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Removal of Hexavalent Chromium from Aqueous Solution by the Pod of *Acacia gerrardii*

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This study aims at investigating the potential of *Acacia gerrardii* pod for the removal of Cr(VI) in batch system. Effect of solution pH, biosorbent dosage, initial concentration of Cr(VI), contact time on the removal process was examined. Complete removal of hexavalent chromium was achieved at pH values 1.0 and 2.0 whereas maximum removal of total chromium was obtained at pH of 3.0. The study showed that the biosorption and bioreduction mechanisms were involved in the removal process. The time required for complete removal of Cr(VI) using the pod of *Acacia gerrardii* was shortened with an increase in biomaterial dosage and decrease in Cr(VI) concentration. Kinetic data was well described using Park kinetic model. Freundlich isotherm model adequately fitted the equilibrium data indication multilayer adsorption of total chromium on the surface of biomaterial. The pod of *Acacia gerrardii* could be used efficiently for the removal of hexavalent chromium from aqueous solutions.

Keywords: Biosorption, chromium, *Acacia gerrardii*, isotherm models, Park kinetic models.

INTRODUCTION

Chromium is widely used in many industrial applications such as electroplating, leather tanning, wood preservation, chromate production, petroleum refining, and oxidants in University laboratories[1]. Chromium is presents in environment in two stable forms, hexavalent chromium (Cr(VI)) and trivalent chromium (Cr(III)). Compared to Cr(III), hexavalent chromium has higher mobility, bioavailability and toxicity[2].

If inadequately treated, chromium-bearing effluents can result in serious environmental health hazard. Toxic effects of chromium include dermatitis, bronchitis, liver dysfunction, renal impairment and cancer[3].

Several organizations and governmental bodies have set regulations and standard to restrict the discharge of toxic chromium to the environment. Though the removal of hexavalent chromium from industrial effluents to be within the regulatory limit is obligatory[4].

Many traditional technologies including chemical precipitation are used to sequester hexavalent chromium from industrial wastewaters[5]. Chemical precipitation of hexavalent chromium involves the chemical reduction of Cr(VI) to Cr(III) at lower pH condition followed by precipitation of Cr(III) as $Cr(OH)_3$ at higher pH values[6]. The chemicals involved in reduction and precipitation process are hazardous and expensive[7]. Furthermore, the toxic sludge generated from this method needs extensive treatment before disposal[8].

The adsorption of heavy metals from wastewaters is obtained using activated carbon and polymer resin, which are expensive[9]. Recently, several researchers have reported the ability of biomaterials to adsorb and reduce Cr(VI) to less toxic Cr(III).

The term "biosorption" was applied to the process by which the contaminants are removed by inactive biomass[10]. This technology utilizes the naturally available, low cost and eco-friendly biomaterial for decontamination of industrial wastewaters[11].

Various biomaterials have been tested for the removal of hexavalent chromium such as *Sargassum cymosum*[12], Oak peel[13], *Prunus serotina* bark[14], husk of *Lathyrus sativus*[15], banana skin[16], *Ficus carica*[17], wood apple shell[18]; dried pineapple leaves [19], *Ecklonia*[20].

The removal mechanism of hexavalent chromium from aqueous medium was considered by several studies as a simple anionic adsorption on the surface of protonated biomass whereas several researchers argued the contribution of reduction to the removal process under acidic conditions.

The pods of *Acacia spp* were reported to contain tannins[21] which exhibited specific affinity to bind metal ions[22]. The pod of *Acacia gerrardii* is naturally available and being produced in plant nursery as a waste materials. In the present study, an attempt has been made to examine the potential of *Acacia gerrardii* pods for the removal of Cr(VI) from contaminated water. The study describes the adsorption and reduction mechanisms involved in the removal process.

