Effect of Substrate Variation on Constructed Wetland System Effectiveness in Reducing Total Chromium Concentration in Water

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Abstract: *The use of chromium (Cr) in various industrial activities may potentially pollute water bodies, therefore water needs to be treated in order to minimize the negative impacts that may be caused by Cr. Constructed wetland systems have the potential to be used as means to remediate chromium (total Cr) in water. However, further research is still needed to enhance the effectiveness of these systems in reducing total Cr concentration in the water. Research is required to optimize the main components of the constructed wetland system, i.e., hydrology, substrate, and vegetation. This study focused on optimizing the substrate media. The specific objective of the study was to determine the effect of adding activated charcoal and charcoal to the soil substrate on the effectiveness of the constructed wetland system in reducing total Cr concentration in the water. Experiments were conducted to compare five different systems treated with simulated Cr wastewater, i.e., system 0 as a control system containing only wastewater; system 1 containing the plant Pistia stratiotes; system 2 containing 100% soil substrate and P. stratiotes; system 3 containing 75% soil + 25% coconut shell charcoal as substrate, and P. stratiotes; and system 4 containing 75% soil + 25% coconut shell activated charcoal as substrate and P. stratiotes. Each system was exposed to simulated waste from $K_2Cr_2O_7$ with total Cr concentration of 15 mg/L for 15 days. Total Cr concentration in the samples was measured by Atomic Absorption Spectrophotometer (AAS). All systems were effective in reducing total Cr concentration. The control system reduced the lowest percentage of total Cr, i.e., 97.4%, while system 4 reduced the most total Cr, i.e., 97.8%. However, the reduction in total Cr was not significantly different among systems ($p > 0.05$). Soil substrate accumulated the highest total Cr, with total Cr accumulation of 12.7%; however, the effectiveness of soil, charcoal, and activated charcoal were not significantly different ($p > 0.05$). Based on the results, it could be concluded that addition of activated charcoal and charcoal to soil substrate did not affect the effectiveness of systems in reducing total Cr concentrations in water within a period of 15 days; although there were significant differences in the decrease of Cr concentrations when viewed at 3-day intervals. The addition of activated charcoal and charcoal also had no effect on the accumulation of Cr in P. stratiotes or in substrate.*

Keywords: *chromium, activated charcoal, constructed wetland, Pistia stratiotes*

1. Introduction

Pollution of water bodies is a global environmental problem. Anthropogenic activities related to industrial, agricultural or domestic activities can be a source of polluted wastewater. According to the UN WWAP, wastewater resulting from human activity in the world can reach a volume of about 1,500 km^3 per year [1]. Industry is one source of wastewater that pollutes water bodies, because the wastewater produced is often not treated properly, but nonetheless discharged into water bodies [2]. UN Water stated that developing countries dispose of 70% of industrial waste into water bodies without prior treatment [1]. This can surely degrade the water quality of water bodies.

Chromium (Cr) is a chemical element that is abundant in the layers of the earth and is often used in various industries [3], such as leather tanning, metal plating, chromium pigment manufacturing, and paint manufacturing [4]. Industrial wastewater containing Cr usually contains a high concentration of total Cr, about 5-20 mg/L [5]. This concentration range exceeds the quality standard or maximum level allowed for total Cr in water, i.e., equal to 0.5 mg/L [6]. High Cr concentration has potential negative impacts, e.g., through the contamination of clean water. Therefore, water contaminated by Cr needs to be processed to minimize the negative impacts that may be

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caused. Total Cr entering a water body can form trivalent chromium, Cr (III), or hexavalent chromium, Cr (VI) [3]. Both types of Cr oxidation numbers are the most stable compared to other Cr forms. The elements Cr (III) and Cr (VI) have opposite characteristics; Cr (VI) is more easily mobilized, more soluble in soil and water, and more oxidative than Cr (III) [3][4][7]. Both Cr (III) and Cr (VI) are potentially hazardous to plant and human health [8][9].

