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ADSORPTION AND DISTRIBUTION OF CADMIUM, CHROMIUM, AND COPPER IN WATER BAMBOO (*EQUISETUM HYEMALE*)

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Abstract

Currently, water contamination by poisonous heavy metals such as cadmium (Cd), chromium (Cr) and copper (Cu), is a severe environmental issue. Water remediation, therefore, is needed, such as by using environmental-friendly phytoremediation method. One of the potential plants to be a phytoremediator in tropical countries like Indonesia is Water Bamboo (*Equisetum hyemale*). This study is aimed to understand the absorption and distribution of heavy metals in Water Bamboo. The research stage include: 1) plant election and acclimation stage; 2) preparation of growth medium; 3) determination of contact time; 4) determination of maximum heavy metals concentration; and 5) determination of heavy metals content in growth media solution, root and stem of water bamboo by Atomic Absorption Spectrophotometer (AAS). As a result, the optimal contact time for the most maximum absorption of all metals is 10 days. Water Bamboo can absorb Cd at the maximum concentration of 10 mg/L, while Cr and Cu at the concentration of 15 mg/L. The distribution of heavy metals is mainly absorbed in the root than in the stem. This work opens the possibility of using the root of Water Bamboo for removal of heavy metals in wastewater

Keywords: Heavy metals, Remediation, Water bamboo.

1. Introduction

Human needs, technology development, and science lead to several negative impacts in terms of environmental issues. The adverse ecological effects are mainly derived from numerous industrial activities, mining, agriculture, and transportation. Several forms of environmental problems include air pollution, water pollution, and soil pollution due to the degradation of environmental quality. One environmental issue that pays much attention to is environmental pollution by disposing of heavy metal waste in the water. Cadmium (Cd), chromium (Cr) and copper (Cu) are several significant heavy metals that are frequently recognized as poisonous contaminants in water [1].

Heavy metals have similar characteristics as other metals [2]. The difference is their effect when they get into the body of a living organism [3]. Some heavy metals have biochemical and physiological functions. Moreover, heavy metals are inorganic compounds that generally have toxic properties. Heavy metals are classified as pollutants in the environment because of their stable form and are difficult to degrade [4]. Besides its toxicity to a living organism, heavy metals will accumulate in sediments and biota through gravity, bioaccumulation, bioconcentration, and bio-magnification processes by aquatic organisms [5, 6].

One of the environmental-friendly recoveries is phytoremediation [1]. Phytoremediation is the utilization of plants to remove, displace, stabilize or destroy the pollutants, whether organic or inorganic compounds, from contaminated soil or waters [1, 7, 8]. One of the tropical plants having potential as a heavy metal phytoremediator is Water Bamboo (*Equisetum hyemale*) [9-12]. Water Bamboo is abundant in Indonesia. Water bamboo has roots that can absorb metal strongly and contain chelating compounds that can bind metals tightly [12, 13] Therefore, in this study, we use Water Bamboo as an adsorbent of heavy metals through phytoremediation [1, 7].

This study is aimed to investigate the absorption contact time of heavy metals Cd, Cr and Cu in Water Bamboo and to understand the absorption and distribution of those heavy metals in Water Bamboo. The main novelty of this research is the information of absorption and distribution of Cd, Cr and Cu in Water Bamboo, which can be used to reduce heavy metal waste in the environment.

2. Experimental

2.1. Materials and chemicals

Materials used in this experiment is Water Bamboo *(Equisetum hyemale)* as a phytoremediator. We also used KH_2PO_4, KNO_3, $Ca(NO_3)_2.4H_2O$, $MgCl_2.6H_2O$, HNO_3, $CuSO_4.5H_2O$, $ZnSO_4.7H_2O$, $CdSO_4$, and K_2CrO_4 as reagents and solution for growth medium. All chemicals were pro analyst grade and purchased from Merck (Germany).

2.2. Apparatus

The concentration of heavy metals in growth medium before and after treatment and in Water Bamboo were measured by Perkin Elmer 5100 PC Atomic Absorption Spectrophotometry (USA). The operational conditions of AAS as described in Table 1.

Table 1. Operational conditions of AAS.

Metals	Cd	Cr	Cu
Wavelength (nm)	228.80	357.87	324.75
Slit width (nm)	0.7	0.7	0.7
Relative noise	1	1	1
Char. concentration (mg/L)	0.028	0.078	0.077
Sensitivity check (mg/L)	1.5	4	4
Linear to (mg/L)	2	5	5
Oxidant	Air	Air	air
Oxidant flow (L/min)	10.0	10.0	10.0
Acetylene flow (L/min)	2.5	3.3	2.5

2.3. Plant election and acclimation stage

Water Bamboo was chosen based on the morphology. The plants should be fresh, challenging, and were not break easily. Before used, the Water Bamboo was cleaned and acclimated. The acclimation stage was an adaptation process for the plant into the new environment. The acclimation stage was conducted in 2 steps. The first step was acclimating the plant to demineralized water for two days. The second step was adapting the plant in nutrition solution for three days.