EXPERIMENTAL

Preparation of biomaterial

The pod of *Acacia gerrardii* was collected from Al-Baha Emirate in Saudi Arabia. The pod was washed by water to remove any debris that might be attached to its surface. The pod then was air dried, grounded by mixer, sieved using 120 mesh and stored in glass bottle.

Preparation of Cr(VI) solutions

The stock solution of Cr(VI) of 500 mg/L was prepared by dissolving analytical grade potassium dichromate in distilled water. Working solutions were prepared by adequate dilution of stock solution with distilled water.

Experiments for Cr(VI) removal

Batch experiments were carried out in 100 ml conical flasks containing mixtures of Cr(VI) solution and pods of *Acacia gerrardii*. The mixture was shaken in shaking incubator till the equilibrium was reached except in the case of kinetic studies where the samples from the Cr(VI) solution were collected at different time intervals. At the end of each experiment, the mixture of biomaterial and Cr(VI) solution was filtered and the filtrates was analyzed for Cr(VI), total Cr and Cr(III) concentrations following standard method[23]. Effect of pH on the removal process was evaluated by varying the pH of Cr(VI) solution in the range of 1.0–7.0. This variation was gained by proper addition of HCl (0.1 M) and 0.1 M NaOH (0.1 M). Hexavalent chromium solution of 20 mg/L was added to 0.1 g of *Acacia gerrardii* pod and mixed in shaking incubator for the period of 18 hours to ensure equilibrium.

In kinetic experiments, various concentration *Acacia gerrardii* pod (1.0–3.0 g/L) was added to Cr(VI) solutions with concentration of 40 mg/L. The samples from the Cr(VI) solution were collected at different time intervals.

To study the adsorption isotherm, different concentrations of Cr(VI) solutions were prepared (20 mg/L, 40 mg/L, 60 mg/L, 80 mg/L, 100 mg/L and 120 mg/L) and mixed with 0.4 g of the pods of *Acacia gerrardii* for the period of 24 hours. All experiments were conducted at temperature of 30°C.

The solution pH was adjusted to the value of 2.0 in both kinetic and adsorption isotherm experiments. The uptake of metals by *Acacia gerrardii* pod calculated using the following equation;

$$q_e = \frac{(C_i - C_e) \times V}{m} \tag{1}$$

where q_e is the total chromium ion adsorbed (mg metal ion/ g biosorbent) at equilibrium, *V is* the volume of the solution (L), C_i and C_e are the initial and equilibrium concentration of Cr(VI) ion (mg/L) and *m* is the dry weight of the *Acacia gerrardii* (g).

Chromium analysis

Hexavalent chromium was analyzed using diphenylcarbazide method in acidic medium. A measured volume of the supernatants were mixed with 3 mL 6 N H_2SO_4 followed by 2 mL of diphenylcarbazide. The total volume was made up to 50 ml using double distilled water. The resulted red-violet complex was measured at 540 nm using spectrophotometer (Spectro 20d Plus Spectrophotometer, Labomed, Inc).

Total chromium concentration was analyzed using flame atomic absorption spectrometer following the instrument operational manual (Agilent 55 AA Atomic Absorption Spectrometer). Trivalent chromium was calculated as the difference between total chromium and hexavalent chromium.

RESULTS AND DISCUSSION

Effect of pH

Solution pH is the most important determinant factor for the removal of heavy metals from aqueous solution. The effect of pH on the removal of Cr(VI) by the pod of *Acacia gerrardii* was presented in Fig.1. The figure demonstrates the complete removal of Cr(VI) from the solution at pH values of 1.0 and 2.0 whereas 90.2% removal was achieved at pH 3.0. The removal efficiency was decreased significantly with increasing the pH from 4.0 to 7.0. This indicates the favorable removal of Cr(VI) using the pod of *Acacia gerrardii* at acidic conditions. Similar trends were reported for the biosorption of Cr(VI) by other biomaterials[24].

