Utilization of Water Hyacinth *(Eichhorniacrassipes)* for Phytoremediation of Hexavalent Chromium in Simulated Wastewater

Asia Pacific Journal of Multidisciplinary Research
Vol. 3 No. 4, 117-123
November 2015 Part IV
P-ISSN 2350-7756
E-ISSN 2350-8442
www.apjmr.com

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Date Received: September 29, 2015; Date Revised: October 29, 2015

Abstract–*One of the most common sources of contamination in surface water is the discharge of waste water containing heavy metals from different industrial applications.Methods in the removal of contaminants like hexavalent chromium, Cr^{+6} ,that are available nowadays are too costly and difficult to operate efficiently. A new approach to solve such problem is Phytoremediation or the use of green plants in the removal of contaminants from wastewater that contains heavy metals.In this study, the effectiveness of water hyacinth (Eichhorniacrassipes) was evaluated for its capability in removing hexavalent chromium from simulated wastewater.The effect of a co-ion, specifically Cu2+ ions, on the percentage removal of Cr6+ was also studied. Diphenyl carbazide colorimetric method was used to quantify the amount of Cr^{6+} left after treatment with water hyacinth.The percentage removal of Cr^{6+} was determined under varying conditions. The parameters varied were concentration of Cr^{6+} (3, 6, & 9 mg/L), contact time (4, 8, and 12 days) and concentration of Cu^{2+} (0, 4, and 8 mg/L). Results showed that the percentage removal of Cr^{6+} is directly proportional to the initial concentration of Cr^{6+} and contact time but inversely proportional to the concentration of co-ions which is Cu^{2+} ions. Results and statistical data showed that the optimum condition for phytoremediation of Cr^{6+} using water hyacinth is 12 days of contact time, and initial concentrations of 9 mg/L and 4 mg/L of Cr^{6+} and Cu^{2+} respectively.Overall results indicated that Eichhorniacrassipes can be used for phytoremediation of Cr^{+6}contaminated wastewater.*

Keywords: *chromium, phyto remediation, water hyacinth, wastewater treatment,*

INTRODUCTION

Hexavalent Chromium, Cr^{+6}, is one of the most common heavy metal being found in surface water caused by discharged of wastewater from industries such as tanning, metal plating and finishing[1]. Due to growing industry, high volume of metal has been used which also accompanied a high amount of contamination in the environment if not removed properly prior to discharge.The concentrations of Cr^{6+} in these industrial wastewaters range from 0.5 to 270 mg/L. The permissible limit of chromium from industrial effluents that can be discharge to surface water is 0.1ppm and 0.05ppm for potable water as defined by DENR Administrative Order No.35.Chromium can exist in two stable oxidation states, trivalent form, $Cr^{3+,}$ which is relatively safe and hexavalent form, $Cr^{6+,}$ which is toxic, carcinogenic and mutagenic in nature once it is exposed in the environment [2]. Aside from it, hexavalent form are also highly mobile in soil and aquatic system and is a strong oxidant capable of being absorbed by the skin[3]. With this, it is therefore essential to remove hexavalent form from wastewaters before being discharged into land and surface water.

According to DENR, Department of Environment and Natural Resources, due to high volume of water hyacinth in the river, it is considered as “pest” This was due to its high productivity of around 200 metric tons of dry matter per 10000 square meter land area under normal condition. Different countries in the world such as Lake Victoria situated in East Africa, Kerala's backwater located in India, Louisiana swamps, Papua New Guinea and Philippines are facing such dilemma. Its mats were deposited on waterways that caused clogging making water activities impossible like fishing and boating.

On the other hand, water hyacinth is found to be the most effective in reducing BOD and COD and removal of nitrogen, phosphorous, suspended solids and heavy metals among water plants [4]. The roots of this plant are found to absor3 copper, lead, silver, cadmium and chromium in enormous quantities and yet show no sign of toxicity [5]. Upon realizing this dilemma, the researchers have come up to utilizing this aquatic pest as an alternative low-cost absorbent of chromium for wastewater treatment.

