and immiscible soil contents. The objective of the study was to determine the ability of Equisetum debile to absorb Cu from the contaminated soil. Cu measurement was conducted by using the AAS (Atomic Absorption Spectrophotometer) method. The study has shown that Equisetum debile can absorb Cu concentrations of up to 25.3 ppm in 60 days after initial planting. However, the Enrichment Coefficient value (0.392) indicated that Equisetum debile was not efficient as a hyperaccumulator plant.

Keywords: *Cu; Equisetum debile; hyperaccumulator; phytoremediation; textile wastewater; enrichment coefficient.*

1 Introduction

The textile industrial area along the Rancaekek-Cicalengka highway (Bandung Regency-Indonesia) has been developing since 1978. This area, which is part of the Citarik sub-watershed, was actually a fertile area of paddy fields. Developments of the textile industry contributed to some determinable impacts on the water and sediment qualities of surface water around those industries, including the Cikijing River. The total area of paddy fields that were directly contaminated by textile wastewater was ± 1215 ha; the area exposed from more than a week-flooding was 254 ha; exposed from less than a week-flooding was 474 ha; and the monthly flooding (rainy season) was 520 ha [1-2].

Suganda, *et al.*, [2] studies show that heavy metals, such as Cu, Zn, Pb, Cd, Co, Ni, Cr were discovered in sludge from textile industrial wastewater. The highest concentration was Cu, Zn and Cr, with concentrations of about 210-680 ppm.

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Cu and Zn concentrations in topsoil (0-20 cm) were between 43-83 ppm and 57-137 ppm, respectively. Their concentrations are higher than other heavy metals' (Pb, Cd and Co).

Heavy metals are natural elements that can contaminate the soil via various human activities, such as mining, industries, atmospheric deposition, excessive use of agrochemicals and waste disposal. The effect of heavy metal toxicity, such as Cd, Ni, Cu and Pb, for animals and plants is well known [3]. Lin, *et al.*, [4] described that heavy metals can come from natural sources, to a certain limit, in water bodies, sediment, and biota; and these heavy metal contents may be increased by industrial wastewater effluents and other human activities.

Based on this background, the contaminated area needs to recover so that it can revert back to its normal condition and function. Rivetta, *et al.*, [5] considered that remediation of contaminated land and groundwater is a common international concern. Salt, *et al.*, [6] concluded that contaminated soils and waters pose a major environmental and human health problem, which may be partially solved by the emerging phytoremediation technology.

Phytoremediation is a site remediation strategy, which employs plants to remove non-volatile and immiscible soil contents. Phytoremediation is also an emerging technology for environmental remediation that offers a low-cost technique that is suitable against different types of contaminants in various media. Phytoremediation is potentially applicable to a diverse range of substances, involving hyperaccumulator plants and radionuclides [7-8]. In this study *Equisetum debile* was used as a hyperaccumulator plant. The plant is a heavy metal tolerant plant species [9]. They are commonly abundant around tailing ponds in mining districts [10].

2 Materials and Methods

2.1 Study Location

This study was conducted in laboratory scale at Industrial Hygiene and Toxicology Laboratory, Environmental Engineering, Institut Teknologi Bandung (ITB). The potted plant was conducted at Environmental Engineering campus area, ITB.

2.2 Soil (Planting Media)

3 (three) soil types were used in this study: contaminated soil (CS), neutral soil (NS), and mixture of soil (MS). CS was taken from Rancaekek paddy fields; NS was taken from Rancagarut, Sumedang; MS was a mixture soil of CS and NS

with ratio CS:NS = 1:5. All soil types were not subjected to rain or water droplets in order to maintain their condition.

2.3 Soil Analysis

Soil texture was analyzed by using Sieve Analysis [11]. Particle size analysis is often used in soil science to evaluate soil texture. Soils rarely consist entirely of one size range. Soil texture is based on different combinations of separate particles of sand, silt, and clay that make up the particle-size distribution of a soil sample [12]. The analysis was conducted to determine soil characteristics.

2.4 Plant Selection

The genus *Equisetum* includes about 25 species and is found throughout the world, except in Australia and New Zealand [13]. *Equisetum* was one of the tolerant plants that grow around tailing ponds and contained 296 ppm Cu in the tailing ash [10]. *Equisetum* can also remove lead and chromium [14]. *Equisetum debile* is a part of the wetland macrophytes, a facultative wetland species, and usually lives in riverbeds, swamps and the fringes of ponds [15-16].

