



## Chromium (VI) biosorption using novel biosorbents from *Calotropis gigantea*

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Biosorption of heavy metals using plant based materials contributes a significant role in reducing environmental pollution. Here, we investigated removal of hexavalent chromium metal [Cr (VI)] from an aqueous solution by alkali treated novel biosorbent prepared from *Calotropis gigantea* (L.) Dryand. ex W.T. Aiton leaves and flower. Batch studies were conducted to examine the process parameters. The effect of pH, biomass dosage, initial metal ion concentration, contact time was evaluated keeping temperature and agitation speed constant. As much as 70% removal of Cr (VI) was observed with a leaf biomass dosage of 4 g/L at pH 2.0 and initial metal ion concentration of 1.0 ppm. Data obtained from the experiment were used to calculate the equilibrium data with two variable isothermal models. Freundlich and Temkin isotherm models suited the process for leaves and petals, respectively. Pseudo second order reaction suited in the kinetic study. The data obtained from the study suggests that biosorbents derived from *C. gigantea* has effective chromium biosorption capability. The results indicate that *C. gigantea* could be used as an efficient, cost effective and environmental friendly biosorbent for the treatment of chromium contaminated water bodies.

**Keywords:** Alkali treatment, Bioaccumulation, Bioremediation, Carcinogenic, Crown flower, Giant milkweed, Heavy metals, Industrial pollution

Industrial effluents when released without prior treatment contaminate the natural habitat by heavy inflow of toxic metal ions affecting public health. Such contaminations are poisonous as they accumulate in plants, animals and humans and cause a permanent toxic and carcinogenic effect. Because of these reasons, presence of heavy metals with higher concentrations in the environment is unacceptable and the pollution legislation directs its removal from such wastewaters. In this context, different biosorption techniques are increasingly gaining interest.

Chromium metal is regarded as a toxic heavy metal having a density of 7.19 g/cm<sup>3</sup> which are found carcinogenic above its permissible concentration of 0.1-0.05 ppm. Hexavalent chromium metal is found to be more toxic than the trivalent form in the effluents. Different industries like metal finishing, electroplating, stainless steel production, chromate preparation industries and textile industries are

releasing chromium waste into water bodies which increases water pollution and raises serious concern on environment<sup>1</sup>. Chromium has many adverse effects on human health and metabolism by accumulating in the food chain. Higher incidents of respiratory cancers and skin allergies are associated with human exposure to chromium metals<sup>2</sup>. Adsorption of heavy metals was found to be an efficient technique in concentrating the metal to a solid surface. The biosorption process depends on surface property of biosorbent as well as chemical property of sorbate. In addition to this, pH, amount of adsorbent, concentration of adsorbate and temperature also contribute to the process. Biosorption mainly depends on the cell wall components such as lignin, cellulose and functional groups — carboxylic acid, alcohol, aldehydes, ketones, etc. on the surface for adsorption of metals<sup>3</sup>. Researchers show interest on biosorption studies due to its low cost implementation, efficiency, adsorbent regeneration and metal resumption ability to explore the potential of different biological material in sequestering metal ions from aqueous solution<sup>4,5</sup>.

Biosorption has been explored utilising various sorbents. Comparative study on biosorption of Cd, Ni, Zn, Pb metals on 30 strains of algae reports maximal

