CONTENT OF HEAVY METALS IN THE WATER AND WATER HYACINTH (*Eichhornia crassipes*) IN WATER BODIES RECEIVING WASTEWATER FROM TEXTILE INDUSTRY (Case study: Cikacembang River, Majalaya Districts, Bandung Regency)

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Abstract: Cikacembang River is including the worst water quality, from a total of 56 industries in the District Majalaya, 22 textile industry throw waste into the Cikacembang River with an average daily discharge 66,058 m^3/day (BPLHD Bandung regency, 2012). Effluents from textile industry contains high amounts of metal, especially cadmium, chromium, copper, and leadthat are harmful to living things. Utilization of aquatic plants for wastewater treatment is an economical method of wastewater treatment contaminated by heavy metals. Therefore, to reduce the content of heavy metal in the Cikacembang River, it isdone phytoremediation by using the water hyacinth (*Eichhornia crassipes*) with two different methods, namely continuous system (field) and continuous system (laboratory). The content of heavy metals Cd, Cr, Cu, and Pb in the water and the water hyacinth (*Eichhornia crassipes*) were measured using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The result showed that the metal content in the water and the water hyacinth (*Eichhornia crassipes*) in batch and continuous systemsis different, the effectiveness of the water hyacinth plant (*Eichhornia crassipes*) to absorb metal in a batch system is better than continuous system because the batch system can reduce Cd metal, Cr, Cu, and Pb respectively 1.19%, 57.95%, 88.18%, and 0.29%. In the continuous system, the water hyacinth plant (*Eichhornia crassipes*) can only reduce about Cd 74.68% and Cu 46.41%, while Pb and Cr increased -138.69% and -28.90%.

Keywords: Cikacembang River, phytoremediation, water hyacinth (*Eichhornia crassipes*), batch system, continuous system

INTRODUCTION

Based on the monitoring results by the Ministry of Environment (MOE) and Environment Monitoring Agency (BPLHD) West Java, along in 2009, 2010 and 2011 status Citarum heavily polluted river water. Iriany and Rachmatiah research (2014) showed that an increase in pollution from upstream to downstream in Upstream Segment Citarum shown by an increase in toxicity in Onion (*Allium cepa*) and a decrease in diversity makrozoobenthos.Citarum River has tributaries which one of them is Cikacembang River which is located on Citarum River Upstream. Based on data from BPLHDs Regency Bandung (2012), the river Cikacembang is including the worst river water quality, from a total of 56 industries in the District Majalaya as many as 22 pieces of textile industry Cikacembang throw waste into the river with an average daily discharge 66,058 m^3/day. Based on Puslitbang research (2010), Cikacembang River upstream side have the quality status of being contaminated, whereas Cikacembang River downstream has heavily polluted the quality status. Textile industry effluent contains high amounts of metal, especially chromium, copper, and cadmium that are harmful to living things (Deepali and Gangwar, 2010).

Textile industrieswhich throw waste into Cikacembang River have done treatment of physics, chemistry, and biology before disposing of waste, but the condition is still toxic Cikacembang River so that the necessary efforts to further processing (Maulani and Rachmatiah, 2014). This is because the textile industry effluent contains high amounts of metal, especially chromium, copper, and cadmium that are harmful to living things (Deepali and Gangwar, 2010). Cikacembang River water is toxic even though no cause of death in Nile Tilapia (*Oreochromis niloticus*), but change the overall parameters of the blood, increasing the number of erythrocyte abnormalities and cause abnormalities in the secondary lamela gills (Azlia and Rachmatiah, 2015).

Utilization of aquatic plants for wastewater treatment which is contaminated by heavy metals is an economical method (Rai, 2010). The response of plants is absorbing metal directly through the roots at a rate absorption of the metal which may reach 90-95% depending on the species, the concentration of the metal, and environmental factors such as pH, temperature, and other (Chakraborty and Mukherjee, 2012). The use of plants to remove, move, stabilize, or destroy contaminants called phytoremediation (Dhahiyat, 2011). The strengths of phytoremediation is environmentally friendly, low cost, sewage treatment aesthetically pleasing, and is especially suitable for developing countries. Plants used in phytoremediation should have a large enough capacity in metal uptake, accumulation, and the ability to process in a short time (Singh *et al.*, 2012).

