

## Biosorption of Cr (VI) from aqueous solutions using *Carum copticum* stem

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### Abstract

The *Carum copticum* stem was used as biosorbent for its ability to remove Cr (VI) from aqueous solutions. The important parameters for the biosorption process such as pH, biosorbent dosage and contact time were investigated. Batch equilibrium experiments showed that a maximum Cr (VI) uptake was obtained at pH 2.0. A dosage of 1.6 g of biosorbent was found to be effective for maximum uptake of Cr (VI). The experimental biosorption data were modeled using both Langmuir and Freundlich biosorption isotherms. The values of the sum of the square of the error (SSE) and root mean squared error (RMSE) showed that the biosorption equilibrium data correlate well with the Langmuir isotherm model with a maximum biosorption capacity of 132.833mg/g. Batch kinetic of biosorption was investigated. The pseudo-first-order and pseudo-second order kinetic models were applied to test the experimental data. The pseudo-first order equation was the best applicable model to describe the biosorption process.

**Key words:** Biosorption; chromium (VI); *Carum copticum*; isotherm; kinetic

**Full length article** Received: 23-10-2011 Revised: 18-11-2011  
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Accepted: 05-11-2011  
Tel: +98 7212230505

Available online: 15-01-2012  
Fax: +98 7212230508.

### 1. Introduction

The pollution of heavy metals is a main problem because of the toxic effects on the environment and living beings. Therefore, it is important to remove these pollutants from water and wastewater before discharge to the environment. Among heavy metals, Chromium is a toxic pollutant in industry wastewaters such as mining, electroplating, metallurgy operations [1]. Chromium exists in two oxidation states, Cr (III) and Cr (VI). The Chromium is mostly found as Cr (III), which is more stable but the Cr (VI) is relatively toxic compared to Cr (III) because the Cr (III) often forms insoluble hydroxides at neutral pH [1]. The high level of Cr (VI) leads to liver damage, pulmonary congestion and oedema [2, 3]. The maximum permissible limit of Cr (VI) for industrial wastewaters varies from 0.05 to 0.1mg/L in different countries [4]. Various methods have been reported for the removal of the Chromium such as chemical precipitation [5], electrochemical precipitation, [6], filtration [7], ion exchange [8], membrane technology [9], etc. However, these technologies have many disadvantages like ineffective or expensive when heavy metals are present in the wastewater at low concentrations. The use of biosorption technology for the treatment of heavy metal contaminated wastewaters has become a useful method to conventional treatments. Several studies related to Kashefi et al., 2012

Chromium removal were carried out using biomaterials such as *Helianthus annuus* stem waste [10], walnut hull [11], *Ocimum basilicum* seeds [12], pomegranate husk carbon [13] and *Aeromonas caviae* [14]. *Carum copticum* is an aromatic plant, which is annual and herbaceous with white flowers and brown fruits with a penetrating smell of thymol that grows in Iran, Pakistan, India and Egypt [15]. However, the stems of the *Carum copticum* can be used as biosorbent for the Cr (VI) removal from aqueous solutions.

The aim of the present study was to investigate the chromium removal efficiency from aqueous solutions by using *Carum copticum* stems as biosorbent, which is a novel sorbent. The experiments were carried out by batch method and the effect parameters on biosorption of the Cr (VI) were studied. In addition, Equilibrium isotherms and kinetic studies were investigated.

### 2. Materials and method

#### 2.1. Materials

The chemicals used for this study were of analytical reagent grade and were purchased from Merck.  $K_2Cr_2O_7$  salt was used to prepare the adsorbate solutions. 0.01M  $H_2SO_4$  and 0.1M NaOH solutions were used for the pH adjustments.

Double distilled water (DDW) was used for the preparation of the standard solutions for the biosorption experiments.

## 2.2. Biosorbent

For biosorbent preparation, the *Carum copticum* stems from Baluchestan region in Iran were collected in October 2008. The samples were dried at laboratory temperature (25°C) for one month. After this period, the samples were grinded by mill and sieved to pass through a 70-mesh (0.210mm). In order to remove impurity on the biosorbent, the samples were washed with DDW. Then, the samples were maintained at 70°C for 12 hours.