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biosorption on the algal strain *Lyngbya taylorii* for all metals<sup>6</sup>. Another study with *Spirulina* sp. demonstrated maximum metal biosorption (90.1 mg/g) at pH 5.0, with 1.0 h contact time<sup>7</sup>. The effect of pH on growth of microalgae and biosorption are important<sup>8</sup>. Activated carbon prepared from *Tridax procumbens* biomass showed 98% removal of Pb(II) and Cd from aqueous solution in 180 min at pH of 6.8<sup>9</sup>. *Portulaca oleracea* showed a maximum of 54.95 mg/g of Cr (VI) ion adsorption at pH 2.0 with 45 min of contact<sup>10</sup>. Cr (VI) biosorption peaked with olive when the pH was brought to 2.0<sup>11</sup>. *Phanera vahlii* fruit biomass exhibits considerable Cr (VI) biosorption potential with zinc chloride activation<sup>12</sup>. Similarly, *Ficus auriculata* leaf biomass showed adsorption of hexavalent chromium under an agitation speed of 120 rpm at pH 2.0<sup>13</sup>. *Spirulina platensis* biomass could remove 98% of Cd (II) from aqueous solution with dosages below 2 g/L for initial concentration of 100 and 200 ppm<sup>14</sup>. Absolute 100% removal of Pb(II) was obtained with *Gelidium amansii* biomass for 200 ppm initial concentration with 1.0 g/L biomass dosage at pH of 4.5 and 318 K for 60 min at static condition<sup>15</sup>. Biomass have consistently being shown to be as good biosorbents against heavy metals<sup>16,17</sup>.

Here, we investigated the potential of the common weed *Calotropis gigantea* (L.) Dryand. ex W.T. Aiton in bioabsorbing chromium metal onto the surface.

## Materials and Methods

Chemicals used for the study were of analytical grade. Single distilled water was used for the whole study.

### Preparation of stock solution

Stock solution was prepared using pure grade potassium dichromate ( $K_2Cr_2O_7$ ) (70.7 mg) dissolved in 500 mL of single distilled water to prepare 50 ppm stock solution. The stock solution is then diluted to make the required experimental concentrations. The stock solution was stored in brown bottle at 4°C before the analysis.

### Preparation of di-phenyl carbazide (DPC) solution

Stock solution was prepared by dissolving 250 mg DPC in 50 mL acetone. The stock solution is stored in brown bottle at 4°C before analysis.

### Preparation of biosorbent

Leaves and flower petals of weed *Calotropis gigantea* plant were collected from a barren land near Kalasalingam Academy of Research and Education, Krishnankoil (9.584035, 77.687142). The collected

leaves and petal samples were washed thoroughly with water followed by distilled water to remove the dirt from the surface of the sample. Samples were then dried in a hot air oven at 70°C for nearly 20 h for leaves and 6 h for flower petals. Dried samples were crushed into fine powders in a commercial blender at 1500 rpm and sieved to get particle size ranging 125-220  $\mu$ m. Fine sample powders were alkali treated with 0.1 N NaOH (100 mL for 1 g), agitated for an hour and kept undisturbed for 24 h. Biomass was then filtered and washed thoroughly with distilled water until pH reaches 7.0. The biomass was then dried and stored in air tight containers for future use.

### Characterization of biosorbent

Surface characterization of the biosorbent was done by SEM for surface morphology, EDX for surface elemental analysis and FTIR for the presence of functional groups<sup>18</sup>. All the analysis was carried out in triplicates.

### Batch biosorption study

The biosorption study was performed with different hexavalent chromium concentrations (0.2, 0.4, 0.6, 0.8 and 1.0 ppm), biomass dosages (1, 2, 3, 4, 5 g/L), pH (2.0, 3.0, 4.0, 5.0, 6.0 and 7.0) contact time (30, 60, 90, 120 min) at constant temperature (303 K) and agitation speed (150 rpm). The effects of each parameter are studied by varying one parameter, keeping others constant. Studies were carried out in 50 mL beakers. Remi multiple beaker shaker was used for constant agitation speed of 150 rpm. The amount of hexavalent chromium biosorbed ( $q_e$ ) in mg/g was calculated using mass balance equation

$$q_e = \frac{(C_i - C_e)V}{m}$$

Percentage removal of hexavalent chromium metal was calculated using the formula:

$$\text{Removal\%} = \frac{(C_i - C_e) * 100}{C_i}$$

$C_i$  = Initial metal concentration (mg/L),  $q_e$  = Amount of metal adsorbed (mg/g),  $C_e$  = Equilibrium metal concentration (mg/L) and  $m$  = amount of biosorbent (g)

### Kinetic experiment

Kinetic studies were done along with the study on contact time with test solutions of different concentrations (0.2, 0.4, 0.6, 0.8, 1 ppm) and contact times (30, 60, 90 and 120 min) keeping other parameters constant [pH-2.0, biomass dosage-4 g/L, temperature (303 K), agitation speed (150 rpm)].