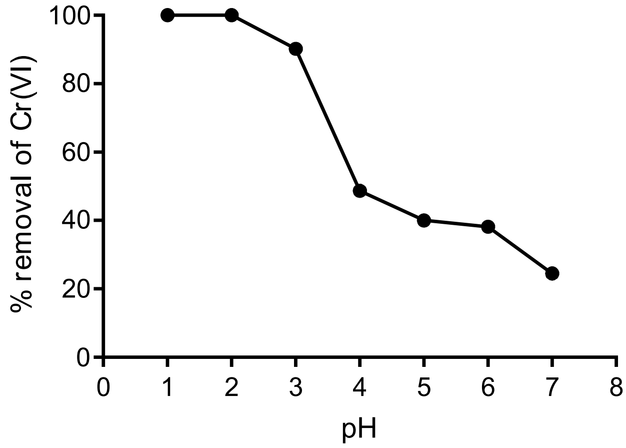

Figure 1. Effect of Solution pH on the removal efficiency of Cr(VI) using the pod of *Acacia gerrardii* (Initial Cr(VI) concentration = 20 mg/L, biomaterial dosage = 1.0 g/L, Temperature = 30°C and rotation speed = 200 rpm.)

It is known that the pH affects the speciation of metal ions in the aqueous solutions as well as the surface chemistry of biomaterials. The expected forms of Cr(VI) in natural water are $HCrO_4^-$, CrO_4^{-2} and $Cr_2O_7^{-2}$ ions with $HCrO_4^-$ is predominant in lower pH values[25]. At strong acidic condition, biomaterials are subjected to the protonation process in which the protons coordinate with functional groups on the surface of biomaterials[20]. Thus, this protonation enhanced the electrostatic attraction of positively charged Acacia *gerrardii* pod and anionic forms of Cr(VI). In contrary, the repulsive force between the anionic form of Cr(VI) and deprotonated pod of *Acacia gerrardii* resulted in low removal efficiency at higher pH values.

For further understanding the removal mechanism of Cr(VI) by the pod of *Acacia gerrardii*, the equilibrium concentrations of Cr(VI), total Cr and Cr(III) are plotted against the studied range of pH values (Fig. 2). The figure shows the appearance of Cr(III) which was not present in the solutions before running the experiments. The concentration of Cr(III) was decreased as the pH of the solutions increased from 1.0 to 7.0 indicating the reduction of Cr(VI) to Cr(III) at lower pH values by the electronic donor groups exists on the surface of *Acacia gerrardii* pod. These results lead to the assumption that both biosorption and bioreduction mechanisms were involved in the removal process of Cr(VI) by the pod of *Acacia gerrardii* pod.

Park proposed two reduction mechanisms (direct and indirect) for Cr(VI) by biomaterials in his subsequent literatures[26–28]. In the direct mechanism, the Cr(VI) is reduced by the biomaterial to Cr(III), which in turn remains in the solution or forms complex with functional group of the biosorbent. Direct reduction mechanism is based on the assumption that the anionic forms of Cr(VI) binds to the protonated functional groups of biomaterials before its reduction to Cr(III) by the adjacent electron-donor groups. The resulted Cr(III) are released to the solution due to repulsive force between protonated biomaterials and cationic Cr(III). The reduction reaction takes place according to the following equations;

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \quad E^0 = +1.33\,V \quad (2)$$

$$HCrO_4^- + 7H^+ + 3e^- \rightarrow Cr^{3+} + 4H_2O \quad E^0 = +1.35\,V \quad (3)$$

$$H_2CrO_4 + 6H^+ + 3e^- \rightarrow Cr^{3+} + 4H_2O \quad E^0 = +1.33\,V \quad (4)$$

As depicted from Fig. 2, the minimum concentration of total chromium was obtained at pH 3.0, which indicates maximum removal of total chromium by the pod of *Acacia gerrardii* at this acidic condition. This can be explained by the fact that higher amount of Cr(III) was added to the solution at pH < 3.0 as a result of Cr(VI) reduction by the pod of *Acacia gerrardii*. On the other hand, the biosorption efficiency of anionic Cr(VI) on the pod of *Acacia gerrardii* was decreased with an increase of pH values to the above of 3.0.

