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Research Article

A Study on Removal of Heavy Metal Chromium from Aqueous Chromium Solution Using *Ipomoea carnea* Root as Biosorbent

S. Krishnaveni*, V. Thirumurugan

Department of Chemistry, A.V.V.M. Sri Pushpam College (Autonomous), Poondi-613 503, Thanjavur (Dt), Tamil Nadu, India.

ABSTRACT

Pollution is the main problem due to heavy metal discharges from industries. In this study *Ipomoea carnea* (Family:Convolvulaceae) is selected to remove the heavy metal chromium from aqueous chromium solution using biosorbent. The present work focuses to evaluate the effectiveness of low cost absorbent *Ipomoea carnea* root powder. Various parameters like pH, biosorbent, dose, contact time and metal ion concentration are investigated using batch studies. A kinetic model study and isotherm model fitting study are studied using Langmuir and Freundlich isotherms. The Thermodynamic parameters ΔG , ΔH and ΔS are also seen. The results reveal that it follows pseudo first order kinetic model and also fit in the Langmuir and Freundlich isotherms. The results are very much encouraging. So, it can be used as low cost biosorbent in controlling the pollution.

Keywords: Pollution, Heavy metal, chromium, *Ipomoea carnea*, Batch adsorption study, Kinetics Langmuir and Freundlich isotherms and Thermodynamic study.

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*Address for Correspondence:

S. Krishnaveni, Department of Chemistry, A.V.V.M. Sri Pushpam College (Autonomous), Poondi-613 503, Thanjavur (Dt), Tamil Nadu, India.

INTRODUCTION

Water pollution is due to the mixing of toxic metals and organic compounds excreted from industries in to the water bodies that cause serious environmental and public problems. Hence this has been becoming an alarming concern and priority of the most industrial sectors to avoid such problem. Heavy metal ions are often found in the environment as result of their wide industrial uses. They are common contaminants in waste water and many of them are known to be toxic or carcinogenic^{1,2}. In addition, heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders. Therefore, their presence in the environment, in particular in water, should be controlled^{3,4}. Strict legislation on the discharge of these toxic products makes it then necessary to develop various efficient technologies for the removal of pollution from waste water. Biological treatments, membrane process, advanced oxidation process chemical and electrochemical techniques, and adsorption procedures are the most widely used for removing metals and organic compounds from industrial effluents⁵⁻¹³. Amongst all the treatments proposed, adsorption using biosorbents is one of the most popular methods since proper design of the adsorption process will produce high-quality treated

effluents. In fact, adsorption is now recognized as an effective, efficient and economic method for water de contamination application and for separation analytical purposes. The adsorbents may be mineral, organic, biological origin, activated carbons, zeolites, clays, silica beads, low-cost adsorbents (industrial by-products agricultural wastes and biomass) and polymeric materials are significant examples.¹⁴ The aim of this research was evaluating the hexavalent chromium, Cr(VI) removal by *Ipomoea carnea* root powder as a new biosorbent from synthetic wastewater and the effect of different parameters on the adsorption process.

MATERIAL AND METHODS

Plant collection

Ipomoea carnea roots were collected from Tiruvarur District, Tamilnadu, India. Collected roots were repeatedly washed with distilled water to remove dirt, dust, and other impurities. The washed materials were shade dried and pulverised. Then the root powder was sieved using 50 mesh and fine biomass obtained. The resulting product was kept in desiccators for further use

Reagents

All the chemicals used in this study were obtained from HiMedia Laboratories Pvt. Ltd. (Mumbai, India). All the chemicals used in this study were of analytical grade.

Preparation of Biosorbent

The 50 g root powder was soaked in 1 liter of 0.1 mol/Lit HNO₃ solution for 24 hour to precipitate out already adsorbed metals on the biomass surface from the environment. It was then filtered and washed with distilled water to remove acid contents, washing was continued till the pH of filtrate become neutral. Filter cake was first dried at room temperature and then in an oven at 105 °C to constant weight. No other chemical and physical treatments were used prior to biosorption experiments. The biomass was then stored in air tight glass bottles to protect it from moisture.