2.5 Plant Acclimatization

Acclimatization is a key step to successful production, because plants need to sufficiently adjust to a new environment [17]. *Equisetum debile* was acclimatized for ± 10 days at 27-28°C, with its normal environment light in greenhouse. 39 pots with volume 1.6 L were provided: 13 pots were filled with CS, 13 pots were filled with NS and 13 pots were filled MS. *Equisetum debile* was cultivated in each pot.

2.6 Sampling

Sample was conducted after the 5th, 15th, 20th, 25th, 30th, 35th, 40th, 50th, and 60th days of planting. In every sampling time, *Equisetum debile* from each type of soil pot was taken, together with the soil. Length, number of stem, number of root, wet weight of *Equisetum debile* were measured. The sample was cleaned and chopped into small pieces, and placed in aluminum foil; the sample was then dried for 2 (two) hours in an oven with a temperature of 120°C.

2.7 Heavy Metal Extractions

Heavy metal concentrations in plant and soil from all samples were measured. Based on the EPA Method 200.2 [18], the analysis was conducted by the acid extraction method. After the dry sample was retrieved, ± 0.25 gram of plant sample and ± 1.5 gram of soil sample were taken. Then, the sample was dissolved in aqua regia (the mixture of HCl : HNO_3 in ratio 1 : 3), and placed on a waterbath for 1 or 2 days. 5 (five) drops of H_2O_2 were given for dissolving any grease and protein. After being left for an hour, the sample solution was filtered and diluted into a volume of 25 ml. The extraction liquid was tested using the Atomic Absorption Spectrophotometer (AAS) method to determine Cu concentration. This procedure was conducted with duplo systems.

3 Results and Discussion

3.1 Soil Condition

The background level method is used in this study; where NS was used as the soil control and the comparison variable to CS. Meanwhile, MS is designed to anticipate the inability of the plants to absorb heavy metals in polluted soil. Based on Paterson [19], the natural background concentrations are those derived solely from natural processes. In the case that there are heavy metal contaminants, these would be derived from weathering of parent materials and redistribution in the soil profile by soil-forming processes.

The result of soil texture analysis is presented in Table 1. The Soil Science Society of America has adopted the USDA classification, that is: sands (< 2000-50 μm), silts (< 50-2 μm) and clays (< 2 μm) [12].

Table 1 Soil texture analysis result.

Soil type	**Particle-size distribution (%)**				**Soil textural classes (Figure 2)**
	Gravel	**Sand**	**Silt**	**Clay**	
NS	1	13	67	19	Silt loam
CS	0	5	57	38	Silty clay loam
MS	1	11	61	26	Silty clay loam

Soil textural classes can be determined by how the value of particle-size distribution from each soil type is represented in the USDA textural triangle [20]. The intersection between the three lines of soil particle-size fraction percent determined the soils' textural classes. NS textural class was silt loam; CS and MS textural classes were silty clay loam. The Soil texture, together with soil structure, helps to determine the supply of water and air in a soil [21]. In general, the higher the percentage of silt and clay sized particles, the higher the water holding capacity. Soil with small particles (clay and silt) has a larger surface area than the larger sand particles. This large surface area allows the soil to hold more of water [22]. In this study, CS textural class indicated a tendency of soil to absorb irrigation water from the Cikijing River, which was polluted.

3.2 Cu Concentration

Soil

Cu concentration in each type of soil at its initial condition is presented in Table 2. Based on Table 2, Cu concentration in CS should be reduced by about 35 ppm to achieve neutral ground state (NS). Cu concentration in each type of soil for the 60 days after planting is presented in Figure 1. The Cu concentration in NS, CS, and MS fluctuated. But the trend showed that the Cu concentration in each soil type decreased from the initial condition.

Table 2 Cu concentration in various type of soil at initial condition.