### Biosorption isotherms

Equilibrium of the biosorption process is studied with five, two variable isotherm models. Biosorption isotherm explains the equilibrium between the adsorbent and adsorbate<sup>13</sup>.

#### Langmuir isotherm model

The model assumes that homogenous adsorption occurs to the adsorption sites which are also assumed to be homogenous in distribution and energy basis<sup>19</sup>. The linear expression of the model is expressed as:

$$C_e/q_e = 1/(Q_0 b_L) + C_e/Q_0$$

where  $C_e$  = equilibrium concentration of Cr (VI) (mg/L),  $q_e$  = the amount of Cr (VI) adsorbed per gram biosorbent at equilibrium (mg/g),  $Q_0$  = monolayer coverage capacity (mg/g),  $b_L$  = is the Langmuir isotherm constant (L/mg). The Langmuir isotherm was also expressed in terms of the dimensionless equilibrium constant  $R_L$ , referred to as the separation factor  $R_L = 1/(1+b_L C_e)$  and  $C_i$  = initial hexavalent chromium concentration (mg/L)

#### Freundlich isotherm model

The model implies heterogeneous surface for multi-layer adsorption<sup>13</sup>. The linear expression is given as:

$$\ln q_e = \ln K_f + (1/n) \ln C_e$$

where  $K_f$  = Freundlich isotherm constant (mg/g)/(mg/L); and  $1/n$  = adsorption intensity

#### Dubinini–Radushkevich model (DR model)

The model relates adsorption to porous structure of adsorbent<sup>16</sup>. The linear expression is given as:

$$\ln q_e = \ln Q_m + K \mathcal{E}^2$$

where  $K$  = the coefficient related to the mean free energy of adsorption ( $\text{mol}^2/\text{kJ}^2$ ),  $Q_m$  = maximum adsorption capacity (mg/g) and  $\mathcal{E}$  is the Polanyi potential  $\mathcal{E} = RT \ln ((C_e+1)/C_e)$  where  $R$  = gas constant (8.314 J/mol K) and  $T$  = temperature (K).

The mean adsorption energy  $E$  (kJ/mol) was calculated using  $K$  values and the equation

$$E = 1/[\sqrt{(2K)}]$$

The physical and chemical nature of adsorption process is explained by mean adsorption energy. If the value is below 8 kJ/mol the process is physical and more than 16 kJ/mol accounts for chemical nature of adsorption if it is between 8-16 kJ/mol it accounts for ion exchange mechanism.

#### Elovich isotherm model

The model implies multilayer adsorption i.e. adsorption increases exponentially with adsorption<sup>17</sup>.

Linear expression of the model is given as:

$$\ln (q_e/q_m) = \ln K_E C_e - q_e/q_m$$

where  $K_E$  = Elovich equilibrium constant (L/mg) and  $q_m$  = Elovich maximum adsorption capacity (mg/g).

#### Temkin model

The model assumes that with coverage heat of adsorption of all the molecules in the layer decreases linearly rather than logarithmically<sup>13</sup>. Linear equation for the model is given as:

$$q_e = (RT/b) \ln A_T + (RT/b) \ln C_e$$

where  $A_T$  = Temkin isotherm equilibrium binding constant (L/mg) and  $b$  = Temkin isotherm constant (J/mol).

#### Kinetics

Kinetic studies gives an insight into the data on mechanism of biosorption<sup>13</sup>.