Some aquatic plants that can be used as phytoremediation plants are kiapu (*Pistia stratiotes L.*), kiambang (*Salvinia molesta*), and water hyacinth (*Eichhornia crassipes*) (Dhahiyat, 2011). *Eichhornia crassipes* can be used to reduce the content of heavy metals Cd, Cr, Cu, Pb, Zn, and Ni (Singh et al, 2012; Yapoga et al, 2013; Komy et al, 2012; Gaherwar and Kulkarni, 2012). In this study, the water hyacinth (*Eichhornia crassipes*) is used to reduce heavy metals in Cikacembang River with continuous system and batch systems in the laboratory. The analysis was conducted to determine the concentration of metals Cd, Cr, Cu, and Pb in water and plants by using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) is compared with the content of water quality standards under Regulation 82 of 2001 Class II, namely 0.01 mg/L, 0.05 mg/L, 0.02 mg/L, and 0.03 mg/L for each of the metals Cd, Cr, Cu, and Pb and quality standards at the plant recommended by WHO 0.02 mg/kg, 1.30 mg/kg, 10 mg/kg and 2 mg/kg for each of the metals Cd, Cr, Cu, and Pb (Nazir *et al.*, 2015). BCF calculation and reduction of metals in water calculated to determine the absorption of metals Cd, Cr, Cu, and Pb in water hyacinth (*Eichhornia crassipes*). Ability of the metal bioaccumulation can be estimated from the classification of bioaccumulation is low (0-100 L / kg), medium (100-1000 L / kg), and high (> 1,000 L / kg) (Van Eszh, 1997 in Amriani et al, 2011). The purposes of this study are knowing the reduction of heavy metals in the river water Cikacembang and accumulation as well as differences in the absorption of heavy metals Cd, Cr, Cu, and Pb by water hyacinth (*Eichhornia crassipes*) in phytoremediation process Cikacembang River using batch and continuous systems.

METHODOLOGY

Continuous Systems Research (Field)

Continuous system research starting from July 2014 through December 2014 with details of a field survey (May 9, 2014), sampling baseline (July 3, 2014 and August 11, 2014), installation trial of the plant net (7 and October 11, 2014), continuous system research in Cikacembang River (November 2014), extraction of metals in Industrial Hygiene Laboratory, Environmental Engineering Institute of Technology Bandung (ITB) (November and December 2014), and testingof heavy metal by using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) in laboratory Service Center for Basic Science, University of Padjadjaran (PPBS-UNPAD) (March, 2015). Equipment used in the continuous system is anet of 2 x 1 x 1.5 m with a mesh size of 5 mm, bamboo, tarpaulin size of 3 x 4 m, 250 ml plastic bottles, plastic zip, shovels, buckets, cool box , blue ice, cameras, DO meter, pH meter and conductivity meter. Water hyacinth (*Eichhornia crassipes*), which is used in a continuous system from Ciparay areas which has a large and small size with an averagewet weight of each size is 71.78 and 24.29 grams. Research continuous system was carried out for 4 weeks, but it will only be explained for 1 week to compare with the batch system. Sampling (water and plants) done on days 0, 3, 5, and 7.

With reference to the SNI 6989.57-2008 water sampling in all the points were done in 0.5 x depth of the surface due to river discharge an average of less than 5 m^3/sec. Samples of water and then put in a plastic bottle of HDPE (High Density Polyethylene) measuring 250 mL. Water hyacinth (*Eichhornia crassipes*)samples were taken by 2 pieces large and small, and put them in a zip plastic. Samples were stored in a cool box to keep cool at 4 ° C.