A constructed wetland system (CWS) is a technology that can be used to treat wastewater, including waste containing Cr [10]. This system has advantages over conventional water treatment systems, e.g., it requires lower manufacturing and maintenance costs, uses less energy, is more environmentally friendly, and has aesthetic value [11]. However, further research is still needed in order to enhance the effectiveness of CWS. This can be achieved by optimizing the three main components of a wetland, i.e., hydrology, substrate, and biota, particularly vegetation [12].

The following study focused on the optimization of substrate with the specific objective of determining the effect of adding activated charcoal and charcoal to soil substrate on the effectiveness of CWS in reducing total Cr concentration in water. Charcoal and activated charcoal are often used in water treatment because they have pores that can adsorb pollutants in water. Activated charcoal is an alternative media which has been found effective in adsorbing pollutants in general because it has a wider porous surface compared to ordinary charcoal [13]. Research on the ability of activated charcoal to adsorb heavy metals in laboratory scale showed that activated charcoal can reduce the concentration of heavy metals in water [14]. Soil is commonly used as the main substrate in CWS. In addition to substrate, the plant *Pistia stratiotes* was used in this study to support biological processes. It was selected as a supporting remediator because of its floating life form, which is expected to absorb total Cr that is not deposited on substrate.

2. Methodology

Experimental CWSs were made from glass aquariums measuring 60x30x35 cm^3. Five systems were compared (Figure 1), i.e., system 0 as a control containing only simulated wastewater (coded W); system 1 containing the plant *Pistia stratiotes* (W+Ps); system 2 containing *P. stratiotes* and 100% soil substrate (W+Ps+S); system 3 containing *P. stratiotes* and 75% soil + 25% coconut shell charcoal as substrate (W+Ps+Ch); and system 4 containing *P. stratiotes* and 75% soil + 25% coconut shell activated charcoal as substrate (W+Ps+Ach). All systems were exposed to simulated Cr waste from $K_2Cr_2O_7$ with total Cr concentration of 15 mg/L. Simulated wastewater was prepared by dissolving 2.12 g of $K_2Cr_2O_7$ in 50 L of water for each system. Systems 2, 3 and 4 were first filled with substrate before given wastewater treatment. System 2 was filled with 12 kg of soil; system 3 was filled with 4 kg of soil, covered on top with a layer of 3 kg of charcoal from coconut shell; system 4 was filled with 9 kg of soil, covered on top with a layer of 3 kg of activated charcoal from coconut shell. *P. stratiotes* was acclimatized for one week and then weighed to obtain four groups with an approximate wet weight of 150 g, which was then added into systems 1, 2, 3 and 4. Running of the experiment was replicated three times.

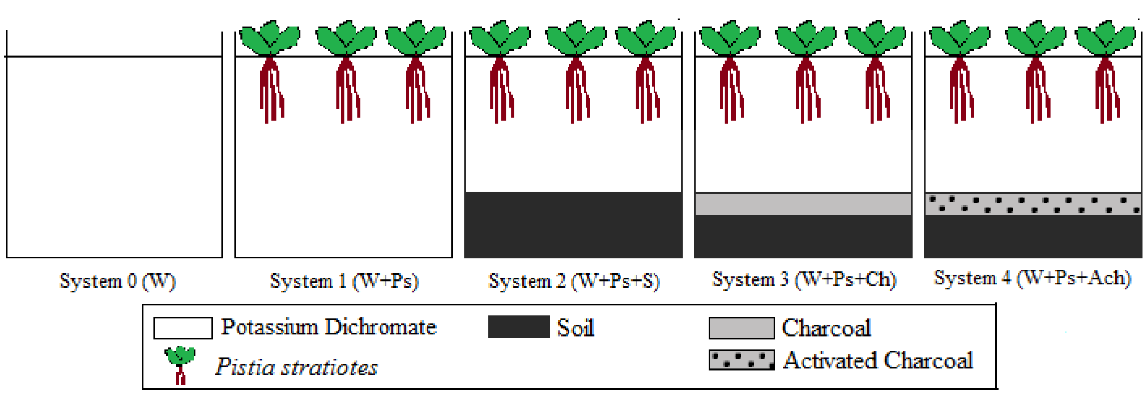

Fig. 1: Design of five systems compared in this study (W=wastewater, Ps=*Pistia stratiotes*, S=soil, Ch=charcoal, Ach=activated charcoal)