OBJECTIVES OF THE STUDY

The study aimed to utilize water hyacinth (*Eichhorniacrassipes*) for phytoremediation of hexavalent chromium in simulated wastewater. It sought to answer the following questions:

1. What is the percentage removal of Cr^{6+} at different concentrations (3 mg/L, 6 mg/L and 9 mg/L) in simulated wastewater upon varying contact time (4 days, 8 days and 12 days) of water hyacinth?
2. Upon varying contact time, is there a significant difference on the percentage removal of Cr^{6+} at different concentrations?
3. What is the percentage removal of Cr^{6+} at different conditions (concentration and contact time) upon the presence of Cu^{2+} at different concentration (0mg/L, 4 mg/L, 8 mg/L)?
4. Is there a significant difference on the percentage removal of Cr^{6+} among varying conditions?
5. What is the best condition in phytoremediation of hexavalent chromium using water hyacinth among varying conditions?

The study will be significant to the environmental sector, to the industries producing chromium contaminated wastewater, and to future researchers.

METHODS

The experimental method of research was utilized in this study. It was composed of a total of twenty - seven (27) set-ups. The parameters varied were contact time (4 day, 8 days, 12days) of the water hyacinth plants with the simulated wastewater, initial concentration (3 mg/L, 6 mg/L, 9 mg/L) of hexavalent chromium (Cr^{6+}) and initial concentration (0 mg/L, 4 mg/L, 8mg/L) of copper ions (Cu^{2+}). A constant volume of 30 L was used for each agitated set-up. The experiment was conducted in Banaba, Padre Garcia, Batangas.

The water hyacinth plants of approximately same sizes were collected from Ambulong, Tanauan, Batangas. The reagents, potassium dichromate ($K_2Cr_2O_7$) and copper sulfate pentahydrate ($CuSO_4{\bullet}5H_2O$) which were used in the experiment proper are of analytical grade supplied by Lipa Quality Control Center. Tap water was used in the adaptation of water hyacinth and distilled water in the preparation of the stock solution. The laboratory tests were carried out at the Lipa Quality Control Center. The said laboratory used the diphenylcarbazide colorimetric method for the determination of hexavalent chromium in the simulated wastewater after phytoremediation.

The simulated wastewater was prepared using analytical grade reagents and distilled water as the solvent. For the chromium contaminated water, a stock solution of 2.0 g/L of potassium dichromate was prepared by dissolving 2000 mg potassium dichromate in 1000 mL of distilled water in a 1000 cm^3 beaker. The solution was then stirred with a glass rod until solutes were totally dissolved. Required concentrations (3.0 mg/L, 6.0 mg/L and, 9.0 mg/L) of Cr^{6+} were prepared by appropriate dilution of the above stock solution.

To account for the 3 mg/L Cr^{6+}, 127.30 mL of the stock solution was diluted to 30L. Likewise, for 6 mg/L and 9 mg/L Cr^{6+}, 254.60 mL and 381.90 mL were each diluted to 30 L respectively.For the required concentrations (4 mg/L and 8 mg/L) of copper ions, 471.156 mg and 942.309mg of copper sulfate pentahydrate ($CuSO_4{\bullet}5H_2O$) were added respectively. The solutions were then stirred until the solute totally dissolves.

Once the water hyacinth plants were collected, tap water will be used to remove surface contamination by washing. They were placed in plastic basins as culture vessels with tap water under natural sunlight to let them adapt to the new environment. Adaptation lasted for seven days. After 7 days of adaptation, the water hyacinth plants which were grown were collected, excess water was removed and the weight of the plant was taken. Approximately 490 to 500 g of water hyacinth plants were put into each glass container with 30 liters of the simulated wastewater at the desired initial concentrations of Cr^{6+} (3.0 mg/L, 6.0 mg/L and, 9.0 mg/L) and Cu^{2+} (0 mg/L, 4.0 mg/L and 8.0 mg/L). The plants were soaked and 250 mL water samples were taken from each container as the desired contact time (4 day, 8 days and, 12 days) were reached. Samples were immediately brought to Lipa Quality Control for Cr^{6+} analysis. The initial volume of water in all agitated set-up containers were equal (30 L) and the changes in volume due to evapotranspiration during the metal uptake were not addressed.