Batch Systems Research (Laboratory)

Batch systems research and metal extraction were done at the Laboratory of Industrial Hygiene, Environmental Engineering Institute of Technology (ITB) in November and December 2014, and the measurement of the concentration of metals using the tool Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) was done in laboratory Service Center for Basic Science University Padjadjaran (PPBS-UNPAD) in March 2015. The object of the research is the water hyacinth (*Eichhornia crassipes*) obtained from rice fields in the area of Ciparaywhich has smaller size than in continuous systems with an average wet weight of 13.47 grams. The equipment used in batch systems research are glass beaker 50 ml, 250 ml Erlenmeyer flasks, flasks of 50 ml and 25 ml, funnel glass, watch glass, spatula, analytical balance, an electric stove, a water bath (water bath), refrigerator, oven, vaporizer cup, plastic zip, glass bottles, plastic bottles of 30 ml and 60 ml, papers, camera, and filter paper whatmann number 42 with a diameter of 90 mm. Materials used in batch systems research were HNO_3, HNO_3 10%, concentrated HCl, concentrated H_2SO_4, H_2O_2 10%, and aquabidest.During the research, plants were stored in racks in the aquatic laboratorywhich provided by the artificial lighting system (TL lamps 40 W, light intensity 900-1200 lux) to replace the function of sunlight. Sampling (water and plants) was done on days 0, 3, 5, and 7.

Extraction of heavy metals in water is based on Standard Methods, 5th edition (2001) following the research conducted by Nurfitri (2010) is by concentrating the 250 mL water sample with 10 ml of HNO_3. Subsequently, the sample was heated to less than 50 mL volume. After that, the sample was diluted with distilled water until reaching the volume of 50 mL. Based on Amalia research (2012), extraction of heavy metals in plants is based on SNI-06-2464-1991 were weighed wet weight of the whole plant samples using an analytical balance. After that, the sample was separated between the leaves and roots. Further samples were chopped and mashed. The sample was then dried in an oven at 105°C for 2 hours. The oven wasused for the research is Precision Oven Economy models. Furthermore, the dry weight of the sample was weighed. Aquaregia (mixture of HCl: HNO_3 with a ratio of 3: 1) of 10 ml for every 1 gram dry weight of the sample is then given to the sample. Samples were heated in a water bath Boekel series models 020 070 1494RS-2 during a day and night. The sample then was filtered and diluted up to 50 mL volume.

Testing and Data Analysis

Testing of content of metals in water samples first of all was done by extracting the metal content in the water and plants. The content of metals in the samples were analyzed using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) brand Agilent Technologies type 700. ICP is a common tool used to detect various kinds of metals in the different samples. The main principle in determining element ICP is the injection of fluid and then element atomization, this technique is based on the spontaneous emission of photons from atoms and ions that have excitation in radio frequencies (Hou and Jones, 2000). The data obtained should be converted to the suitability of the data by the weight of samples using **Equation 1** until**Equation 6**.

$$\text{Concentration of heavy metals in water}\left(\frac{\text{mg}}{\text{kg}}\right) = \frac{\text{ICP Result (ppm) x 50 mL}}{\text{250 mL}} \quad \textbf{(Equation1)}$$

$$\text{Concentration of heavy metals in the roots}\left(\frac{\text{mg}}{\text{kg}}\right) = \frac{\text{ICPResult (ppm) x 25 m}}{\text{Weight of dry sample (g)}} \quad \textbf{(Equation2)}$$

$$\text{The concentration of heavy metals in the shoots}\left(\frac{\text{mg}}{\text{kg}}\right) = \frac{\text{ICP Result(ppm) x 25 m}}{\text{Weight of dry sample (g)}} \quad \textbf{(Equation3)}$$

$$\text{Efficiency of metal reduction} = \left(\frac{\text{Co}-\text{Cx}}{\text{Co}}\right) \text{x } 100\% \quad \textbf{(Equation4)}$$