## 2.3. Batch experiments

The effect of pH on chromium biosorption rate was studied by varying the pH from 2 to 7.5 (which was adjusted with 0.01M H<sub>2</sub>SO<sub>4</sub> or 0.1M NaOH at the beginning of the experiment). The concentration of chromium solution used for this study was 100mg/L. The volume of chromium solution was 100mL. The biosorbent dosage was 0.5 g dry weight of biosorbent. The shaker speed was 450rpm and contact time was 10 min. To study the effect of biosorbent dosage on chromium removal from solution by the biosorbent, experiments were conducted by varying the biosorbent dosage from 0.2g to 1.6g. The concentration of chromium solution used for this study was 100mg/L. The volume of chromium solution was 100mL. The pH of solutions was adjusted at 2. The shaker speed was 450rpm and contact time was 10 min. Kinetic studies were achieved by shaking of biosorbent (1.6 g) with 100mL of chromium solution (100mg/L) at 25°C and solution pH (2.0). The samples were collected at time intervals between 5 to 50min and filtrated by filtrate paper. Biosorption isotherm experiments were carried out at 25 °C on a shaker for 30min. The biosorbent (1.6 g) were thoroughly mixed with 100mL of chromium solutions. The isotherm studies were performed by varying the initial chromium concentrations from 20 to 100mg/ L at pH 2.0. The pH value was adjusted using 0.01M H<sub>2</sub>SO<sub>4</sub> or 0.1M NaOH before addition of biosorbent and was maintained throughout the experiment. The concentrations of residual Cr (VI) ions in the solution were determined by an atomic adsorption spectrophotometer (PHILIPS PU9100X).

## 3. Results and discussion

### 3.1. pH effect

The pH is the most important parameter for the biosorption process. For the study of the pH effect on biosorption, the experiments were carried out in the pH range of 2.0–7.5 keeping all other parameters constant (chromium concentration = 100 mg/L; biosorbent dosage = 0.5 g/100mL; shaker speed = 450 rpm; contact time = 10min; temperature = 25°C). Fig. 1 shows the results of this study. As seen from this figure, the pH has important effect

on biosorption of Cr (VI) from aqueous solution. The maximum Cr (VI) removal by biosorbent was 30% at pH 2. There was a sharp decline in percent biosorption with increase in pH from 2 to 6. Chromium removal decreased from 30 to 10% as pH increased from 2 to 6. Therefore, the maximum Cr (VI) removal was 2 and It was selected as the optimal pH value. The pH dependence of chromium biosorption can be related to the type and ionic state of functional groups on the biosorbent and chromium speciation in solution. The dominant chromium compound within the solution at pH 2 is HCrO<sub>4</sub><sup>-</sup> (CrO<sub>4</sub><sup>2-</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> exist) [2]. At low pH values, the surface of biosorbent would be covered by H<sup>+</sup> ions, which increase electrostatic attraction between negatively charged Cr (VI) ions and binding sites of biosorbent [16]. At high pH, low biosorption of Cr (VI) may be due to dual competition of both anions (CrO<sub>4</sub><sup>2-</sup> and OH<sup>-</sup>) to be adsorbed on the surface of biosorbent [17].

### 3.2. Effect of biosorbent dosage

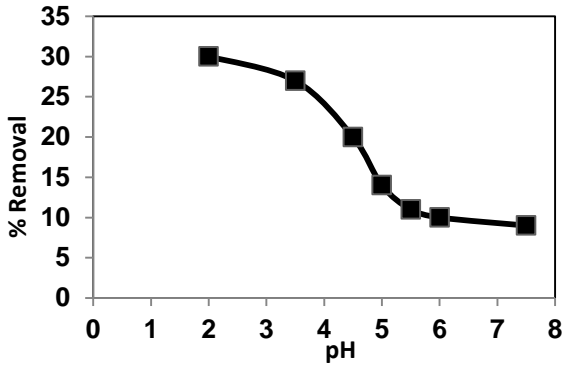
The removal of metal ions is a function of adsorbent dosage. For this study, the efficiency of biosorbent was studied at different biosorbent dosages for the percent removal of chromium. The experiments were conducted at constant initial Cr (VI) concentration (100mg/L), contact time (10min), pH 2, temp. (25°C), shaker speed (450 rpm) with varying biosorbent dosages (0.2–1.6 g). Fig. 2 shows the results of the effect of biosorbent dosage on the removal of Cr (VI). As seen from this figure, with increasing of biosorbent dosage, the removal of Cr (VI) increased up to 50%. Increase in chromium removal with biosorbent dosage can be attributed to increased surface area and the availability of more biosorption sites [18].

