Effectivity of Vertical Sub-Surface Downflow Constructed Wetland System with Varying Composition in Reducing Chromium and Color in Synthetic Textile Wastewater

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***Abstract*-**Textile and leather tannery wastewater pollute water bodies with their content of chromium metal (Cr) and synthetic dyes which are highly toxic. The use of constructed wetland systems is an approach to treat such wastewater before being discharged directly into the environment. This study was conducted to examine the effectiveness of vertical sub-surface downflow constructed wetlands with varying composition in decreasing Cr concentration and color thickness (value) in synthetic textile wastewater. Systems were varied by substrate composition and presence of the plant *Leersia hexandra*. Synthetic textile wastewater containing $K_2Cr_2O_7$ and reactive dye were flowed downward into five systems: (1) soil-sand-gravel substrate, without plants; (2) soil-sand-wood chips substrate, without plants; (3) soil-sand-gravel substrate, and *L.hexandra* plants; (4) soil-sand-wood chips substrate, and *L. hexandra* plants; and (5) a system without substrate or plants as control. Chromium concentration and color thickness were measured at 8, 16, 24, 32 and 40 hours after treatment. Measurements at 8 hours showed that systems no. 1, 2, 3, and 4 decreased Cr concentration in effluent as much as 87,6%; 79,1%; 81,4%; and 89,2% respectively. Meanwhile Cr concentration in the control system's effluent remained relatively constant. Systems no. 1, 2, 3, and 4 decolorized the effluent up to 94,6%; 89,6%; 93,4%; and 86,0% respectively; meanwhile, color in the control system was unchanged. All four treatment systems could effectively reduce Cr concentration and color thickness in synthetic textile wastewater. However, results did not support the hypothesis that the presence of plants would significantly affect Cr removal, or that the addition of wood chips to substrate would enhance decolorization effects.

K*eywor*ds-Vertical sub-surface downflow constructed wetland, *Leersia hexandra*, textile wastewater, chromium, decolorization

I. INTRODUCTION

Chromium (Cr) and reactive dye are used in the production of textile, dye, and tanned leather products. Chromium is known as a trace element in plant and animal metabolism and has two stable forms, i.e., the trivalent form and the hexavalent form, which is regulated tightly in its use [1].

Chromium is often used in chemical industries, for example, it is used for electroplating, leather tanning, and dye production. As waste, chromium is toxic to living organisms [2]. In Indonesia, the maximum allowable concentration (mg/L) of chromium as leather tanning waste is limited to 0,6 mg/L [3].

Reactive dye is soluble in water and strongly binds to fabric fibers and leathers [4]; it produces a dense color in water [5]. Every year, a high amount of reactive dyes is produced, 10-15% of which is released back to the environment, i.e., water bodies, and most are carsinogenic [5]. If wastes containing chromium and reactive dyes are not controlled, they could lower the water quality, and thus must be treated properly as soon as possible. Use of a constructed wetland system is an alternative for processing wastewaters of textile and leather tanning factories. The system's effectivity is affected by physical, chemical, and biological factors [6].

The objective of this study was to assess the effectivity of constructed wetland systems in reducing chromium and color density in synthetic wastewater. The systems tested were varied by the presence of plants and by substrate composition.

II. METHODOLOGY

A. Constructed wetland and synthetic wastewater

Constructed wetland systems were built as vertical sub-surface downflow systems (batch). Five systems were built in the form of glass aquariums with 0.8 mm glass thickness and dimensions of 20x20x50 cm^3 with a valve at the bottom. Rubber buckets were made into wastewater containers, with holes at the bottom of each container to control the outlet water flow, the flow was kept stable between 0.41 and 0.5 mL/s. *Leersia hexandra* plants were used as chromium phyto-accumulator [1]. Plants were acclimated for one week before being integrated into the systems. Substrate was stratified in layers of similar weight and thickness, each layer weighed 4 kg or 10 cm in thickness. The five systems compared were (Figure 1): (1) a system with substrate composed of soil-sand-gravel (SSG); (2) a system with substrate composed of soil-sand-woodchips (SSW); (3) a system with substrate composed of soil-sand-gravel and planted with *Leersia*

Manuscript received 18 January 2016.