Where Co = Concentration of metal on day 0

Cx = metal concentrations on day 7

Bioconcentration factor (BCF) can be determined using the following equation (Soemirat, 2005):

$$\text{BCF (L/kg)} = \frac{\text{concentration of metals in plants}\left(\frac{\text{mg}}{\text{kg}}\right)}{\text{concentration of metals in water}\left(\frac{\text{mg}}{\text{L}}\right)} \quad \textbf{(Equation5)}$$

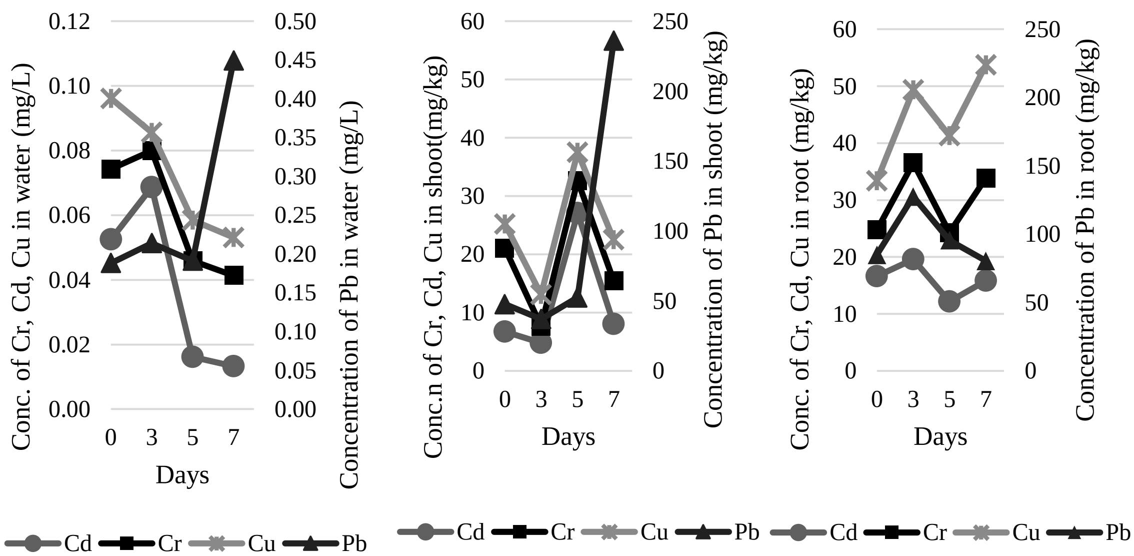
RESULTS AND DISCUSSION

Results of Continuous Systems Research (Field)

Metal content in the water and the plants in continuous system were fluctuated within 7 days because of the activity of the textile industry which dispose of wastewater into the river. Fluctuation of water metal content in Cikacembang River can be seen in **Figure 1**.

a. Cadmium (Cd)

Content of Cd in the water exceeded the quality standard (0.01 mg/L) which is between 0.01 to 0.07 mg/L. According to Siantiningsih (2005), Cd binds with small minerals so it's easily lifted from the bottom to the river. Cd uptake by roots and shoots will increase with increasing of metal concentration in the media. Cd concentrations in



a) Water b) Shoot c) Root

Figure 1. Content of Cd, Cr, Cu, and Pb in Continuous System Research

the shoots increases and decreases in the range 6.70 to 27 mg/kg, while the roots in different ranges which are not too far away that is from 12.1 to 19.6 mg/kg. Water hyacinth (*Eichhornia crassipes*) reduced Cd metal in water by 74.68%. Mobility and Cd metal solubility in water is high (Delcorso, 2008). Bioaccumulation of metals Cd in shoots were moderate that is 606.81 L/kg and in the root were high bioaccumulation with a value of 1190.91 BCF L/kg.

b. Chromium (Cr)