#### Pseudo first-order kinetics

Pseudo first-order kinetics is given by the equation<sup>20</sup>:

$$\log (q_e - q) = \log q_e - K_1/2.303 t$$

where  $q_e$  and  $q$  are the amounts of Cr (VI) adsorbed (mg/g) at equilibrium and at any time  $t$ . and  $k_1$  = (L/min) is the pseudo first-order rate constant.

#### Pseudo second-order kinetics

Pseudo second-order kinetics is expressed by the equation<sup>13</sup>:

$$t/q_e = 1/(k_2 q_e^2) + t/q$$

where  $k_2$  (g/mg min) is the pseudo second-order rate constant.

## Results and Discussion

### Characterization of biosorbent

The biosorbent was prepared from the dried, powdered, alkali treated leaves and flowers of *Calotropis gigantea* (Suppl. Fig. S1. All supplementary data are available only online along with the respective paper at NOPR repository at <http://nopr.res.in>). Surface characterization of the sorbent is done by SEM for surface morphology, EDX for elemental analysis and FTIR was conducted for the detection of functional groups. SEM analysis of plant leaf and petal biomass before and after alkali treatment was performed and a detectable variation can be observed between the conditions, the surface of untreated biomass is irregular and is inconsistent, whereas for the treated plant biomass surface is regular and is well organized, which is a prior requirement for effective adsorption of adsorbate onto the

pores of the sorbents (Fig. S2). A notable difference is found in the weight percentage of carbon element before and after treatment which could be a reason for the proper organization of pores aiding the adsorption process (Fig. S3).

An alkane stretching, phenol bending, sulfoxide stretching, alkene bending, alcohol bending are the notable differences that are made from the FTIR analysis of both leaf and petal biomass (Fig. S4). The results of FTIR could be read along with difference in weight percentage of carbon, oxygen, and sulfur elements from the EDX results.

Broad alcohol stretching at  $2899\text{ cm}^{-1}$ , N-O stretching in  $1516\text{ cm}^{-1}$ , carbon dioxide stretching in  $2366.66\text{ cm}^{-1}$  were the notable difference from alkali treated and untreated plant biomass. From the FTIR analysis of biosorbent before and after biosorption leaf biomass, N-O stretching in  $1516\text{ cm}^{-1}$ , carbon dioxide stretching in  $2366.66\text{ cm}^{-1}$ , anhydride stretching in  $1735\text{ cm}^{-1}$  was majorly found in leaf biosorption process. N-O stretching in  $1541\text{ cm}^{-1}$ , alcohol bending at  $1361\text{ cm}^{-1}$ , alkane stretching at  $2941, 952$  and  $667\text{ cm}^{-1}$ , carbon dioxide stretching at  $2362\text{ cm}^{-1}$ , alkene stretching at  $1653\text{ cm}^{-1}$  were found from the petal biosorbed biomass. From the data it is clear that changes in occurrence and disappearance of functional groups has occurred and has aided the process of biosorption process.

#### Effect of pH

The influence of pH over adsorption process is higher than other biosorption parameters. pH influences the surface charge of the biosorbent and the degree of ionization which causes an impact on the process<sup>10</sup>. To determine the influence of pH on biosorption, an experiment was carried out keeping other parameters like initial ion concentrations, dosage, temperature, contact time constant and pH was varied from 2.0 to 7.0. The result of the experiment is depicted in Fig. 1. Standard graph for Cr (VI) was prepared by plotting test concentrations with absorbance at 540 nm. Graph with Co-efficient of co-relation ( $R^2$ ) value of 0.99 was obtained.

