Biosorption of Cr (VI) From Wastewater Using Dried Leaves of Jatropha Curcas

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ABSTRACT

The sorption property of dried and powdered leaves of Jatropha plant for Cr(VI) from wastewater was investigated by conducting batch mode biosorption experiments. The effect of pH, contact time, dose of biosorbent and initial concentration of the sorbate was studied in a series batch mode sorption experiments. Acidic medium favored the sorption process with maximum sorption capacity of 79.23% at pH 2. The sorption experiment attained equilibrium or saturation at 1hr and the biosorption equilibrium data obtained at a pH 2 was found to better fit the Langmuir adsorption isotherm with maximum biosorption efficiency of 0.313 mg/g. The efficiency of the biosorbent was also tested in real wastewater collected from tannery following the same procedures and using the optimum conditions obtained in the laboratory-made sample and found to be reasonable with biosorption efficiency of 59.9%.

Keywords: Biosorption, Cr(VI), wastewater, sorption capacity, Langmuir Isotherm

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INTRODUCTION

Rapid industrialization and increase in population have resulted in a large amount of discharge either in the form of municipal or industrial wastewater and this has led to the inclusion of heavy metals in the environment. Consequently, these metals are usually found well above the tolerance limit in the aquatic environment [1].

Heavy metals, from their point of origin and other sources, can be transported to distant environments. These all pose contamination in the receiving water system and land resulting in serious environmental pollution even threatening human life [2-4]. Contamination of the environment by heavy metal ions causes severe socio-environmental problems. Thus in a view of their toxicity and persistent nature, protecting the environment from contamination by these pollutants is crucial for global sustainable development [1].

Chromium is one of the common heavy metals, discharged and accumulated in large quantity into the environment as a result of various industrial activities such as leather tanning, dyes, paints and pigment manufacturing, wood preservation, electroplating etc. which in turn has posed deleterious impact on the public health and the ecosystem at large [5-7].

Chromium like the other transition metals exists in various oxidation states. However, in the aquatic environment it mainly occurs in two stable oxidation states: Cr(III) and Cr(VI). These oxidation states of chromium have contrasting toxicity, mobility and bioavailability [8-11]. The Cr(VI) is of particular concern because of its toxicity than that of the other species Its toxicity is 500 times than that of the trivalent chromium, which is relatively innocuous and an essential micronutrient in the diet. Cr(VI) readily moves through soil and aquatic environments and is a strong oxidizing agent capable of being absorbed through the skin [1, 8-12]. According to the United States Environmental Protection Agency (USEPA), the maximum recommended limit of Cr(VI) in potable water is 0.05 mg/L.

However, wastewater resulting from various industrial activities contains much higher concentrations of this toxic metal as compared to the above permissible limits. Thus, treatment of these effluents to reduce/remove this pollutant before discharging into the environment becomes inevitable [1, 9, 13-17].

Different techniques like chemical precipitation [18, 19], membrane filtration[20], ion exchange[21-23], reverse osmosis[24] and activated carbon [24-27] adsorption have been suggested for the removal of Cr(VI) from industrial wastewater . However, these approaches are not cost effective and difficult to implement in developing countries like that of Ethiopia where resources are limited [9, 10 &16]. Apart from this, most of these conventional techniques generate secondary effluent impacts on the recipient environment and some of these methods become inefficient especially when the metal concentration is low. Therefore, there is a dire need for a treatment method for Cr(VI) removal from wastewater which is simple, effective and inexpensive [25, 28-31].

With regard to this, biosorption, which involves biological materials for the removal of heavy metals from industrial effluents, can be considered as an alternative way. Different investigations have proved it efficient, economical and technically feasible. Hence has gained increased credibility during recent years [32-39]. Natural (biological) materials that are available in large quantities or certain waste from agricultural and industrial operations may have potential to be used as low-cost sorbents, as they represent unused resources, widely available and are environmental friendly [37, 38].

Hence, there is a need to explore new low-cost sorbents having improved Cr(VI) sorption capacity. In this study an attempt was made to investigate the Cr(VI) sorption property efficiency of the dried leaves of *Jatropha curcuas L.(DPLJ)*. In addition its natural abundance in mid to low altitudes areas, the plant is also deliberately cultivated for biofuel purpose.

MATERIAL AND METHODS

All the chemicals used in this experiment are of an analytical grade. Potassium dichromate, Hydrochloric acid, sodium hydroxide, acetone (UV-Vis grade) 1,5diphenylcarbazide (DPC) Nitric acid, Sulfuric acid were obtained from Fissions, India.