Chromium is used in the textile industry as a mordant which has resistance to fade so resistant to water, light, and sweat (Kozlowski, 2012). Range of Cr content in water is 0.01 to 0.03 mg/L, which still fulfills the quality standard (0.05 mg/L). Cr concentration in the roots continue to increase from 8.10 mg/kg to 18 mg/kg, while in the shoots decreased from 14.3

mg/kg (day 0) reaches the lowest point of 2.83 mg/kg (day 3) and increased again. Absorption of Cr in water depends on pH, oxidative Cr and concentration, salinity, and the presence of dissolved salts (Singh *et al.*,2012). There is no Cr reduction by plants due to the concentration in the water increases, so the percentage of Cr reduction is -28.90%. Cr metal accumulation levels in leaves on day 7 is in the amount of 262.19 L/kg and in the root of 643.12 L/kg, both of them are including moderate bioaccumulation.

c. Copper (Cu)

Cu contained in the dyes used by the textile industry, each dye is containing Cu as an internal part of the molecular structure of the chromophore (Andarani, 2009). Cu concentrations in water between 0.01- 0.02 mg/L is still in accordance with the quality standards supposed to (0.02 mg/L). Percentage of reduction of Cu by the plants is 46.41%. Cu concentration at shoots increased from 4.20 mg/kg to 7.06 mg/kg and at the root increased from 8.66 mg/kg to 19.08 mg/kg. The rate of accumulation of Cu in the shootsof 601.42 L/kg is including moderate bioaccumulation and at the root of 1691.74 L/kg including high bioaccumulation.

d. Lead (Pb)

Pb metal content range in water is 0.19 to 0.45 mg/L. The high concentration of Pb is because Pb compound is used as a pigment, including white lead (lead carbonate and sulfate), red lead (lead oxide), a variety of lead chromate and lead cyanamide (Eagleson, 1993). Pb concentrations in the roots were in the range 75.67 to 127.59 mg/kg and concentrations in the leaves between 37.04 to 236.17 mg/kg. BCF values of Pb in leaves and roots still relatively moderate bioaccumulation that is 525.32 L/kg in the shoot and 178.88 L/kg at the root. There is no reduction of metal, the concentration of Pb increased by 138.69% from the initial concentration, so the percentage of reduction is -138.69%.

Reduction of Cd, Cr, Cu, and Pb in the continuous system can be seen in Figure 2. It can be concluded that the water hyacinth (Eichhornia crassipes) can absorb the metal content of Cd and Cr for continuous systems research.

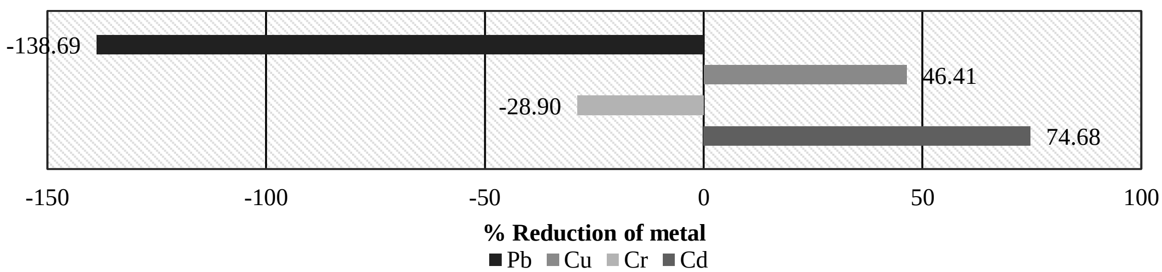


Figure 2. Reduction of Cd, Cr, Cu, and Pb in Continuous System Research

Results of Batch Systems Research (Laboratory)

Metal content in water of Cikacembang river in batch system can be seen in **Figure 3**.

a. Cadmium (Cd)