Preparation and analysis of Cr(VI) solutions

For biosorption experiments, stock chromium (VI) solution of 1000mg/L, was prepared by dissolving an appropriate amount of Chromium (VI) salt in deionized distilled water. Cr(VI) solutions of different concentrations were prepared by adequate dilution of stock solution with deionized distilled water. Before and after the experiments Cr(VI) content in the solutions were determined by spectrophotometer (Systronics-169).

Batch biosorption Experiments

The affinity of biomass to adsorb Cr(VI) ions was studied in batch experiments. In all sets of experiments fixed volume of Cr(VI) solution (50mL) was stirred with desired biosorbent dose (2g/L) of 50 mesh size at 310K and 450 rpm for 2 hour. Different condition of pH (1 to 10), initial metal concentration (20 to 100 mg/L) and contact time (15min to 120 min) were evaluated during study. In order to regulate pH of the medium 0.1 mol/lit HNO₃ were used. The 100 mL, flasks were placed on magnetic stirrer with constant shaking rate for 2 hours with 450 rpm. The solutions were separated from biomass by filtration through filter paper (Whatmann 41). For the sorption time of equilibrium on Cr(VI) uptake was calculated by difference in concentration. The initial concentration C_i (mg/L) and metal ion concentrations at various time intervals, C_e(mg/L) were determined and the metal ion uptake q_e(mg metal adsorbed/g adsorbent) was calculated from the mass balance equation given below

$$q_e = \frac{(C_i - C_e) V}{W} \quad \dots\dots\dots(1)$$

The formula below provides to calculate the percentage of the Cr removed:

$$\text{Removal \%} = \frac{(C_i - C_e)}{C_i} \times 100 \quad \dots\dots\dots(2)$$

Where W is the mass of the sorbent (g), V is the volume of the solution (L), C_e is the equilibrium concentration of the Cr solution (mg/L), and C_i is the initial Cr metal ion concentration (mg/L).

RESULTS AND DISCUSSIONS

Effect of pH:

pH is one of the important factors affecting the biosorption of metal ions in the solution. The effect of on the biosorption Cr(VI) onto *Ipomoea carnea* was studied at pH 1-10 for initial metal ion concentration 20 ppm for biosorbent dose 1g/L at time 60mts and Temperature 310K.

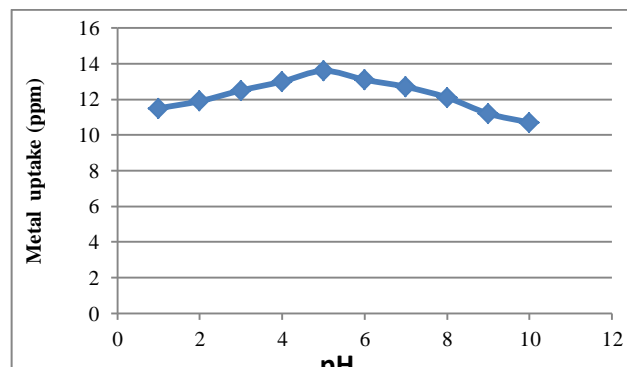


Fig.1: Effect of pH on the metal ion uptake (Time : 60 min, Biosorbent dose : 1.0 g/L, Volume of the solution: 50ml, Temp. : 310K)

The metal ion uptake increases, as the pH of the solution increases from 1 to 5 and then decreases with increase of pH up to pH 10. The maximum metal ion uptake was found to be 13.6 at pH 5.

Effect of adsorbent dosage

The percentage of Cr(VI) metal ion adsorption increases with adsorbent dosage increases from 0.5g/L to 3.0 g/L by giving removal efficiency from 58.4 % to 74.0 % . The maximum biosorption 74%, obtained at adsorbent dosage 2g/L. After that adsorbent dose 2g/L there is no increases in adsorption.