Sampling and Preparation of the Biosorbent

Jatropha (*Jatropha curcuas* L.) leaves collected from Benshangul Gumuz regional state (Ethiopia) were air-dried and manually crushed to make them manageable for plastic packing and transport. The air-dried leaves were brought to the laboratory and repeatedly washed with distilled water to remove dust from the surface. Then the cleaned biomass was left to dry in an oven for 24 hrs at $105\pm5^{\circ}$ C. The oven-dried biomass was grinded with an electric grinder. In order to get the uniform size of the biosorbent, the powder was passed through a steel sieve of mesh size 810 µm. Finally part of the powder that passed through the sieve was preserved in dry and clean plastic bottle for the subsequent biosorption experiment.

Preparation of Cr (VI) Stock Solution

1000 mg/L Cr(VI) stock solution was prepared by dissolving 2.8246 g of $K_2Cr_2O_7$ with distilled water in a 1 L volumetric flask and then filled up to the mark. Later this solution was used as laboratory made (synthetic) wastewater sample for the subsequent biosorption experiments to serve as a source of Cr (VI) ions. From this stock solution further working solutions were prepared as needed by appropriate dilution. In this study, all biosorption experiments were conducted using 100 mL solution volume.

Biosorption Experiments

Batch mode biosorption studies were conducted at room temperature (22 °c) using 250 mL conical flasks. A known amount of dried and powdered leaves of Jatropha plant, which

hereinafter be called *DPLJ*, was added to 100 mL of known concentration of Cr(VI) solutions. The pH of the Cr(VI) solutions was adjusted by using 0.5 N NaOH and HCl solutions prior to mixing with the biosorbent. The mixture was then agitated at 200 rpm using a mechanical shaker depending upon the contact time of interest, allowing sufficient time for mixing. After the desired time the mixture was filtered using Whatman Number 541,125 mm filter paper. The concentrations of Cr(VI) in the filtrates were then measured using UV-Vis spectrophotometer by developing a purple color using 1,5-diphenylcarbazide, a common complexing agent.

The effects of different parameters on the biosorption process were studied by varying pH (2, 4, 6 and 8), contact time (15, 30, 45, 60 and 120 minutes), amount of the biosorbent (2, 4, 6, 8 and 10 and 12 g) and initial concentration of Cr(VI) ions (5, 10, 15, 20 and 25 mg/L). The effect of each parameter was studied by varying one of the factors at a time while keeping the rest constant at a constant volume of solution and room temperature.

Each biosorption experiment was conducted in triplicate and the chromium removal efficiency of the DPLJ at any instant of time was determined and presented by using the following equation:

% removal =
$$\frac{C_0 - C_f}{C_f}$$
 (1)

Where, C_0 is the initial concentration of Cr(VI) ion and C_f is a final concentration of Cr(VI) ions (concentration in the filtrates)[40]. The amount of metal removed, q (mg metal/gram sorbent) was computed using the following equation [16].

$$q = \frac{(C_0 - C_f)V}{m}$$
(2)

Where C_o and C_f are the initial and final Cr(VI) concentrations, the m= mass of the biosorbent and V= volume of the solution. The biosorption equilibrium data obtained at a

fixed dose of the biosorbent and varying initial Cr(VI) ions at constant pH have been fitted into the two well-known adsorption isotherms: Langmuir and Freundlich adsorption isotherms in order to see whether the biosorption equilibrium obeys these models and determine the maximum uptake capacity of the biosorbent (DPLJ).

Cr(VI) Analysis

Studying chromium removal efficiency of the DPLJ involves measuring the Cr(VI) ions concentration in the wastewater before and after the biosorption process takes place. For the laboratory made sample, Cr(VI) ion concentration before the biosorption process was already known and what remained was determining the concentration after the biosorption process. Therefore, this was done spectrophotometrically by developing a purple-violet color with 1, 5-diphenylcarbazide in acidic solution as a complexing agent. The absorbance of the purple-violet colored solution was read at 540 nm after 20 minutes[1].