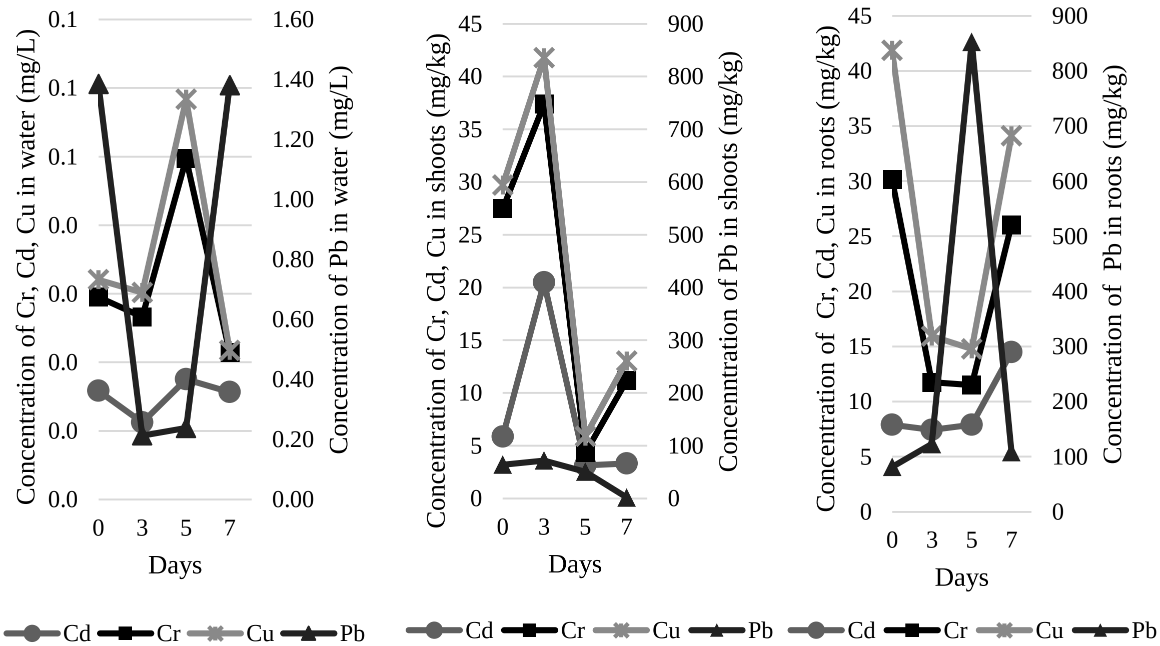
Cd metal concentrations in water that fulfill the quality standard (0.01 mg/L) is on the 3rd day, while the other days exceeded the quality standard which is 0.02 mg/L. Cd concentration in shoots between 0.02 to 5.88 mg/L, and the roots between 7.91 to 10.7 mg/L. It is estimated that the water hyacinth (*Eichhornia crassipes*) which are used already contains metals Cd, so after 3 days Cd metal diffusion was out of the plant. Percentage of reduction Cd metal in water is 1.19%. Cd mobility in the water is high enough, low content of Cd in the water showed uptake by plants. Levels of Cd accumulation in shoots and roots were moderate which is 211.67 L/kg and 924.70 L/kg.

b. Chromium (Cr)

All of Cr concentration in water does not exceed the quality standard (0.05 mg/L), it's only in the range of 0.01 to 0.03 mg / L. Initial concentration of Cr in shoots and roots is high that are 21.6 mg/kg and 22.2 mg/kg. Cr concentration decreases to be contained by 2.76 mg/kg in shoots and 5.02 mg/kg in the roots. Cr concentrations in roots is higher than Cr concentration in shoots, because the mobility of Cr from the root to the shoots is low, the concentration of Cr is dominant in the root (Shanker, 2005). Cr metal accumulation levels in leaves and roots is high which are 1,365.21 L/kg and 2,008.05 L/kg. Water hyacinth (*Eichhornia crassipes*) can reduce Cr in the water as much as 57.95%.

c. Copper (Cu)