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http://dx.doi.org/10.15242/IJACEBS.AE0216136

hexandra (SSG+L); (4) a system with substrate composed of soil-sand-woodchips and planted with *L. hexandra* (SSW+L); and (5) a control without any substrate or plants. Woodchips were used as adsorbent although they need a long retention time to take effect [7].

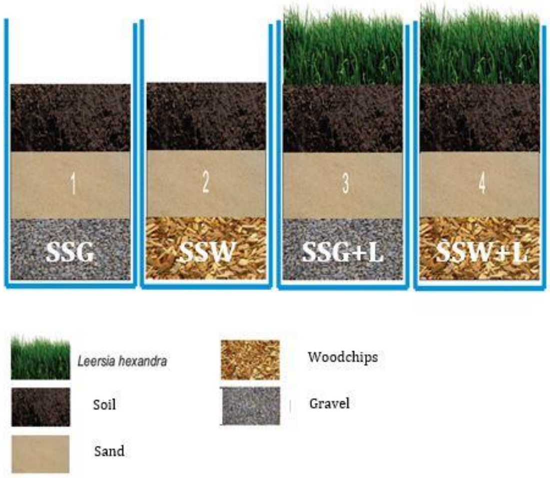

Fig. 1 Constructed wetland model

Synthetic wastewater was made of dissolved hot reactive dye (Procion H-E) with a concentration of 50 mg/L and $K_2Cr_2O_7$ concentration of 20 mg/L, with deionized water as solvent.

B. Experiment

Each system was run with three replications. Wastewater was trickled intermittently from above the systems through the holes at the bottom of the buckets. Physical conditions such as air temperature, water temperature, and substrate (soil) acidity were measured during the experimental run. Air temperature was measured using a sling psychrometer, water temperature using a DO-meter, and substrate acidity using a soil tester. The amount 100 mL of effluent was sampled through the valve using a beaker glass five times in 40 hours (sampled every 8 hours, at 8^{th}, 16^{th}, 24^{th}, 32^{nd}, and 40^{th} hours). Dissolved oxygen (DO) measurement was conducted immediately after the effluent was sampled, followed by pH and conductivity measurements.

Substrate and plants were sampled at t-5 (40^{th} hour) using an auger, then mixed. Plant and substrate samples were dried at 75°C in an oven for 24 hours.

C. Sample preparation and analysis

Sample preparation is the first step before measuring metal content in samples using atomic absorption spectrophotometer (AAS). For effluent samples, 5 mL of HNO_3 65% were added to 50 mL samples each in a beaker glass. Each glass was closed using a watch glass and vapored until 20 mL of sample remains and the sample appears clear (if the sample is not clear enough, 5 mL of HNO_3 could be added once). Condensed vapors on the watch glass was rinsed using aquadest and stored into the remaining sample until the volume reached 50 mL. Samples were moved into a volumetric flask and homogenized. The homogenized samples were then filtered through filter papers and stored in labelled bottles.

Preparation of substrate samples was conducted by dissolving the samples into 50 mL HNO_3 65% and heated at 60°C for two hours. The samples were filtered then stored in labelled bottles. For plant samples, 10 mL HNO_3 65% were added to 0.5 gr of dried plant samples and heated at 60°C for two hours, filtered afterwards, and stored in labelled bottles.

Metal content analysis was conducted using AAS. Meanwhile decolorization percentage was measured using the absorbance data of effluent samples. Absorbance data were measured at wavelength of 520 nm using an UV-VIS spectrophotometer. Data were then analyzed statistically using one-way ANOVA.

III. RESULTS AND DISCUSSION

A. Reduction of chromium

Measurements for pH and DO of sampled effluents from each system in 40 hours are presented in Figure 2. Average pH varied between 6.3 and 6.6; while DO levels decreased with time, with DO in systems 1 to 4 at 40 hours measuring 2.6; 1.6; 2.5; and 0.9 mg/L respectively.

Chromium concentration of effluents measured between 2.17 and 5.0 mg/L at 40 hours, with the lowest chromium concentration recorded in system no. 4 (SSW+L) (Fig. 2). The graph shows the reduction of chromium in each system since the 8^{th} hour. Systems 1 to 4 reduced chromium concentrations as much as 87.6%; 79.1%; 81.4% and 89.2% respectively. However, at the 16^{th}, 24^{th}, 32^{nd}, and 40^{th} hours of observation, the systems did not exhibit significant changes in the concentration of chromium in effluents.