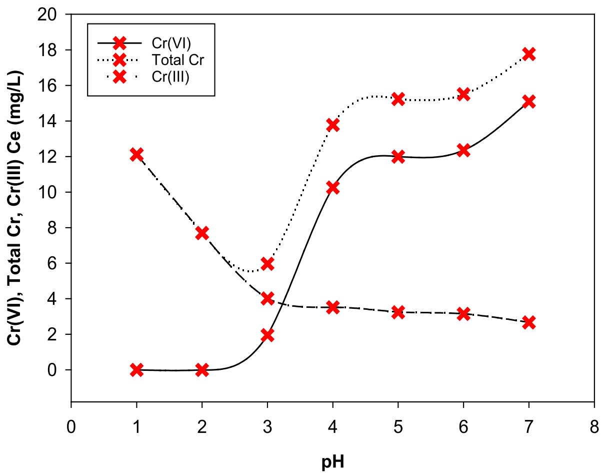

Figure 2. Chromium concentration profile during the removal of Cr(VI) using the pod of Acacia gerrardii at different acidic conditions (Initial Cr(VI) concentration = 20 mg/L, biomaterial dosage = 1.0 g/L, Temperature = 30°C and rotation speed = 200 rpm.)

Kinetic studies of Cr(VI) removal

Effect of contact time and adsorbent dosage on the removal of Cr(VI) using the pod of *Acacia gerrardii* was presented in Fig. 3. It is indicated from the figure that higher concentration of *Acacia gerrardii* pod shortened the required time to reduce the concentration of Cr(VI) to the below of its detection limit. Fig. 3 shows the increase of Cr(III) concentration with time indicating the reduction of Cr(VI) to Cr(III). On the other hand, it has been observed that the amount of Cr(VI) removed from solution was higher than the amount of Cr(III) at each point of time demonstrating the simultaneous adsorption and reduction of Cr(VI) using the pod of *Acacia gerrardii*. After disappearance of Cr(VI) in the solution, there was no significant removal of total chromium with time suggesting the low adsorption capacity of Cr(III) on the surface of biomaterial at acidic condition. This can be due to repulsive force between the cationic ions of Cr(III) and protonated biomaterial at lower pH values.