Cu concentration in water is very low, of 0 - 0.01 mg/L, it did not exceed the quality standard (0.02 mg/L). Cu concentrations in the shoots ranges of 1.70 to 2.63 mg/kg and in the roots of 6.22 to 11.7 mg/kg. Cu concentrations that higher in roots than in the leaves is one of the mechanisms of plant tolerance to Cu metal. This is done to avoid the accumulation of toxic concentration by stopping excess of Cu in the root, so it does not enter the interior of the leaf (Yruela, 2009). Cr metal accumulation in shoots 6273.99 L/kg and the root 27455.39 L/kg including high bioaccumulation. This demonstrates the high demand for Cu in plants for photosynthesis. The location of Cu metal accumulation in plants is chloroplasts, Cu metal is needed for photosynthesis (Maksymiec, 1997). The need of Cu needs that are high on the water hyacinth (*Eichhornia crassipes*) is also shown on the Cu metal removal percentage is highest among the other metals is 88.18%.



a) Water b) Shoot c) Root

Figure 3. Content of Cd, Cr, Cu, and Pb in Batch System Research

d. Lead (Pb)

Pb concentration in water is much higher than the concentrations of Cr, Cd, and Cu. Pb concentration in water is between 0.21 to 1.38 mg/L exceeded the quality standard (0.03 mg/L). Absorption of Pb by the water hyacinth is higher than absorption of metals Cd, Cr, and Cu. Pb concentration in shoots is between 61.2 to 67.1 mg/kg and in the roots of 81.52 to 118 mg/kg. High Pb concentrations in water damage barrier function of plasmalemma so Pb gets into the cells in large numbers (Sharma and Dubey, 2005). However, if calculated bioaccumulation of Pb in the leaves and roots are low ehich are 1.48 L/kg and 78.57 L/kg. It was because of high differences between metal content in the water and in plants. Pb metal absorption by plants were classified as very low at 0.29%.

The results of the percentage reduction of heavy metals in the water due to metal uptake by plants existing batch systems can be seen in Figure 4.

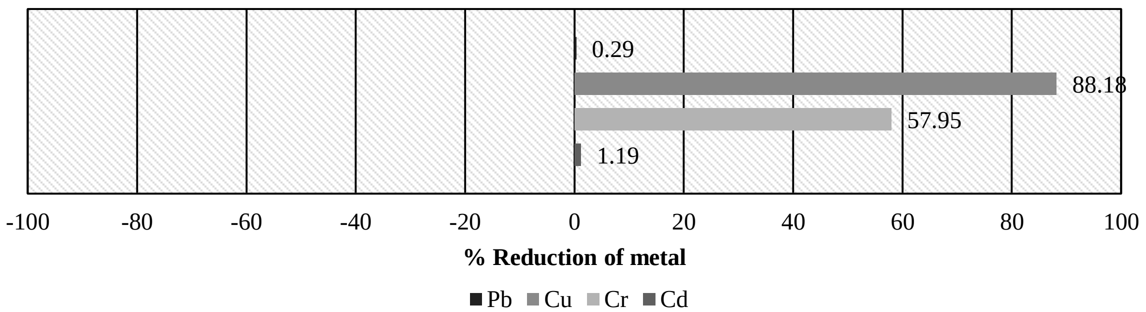


Figure 4. Reduction of Cd, Cr, Cu, and Pb in Batch System Research

Comparison of Batch and Continuous System

Content of heavy metals in the water and plant were different. Content of heavy metals in water less than inshoots and roots of the water hyacinth (*Eichhornia crassipes*). Although the metal content in water less, but many parameters Cd, Cr, Cu, and Pb were exceeded the quality standards that are harmful to living things. The trend of increase and decrease of Pb in water and plants on both systems is inversely proportional to the metal Cd, Cr, Cu. Lead availability is also affected by the presence of other heavy metals. Orronoa *et al*. (2012) in Fahr *et al*.(2014) reported that Pb availability was reduced when it was supplied with five heavy metals (Cd, Cr, Cu, Zn, and Ni) that have an antagonist effect. When Pb supplied alone or in ternary combination (with Zn and Cu), its availability increased due to the antagonistic interaction between Cu and Zn, which made Pb more available for plant uptake (Fahr *et al*, 2014).