2.4. Growth medium

Nutrition solution for the growth medium was made by mixing 0.00676 g of KH_2PO_4; 0.252 g of KNO_3; 0.59 g of $Ca(NO_3)_2.4H_2O$; and 0.20 g of $MgCl_2.6H_2O$ [14-16] and diluted in one Litre of aquabidest. The growth media was an opened cylinder vessel containing 500 mL of synthetic wastewater (Cd, Cr, and Cu). Water Bamboo was then placed in the vessel to determine the optimum contact time using heavy metals concentration of 5 mg/kg for a duration of 5, 10, and 15 days, respectively. After the optimum contact time was determined, the maximum concentration of metals absorbed were optimized using synthetic wastewater solution of 5, 10, and 15 mg/kg. Figure 1 shows the research flow chart.

2.5. Heavy metals analysis in growth media solution and water Bamboo

Each polluted water in the vessel was drawn as much as 50 mL and filtered to get a clear sample. The actual sample was then destructed using 1 mL of concentrated HNO_3 63% at a temperature of 150°C until the volume was reduced by 10 mL and the solution became clear. The destructed samples were then cooled and diluted in a 25 mL volumetric flask using demineralized water for further AAS analysis.

Digestion of Samples. The root and stem of Water Bamboo was cleaned and cut into small parts. It was then dried at a temperature of 105ºC around 1.5 hours to remove water content. The dried sample was then grounded to obtain a fine powder. One gram of this fine powder was mixed with 10 mL of concentrated HNO_3 63% and then heated in a hotplate[15]. The temperature used was 90°C for 20 minutes and increased to 150°C for 1 hour until all dissolved and became a clear solution. The resulting solution was then diluted in a 25 mL volumetric flask using demineralized water for further AAS analysis

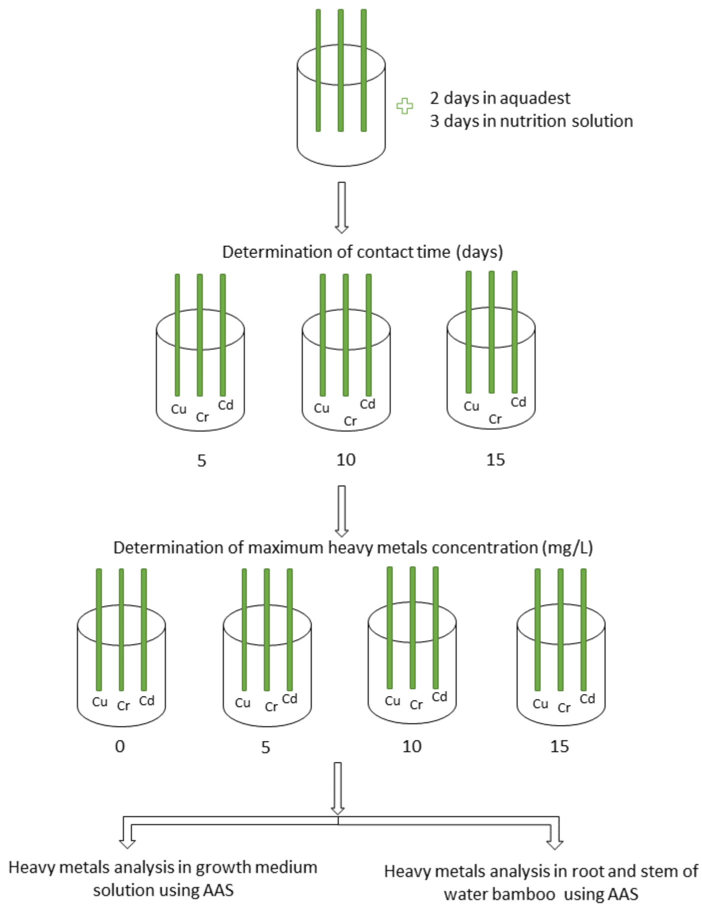

Fig. 1. Research flow chart.