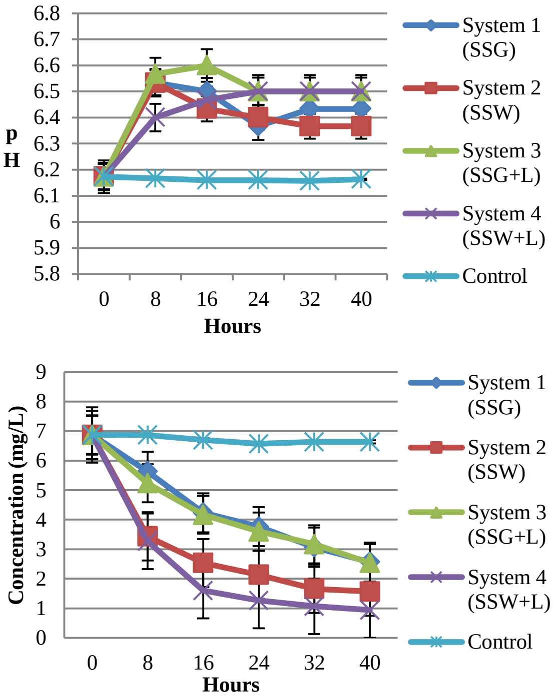

Fig. 2 pH and DO conditions of each system sampled at 8^{th}, 16^{th}, 24^{th}, 32^{th}, and 40^{th} hours

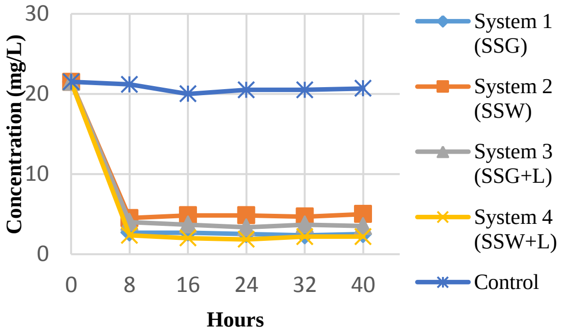

Fig. 3 Chromium concentration of effuents at 8th, 16th, 24th, 32nd, and 40th hours

Chromium reduction in effluents could be caused by reduction mechanisms by other metals, electron transfer, or adsorption. In the system containing soil and sand, Cr(VI) could be reduced by Fe(II) and organic matters to produce Cr(III) which is immobile and not soluble in water. Reduction caused by Fe(II) occurs at neutral pH and hipoxic condition [8], meanwhile reduction rate induced by organic matter is proportional to the amount of Cr(VI) and organic matters[8]. Cr(VI) could be mobilised in anaerobic/hipoxic condition [8]. In the observed systems, Cr(VI) could be reduced into Cr(III) by Fe(II) and organic matters, while pH and DO conditions support the reduction mechanism by Fe(II) [8].

Chromium reduction in effluent is supported by the substrate's ability to reduce chromium mobility. Consecutively, systems 1 to 4 could contain 510; 488; 435; and 450 mg/kg of chromium (Fig. 4). Chromium level in substrate increased because Cr(VI) and Cr(III) could be well absorbed by substrate particles. The difference in chromium levels could be related to the different capabilities of the different substrate types. Sand could adsorp Cr(VI) in a pH range between 5 and 7,5 because in that range the sand's surface is mostly positively charged. Moreover Cr(VI) reduction mechanism by Fe(II) in soil occurred easily in neutral pH, the mobile and soluble Cr(VI) could be reduced into Cr(III) which is immobile and not soluble in water in neutral pH. Cr(III) could be absorbed and bind in soil with the help of iron oxide, clay, and sand [8]. Adsorption of Cr(III) rapidly occurred in soil when pH level increased [9].

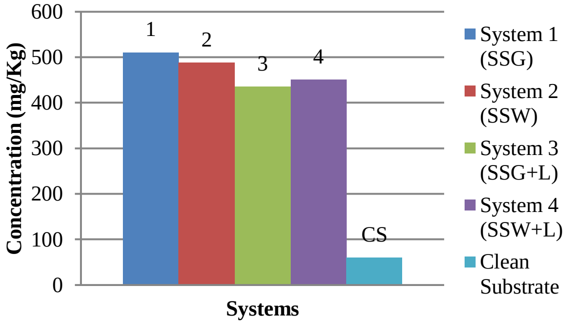

Fig. 4 Chromium concentration in substrate at 40th hour.