Similar results were obtained for both the biosorbents. Maximum percent removal of Cr (VI) was observed at pH 2.0 (Fig. 1). Maximum percent obtained was 47%. Cr (VI) exists as chromate ion or dichromate ion i.e. they exist as anion in aqueous solution. They will be more bind to positive sites of sorbent. At lower pH more hydronium ions will be

present and will bind to functional groups present on the surface making the biosorbent surface charge positive. The positive charged surface favors negative chromate ion to bind to the surface. At higher pH there will be less hydronium ion resulting negative charged sorbent surface which repulses the negative metal ion<sup>12</sup>. The optimized pH was then used for further experiments.

#### Effect of biomass dosage

Biomass dosage is the amount of adsorbent per liter of solution. Effect of dosage has its own importance in biosorption process. During biosorption the adsorbate occupies the pores of the sorbents upon their chemical affinity. With the increase in the number of adsorption site, the percent of adsorption increases. To justify the concept, experiment was done with varying biomass dosage (1-5 g/L) keeping other parameters constant. The result is portrayed in the graph.

As much as 49.56% of chromium ion removal occurred at dosage 2 g/L of leaf biomass. Removal of chromium (VI) increased from 24% to 49% when there was increase in dosage from 1 to 2 g/L. At 2 g/L equilibrium was reached (Fig. 2). When the dosage was increased to 3 an anomalous decrease and later increase in percent removal was observed. About 65% of percent removal was observed at 4 g/L dosage. Further increase in dosage caused not much change in percent removal.

A similar trend is also found in case of petal biomass with the increase in dosage from 1-2 g/L, there was increase in percent removal of Chromium ion. Maximum percent removal was 44% at 2 g/L dosage (Fig. 1B). With the increase in dosage the percent removal of chromium ion was declined and later increased to reach 64%. This anomaly might be due to any mistake during the experiment or any other reasons.

#### Biosorption isotherm data

The isothermal study was done by five, two variable isotherms. Out of five, Freundlich showed the maximum co-efficient of determination for *C. gigantea* leaf biomass, which was about 0.73. The

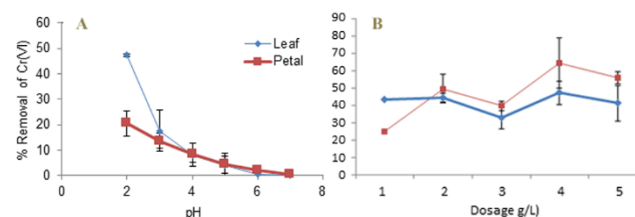


Fig. 1 — Effect of (A) pH; and (B) dosage on percent removal of Cr (VI) ions by *C. gigantea* leaf and petal biomass

Table 1 — Isotherm models and constants

Two-variable Isotherm Model Parameters					
Model	Variables	<i>Calotropis</i> leaf biomass		<i>Calotropis</i> petal biomass	
		Values	R <sup>2</sup>	Values	R <sup>2</sup>
Langmuir	Q <sub>0</sub> (mg/g)	-0.37	0.05	7.7639752	0.51
	b <sub>L</sub> (L/mg)	-0.54		-0.0775436	
	C <sub>i</sub>	R <sub>L</sub> values			
	0.20	1.12		1.00	
	0.40	1.27		1.00	
	0.60	1.47		1.00	
Freundlich	N	0.89	0.73	1.32	0.70
	K <sub>f</sub>	0.30		7.86	
Dubnin-Radushkevich	Q <sub>m</sub>	0.17		0.17	0.38
	K	0.00		-1E-07	
Elovich	E	2886.75			
	K <sub>e</sub>	-1.02	0.58	-0.49	0.37
Temkin	q <sub>m</sub>	-0.17		-0.02	
	K <sub>T</sub>	1.00	0.58	1.00	0.72
	b	36829.56		116627	