For the real samples, composite wastewater was collected from WALIA tannery (Addis Ababa, Ethiopia). Before conducting the biosorption experiment, the concentration of Cr(VI) in the raw wastewater was determined as follows: the first part of the wastewater was taken and filtered using a Whatman filter paper(number 541,125 mm). From 50 mL of the filtrate collected, 10 mL aliquot was taken and diluted to 100 mL. Next, from this solution 10 mL aliquot was taken in a conical flask and acidified with 0.5N sulphuric acid and its absorbance was measured spectrophotometrically at 540 nm after developing a purple-violet color with 1, 5- diphenylcarbazide. After determining the concentration Cr(VI) ions in the raw wastewater, biosorption experiments were conducted in triplicate using the optimum conditions of the parameters obtained in the laboratory made a sample, i.e. pH 2, 10 g biosorbent , contact time 1hr and solution volume of 100 mL. Finally, the residual Cr(VI) ion concentrations in the filtrates were measured in the same way as described above in the experimental section.

RESULTS AND DISCUSSION

Batch mode biosorption experiments were conducted to study the Cr(VI) removal efficiency of DPLJ, by developing a method using a laboratory made wastewater solution. The batch sorption experiments were studied as a function of four parameters viz. pH, contact time, amount of biosorbent and initial Cr(VI) concentration. Finally, in order to see the applicability of the method in real situations when there are competing ions the optimum conditions obtained in these experiments were applied into real wastewater sample collected from WALIA Tannery (Addis Ababa, Ethiopia). The biosorption experiment at each parameter was studied in triplicate and the residual concentration was determined from a linear calibration curve.

Effect of pH on the Removal Efficiency

The pH of the solution is an important factor that controls the uptake of metal ions from the solution by a biosorbent. This is because that the pH of the solution can change the surface charge of the sorbent and degree of ionization of the sorbate [11, 46].

It has been found that the percent removal of Cr(VI) ions increased with decreasing the pH of the solution, reaching its maximum (79.23%) at pH 2. However, when the pH of the solution was increased the removal efficiency was found to reduce reaching 27.54% at pH 8.

The mean residual Cr(VI) concentrations at consecutive pH values showed a significant difference when statistically analyzed using LSD (Least Significant Difference) at 95% confidence level. This indicates that the removal efficiency of DPLJ differs as the pH of the solution is varied. Fig. 1 depicts this decreasing trend of percent removal with increasing pH, attaining its peak and minimum removal efficiency at pH 2 and 8

respectively. The reason for the observed trend can be explained as the pH of the solution is lowered, the surface of the biosorbent material gets protonated as a result, the electrostatic attraction towards the predominant oxyanions of Cr(VI) in acidic solutions $(Cr_2O_7^{2-} and HCrO_4^{-})$ is enhanced. The decrease in percent removal with higher pH can be explained in three different ways:

- As the pH increases the degree of protonation decreases hence the anionic electrostatic attraction is reduced
- 2) As the pH increases the competitiveness of the OH⁻ ion increases and
- It may be due to the prior occupation of adsorption sites of the biomaterial by the sorbate [8, 11 & 23].

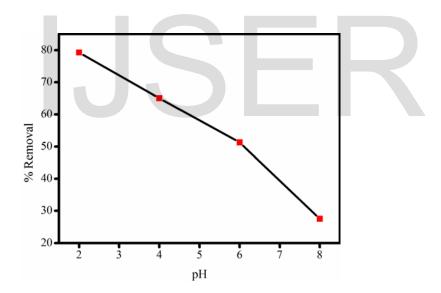


Fig. 1: Percent removal as a function of pH (initial concentration 10 mg/L, biosorbent dose 4 g, contact time 1 hr)

Effect of Contact time on the Removal Efficiency

It has been observed that the sorption process in the first 15 minutes was very fast, and 58.72% of the Cr(VI) ions from the solution were removed in 15 minutes. The percent removal proceeded to increase and started to stabilize after 60 minutes (Fig.2). Here it is

worth to note that after 60 minutes the biosorption process became almost independent of contact time signifying that the process tends to attain its sorption equilibrium at the experimental conditions. This is evident from Fig.2 that after 60 minutes for an increase in a contact time of 1 hr a 0.22% increment in percent removal was recorded, which is very small as compared with the contact time.

In addition, after 90 minutes of contact time the difference in the mean residual concentrations between the consecutive contact times was found to be insignificantly different at 95% confidence level when statistically analyzed by LSD indicating the saturation of the biomaterial.

Fig.2 illustrates the general trend observed in this experiment. This can be explained as that, under the experimental conditions used in this study the active surface sites of the biosorbent became saturated hence, the uptake of the remaining Cr(VI) ions became impossible/retarded.