Type of soil	Cu concentration (ppm)
NS	26.20
CS	61.3
MS	26.5

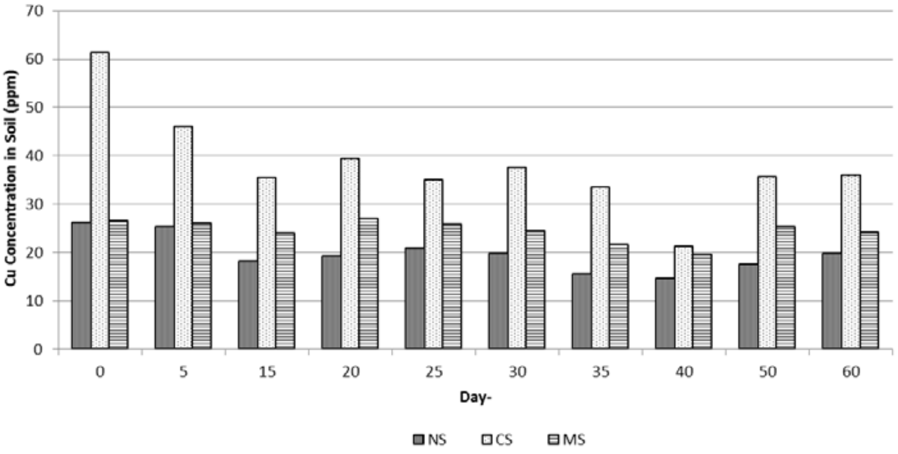

Figure 1 Cu concentration in various type of soil for 60 days of planting.

In CS, Cu concentration at the 60th day was 36 ppm. The concentration decreased by ± 25.3 ppm from initial condition. The biggest concentration decrease was between the 35th and the 40th days, with a value of 12.29 ppm. At the 40th day, Cu concentration decreased below the NS initial condition with a value of 21.24 ppm. It can be concluded that *Equisetum debile* can absorb Cu concentration from the soil, and the effectiveness of *Equisetum debile* in absorbing Cu peaked 40 days after planting.

Plants

Cu concentrations in the root, for the 60 days after planting, is presented in Figure 2 and the Cu concentration in the stem is presented in Figure 3.

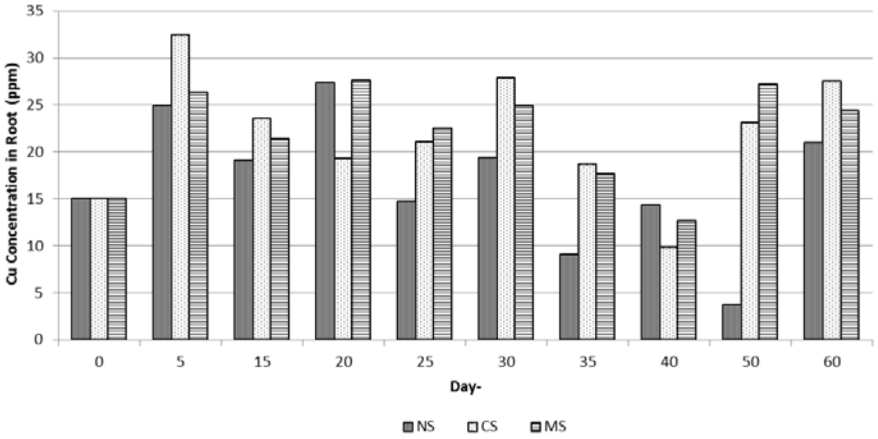

Figure 2 Cu Concentration in Root for 60 days of planting.

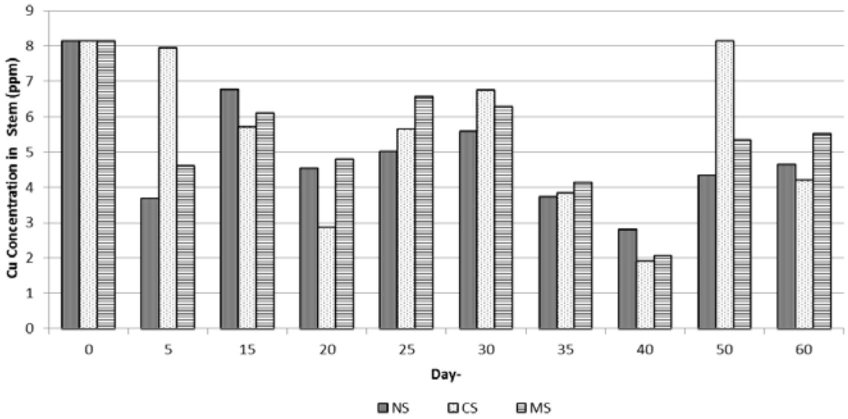

Figure 3 Cu Concentration in Stem for 60 days of planting.

Plants need Cu in small concentrations. The Cu concentration in a plant, in general, is only about 5-20 mg/kg of dry biomass [23]. High levels in accumulation of such heavy metals is highly toxic and would certainly kill the common nonaccumulator plant [24].