3. Result and Discussion

3.1. Optimum contact time of heavy metals

Determination of the optimum contact time was used as a reference to identify the metal exposure limit on how much the plant was able to absorb optimally. In this study, the initial concentration of growth medium used was 5 mg/L with different contact times; 5, 10, and 15 days. The rest concentration of heavy metals in growth medium was then measured, as shown in Fig. 2. Figure 2 shows that Water Bamboo can absorb heavy metals. The longer the contact time, the metal concentration in the growth medium solution decreases. The concentration of heavy metals in growth medium solution were significant decrease after five days of contact. This showed that after 5 days, 97-99% of the metal has been absorbed by the plant. This shows that in the first 5 days,

Water Bamboo has the ability to quickly absorb almost all metals. After 10 days, mostly all heavy metals have been absorbed by the Water Bamboo, except Cd. The rest Cd in growth solution is about 0.06 mg/L. However, after 15 days of contact time, some Copper is desorbed back into the growth medium. Water Bamboo could release back the absorbed copper. It is inferred that Water Bamboo has a saturation point to absorb copper. The saturation point is the maximum time limit of plants in absorbing contaminants [7, 17]. The ability of plants to absorb the contaminant decreases after the plants pass the saturation point. The plants released back the absorbed heavy metals [18, 19]

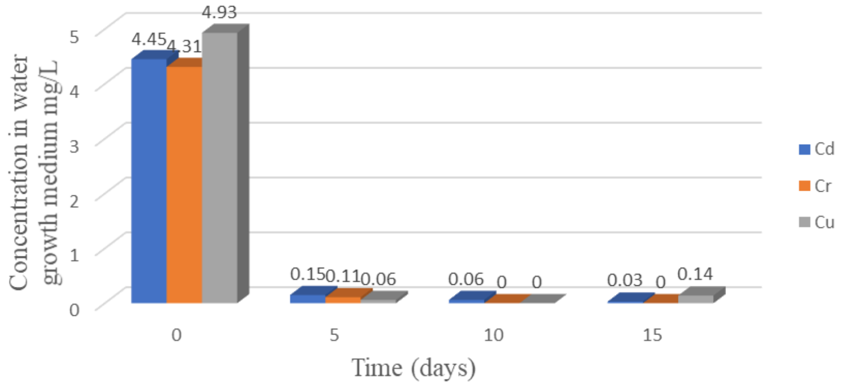

Fig. 2. The concentration of Cd, Cr, and Cu in growth medium solution after metals absorption by Water Bamboo.

3.2. Absorption and distribution of heavy metals in water Bamboo

Water Bamboo's ability to absorb and distribute heavy metals Cd, Cr, and Cu had been known [12]. Absorption activity is based on the concentration of heavy metals in the growth medium and absorption treatment. In this study, the absorbed heavy metals are based on the absorption using root and stem with various concentrations of heavy metals (5 mg/L, 10 mg/L, and 15 mg/L).

The contact time used was 10 days for all metals. Table 2 shows the concentration of heavy metals in growth medium and Water Bamboo after absorption. Water Bamboo can adapt and survive in water containing heavy metals Cd, Cr, and Cu. Water Bamboo can absorb and distribute heavy metals. The absorption and distribution of heavy metals by Water Bamboo are divided into 3 processes: the heavy metals are absorbed by root, translocation of metals from root to another plant part, and metals localization in plant cell [6, 12, 19].

Figure 3 shows the mechanism of heavy metals absorption. The hair roots of Water Bamboo have a plasma-membrane, which can absorb heavy metals strongly. The adsorbed metal is then bonded by the chelating compound and distributed to the stem through the xylem [18].

Table 2 also reveals the concentration of heavy metals in growth medium solution after metal absorption varies depending on the type of metal. The concentration of Cd, Cr, and Cu in the growth medium solution after absorption, below 0.06 mg/L for initial concentration of 5 mg/L and below 0.50 mg/L for initial concentration of 15 mg/L. This indicates that almost all of those metals (up to 98.8%) was absorbed by Water Bamboo. Other study also used Water Bamboo to reduce Fe in leachate. The results of the research showed that after 7 days, the Fe concentration was only reduced by 11% [13].

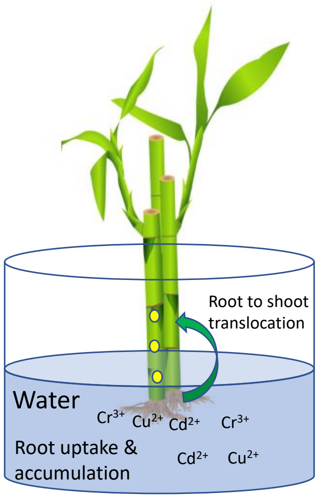

Fig. 3. Absorption and distribution of heavy metals by water Bamboo.

Table 2. The concentration of heavy metals in growth medium and water Bamboo after absorption.