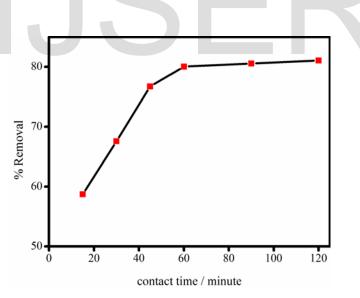


Fig.2: Percent removal of Cr(VI) as a function of contact time (initial concentration 10 mg/L, initial pH 2 and biosorbent dose 4 g)

The trend observed in this study is in agreement with several previously reported studies on different biomaterials. For example, a study conducted on assessment of the removal efficiency of Cr(VI) using wheat bran and the results revealed that the sorption process reached equilibrium in 1 hr and after that small change in the removal efficiency was observed. Biosorption of Cr(VI) conducted using different agricultural wastes showed a 40% increment for an increase in a contact time of 4 hrs after a saturation/ equilibrium time [11, 14].

Generally studying the effect of contact time enables to develop a kinetic model for the sorption process in using a particular biosorbent, which in turn is an important parameter for designing sorption systems [23].

Effect of Dose of the Biosorbent on the Removal Efficiency

A100 mL of 10 mg/L Cr(VI) solution at a pH of 2 was subjected to a batch mode biosorption experiment for 1 hr (the time which the rate of sorption started to stabilize in the previous experiment). The experiment was conducted in triplicate with 2, 4, 6, 8, 10 and 12 g of DPLJ. Under the experimental conditions used in this study, it was possible to remove more than half of the initial concentration of the sorbate with 2 g of the biosorbent. Fig.2 clearly shows the extent of percent removal obtained in this study as the amount of biosorbent increases. And from the results it can be concluded that almost complete removal (> 95%) was obtained from a 100 mL of 10 mg/L Cr(VI) by using 10-12 g of DPLJ. Statistical analysis of the mean residual concentrations by LSD at 95% confidence level showed that after using 10 g of DPLJ, the differences between the mean residual concentrations became insignificantly different. From this, we can conclude that 10 g of DPLJ is the optimum amount under the experimental conditions used in this work. However, it is worth to look that there might be a possibility to increase the removal efficiency more than the reported figure either by modifying the surface of the biosorbent

IJSER © 2018 http://www.ijser.org or adding some extra DPLJ (i.e. > 12 g). However, surface modification helps to reduce the amount of biosorbent used for treatment as it increases the removal efficiency of the biosorbent.

Generally, the increase in removal efficiency as the amount of the DPLJ was increased can be attributed to an increase in a number of active surface sites capable of attracting the Cr(VI) ions [11, 12].

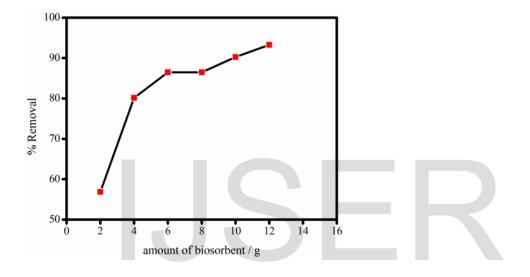


Fig. 3: Percent removal of Cr(VI) as a function of biosorbent dose (initial concentration 10 mg/L, initial pH 2 and contact time 1 hr)

Effect of Initial Concentration of Cr (VI) ions on the Removal Efficiency

Batch mode experiments at different initial concentration levels of Cr(VI) ions (5, 10, 15, 20 and 25 mg/L) were carriedout while maintaining the rest three parameters constant. Experimental results revealed that, for the concentration range studied (5-25mg/L), percent biosorption was found to decrease from 91.20- 47.36 %. The maximum percent removal was achieved at 5 mg/L Cr(VI) ion concentration with 4 g of the DPLJ while the minimum (47.36%) being the highest concentration level studied (25 mg/L). From this

trend it can be concluded that the percent removal will even be lower if the Cr(VI) ion concentration was increased further.

In general it can be inferred from Fig.4 that the percent biosorption was higher with lower concentration levels studied (5-15 mg/L), than that of the higher concentration levels (20 and 25 mg/L), which had 58.89 and 47.36% removal efficiency respectively. It is also interesting to note from Fig.4 that there was a sharp decline in percent removal when the initial concentration of Cr(VI) was increased from 15 to 20 mg/L.

The decrease in percent removal when the concentration of the Cr(VI) ions was increased can be attributed to the fact that the binding sites at the surface of the sorbent, which was kept constant, became saturated and the tendency to uptake additional ions became reduced even though there were extra sorbate ions left in the solution. Meaning, at higher concentrations, the available sites for sorption become fewer, and hence the percentage removal of metal ions, which depends upon the initial concentration, decreases [8, 14& 23].