Based on Figure 2, on the 5th day, the Cu concentration in the root was increasing; NS was increasing at 9.9 ppm, CS was increasing at 17.42 ppm and MS was increasing at 11.35 ppm. Up until the 60th day, the trend of Cu concentration in the root was increasing. The translocation of heavy metal that occurred in roots and others plant tissue above the soil is: first, the heavy metal is absorbed at the surface of the roots and then it broke through and moved into the root's cells [25]. The chemical elements that were absorbed by the plant's roots are in ions form, which means it was a cation or anion. Root branches are the active part of the roots, and directly touches the chemical element when absorption happens. The amount that can be absorbed by the plants depend on the growth and development of the roots itself. With more roots, the contact surface is wider. It can give more chances for the chemical element to be absorbed [23].

The uptake of metals into root cells, the point of entry into living tissues, is a step of major importance for the process of phytoextraction. However, for phytoextraction to occur, metals must also be transported from the root to the shoot [24].

The initial Cu concentration in the stem was 8.15 ppm. In contrast to the roots, Cu concentration in the stem was decreasing at the 60th day. The absorption mechanism of heavy metals is conducted by roots and then translocated to another tissue or different parts above the soil (shoot) [26]. Translocation of Cu concentrations from the root to stem is hard. Lasat [24] studies show that metals can also be complexed and sequestered in cellular structures (e.g. vacuole), thus becoming unavailable for translocation to the shoot. The movement of metals from the root to the shoot, termed translocation, is primarily controlled by two processes: root pressure and leaf transpiration.

The results showed that Cu had accumulated more in the root part, than the stem part. Arduini, *et al.*, [27] has studied that the poor translocation to the aerial parts may be part of a defense strategy to avoid serious shoot damage. The result also agreed with Hidayati [8], which said that excess Cu will accumulate in the roots, with few Cu translocations into other parts of the plant.

3.3 Enrichment Coefficient

Enrichment Coeffient (EC) of heavy metals in the plant is presented in Eq. (1) [28]:

$$EC = \frac{[Element]_{shoot}}{[Element]_{soil}} \tag{1}$$

EC is the important factor to show the potential of plant that used as hyperaccumulator [28].

From Table 3, it can be concluded that for CS, the EC value was decreasing until the 20th day, and then after the 30th day. According to Haque, *et al.*, [29], the decreasing of the EC could be due to saturation, in the transfer of the plant's metal uptake into other plant tissues, of high metal concentrations. This result agrees with the previous discussion. Figure 2 has shown that after the 5th day and 30th day, the root's Cu concentration was decreasing.

Table 3 Enrichment Coefficient (EC).

Day-	EC stem to soil			EC root to soil			EC plant to soil		
	NS	**CS**	**MS**	**NS**	**CS**	**MS**	**NS**	**CS**	**MS**
5	0.146	0.173	0.176	0.985	0.703	1.01	0.574	0.433	0.628
15	0.371	0.161	0.255	1.05	0.665	0.892	0.822	0.408	0.583
20	0.235	0.073	0.177	1.419	0.491	1.018	0.919	0.3	0.641
25	0.24	0.161	0.255	0.702	0.601	0.873	0.487	0.418	0.556
30	0.284	0.18	0.256	0.983	0.742	1.014	0.64	0.469	0.668
35	0.36	0.114	0.191	1.249	0.557	0.814	0.819	0.337	0.515
40	0.193	0.091	0.106	0.98	0.464	0.644	0.617	0.284	0.405
50	0.248	0.228	0.212	0.216	0.648	1.075	0.232	0.448	0.654
60	0.236	0.117	0.23	1.064	0.763	1.012	0.684	0.433	0.663
average	**0.257**	**0.144**	**0.206**	**0.961**	**0.626**	**0.928**	**0.644**	**0.392**	**0.590**

The previous discussion also mentioned that *Equisetum debile* can absorb Cu content in contaminated soil. However, the result from Table 3 shows the the average EC value of CS from plant to soil was below 1 (0.392). It was implied that even though *Equisetum debile* has an ability to absorb Cu, it was not efficient as a hyperaccumulator plant for contaminated soil. The efficiency of *Equisetum debile* in absorbing heavy metal could be improved by stimulating the growth of rhizospheric microorganisms at the root, and enhancing the metal bioavailability with synthetic chelators [24].

4 Conclusions

The study has shown that *Equisetum debile* is a Cu tolerant plant and can absorb Cu concentrations. 40 days after planting was the most optimal day for *Equisetum debile* to absorb Cu. The Enrichment Coefficient (EC) value from plant to soil, which was 0.644 for NS, 0.392 for CS and 0.59 for MS, indicated that even though *Equisetum debile* can absorb Cu in the soil, the plant was not efficient as a hyperaccumulator plant. Other hyperaccumulator plants could be used to recover the contaminated area.

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