Other than substrate, *Leersia hexandra* had a role in absorbing and storing chromium. In 40 hours *L. hexandra* in systems 3 and 4 could absorb 186±23,1 mg/kg and 200±40 mg/kg into their roots, but not their leaves or stems (possibly stored in a tiny amount in leaves and stems).

Compared to the result of Zhang's experiment in 2007 [1] (in which he reported storage of 6978 mg/kg chromium in *L. hexandra* roots), the amount of chromium absorbed in our results is lower, because of the batch system (without further addition of synthetic wastewater) and the applied retention time. Substrate's role in capturing/binding chromium ions could lower the probability of chromium absorption by *L. hexandra*'s roots; other than that, the low amount of absorbed chromium could be caused by metal competitors absorbed through the same pathway of transport, for example Fe(III). Fe (III) is a reductor in the reduction process of Cr(VI) into Cr(III); if reduction rate of Cr(VI) increases, then the production rate of Fe(III) as a competitor metal for Cr(III) increases as well, this process could hinder Cr(III) uptake by plants, and thus result in the accumulation of Cr(III) in substrate [10].

TABLE 1: CHROMIUM CONCENTRATION IN *Leersia hexandra*

System	*Chromium content*		
	Root	*Stems*	*Leaves*
System 3 (SSG+L)	186,7±23,1 mg/kg	N/A	N/A
System 4 (SSW+L)	200±40 mg/kg	N/A	N/A

**N/A= Not detected*

B. Decolorization

Decolorization in effluent was apparent since the 8th hours. Then measurements remained relatively unchanged at the 16th, 24th, 32nd and 40th hour observations. Decolorization percentages in systems 1 to 4 were consecutively 94.6%; 89.6%; 93.4%; and 86.0%, while there was no change in the control system. In comparison, system 1 (SSG) and system 3 (SSG+L) produced better decolorization results than system 3 (SSW) and system 4 (SSW+L). This was due to the woodchips giving a yellowish color to the effluent and thus raising the absorbance measurement when assessed using spectrophotometer at the same wavelength. Decolorization occurred because adsorption by soil particles, organic matter, and sand particles went well [11], but not when the water reached the woodchips layer.

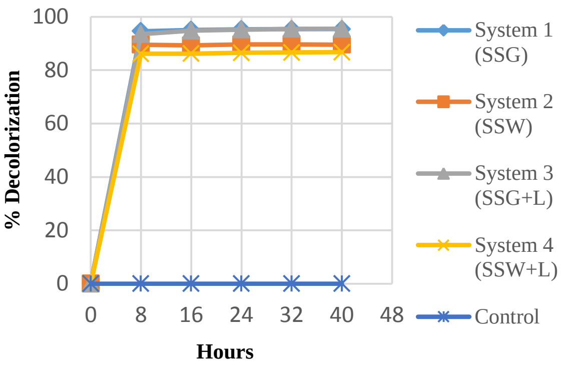

Fig. 5 Decolorization percentages sampled at 8th, 16th, 24th, 32nd and 40th hours.

Other than adsorption, degradation by proteins secreted by living organisms could affect the level of decolorization, because when substrates were sampled and re-dissolved into water, no color was produced; this indicates that not only adsorption occurred in the systems (because adsorbed materials could be released back into the environment and create the same effect as before) [11].

IV. CONCLUSION

Constructed wetland systems in this study effectively lowered chromium concentration in wastewater effluents. In 8 hours, systems 1, 2, 3, 4, varied by substrate and presence of plants, could lower chromium concentration as much as 87.6%; 79.1%; 81.4%; and 89.2% respectively. Although the results showed no significant differences among systems, substrate had an important role in holding chromiun and preventing it from polluting the outer system. In this system *Leersia hexandra* as accumulator did not have much effect in the short term. This could be caused by the metal competitors (Fe(III)) that hindered the uptake of Cr(III) by roots.

System 1, 2, 3, and 4 lowered the color density of wastewater as much as 94.6%; 89.6%; 93.4%, and 86.0% respectively, while the control system did not have any effect in decolorizing effluents. Based on decolorization percentage, woodchips were not effective in reducing color density of density, because woodchips produced a yellowish color to the effluents. Adsorption and degradation activities in the systems are expected to play an important role in decolorizing effluents.

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