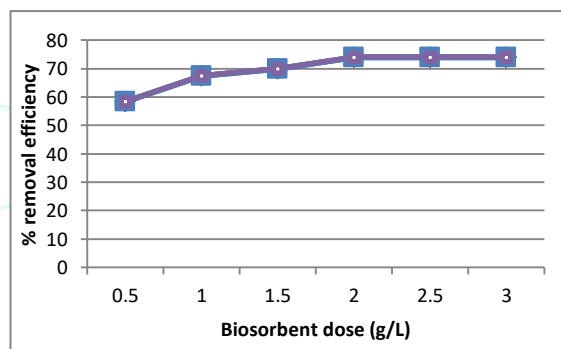


Fig.2: Effect of adsorbent dose on removal efficiency (%) of Cr(VI) (Time:60 min, pH:5, Volume of the solution:50mL, Initial metal ion concentration:20ppm, Temp.:310K)

Effect of contact time

The effect of contact time on removal of Cr ion is shown in Fig.3. According to results, an increase at contact time led to increase at surface adsorption rate to 90 min and then remains unchanged. Maximum adsorption occurred in the 90 min for pH5, biosorbent dose 2g/L at Temp 310 for initial ion concentration 20ppm.

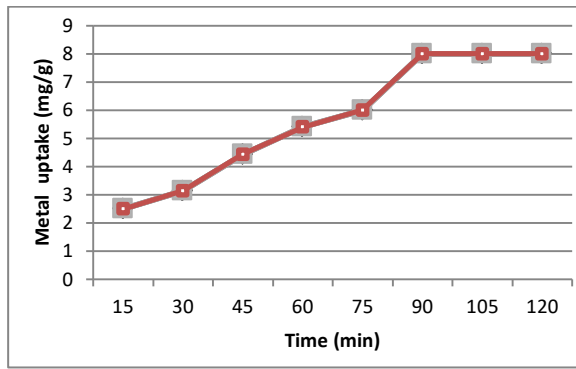


Fig. 3: Effect of contact time for Cr(VI) biosorption (Biosorbent dose: 2.0 g/L; pH:5, Volume of the solution: 50mL, Initial metal ion concentration: 20ppm, Temp.:310K)

Effect of initial concentration

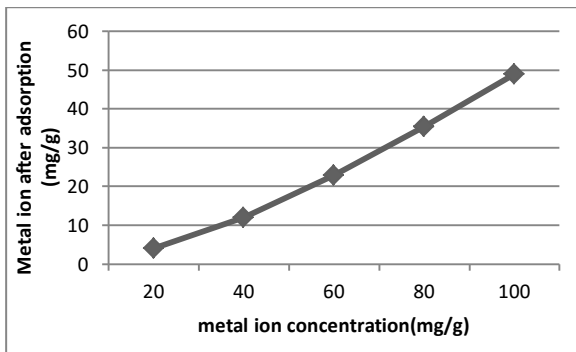


Fig.4: Effect of initial metal ion concentration on biosorption after adsorption of Cr(VI), Time: 90 min; pH 5; Volume of the solution; 50mL, Biosorbent dose: 2.0 g/L; Initial metal ion concentration: 20ppm, Temp.:310K

From the above study optimised condition for biosorption are activated the pH is 5, biosorbent dose 2g/L and equilibrium time is 90mts.

Kinetic study

The kinetics of Cr (VI) sorption on adsorbent was analyzed using two kinetic models. The pseudo First order equation

$$\text{Log}(q_e - q_t) = \log q_e - k_1 t / 2.303 \dots\dots\dots(6)$$

Where, q_e is the mass of the material ion adsorbed (mg/g) at equilibrium time, q_t is the amount of the metal ion adsorbed at time 't' (min). For pseudo first order kinetic model, the sorption coefficient and equilibrium capacity q_e can be determined from the linear plot of $\log (q_e - q_t)$ versus time at different concentrations. The graph is shown in the Fig.6.

The pseudo second-order equation²⁰ is given by

$$t/q_t = 1 / k_2 q_e^2 + (1/q_e)t \dots\dots\dots(7)$$

where k_1 and k_2 symbolize the pseudo first-order and pseudo second-order rate constants respectively. For pseudo second order kinetic model, the sorption coefficient and equilibrium capacity q_e can be determined from the linear plot of t/q_t versus time at different concentrations. The graph is shown in Fig.7.