To evaluate the significant effect in the percentage removal of hexavalent chromium among varying conditions (contact time and concentration of Cr^{6+} and Cu^{2+}), Two-Way Analysis of Variance was used (*Sigmaplot® v12.0)*.

RESULTS AND DISCUSSION

Percentage removal of Cr^{6+} at different concentrations in simulated wastewater upon varying contact time of water hyacinth

Table1 presents the percentage removal of chromium VI at different concentrations in simulated wastewater upon varying contact time. The highest percentage removal (90.11%) is obtained in 12 days contact time and 9 mg/L of Cr^{6+} while the lowest percent removal (75.33%) is 4 days and 6 mg/L Cr^{6+}. The amount of the absorbed metal ions increased as the time lapses. The plant showed a rapid metal reduction for the first 4 days of contact time. The high percentage removal of chromium or its fast absorption by the water hyacinth plants at the initial stage of the process were due to high volume of available vacant sites in which the heavy metal adhered.

Table 1. Removal of Cr^{6+} at Different Concentrations in Simulated Wastewater upon varying Contact Time

Initial Concentration of Cr^{6+}	Contact Time		
	4 days	8 days	12 days
	Percentage Removal of Cr^{6+}		
3 mg/L Cr^{6+}	78.00%	78.33%	82.67%
6 mg/L Cr^{6+}	75.33%	81.33%	84.50%
9 mg/L Cr^{6+}	80.78%	86.44%	90.11%

Meanwhile, Figure 1 shows the trend generated by plotting the percentage removal of Cr^{6+} against the initial concentration and contact time.

In general, an increasing trend in the percentage removal as the contact time and concentration of Cr^{6+} is increased is evident in the figure. This is due to the fact that absorption of metal ions continues until a certain period of time when the saturation point is reached.

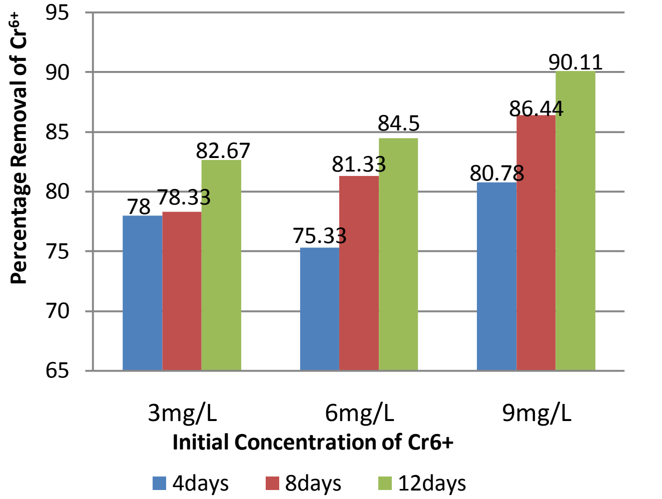

Figure 1.Percentage Removal at Varying Concentration of Cr^{6+} and Contact Time

This is when the sorption sites of the absorbent become saturated with the metal ions and no more space is available for more ions. To support this, many researchers have proven that increasing the contact time also increases the percentage removal of heavy metal in phytoremediation.

The increase in the percentage removal of Cr^{6+} with increasing concentration of chromium VI in simulated wastewater were to be expected since as the number of dichromate ions increased in the simulated wastewater, there were increased chances of those ions making contact with the plant roots. Therefore, the chances of chromate ions being absorbed were increased and if there were any competition for binding sites among the various ions present in the media being treated, chromate ions were more likely to occupy many of those sites when present in the media at higher concentrations.

In contrast, on day 4 a decrease in the percentage removal, from 78% to 75.33%, can be observed on the figure as the concentration was increased from 3 mg/L to 6 mg/L, respectively which opposes the established trend. This could mean that the contact time of 4 days is not enough to let most of the metal ions bind to the water hyacinth plant's binding sites. This is somewhat comparable with the study of Win D Than wherein he measured the lead, Pb^{2+}, content in the plant root for third and fourth day containing 281 ppm to 339 ppm respectively which means that the roots undergo desorption of lead ions.[6].This means that at this point, roots were already saturated and the tendency is that the metals will be pushed out of the binding sites.