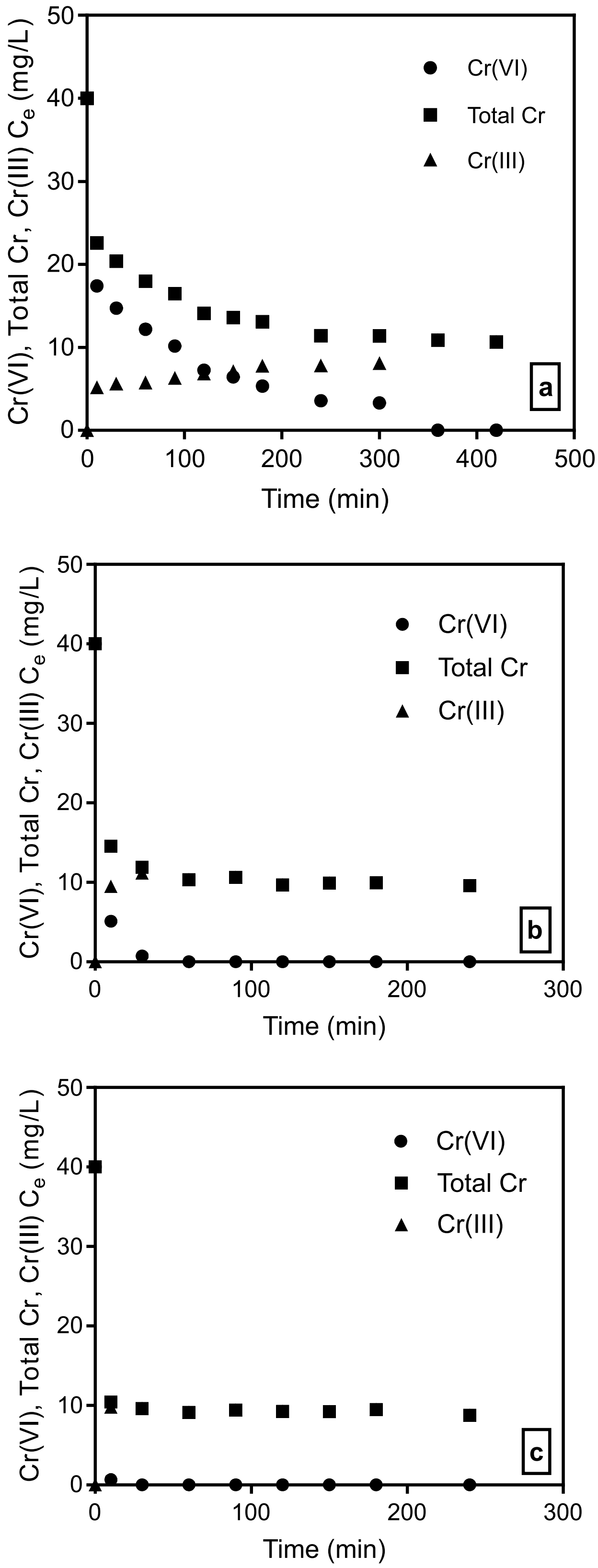

Figure 3. Chromium concentration during the removal of Cr(VI) using the pods of *Acacia gerrardii*. pH =2, initial Cr(VI) concentration = 40 mg/L, Temperature = 30°C, rotation speed = 200 rpm and biomaterial dosage was (a) 1.0 g/L and (b) 2.0 g/L (c) 3 g/L

Kinetic modeling

Since the biosorption and bioreduction mechanisms were involved in the removal of Cr(VI) from aqueous solutions, Park kinetic model[27] was used to describe the removal kinetic of Cr(VI) by the pod of *Acacia gerrardii*. This model is based on the following redox reaction between biosorbent and Cr(VI) during the biosorption process:

$$biomass + Cr(VI) \rightarrow biomass(oxidized) + Cr(III) \quad (5)$$

The model considers the following assumption: (1) organic compounds on the surface of biomaterials are responsible for Cr(VI) reduction (2) one type of organic compounds has the ability to reduce Cr(VI) (3) the rate equation of Cr(VI) reduction is first order (Eq. 6)

$$\frac{d[Cr(VI)]}{dt} = -k[OC][Cr(VI)] \quad (6)$$

Where OC is the concentration of organic compounds at time t (minute) which is capable of reducing Cr(VI) in (mmol/L), Cr(VI) is the concentration of hexavalent chromium at time t (mmol/L), is the rate constant (L $mmol^{-1}$ m^{-1}).

The general form of Park model can be expressed as follows;

$$[Cr(VI)] = \frac{C_{OC}^{*}[B][Cr(VI)]_0 - [Cr(VI)]_0^2}{C_{OC}^{*}[B]\exp(k(C_{OC}^{*}[B] - [Cr(VI)]_0)t) - [Cr(VI)]_0} \quad (7)$$

Where C_{OC}^{*} is the content of equivalent organic compound per unit gram of biomass (mmol/g) $[Cr(VI)]_0$ is the initial concentration of Cr(VI) (mmol/L) and is the concentration of biomaterial (g/L).

Fig. 4 shows that the Park model could describe the Cr(VI) reduction kinetic at different dose of the pod of *Acacia gerrardii*. The constant values of C_{OC}^{*} and are determined using the nonlinear equation regression with the help of GraphPad Prism 7.04. The parameters calculated values from the model are listed in Table 1. The removal rate constant increased with an increase in the biomaterial dosage from 1.0 to 3.0 g/L. This can be attributed to the higher availability of electrons required for reduction reaction with increasing the biomaterial concentration[29].