In the continuous system, water hyacinth (*Eichhornia crassipes*) can eliminate most major metal that is Cd as much as 74.68% and Cu as much as 46.41%. However, Pb and Cr did not decrease but rather an increase in the concentration of each metal which is added as much as -138.69% and -28.90%. The reduction of Cd and Cu that were good by the water hyacinth (*Eichhornia crassipes*) is evidenced by the high bioconcentration factor at the root. Thus obtained that in the continuous system, water hyacinth (*Eichhornia crassipes*) is a good hyperaccuumulator for metals Cd and Cu. However, bioaccumulation of metals in the shoots is still relatively moderate, this is due to fluctuations in river water makes metal content in water varies so that the plant is unable to absorb metal maximum. BCF generated was compared with research by Swain *et al*.(2014), which gave exposure to the metal for 25 days, BCF for the Cd concentration of 0.27 mg/L were medium, which is 653 L/kg and at a concentration of 0.35 mg /L Cu which is 1,230 L / kg. Provided that metal exposure within 7 days of the study is very highalmost the same as research of Swain (2014), due to the routine of the textile industry effluent dispose of waste into water bodies.

Water hyacinth (*Eichhornia crassipes*) in a batch system can reduce metal content. Although metals Cd and Pb are relatively low at 1.19% and 0.29%, Cr and Cu are high, namely 57.95% and 88.18% , Water hyacinth (Eichhornia crassipes) is able to absorb large amounts of metal in accordance with the research Prasad (1983) that the water hyacinth can reduce Cr 60-80% within 8-16 days and in research Scheider (1995) which stated that for 30 minutes at 5.5 pH conditions as much as 2 g / L of roots and shoots of water hyacinth (*Eichhornia crassipes*) can be designated respectively 100% and 97%. The high eduction of Cr and Cu in water can be seen by high BCF values in shoots and roots. Different with continuous system where high accumulation is only on the root. Thus obtained that the water hyacinth plant (*Eichhornia crassipes*) is an excellent hyperaccumulator for Cr and Cu. When compared with the Odjegba and Fasidi research (2007), the BCF value generated in the exposure of 0,3 mM of heavy metals in the water hyacinth (*Eichhornia crassipes*) for 3 weeks (21 days) produced BCF values which included in high bioaccumulation, BCF values for metals Cd exposure is 2093.80 L/kg, Cr metal is 1515.67 L/kg , Cu is 1298.20 L/kg, and Pb is 1048.20 L/kg. Cr and Cu metal content during the 7 days is very high so the BCF value is high as in research by Odjegba and Fasidi for 3 weeks

Cu was absorbed by the water hyacinth (*Eichhornia crassipes*) in batch and continuous system. Increasing concentrations of this Cu continues to happen because Cu is needed by plants in various tissues. Since the plants needit constantly then the roots and shoots of the plant was continuously absorbing Cu into the network. Yruela (2009) stated that plants need Cu for normal growth and development, when these ions are not available, the plant experienced certain symptoms of deficiency, which mainly affect the leaves and reproductive organs. On the other hand, the redox properties that make Cu as essential elements also contribute to toxicity, in which the redox reaction between Cu^{2+} and Cu^{+} can catalyze the production of hydroxyl radicals which are highly toxic which can cause cell damage in lipid levels, membranes, nucleic acids, proteins and other biomolecules.

CONCLUSION

Metal content in the water and the water hyacinth (*Eichhornia crassipes*) in batch systems is influenced by the flow of water, while the metal content in the batch system is more stable the absorption will be maximum. The highest reduction of metal occurs in a batch system is of 88.18% Cu.Water hyacinth (*Eichhornia crassipes*) is an excellent hiperakumulator for Cu compared to metals Cd, Cr, and Pb in the batch and continuous system which is viewed by high value BCF.

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