### 3.3. Effect of contact time

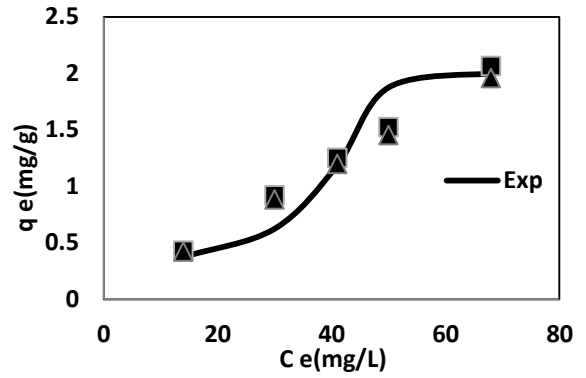
The effect of changing contact time on biosorption, while keeping the biosorbent dosage (1.6 g), pH (2.0) and shaker speed (450 rpm) at 25°C illustrated in Fig. 3. The removal of Cr (VI) by biosorbent increased with increasing contact time and attains a maximum value at 30min and thereafter, it remains almost constant. After the equilibrium time, no more Cr (VI) was removed.

### 3.4. Biosorption isotherm

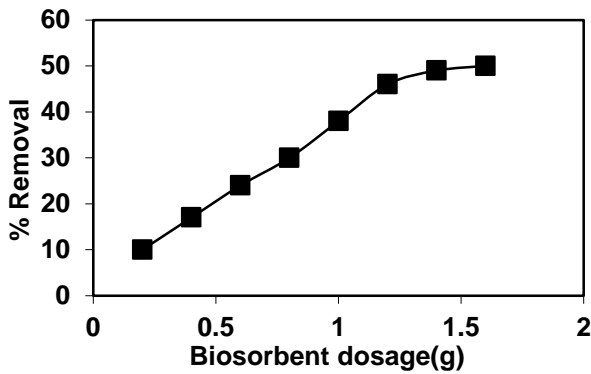
Cr (VI) biosorption isotherms were obtained at constant pH, biosorbent dosage, contact time and temperature. The biosorption of chromium ions was carried out at different initial chromium ion concentrations ranging from 20 to 100mg/L, at optimum pH (2.0), at 450 rpm for 30min. The biosorbent dosage was 1.6g. Analysis of the equilibrium data is important to develop an equation which accurately represents the biosorption process and which could be used for biosorption process design. To test the fit of data, the Langmuir, Freundlich and Redlich-Peterson isotherm models were applied for this study.



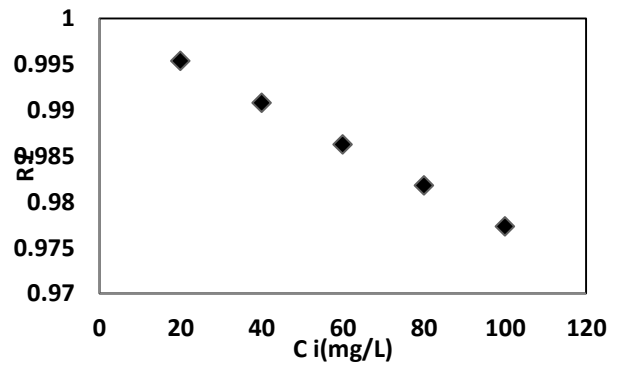
**Fig.1.** Effect of pH on Cr (VI) removal (chromium concentration = 100 mg/L; biosorbent dosage = 0.5g; shaker speed = 450 rpm; contact time = 10min; temperature = 25°C).



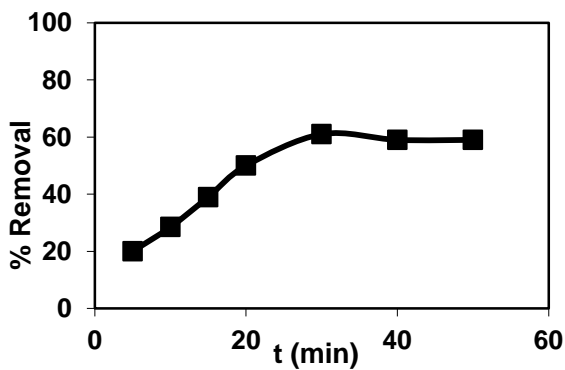
**Fig.4.** Comparison Langmuir and Freundlich equilibrium isotherms ( $q_e$ ) plots with the experimental data of Cr (VI) (20–100mg/g) biosorption (pH=2; shaker speed = 450 rpm; biosorbent dosage=1.6g; contact time=30min; temperature = 25°C).