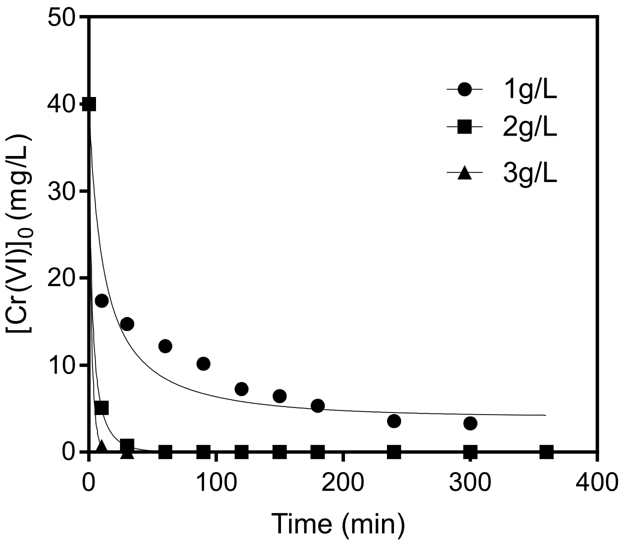

Figure 4. Chromium concentration during the removal of Cr (VI) using the various concentration of the pods of *Acacia gerrardii*. pH =2, initial Cr (VI) concentration = 40 mg/L, Temperature = 30ºC, rotation speed = 200 rpm and biomaterial dosage was (a) 1.0 g/L and (b) 2.0 g/L (c) 3 g/L. Symbols are the experimental data whereas lines are the predicted data from the model

Table 1. Estimated parameters of Park kinetic model for the removal of Cr (VI) using the pod of *Acacia gerrardii*. pH = 2, initial Cr (VI) concentration = 40 mg/L, temperature = 30 0C, rotation speed = 200 rpm and biomaterial dosage was (a) 1.0 g/L and (b) 2.0 g/L (c) 3 g/L

Biosorbent dosage	Park kinetic model parameters		
	C_{OC}^{*}(mmol/g)	K (L $mmol^{-1}$ m^{-1})	R^2
1 g/L	0.69	0.002	0.934
2 g/L	0.09	0.009	1.00
3 g/L	0.28	0.040	1.00

Adsorption isotherm modeling

Since it is difficult to determine the form of chromium ions on the surface of biomaterial, adsorption isotherm models were used to describe the adsorption of total chromium on the surface of the pod of *Acacia gerrardii*. These models link the amount of metal ions adsorbed on unit mass of biosorbent at specific temperature. The models applied to obtained equilibrium data are namely; Langmuir adsorption isotherm model and Freundlich adsorption isotherm model.

The linear forms of Langmuir and Freundlich adsorption isotherm models are expressed in Eq. 8 and Eq. 9 respectively.

$$\frac{C_e}{q_e} = \frac{1}{K_L \times q_{max}} + \frac{C_e}{q_{max}} \quad (8)$$

Where q_{max} is the maximum biosorption capacity of adsorbent (mg/g) and K_L is the Langmuir biosorption constant (L/mg). The values of q_{max} and K_L are calculated from the slope and intercept of the linear plot of C_e/q_e versus C_e (Fig. 5) respectively.

$$\frac{C_e}{q_e} = \frac{1}{K_L \times q_{max}} + \frac{C_e}{q_{max}} \quad (9)$$