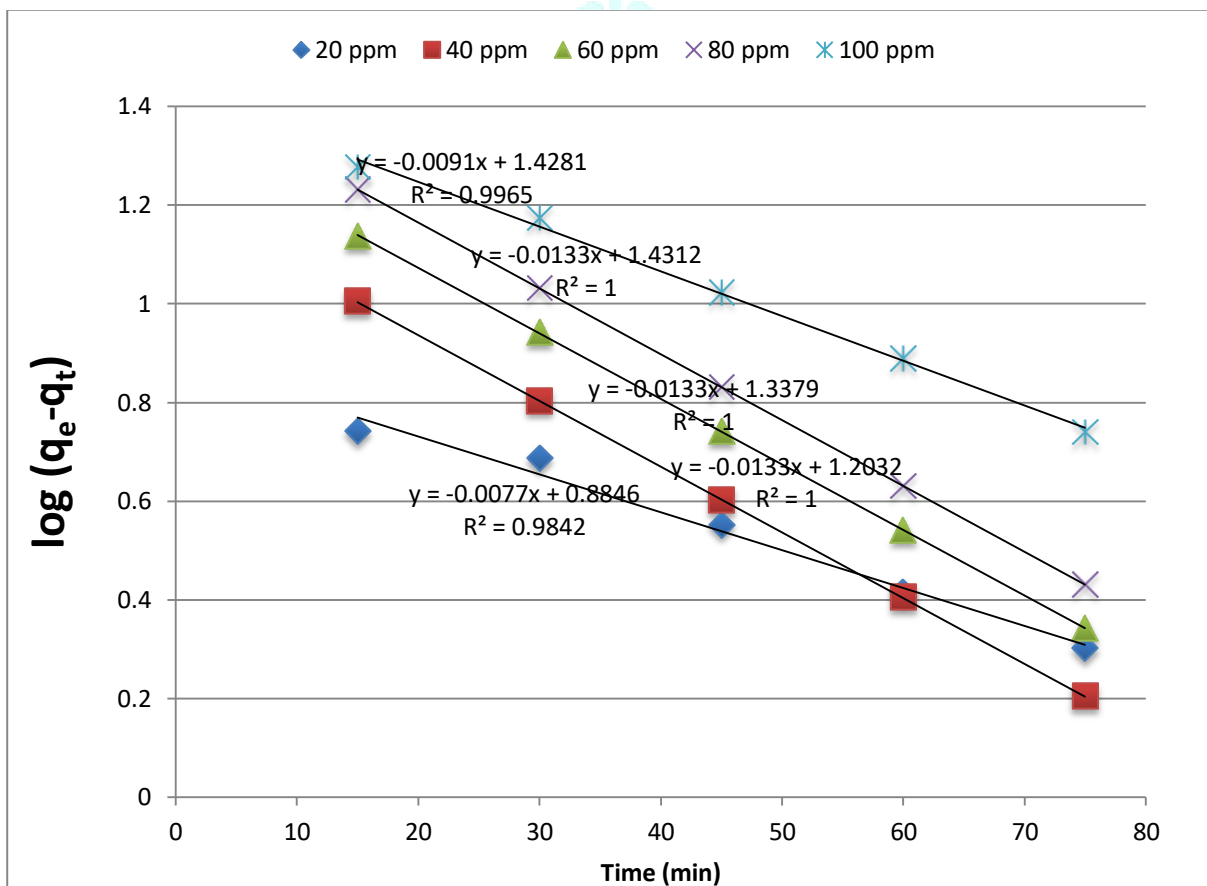


Fig.6: Time Vs log (q_e - q_t) for pseudo first order kinetic model at 310K

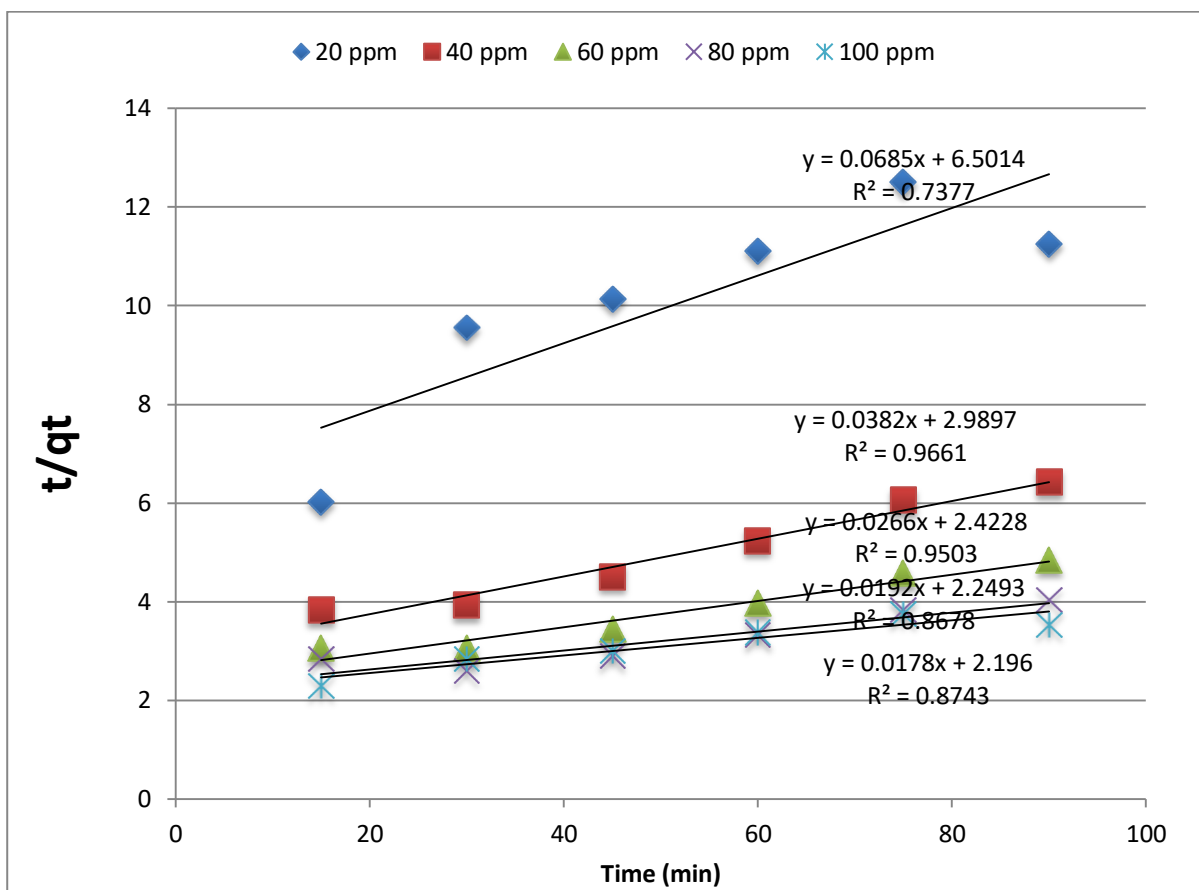


Fig.7: Time Vs t/qt for pseudo second order kinetic model at 310K

From the kinetic study, the fact suggests the sorption of Cr (VI) ion follows pseudo- first order kinetic model than pseudo-second order kinetics. The result indicated that it doesn't follow pseudo second order kinetics because, its coefficient correlation R^2 values are from 0.737 to 0.966. For the pseudo first order kinetics, coefficient correlation R^2 values are from 0.984 to 1. Closure agreement between experimental and calculated kinetic constants and coefficient of correlation closure to unity indicated that the pseudo first order model better represents the experimental data. So, *Ipomoea carnea* biosorbent follows pseudo first order kinetic model. The theoretical and q_e experimental values are very close for the pseudo first order kinetic model. Example: for 20ppm q_e theoretical value is 8 and q_e experimental value is 7.7. whereas, the q_e theoretical and q_e experimental values are not very close for the pseudo second order kinetic model. Example: for 20ppm q_e theoretical value is 8 and q_e experimental value 14.7. so *ipomoea carnea* biosorbent follows pseudo first order kinetic model. The above inference indicate is follows physic-sorption