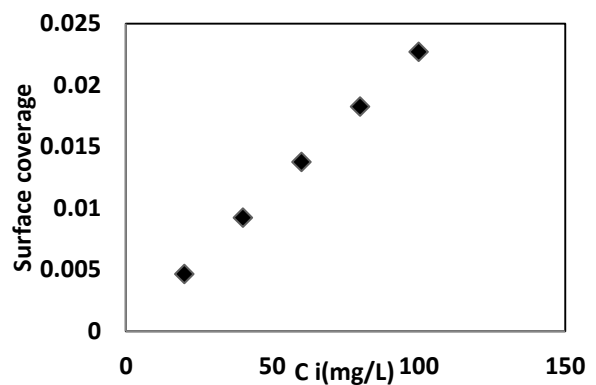
**Fig.2.** Effect of biosorbent dosage on Cr (VI) removal (chromium concentration = 100 mg/L; pH=2; shaker speed = 450 rpm; contact time = 10min; temperature = 25°C).



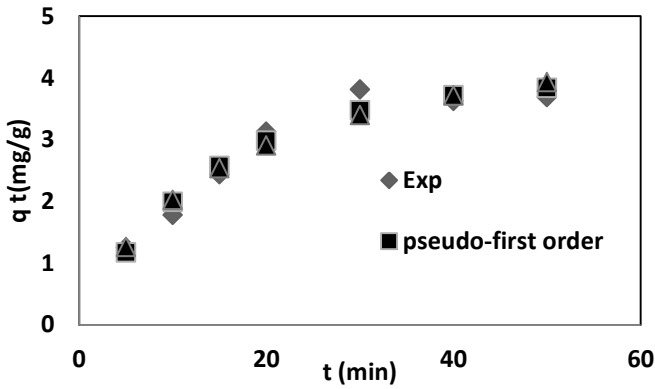
**Fig.5.** The calculated  $R_L$  values against initial Cr (VI) concentration.



**Fig.3.** Effect of contact time on Cr (VI) removal (chromium concentration = 100 mg/L; pH=2; shaker speed = 450 rpm; biosorbent dosage=1.6g; temperature = 25°C).



**Fig.6.** The calculated surface coverage values against initial Cr (VI) concentration.



**Fig.7.** Pseudo-first order and pseudo-second order plots for biosorption of Cr (VI).

In order to find out the best applicable model from the goodness of fit with the experimental data, it is necessary to study the data using error analysis. The error analysis methods such as the sum of the square of the error (SSE) and root mean squared error (RMSE) were used to find out the model, which is best fit to the experimental data. The mathematical statement for SSE and RMSE are as follows [19, 20]:

$$SSE = \sum (q_m - q_e)^2 \tag{1}$$

$$RMSE = [(1/n) \sum (q_m - q_e)^2]^{0.5} \tag{2}$$

Where  $n$  is the number of experimental data points,  $q_m$ (mg/g) is the calculated data from model and  $q_e$ (mg/g) is the calculated data from the experimental data. A small number of SSE and RMSE is the more applicable model to the isotherm of Cr (VI) biosorption. In addition to  $r^2$  values denote the correlation between the experimental and model values. The  $r^2$  value was determined by Eq. (3) [21]:

$$r^2 = \frac{\sum (q_m - q_{e,m})^2}{\sum (q_m - q_{e,m})^2 + \sum (q_m - q_e)^2} \tag{3}$$

Where  $q_{e,m}$  is the average of  $q_e$ .

Langmuir equation relates the coverage of adsorbate on a solid surface to concentration of a medium above the solid surface at a fixed temperature. The Langmuir model can be written in the following form [22]:

$$q_e = q_{max} \frac{K_L C_e}{1 + K_L C_e} \tag{4}$$

Where  $q_{max}$  (mg/g) and  $K_L$ (L/mg) are the maximum biosorption capacity and the affinity of the binding sites, respectively.

Freundlich isotherm is capable of describing the adsorption of organic and inorganic compounds on a wide variety of biosorbent. The empirical Freundlich isotherm model based on a heterogeneous surface and it can be written in the following form [23]:

$$q_e = K_f C_e^{1/n} \tag{5}$$

Where,  $K_f$  and  $n$  are the Freundlich constants, which represent biosorption capacity and biosorption intensity, respectively.

The curve in Fig. 4 was generated from Freundlich and Langmuir model equations. As seen from Fig. 4, both these models were suitable for describing the biosorption of Cr (VI) by *Carum copticum*. Table 1 shows the model constants along with the values of  $r^2$ , SSE and RMSE for biosorption of Cr (VI) on *Carum copticum*. The smaller values of SSE and RMSE show that the Langmuir model fitted well to the experimental data of Cr (VI) biosorption. The maximum biosorption capacity,  $q_{max}$ , was found to be 132.833mg/g at 25 °C. The value of  $K_L$  was obtained 0.000232L/mg. The value of Freundlich constant,  $n$ , in the range 1–10 indicates the favorable biosorption. In this study, it was obtained 1.0281. The value of  $K_F$  was found 0.0323.