Since the researchers only consider the weight of the plants used for the treatments, other qualities of the water hyacinth plants that may affect their absorption capacity possibly caused this deviation.

Comparison on the percentage removal of Cr^{+6} at different concentrations upon varying contact time

For the comparison of percentage removal of Cr^{6+} under varying initial concentration of Cr^{6+} and contact time as shown in Table 2, Two-Way Analysis of Variance (ANOVA) was applied.

Table 2.Summary of F values between percentage removal of Cr^{6+} with varying initial concentration of Cr^{6+} and contact time*

Source of Variation	F_{value}	$F_{critical}$ **	P_{value}	Decision	Interpretation
Contact Time	39.14	3.55	<0.001	Reject Ho	Significant
Concentration of Cr^{6+}	50.56	3.55	<0.001	Reject Ho	Significant
Contact Tine x Concentration of Cr^{6+}	3.45	2.93	0.03	Reject Ho	Significant

**Analyzed by SigmaPlot V12.0*
***Fcritical obtained from Microsoft Excel 2007*

It is evident on the table that the F values (39.14, 50.56, and 3.45) of the sources of variation were all higher than the critical F value (3.55 and 2.93). Also, the p-values (<0.001, <0.001 and 0.03) were all lower than 0.05 level of significance at a total of 26 degrees of freedom. Hence, the null hypothesis is rejected. This means that there is a significant difference in the percentage removal of Cr^{6+} upon varying the initial concentration of Cr^{6+} and contact time. Both of the varying parameters affect the percentage removal of Cr^{+6} metal using water hyacinth plant as absorber.

Removal of Cr^{+6} at different conditions (concentration and contact time) upon the presence of Cu^{+2} at different concentrations

Presented in Table 3 is the calculated percentage removal of chromium VI at different conditions (concentration and contact time) upon the presence of copper ions at varying concentrations. This shows how the presence of other ions specifically Cu^{+2} at different concentration affect the absorption capability of water hyacinth plant or percentage removal of Cr^{+6} in simulated wastewater.

The trend generated by plotting the percentage removal of Cr^{6+} against the contact time and initial concentrations of chromium ions and copper ions is shown in Figure 2.

Evident in the graph is the decreasing trend in the percentage removal of Cr^{6+} as the concentration of copper ions is increased. As shown in the graph, the highest percentage removal of Cr^{+6} at the presence of Cu^{+2} ions was observed at 12 days contact time.

The decreasing percentage removal as the concentration of copper ions is increased is due to the competition of copper ions with the chromium ions to bind on the absorption sites. This means that the more copper ions in the simulated wastewater the lesser tendency for the chromium ions to be absorbed by the water hyacinth. Also, the binding sites for the absorption of the chromium ions were occupied by the copper ions.

On the contrary, a fluctuating trend can be observed from Figure 2 for the percentage removal of Cr^{6+} upon 4 days contact time as the concentration of copper ions is increased.

Table 3.Percentage removal of Cr^{6+} at different concentration and contact time upon the presence of Cu^{+2} at different concentrations

Concentration of Cu^{2+}	**Concentration of Cr^{6+}**								
	3 mg/L Cr^{6+}			**6 mg/L Cr^{6+}**			**9 mg/L Cr^{6+}**		
	Contact Time								
	4 days	8 days	12 days	4days	8days	12days	4days	8days	12days
	Percentage Removal of Cr^{6+}								
0 mg/L Cu^{2+}	78.00%	78.33%	82.67%	75.33%	81.33%	84.50%	80.78%	86.44%	90.11%
4 mg/L Cu^{2+}	74.33%	79.00%	81.33%	77.33%	79.83%	81.67%	82.33%	84.44%	88.78%
8 mg/L Cu^{2+}	76.67%	76.33%	79.33%	76.00%	79.17%	76.17%	80.78%	84.67%	81.22%