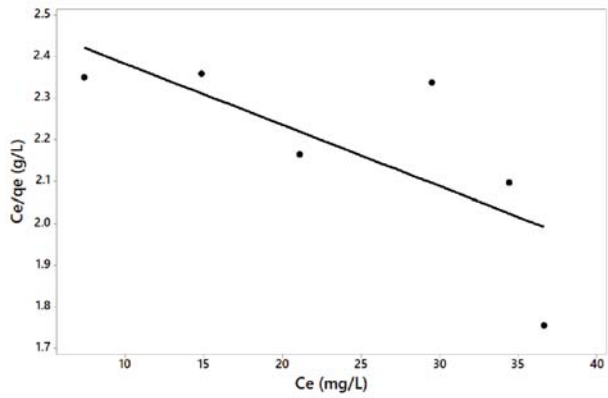

Figure 5. Langmuir adsorption isotherm for the sorption of total chromium by the pods of *Acacia gerrardii*

The Freundlich isotherm constants *1/n* and K_f (L/g) are calculated from the slopes and intercepts of the linear plot of log q_e versus log C_e (Fig. 6).

The calculated values of the models constants are presented in Table 2 and the graphical presentations of . The Freundlich adsorption isotherm model showed better applicability (R^2 = 0.984) to equilibrium data indicating multilayer adsorption of chromium on heterogeneous surface. The higher value of 1/n (*1/n* > 1) indicates biosorption over the studied range of concentrations was not the favorable.

Table 2. Adsorption isotherm models for the biosorption of total chromium by the pod of Acacia gerrardii. pH = 2, biomaterial dosage = 4 g/L, temperature = 30°C and rotation speed = 200 rpm

Adsorption model	Langmuir isotherm model			Freundlich isotherm model		
Parameters	q_{max} (mg/g)	K_L (L/mg)	R^2	K_f(L/g)	1/n	R^2
	68.21	0.005	N.F*	3.09	1.11	0.984

* Not fitted

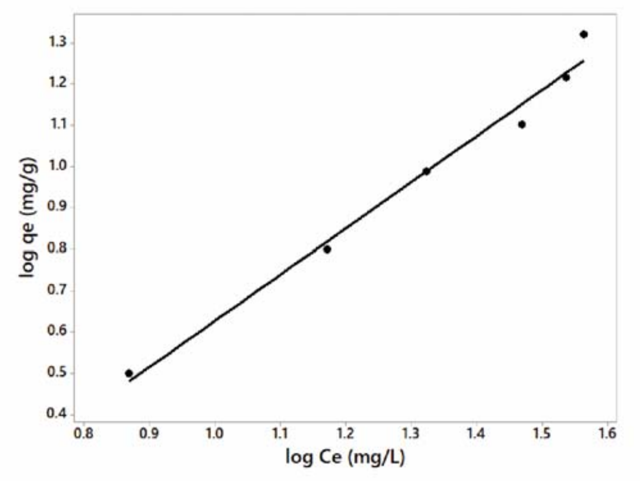

Figure 6. Freundlich adsorption isotherm for the sorption of total chromium by the pods of *Acacia gerrardii*

CONCLUSIONS

The pod of *Acacia gerrardii* has proved to be an efficient biomaterial for the removal of hexavalent chromium from aqueous solutions. The removal efficiency was dependent on the acidic conditions of the solutions. An increases in the pH of the solution resulted in the decrease of the removal of Cr(VI) by the used biomaterial. Complete removal of Cr(VI) was observed at the acidic conditions (pH ≤ 2.0) whereas maximum removal of total chromium was observed at pH of 3.0. Trivalent chromium which was not available initially in the solutions appeared after biosorption process indicating the reduction of Cr(VI) to Cr(III) by the pod of *Acacia gerrardii* at strong acidic conditions. The Park model fitted well with the kinetic data at all ranges of the biosorbent dosages. An increase in the biosorbent dose resulted in increasing the removal rate of Cr(VI) by the pod of *Acacia gerrardii*. The uptake of Cr(VI) by the used biomaterial increased with increasing the dose of biosorbent and shortened the equilibrium time. The equilibrium data of total chromium removal was described well using the Freundlich adsorption model suggesting multilayer adsorption mechanisms.

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