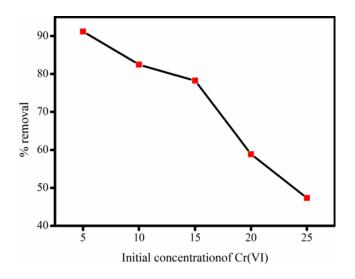
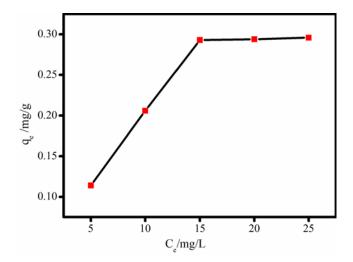


Fig. 4: Percent removal as a function of initial concentration of chromium ions (pH 2, contact time 1 hr, dose of biosorbent 4 g).



However, if we look at a number of sorbate ions removed per gram of the biosorbent, it was found to rise with initial Cr(VI) ion concentrations (Fig.5) which may be ascribed to the availability of more number of Cr(VI) ions in solution for sorption. Moreover, higher initial sorbate concentration provided higher driving force to overcome all mass transfer resistances of the metal ions from the aqueous to the solid phase resulting in higher probability of collision between Cr(VI) ions and the active sites [1].

After 15 mg/L of Cr(VI) ions, the actual amount removed was found to be nearly constant (Fig.5). This shows that under the experimental conditions used in this study, 4 g of DPLJ was capable of removing 0.293- 0.296 mg of Cr(VI) ions /g DPLJ from 100 mL of solution. This can be attributed to the fact that the after 15 mg/L of Cr(VI) the binding sites at the surface became saturated and the tendency to uptake additional ions became reduced. Similar trends were also reported on studies conducted using treated sawdust, wheat bran and durian peel on Cr(VI) and reported similar trends even though the operating conditions used were different [1, 13].



IJSER © 2018 http://www.ijser.org **Fig. 5:** Amount of Cr(VI) removed per gram of the biosorbent (pH 2, contact time 1 hr, dose of biosorbent 4 g)

Adsorption Isotherms

In this study all the equilibrium data obtained at different Cr(VI) ion concentrations and a fixed mass of the biosorbent at room temperature were fitted into the most widely used Langmuir and Freundlich adsorption isotherm models so as to describe the biosorption equilibrium and obtain the maximum biosorption capacity of the biosorbent. Linear regression was used to determine the better fitting isotherm and coefficient of determination (\mathbb{R}^2) was used as a fitting criterion in this study [11, 14 & 23].

Langmuir Isotherm

The linear form of Langmuir model, which is valid for monolayer adsorption on the surface of the biosorbent, is given by:

$$\frac{C_e}{q_m} = \frac{1}{bq_m} + \frac{C_e}{q_m}$$
(3)

Where: C_e , the equilibrium concentration, **b**, energy of biosorption and q_m , maximum biosorption capacity (mg/g) corresponding to complete monolayer coverage [14, 23]. The constants b and q_m were determined from the y intercept and slope of the regression equation obtained from the linear plot of C_e/q_e vs. C_e of the equilibrium data respectively (Fig.6).

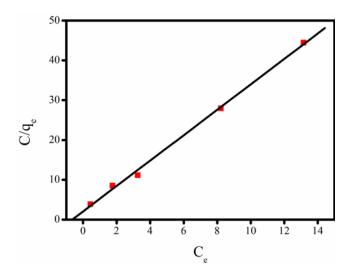


Fig. 6: Langmuir isotherm for the biosorption of Cr(VI) with DPL (biosorbent dose 4 g, contact time 1 hr and pH 2)

The results obtained shows that the Cr(VI) –DPLJ biosorption system follows well to the Langmuir adsorption model with maximum biosorption capacity 0.313 mg/L and biosorption energy of 1.55 L/mg. The essential features of Langmuir adsorption isotherm is expressed in terms of a dimensionless constant called separation factor or equilibrium parameter (R_L), which is defined by:

$$R_{\rm L} = \frac{1}{b_{\rm C_0}} \tag{4}$$

Where C_o is the initial Cr(VI)ions concentration (mg/L) and b energy of biosorption. R_L value indicates the shape of the isotherm to be irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 0$) or unfavourable ($R_L > 1$) [11, 14, 23]. R_L values at all concentration levels

used in this study were computed and found to be in between 0 and 1, indicating the favourability of the Cr(VI)-DPLJ biosorption system under the experimental conditions used in this study.