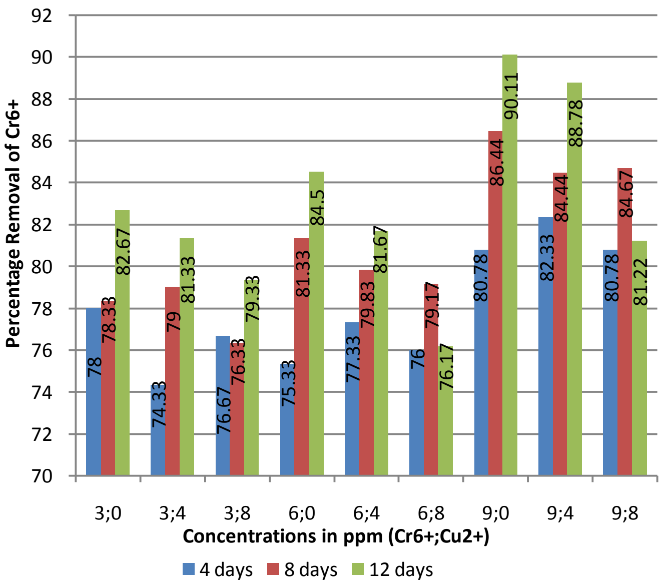

Figure 2.Percentage removal at varying contact time and concentration of Cr^{6+} and of Cu^{2+}

This deviation in the result may have been due to some uncontrolled factors like the absorption capacity of the plants used and insufficient contact time. It is also possible that the plants used in these set ups have shorter roots which could mean lesser absorption capacity. By this, it was determined by the researchers that the absorption of metals are mainly occur in the roots of the plants

Also noticeable in the Figure is the decrease in the percentage removal of Cr^{6+} in those set up with the highest concentration (8mg/L) of copper ions. As in these cases, hindering mechanisms became completely dominant and Cr^{6+} excretion occurred as plant cells where saturated with both copper and chromium ions in the passage of time.

Biological and physical processes are both involved in the uptake of ions by aquatic plants. One example of physical process involved is diffusion which allows the positively charged ions from higher concentration to a lower concentration such as plant cell. Another physical process is osmosis which move the water molecule in the opposite direction as it passed through the semi-permeable membrane of the plant and hinder the positive ions uptake. Ion exchange and complex formation are other physical processes that can be involved in the uptake of ions in the aquatic plant. Positively charged ions such as metals would greatly influencedby the property of the plants to allow the passage of fluid since both the process of diffusion and osmosis were across the cell wall.The rate of adsorption of positively charged ions such as metal was by Ion exchange process. Formation of other ions or co-ions would prevent the uptake of the Cr+6 into the plant cell wall as it interfere in the process by occupying available sites for adsorption, thereby large complex ions were being absorb instead of the chromium. Prevention of the uptake of ions in the plant cell or removal from the plants could be resulted in biological process. Thus, two classes of processes could be happen; an adsorption of the positively charged ions into the cell wall by physical processes and prevention and removal of the ions from the cell wall by biological processes.

As in these cases reflected in figure 2, hindering mechanisms or prevention of the cautions to adsorbed on the cell wall became completely dominant and Cr^{6+} excretion occurred as plant cells where saturated with both copper and chromium ions in the passage of time.

Comparison on the percentage removal of Cr^{+6} among varying conditions

All calculated p-values from different sources of variations were lower than 0.05 level of significance at a total of 17 degrees of freedom. Based on these, there is a statistically significant interaction between contact time and concentrations of copper and chromium VI ions with a p-value of <0.001. It can also be inferred from the table that F values of the sources of variation were all higher than the critical F value (64.42>3.17; 35.60>2.12; 4.96>1.83). This also implies that there is a significant difference on the percentage removal of Cr^{6+} upon varying the contact time and concentrations of Cr^{6+} and Cu^{2+} during phytoremediation of water hyacinth.

Table 4. Summary of F values between percentage removal of Cr^{6+} with varying initial concentration of $Cr^{6+}$and Cu^{2+} and contact time*

Source of Variation	F_{value}	$F_{critical}$ **	P_{value}	Decision Ho	Interpretation
Contact Time	64.42	3.17	<0.001	Reject	Significant
Concentration Of Cr^{6+} and Cu^{2+}	35.60	2.12	<0.001	Reject	Significant
Contact Time x Concentration Of Cr^{6+} and Cu^{2+}	4.96	1.83	<0.001	Reject	Significant

**Analyzed by SigmaPlot V12.0*

***Fcritical obtained from Microsoft Excel 2007*

Table 4 shows that the null hypothesis is rejected which means that the presence of varying concentration of copper ions (Cu^{2+}) in the simulated wastewater under varying conditions significantly affect the percentage removal of hexavalent chromium. As the concentration of the copper ions increases, a significant decrease in the absorption of chromium ions was observed.