**Table 1:** Freundlich and Langmuir model parameters for biosorption of Cr (VI) by *Carum copticum* stem (Temperature= 25°C).

Langmuir model	
$q_{max}$ (mg/g)	132.833
$K_L$ (L/mg)	0.000232
RMSE	0.210
SSE	0.221
$r^2$	0.977
Freundlich model	
$K_F$	0.0323
$n$	1.0281
RMSE	0.224
SSE	0.250
$r^2$	0.974

The separation factor ( $R_L$ ) is an essential characteristic of the Langmuir isotherm. It can be used to predict whether a sorption system is favorable or unfavorable. The  $R_L$  is defined by the following relationship [24]:

$$R_L = 1 / (1 + K_L C_i) \tag{6}$$

Where  $K_L$  and  $C_i$  are the Langmuir constant and the initial concentration of metal, respectively. The isotherm is favorable when  $0 < R_L < 1$  and the isotherm is unfavorable when  $R_L > 1$ . The values of  $R_L$  for Cr (VI) were calculated and plotted against initial metal ion concentration. The calculated  $R_L$  values versus initial Cr (VI) concentration were represented in Fig. 5. From this figure, it was observed that biosorption was found to be more favorable at higher concentrations ( $0 < R_L < 1$ ). The sorption process was favorable for Cr (VI) removal at all concentrations investigated (20 to 100 mg/L).

The surface coverage ( $\theta$ ) is the fraction of biomass surface covered by metal. It was studied using Langmuir type equation [25]:

$$\theta = K_L C_i / (1 + K_L C_i) \quad (7)$$

The plot of the surface coverage against initial concentration of Cr (VI) is presented in Fig. 6. The increase in initial Cr (VI) concentration from 20 to 100 mg/L for the *Carum copticum* increases the surface coverage on the biosorbent. The surface coverage was obtained very low. It may be because of high  $q_{max}$  of the *Carum copticum*.

### 3.5. Biosorption kinetics

In order to investigate the kinetics of Cr (VI) biosorption by *Carum copticum*, the pseudo-first order model [26] and pseudo-second order model [27] were used. The non-linear form of the pseudo-first-order model can be expressed as:

$$q_t = q_e (1 - \exp(-K_1 t)) \quad (8)$$

Where  $q_e$  and  $q_t$  are the adsorption capacity at equilibrium and at time  $t$ , respectively (mg/ g), and  $k_1$  is the rate constant of pseudo first-order model ( $\text{min}^{-1}$ ).

The pseudo-second order kinetic can be expressed as:

$$q_e = q_e^2 K_2 / (1 + q_e K_2 t) \quad (9)$$

Where  $K_2$  is the pseudo-second order rate constant (g/mg min). Table 2 shows the predicted model constants for the above kinetic equations. Fig. 7 is shown the fitting of experimental data with two models. From Table 2, the values of SSE and RMSE indicate a better fit of pseudo-first order model with the experimental data compared with the pseudo-second order model. Moreover, the equilibrium biosorption capacity calculated from the pseudo first-order kinetic model fitting is nearer equilibrium biosorption capacity from the experiments ( $q_{e, \text{exp}}$ ) than the pseudo-second order kinetic model fitting.

### 4. Conclusion

The *Carum copticum* stem was used as biosorbent for the removal of Cr (VI). Effects of pH, biosorbent dosage and contact time on the biosorption of the Cr (VI) were studied. The isotherms and kinetics of the biosorption process were further investigated. The following conclusions were drawn from the present study:

1. The obtained results showed that pH, biosorbent dosage and contact time highly affected the Cr (VI) removal from aqueous solutions.
2. The maximum biosorption of the Cr (VI) from aqueous solutions occurred at pH 2, 1.6 g biosorbent dosage and 30 min contact time for the initial concentration of Cr (VI)=100mg/L.
3. Langmuir biosorption model adequately described the biosorption of Cr (VI) by The *Carum copticum* stem.
4. Kinetics results were well described by pseudo-first order model.

**Table 2:** Comparison of the pseudo-first order- and pseudo-second order models constants and calculated and experimental  $q_e$  values for biosorption of Cr (VI) by *Carum copticum* stem.

Experimental Value	$q_{e, \text{exp}}$ (mg/g)	3.813
Pseudo- first order model		
	$q_e$ (mg/g)	3.956
	$K_1$ ( $\text{min}^{-1}$ )	0.0701
	RMSE	0.184
	SSE	0.236
	$r^2$	0.996
Pseudo-second order model		
	$q_e$ (mg/g)	5.141
	$K_2$ (g/mg min)	0.0126
	RMSE	0.226
	SSE	0.357
	$r^2$	0.994

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