Water, substrate and *P. stratiotes* tissue were sampled periodically and analyzed for Cr content. Water and substrate were sampled every three days for a period of 15 days, i.e., from day 0 (t = 0) to day 15 (t = 15). Plants were sampled twice, i.e., on day 0 (t = 0) and day 15 (t = 15). Sampled water was measured into a 100 mL beaker. Substrate samples were taken from five points in the uppermost layer of the substrate. Other physicochemical and microclimatic parameters were also measured, including water temperature, substrate temperature, water pH, substrate pH, air temperature, air humidity and light intensity.

Shoots and roots of *P. stratiotes*, as well as substrate were dried in an oven at a temperature of about 80°C for 24 hours. After drying, shoot and root samples were weighed to 0.5 gram samples and placed in a 50 mL beaker. Samples that have been weighed and then soaked in a solution of 50 mL concentrated HNO_3 were then stored in the fume hood for 24 hours. Sampled water was added with 5 mL of HNO_3 solution, and also stored in the fume hood for 24 hours. Samples of water, plant tissue and substrate that have been soaked in a solution of HNO_3 were then heated on an electric stove with a temperature of approximately 100°C for one hour, then given 2 mL of 70% H_2O_2 solution, then heated again. Addition of H_2O_2 70% and heating was repeated until the sample solution became clear [15][16]. Total Cr concentration was measured using an atomic absorption spectrophotometer (AAS GBC Avanta) with a wavelength of 357.9 nm. Data were processed using SPSS independent T-test and one-way ANOVA with Duncan advanced test.

3. Results and Discussion

Total Cr concentration in water of all systems decreased within a period of 15 days (Figure 2). The lowest percentage of reduction in total Cr concentration at day 15 occurred in System 0 or control (W), amounting to 97.4%, while the highest percentage reduction was found in system 3 (W+Ps+Ch), amounting to 97.8%. System 2 (W+Ps+S), System 3 (W+Ps+Ch), and System 4 (W+Ps+Ach) which were varied by substrate showed no significant difference in decreasing total Cr concentration in water. Total Cr concentration on day 15 in the three systems were not significantly different (p>0.05), suggesting that the addition of activated charcoal and charcoal did not affect the system in lowering total Cr concentration in water. Although substrate variation had no effect on the system's effectiveness in decreasing total Cr concentration, final Cr concentration in the systems met the quality standard value; final measurements were below the maximum level allowed for water, i.e., 0.5 mg/L (Figure 3). Final total Cr concentration in the systems ranged from 0.32 to 0.35 mg/L (Figure 3).