Adsorption Isotherms

The study of adsorption has been of great importance and significance in the treatment of water and waste water by adsorption principle in selecting an adsorbent for the removal of dyes and colorants¹⁹. The adsorption data for the removal of cr metal ion on biosorbent were used to fit the Freundlich and Langmuir isotherms

Freundlich isotherms: $\log q_e = \log k + (1/n) \log C_e$
(3)

Langmuir isothermes : $(C_e/q_e) = (1/Q_0 b) + (C_e/Q_0)$
(4)

Where, k and $1/n$ are the measures of adsorption capacity and intensity of adsorption, respectively. q_e is the amount Cr metal ion adsorbed per unit mass of adsorbent(in mg g^{-1}) and C_e is the equilibrium concentration of metal ion (in mg L^{-1} or ppm); Q_0 and b are the adsorption capacity(in mg g^{-1}) and b is the Langmuir constant, which are the measures of monolayer adsorption capacity (in mg g^{-1}) and surface energy (in g L^{-1}), respectively.

Further, the essential characteristics of the Langmuir isotherm can be described by a separation factor, R_L , which is defined by the following equation [5].

$R_L = [1 / (1 + bC_i)]$ (5)

Where, R_L is the separation factor, C_i and b are the initial concentration of metal ion (in mg L^{-1} or in ppm) and Langmuir constant (in g L^{-1}). The value of R_L , indicates the shape of the isotherm and nature of the adsorption process as given below;

<u>R_L value</u>	<u>Nature of adsorption process</u>
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

Table 1. Adsorption Isotherm parameters for the removal of Cr(VI)

Isotherms	Parameters	
Langmuir	Q _{max} (mg/g)	32.26
	R ²	0.988
	K _L (L/mg)	0.0689
	R _L	0.1125
Freundlich	1/n _f	0.4620
	n _f	2.1645
	R ²	0.997
	K _f (L/mg)	4.305

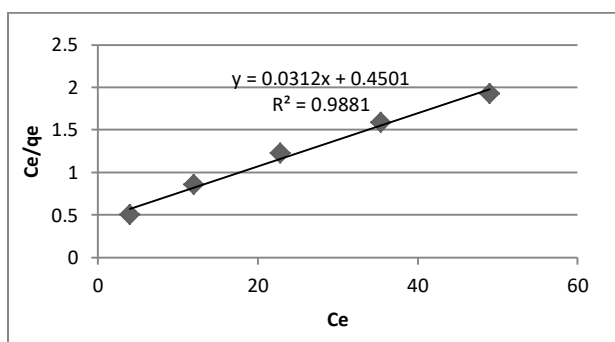


Fig.5: Langmuir adsorption isotherm plot

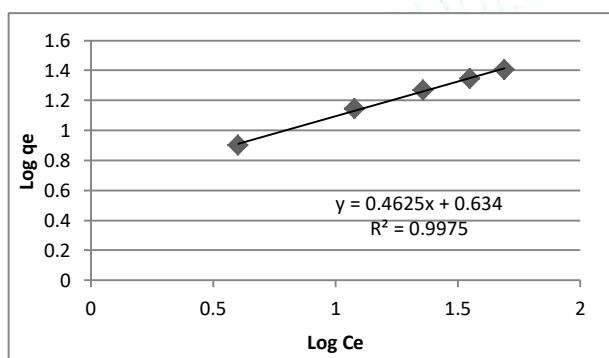


Fig.5: Freundlich adsorption isotherm plot

The present results show that both Langmuir and Freundlich model fits perfectly from the adsorption equilibrium data. Among these two Freundlich isotherm model fits better than Langmuir isotherm model R_L value is below 1 (R_L=0.1125). So it indicates favourable adsorption. For Freundlich isotherm model 1/n_f value is 0.4620. It is between 0 to 1 which represents favourable adsorption of the adsorbent and also n_f value is 2.1645 which indicates high tendency forward adsorbing the metal ion onto the adsorbate.