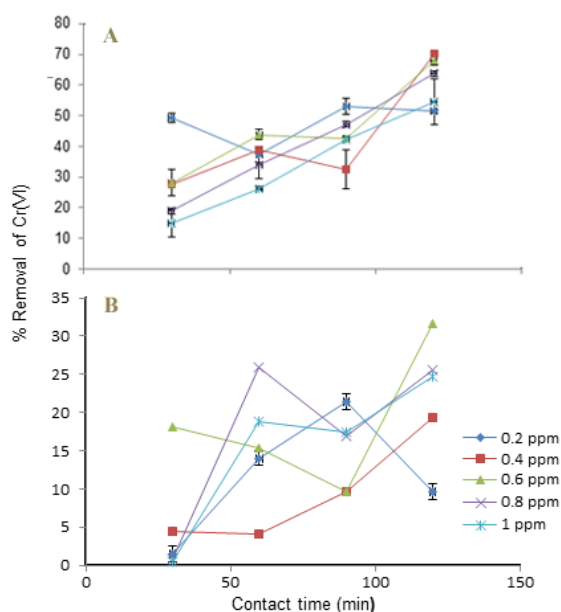


Fig. 2 — Effect of initial ion concentration and contact time on percent removal of Cr (VI) by *C. gigantea* leaf (A) leaf; and (B) petal biomass

Freundlich constants  $n$  and  $K_f$  values are 0.89 and 0.30, respectively. From the data it should be assumed that the biosorption favors multilayer adsorption. For petal biomass Temkin model best fitted the process. The  $R^2$  value for the same is 0.72.  $K_T$  value and  $b$  value are 1 and 116627, respectively (Table 1).

Table 2 — Kinetic constants for pseudo second order reaction for leaf and petal biomass

Initial conc. of Cr (VI)	<i>C. gigantea</i> leaf kinetic constants			<i>C. gigantea</i> petal kinetic constants		
	R <sup>2</sup>	q <sub>e</sub>	K	R <sup>2</sup>	q <sub>e</sub>	K
0.2	0.91	0.03	0.34	0.6	-0.006	1.28
0.4	0.32	0.1	9.37	0.24	-0.02	6.52
0.6	0.63	0.16	14.6	0.22	0.04	1.67
0.8	0.44	0.83	549	0.54	-0.01	0.70
1.0	0.21	1.88	2912	0.58	-0.004	0.04

### Kinetic study

Effect of initial concentration of Cr (VI) was found by carrying experiment keeping other parameters except initial metal ion concentration constant. The result is depicted in the graph along with the effect of contact time (Fig. 2 A & B). Increased concentration of metal ions decreases the removal of chromium ions from the solution. This might be due to the difficulty of sorbent to adsorb to the entire chromate ion. The anomaly in the result is yet to be discovered.

The kinetic constants for the pseudo second order reaction for leaf biomass and petal biomass is shown in the Table 2. Comparing pseudo first and pseudo second order reaction kinetics pseudo second order reaction fits into the fits into the biosorption process.

### Conclusion

Alkali treated leaf and petal biomass of *Calotropis gigantea* could be used as biosorbent of hexavalent chromium. Alkali treatment of the powdered sample gave a uniform, organised surface which aids the process of Biosorption. Dried alkali treated biomass of *C. gigantea* leaves and petals served the purpose for its hexavalent chromium metal removal by batch studies with different parameters, followed by kinetic and equilibrium study. FTIR analysis depicted the presence of functional groups on the surface of the sorbent. For those metals forming anionic compounds in aqueous solution favours lower pH like hexavalent chromium which forms dichromate ions in lower pH. Maximum biosorption was found at pH 2.0 at a dosage of 2 g/L. With the increase in the initial concentration of metal ion, percent removal decreased. Freundlich and Temkin isothermal model fitted the biosorption study for leaf and petal biomass respectively. Which gave  $R^2$  value not more than 0.75 (0.73 and 0.72). In kinetic study pseudo second order reaction was best suited. These results are comparable with other biosorbents,

thus from the study it can be concluded that the *Calotropis gigantea* plant leaf could be used as an efficient biosorbent for future applications.

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### Conflict of Interest

Authors declare no conflict of interests.

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