Best condition based on the aforementioned variations

Table 5 shows that treatment using 9 mg/L of Cr^{6+} and 0 mg/L Cu^{2+} for 12 days have the highest computed average (90.07). This means that the percentage removal of hexavalent chromium is maximized at this condition.

It was already proven earlier that the three factors (contact time, concentration of Cr^{6+} and concentration of Cu^{2+}) varied in this study were statistically significant to the percentage removal of Cr^{6+} ions in the phytoremediation of Cr^{6+} using water hyacinth. Also, it was observed that the contact time and concentration of Cr^{6+} are directly related to the percentage removal of Cr^{6+}. This meant that as the contact time was increased from 4 to 12 days, the percentage removal also increased. Thus, the percentage removal was maximized at the 12th day. Likewise, the percentage removal of Cr^{6+} increased as the concentration of Cr^{6+} was increased from 3 mg/L to 9 mg/L. Accordingly, the best condition was achieved at the treatment with the highest initial concentration of Cr^{6+} (9 mg/L). On the other hand, a decreasing trend was observed as the percentage removal of Cr^{6+} was plotted against varying concentrations of Cu^{2+}. The percentage removal ofchromium VI decreases as the concentration of Cu^{2+} was increased from 0 mg/L to 8 mg/L. Thus, treatment with 0 mg/L of copper ions gave the highest result.

Table 5.Summary of averages among percentage removal of Cr^{6+} with varying initial concentration of Cr^{6+} and Cu^{2+} and contact time

Concentration in ppm (Cr^{6+}:Cu^{2+})	**Contact Time**		
	4 Days	*8 Days*	*12 Days*
		Averages	
3:0	78.00	78.22	82.56
3:4	74.44	79.00	81.33
3:8	76.67	76.33	79.22
6:0	75.39	81.33	84.56
6:4	77.33	79.83	81.61
6:8	76.00	79.22	76.11
9:0	80.81	86.52	**90.07**
9:4	82.30	84.44	**88.78**
9:8	80.74	84.70	81.26

Based on the calculated percentage removals and statistical treatment of data, the best condition was established to be 12 days of contact time in simulated wastewater with 9 mg/L initial concentration of Cr^{6+} and 0 mg/L of copper ions. But it was also plausible to conclude that the optimum condition in the presence of copper ions was achieved at 12 days of contact time in simulated wastewater with 9 mg/L initial concentration of $Cr^{6+}$and 4 mg/L of copper ions.

CONCLUSION AND RECOMMENDATION

In general, an increasing trend is observed as the percentage removal of Cr^{6+} is plotted against the concentration and contact time. Therefore, the percentage removal of Cr^{6+} has a direct relation with contact time and concentration of chromium VI in simulated wastewater.

There is a significant difference on the percentage removal of Cr^{6+} at different concentrations in simulated wastewater upon varying contact time.

Though the results showed some deviation in the established trend, generally, it can be concluded that the percentage removal of Cr^{6+} in simulated wastewater decreases as the concentration of copper ions increases.

There is a significant difference in the percentage removal of Cr^{6+} at different conditions (concentration and contact time) upon the presence of Cu^{2+} at different concentrations.

Based on the experimental and statistical results, the optimum condition for phytoremediation as per the given parameters varied is 12 days of contact time, chromium VI concentration of 9 mg/L and 4 mg/L copper ions.

It is recommended that future researchers can consider using longer contact time and higher initial concentrations of chromium VI as the plants were able to survive during the experiment proper.

Other plant characteristics (i.e. age, weight, height, roots size, etc.) may be varied to know their effect in phytoremediation.

The study also suggests using water hyacinth plants in the treatment of industrial waste water containing considerable amount of Cr^{6+}.

It is also endorsed that future researchers use water hyacinth in the determination of other chemical characteristics of waste water like BOD and COD.

Future researchers can also consider using other aquatic plants for phytoremediation of hexavalent chromium and compare it with water hyacinth.

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