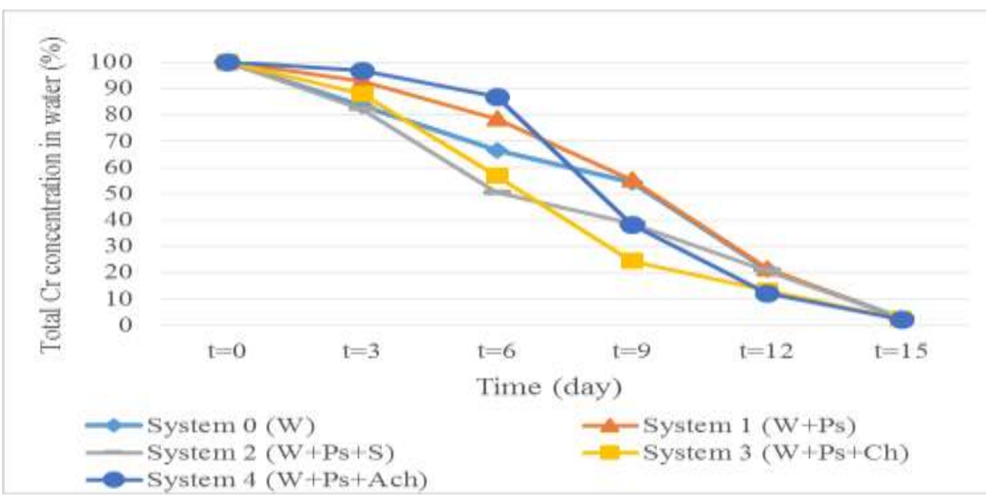

Fig. 2: Percentage of total Cr concentration in water, relative to the initial amount given as treatment.

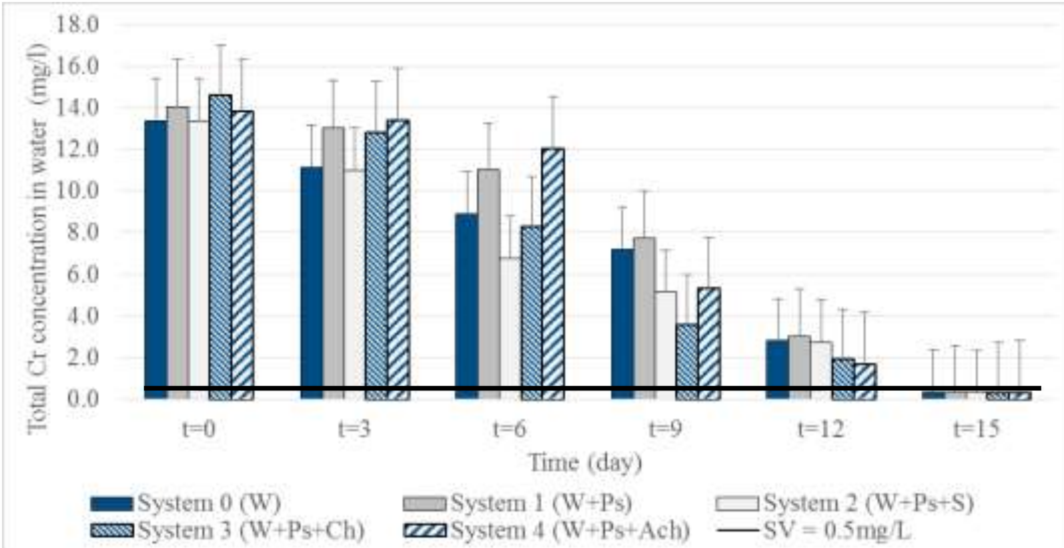

Fig. 3: Total Cr concentration in water. On day-15, concentrations have reached below the maximum level allowed for water, shown by the SV (quality standard value) line.

The mechanism in decreasing total Cr concentration in all systems involves three main processes, i.e., chemical, physical and biological processes [17]. Chemical processes include the reduction of Cr (VI) to Cr (III). Reduction is the most important process in decreasing total Cr concentration because it will affect the characteristics of Cr in water [7]. Cr (III) that results from the reduction process is more insoluble, more stable, and more difficult to mobilize than Cr (VI) [12]. Physical processes in the form of precipitation backed by the force of gravity can accumulate total Cr at the bottom of the system. Precipitation is an important process in treating wastewater prior to further biological processing [18]. In this case, biological processes include the accumulation of Cr by *P. stratiotes*. However, it would appear that chemical and physical processes were more dominant.

The element Cr (VI) can be reduced to Cr (III) if there is Fe (II) and dissolved organic compounds present [3][19]. The Cr form which was predominant at the initial treatment exposure was Cr (VI), in the form of dichromate ($Cr_2O_7^{2-}$) derived from the decomposition of $K_2Cr_2O_7$ in water. Dichromate was reduced by Fe (II) to become Cr (III). Fe (II) may have originated from tap water and/or soil used in the systems. The presence of Fe (II) is abundant in the environment [20], e.g., in water [21].