Freundlich Isotherm

The linear form of Freundlich isotherm, which is an indication of heterogeneity of the biosorbent, is given by:

$$\log q_{e} = \log K_{f} + \frac{1}{n} \log C_{e}$$
⁽⁵⁾

Where, $\mathbf{K}_{\mathbf{f}}$ stands for adsorption capacity and \mathbf{n} adsorption intensity (heterogeneity factor) [14, 23]. In a similar manner, the value of $\mathbf{K}_{\mathbf{f}}$ and \mathbf{n} were determined from the slope and the y-intercept of the plot of logq_e vs. logC_e of the equilibrium data (Fig.7) to be 0.165 mg/g and 3.51. The value of biosorption intensity (n) greater than one indicates the favourability of the sorbate- sorbent system [41]

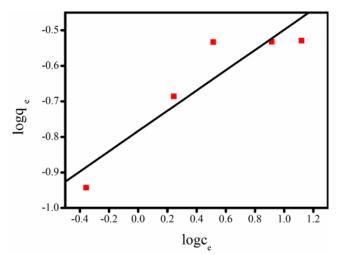


Fig. 7: Freundlich isotherm for the biosorption of Cr(VI) with DPLJ (dose of biosorbent 4g, contact time 1hr and pH 2)

Results of the linear regression of the equilibrium data (Table 1) revealed that the Langmuir models better conforms to the Cr(VI)-DPLJ biosorption system, with a coefficient of determination; $R^2 = 0.9976$. This indicates that under the experimental conditions used in this study, the Cr(VI)-DPLJ biosorption system exhibits uniform monolayer biosorption process.

Table 1: Linear regression data for Langmuir and Freundlich isotherms of Cr(VI) biosorption with DPLJ

Isotherm type	Parameter	R ²
Langmuir	$q_{\rm m} = 0.313 \text{ mg/g},$	0.9974
	b =1.55 L/mg	
Fredulich	$K_{\rm f}$ =0.165 mg/g,	0.8514
	n=3.51 L/mg	

APPLICATION OF THE METHOD IN REAL WASTEWATER (CASE STUDY)

In order to see the applicability of the method in real situations when there are competing ions for the possible binding sites, biosorption experiments were conducted using wastewater collected from the Walia Tannery (Addis Ababa). After sample preparation as explained in the experimental part the wastewater was tested for its Cr(VI) content. Finally, biosorption experiments were conducted in triplicate for 1hr using 10 g of the biosorbent. The removal efficiency was found to be 59.59% showing the applicability of DPLJ for the treatment of Cr(VI) in real wastewater as its reasonably good figure. However, here it is worth to note that the percent removal was found to be less than that of the laboratory made sample. This is because of the presence of other ions in the wastewater, which competes for the binding of oxyanions of chromium on the surface of the biosorbent.

CONCLUSIONS

Biosorption of Cr(VI) by using dried leaves of Jatropha plant (DPLJ) without any surface modification of the biomass was conducted in a batch mode experiment. The findings of this study showed that the four parameters studied viz. pH, contact time, a dose of the biosorbent and initial Cr(VI) ion concentration affect the removal efficiency. Under the experimental conditions used in this study it was possible to remove 79.23% of Cr(VI) from a 100 mL of solution using 4 g of the biosorbent at pH 2. The results indicated that the biosorption of Cr(VI) by DPLJ was found to be higher in acidic medium. Langmuir adsorption isotherm was found to better fit the equilibrium of the biosorption data and maximum biosorption efficiency of the DPLJ found to be of 0.313 mg/g. The biosorbent was also tested in real wastewater sample collected from Walia Tannery and showed reasonably good removal efficiency (59.9%). The decrease in removal efficiency as compared to the laboratory made sample is ascribed to the presence of competing ions for the possible binding sites on the surface of the biosorbent. However, this study did not cover investigation of the actual mechanism involved by the biosorbent and it only took into account biosorption in terms of electrostatic attraction of the sorbate. Any possible reduction of Cr(VI) into Cr(III) was not considered and all Cr analysis and percent removal were made for residual Cr(VI) ions. Finally, Jatropha leaves can be an alternative source for hexavalent chromium remediation in wastewater from tanneries or other industrial operations as the plant is easily cultivated for biofuel development or environmental protection proposes apart from this purpose.

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Conflict of Interest: The authors declare no conflict of interest

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