Heavy metals	Optimum time (days)	Initial concentration (mg/L)	Concentration after absorption		
			Growth medium (mg/L)	Root (mg/kg)	Stem (mg/kg)
Cd	10	5	0.06	90.69	2.13
		10	0.28	162.53	12.76
Cr	10	5	0.00	189.46	7.54
		10	0.03	320.54	9.72
		15	0.13	689.90	29.52
Cu	10	5	0.00	136.30	0.12
		10	0.30	370.10	17.47
		15	0.49	544.88	23.99

The absorption of heavy metals increases as increasing the concentration of heavy metals in the growth medium solution. The concentration of Cd in roots was 90.69 mg/kg in the first 5 days and increased to 162.53 mg/kg after 10 days. The concentration of Cd in stem was 2.13 mg/kg in the first 5 days and increased to 12.76 mg/kg after 10 days. The same thing happened to Cr and Cu absorption, where the maximum concentration of Cr and Cu in the roots was 689.90 mg/kg and 544.88 m/kg after 15 days, whereas in the stem only reach a maximum of 20.00 mg/kg after 15 days. This indicates that Cd, Cr, and Cu are more distributed in the roots than in the stems[18].

Metal localization Mostly occurs in roots, anticipating toxicity effect to other plant cells. Root shows high heavy metal distribution due to contact of this plant part with growth medium directly, and the first part absorbs the heavy metal contaminants. Absorption process of nutrition solution is done by root tip using meristem tissue [6, 20]. It happens because of the attractive force of water molecules in the plant. Heavy metals are absorbed by roots in the form of soluble ion and nutrients [21]. The absorbed metals transport into xylem and enter the stem [16, 22-25].

Based on data in Table 2, it can be seen that Water Bamboo absorbs more Cr than Cu and Cd. As it is known that the atomic relative of Cr = 52 gram/mol, Cu =

63 gram/mol, and Cd = 112 gram/mol, this shows that lighter metals are absorbed more quickly into the roots and stems of Water Bamboo than the heavier metals. In addition, beside relative atomic, metal toxicity level also affects metal absorption by Water Bamboo. Water Bamboo has survival power, which is more toxic metals will be absorbed less [24, 25]. Water Bamboo absorbs less Cd, because Cd is more toxic and inhibits nutrient absorption [22, 23].

To understand the mechanism of heavy metals by Water bamboo, we tested absorption models. The kinetic models of heavy metals absorption can be determined by plotting the concentration versus contact time data. Table 3 shown the regression coefficient (R^2) of heavy metal absorption kinetics (Cd, Cr, and Cu) in Water Bamboo. As shown in Table 3, the kinetic model of heavy metals absorption in Water Bamboo refers to Pseudo second order.

Table 3. The regression coefficient (R^2) of heavy metal absorption kinetics (Cd, Cr, and Cu) in Water Bamboo.

Heavy Metal	**R^2**					
	First Order	**Second Order**	**Third order**	**Pseudo first order**	**Pseudo second order**	**Korsmeyer-Peppas**
Cd	0.8594	0.9574	0.7949	n/a	0.9999	10^{-5}
Cr	0.0345	0.0786	0.0670	n/a	0.9999	0.0667
Cu	0.2627	0.0047	0.0148	n/a	0.9996	0.4926

Based on Table 3, we calculated the constants of absorption rate of heavy metals. Table 4 shows the constants of absorption rate of heavy metals in Water Bamboo, which it follows a pseudo second-order model. This phenomenon can be assumed that the heavy metal absorption occurs in a large concentration in a short time [28, 29]. This is evidenced by the absorption of 98.8% heavy metals in the first 10 days. Generally, the concentration of heavy metals (Cd, Cr, and Cu) uptake within the plant increased as time progressed. Other study also found that the best fit was obtained with the pseudo-second-order kinetic model for Water Bamboo [26].

Table 4. The constants of absorption rate of heavy metals in water Bamboo.

Heavy Metal	**Pseudo second order**	
	R^2	**k (mg^{-1} day^{-1})**
Cd	0.9999	1.016
Cr	0.9999	1.006
Cu	0.9996	1.012

4. Conclusions

The Water Bamboo can absorb 98.8% Cd and all Cr and Cu after ten days of contact time. The Water Bamboo has the ability to absorb Cd at a concentration of 10 mg/kg, otherwise Cr and Cu at 15 mg/kg for 10 days. Chromium and copper are absorbed more than cadmium. The Cd, Cr, and Cu are mostly distributed in the root. Absorption of Cd, Cr, and Cu by Water Bamboo can be well described by the pseudo-second-order model equation. This study implies that Water Bamboo could be a potential environmental-friendly phytoremediator for heavy metals contaminated water in a tropical country like Indonesia

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