The reduction of Cr (VI) can occur in a pH range of 3 to 7 [3]. The measured pH value of water in the the experimental CWSs ranged from 5.4 to 6.1. Fe^{2+} ions may possibly be the reductant agent of dichromate in the five systems [23]. Fe^{2+} can form Cr (III) which has properties more insoluble than Cr (VI), so that Cr (III) can be settled more easily. Besides Fe^{2+}, organic compounds can reduce the concentration of Cr (VI) in the system. Dissolved organic compounds, such as fulvic acid is likely to come from the soil [25][26]. Organic compounds derived from the soil have a very stable trait that can produce Cr (III) complex as a product of the reduction process [3]. Cr (III) resulting from the reduction of Cr (VI) is a solid that is less soluble in water [22]. This allows deposition by gravity to occur more easily. Precipitation of Cr (III) to Fe (III) occurs at a pH greater than 4 [26]. This was the pH condition found in the systems, as mentioned previously. The reduced Cr (III) formed is then deposited to the bottom of the system.

Figure 4 shows the decrease in percentage of total Cr concentration in water at different time intervals. When viewed according to time intervals, systems 2, 3 and 4 exhibited significant difference in the amount of Cr removed from the water ($p < 0.05$). System 2 which contained only soil as substrate was most effective in decreasing total Cr concentration between day 3 and day 6. System 3 containing charcoal worked most optimally between day 3 and day 9, whereas System 4 which contained activated charcoal worked optimally between day 6 and day 9. This difference may have been affected by difference in the amount of Cr (VI) reduced to Cr (III) each day.

Pistia stratiotes contributed to lowering total Cr concentration in water, amounting to 250–327 µg/g in 15 days. The highest Cr concentration was accumulated by *P. stratiotes* in System 3, while the lowest accumulation occurred in System 1 (Figure 5), although the values were not significantly different (p> 0.05). This was also true for systems 2 and 4, thus it can be concluded that the addition of activated charcoal and charcoal did not affect total Cr accumulation by *P. stratiotes*. Total Cr accumulation in roots tended to be greater than in shoots; however the difference was not significant (p> 0.05) (Figure 5).

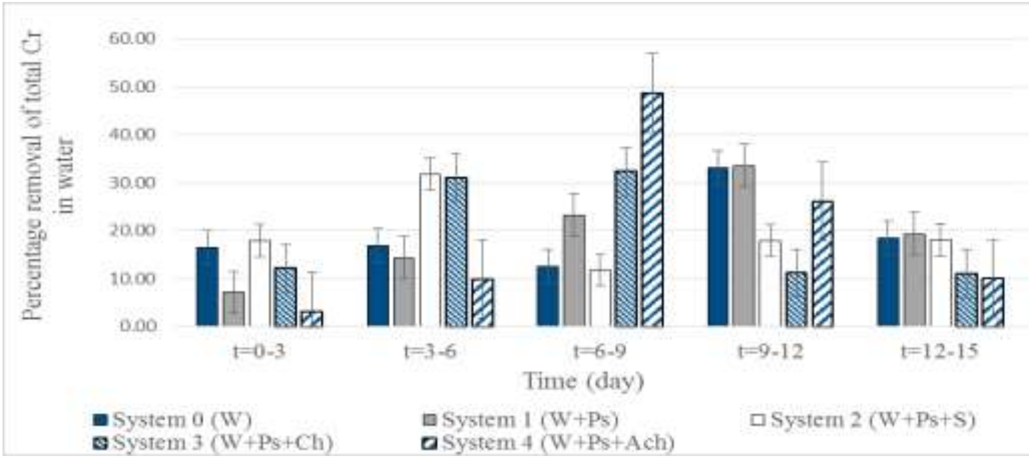

Fig. 4: Percentage removal of total Cr concentration in water at every three-days interval.