Langmuir and Freundlich plots are shown in Fig. 5 and Fig. 6. Even though both Langmuir and Freundlich model better fit the experimental results over the experimental range with good correlation coefficient, the Freundlich isotherm model is best fitted due to best R² value. In Langmuir isotherm R_L value is below 1 i.e. 0.1125. So, this is a favourable isotherm. Since it follows Freundlich isotherm. The value 'n_f' coefficient found in Freundlich isotherm is 2.1645 which indicates high tendency forward adsorbing the metal ion onto the adsorbate. The value coefficient '1/n_f' in the Freundlich isotherm model is between 0 to 1 which represents adsorption intensity of adsorbate to adsorbent. In this study 1/n_f = 0.462 which indicates the favourable adsorption of the adsorbate.

Thermodynamic studies

Using the following equations, the thermodynamic parameters, which are standard free energy change (G), enthalpy (H), and entropy (S), were obtained to examine the Cr(VI) adsorptions on biosorbent thermodynamically.

$$\Delta G^{\circ} = -RT \ln K_d \dots\dots\dots (8)$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \dots\dots\dots (9)$$

$$\ln K_d = (-\Delta H^{\circ}/R)1/T + (\Delta S^{\circ}/R) \dots\dots\dots(10)$$

where, R is the universal gas constant (8.314 J/mol K), T is the absolute temperature in Kelvin, and K_d is the equilibrium constant obtained from Langmuir constant K_L. By drawing the van't Hoff plot of lnK_d versus 1/T, the H and S values were found from the slope and intercept. Table 2 lists the H, S, and G values at various temperatures for Cr(VI) adsorption on biosorbent.

Table 2: Thermodynamic parameters ΔG° ΔS° and ΔH° values for the adsorption of Cr(VI) at various temperatures

Metal ion concentration (ppm)	310K	320K	330K	ΔS°	ΔH°
	ΔG°	ΔG°	ΔG°		
20	-3572	-4511	-5736	106.00	29281
40	-2179	-2994	-4549	115.73	33771
60	-1261	-2066	-3803	123.96	37279
80	-582	-1358	-3200	126.95	38884
100	-102	-771	-2591	121.21	37595

The values of thermodynamic parameters are calculated for the present systems are shown in Table 2. The negative ΔG° value reveals the Cr adsorption on *Ipomoea carnea* biosorbent is favourable. The positive value of ΔH° indicates an endothermic process and positive value of ΔS° indicates the spontaneous nature of adsorption.

CONCLUSION

The effect of different factors on the sorption abilities of inexpensive wild plant *Ipomoea carnea* root powder is studied for the removal of Cr(VI) from aqueous solutions. The following conclusions are drawn from the present studies. *Ipomoea carnea* root powder is a suitable material for Cr(VI) adsorption. pH, biosorbent dose, contact time and initial

metal ion concentration highly affect over all metal uptake capacity of biosorbent. The sorption is pH dependent and sorption capacity increased in pH value upto 5 after that there is a decrease in sorption. So, this indicates pH 5 is more suitable medium for adsorption of Cr (VI). The optimum time is observed to be 90min with sorption capacity of 16g/L the optimum dosage is 2 g/L and the percentage of removal is 80 so in this optimised condition for their studies are carried out. In the examined concentration range 20-100mg/L the results also reveal, it follows pseudo first order kinetic model than pseudo second order kinetic. Since R² value near 1 and also theoretical and experimental values of q_{max} are close to each other. So it reveals it follows physico-sorption. Present results show that

both Langmuir and Freundlich model fits perfectly from the adsorption equilibrium data. Among these two Freundlich isotherm model fits better than Langmuir isotherm model R_L value is below 1 ($R_L=0.1125$). So it indicates favourable adsorption. For Freundlich isotherm model $1/n_f$ value is 0.4620. It is between 0 to 1 which represents favourable adsorption of the adsorbent and also n_f value is 2.1645 which indicate high tendency forward adsorpting the metal ion onto the adsorbate. Thermodynamic parameters (ΔG , ΔH and ΔS) reveals that it is favourable endothermic spontaneous reaction. In the future *Ipomoea carnea* root powder can be used to remove heavy metal from the effluent. Engineering technologies can be developed by using the results of isotherm model and thermodynamic parameters for removal of effluent in most efficient way.

Conflict of interest

The authors declare no conflict of interest.

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