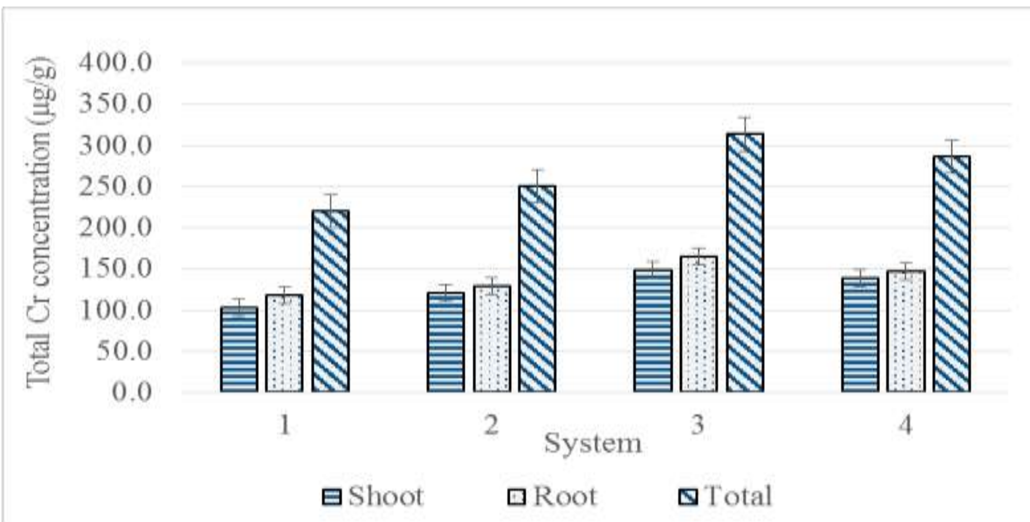

Fig. 5: Total Cr concentration in *Pistia stratiotes* after 15 days.

Substrate in systems 2, 3 and 4 did not show significant differences in accumulating total Cr (p> 0.05) after 15 days (Figure 6). This may be due to the dominant role of physical processes, specifically deposition by gravitational force, so that the concentration of total Cr deposited into substrate was relatively the same for 15 days. As a result, the addition of activated charcoal and charcoal did not affect substrate in accumulating total Cr.

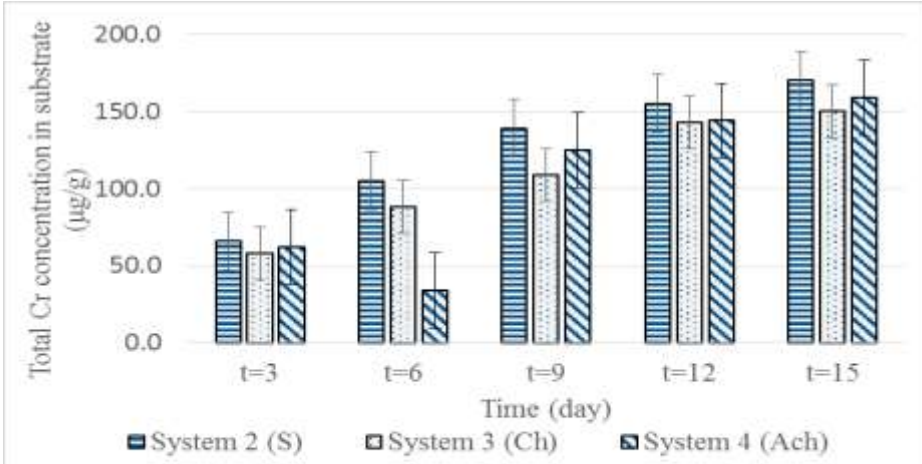

Fig. 6: Total Cr concentration accumulated in substrate after 15 days

4. Conclusion

Results of this study have shown that varying substrate, in this case by adding activated charcoal and charcoal to soil, did not affect the constructed wetland system's effectiveness in decreasing total Cr concentration in water after 15 days, although there were differences in the amount of total Cr removed at 3 day intervals. The addition of activated charcoal and charcoal also had no effect on the accumulation of Cr in *Pistia stratiotes* or in substrate.

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