

Chromium biosorption from aqueous environments by mucilaginous seeds of *Cydonia oblonga*: Kinetic and thermodynamic studies

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Abstract

Hexavalent chromium Cr(VI) is one of the most toxic heavy metals in aqueous solutions, hence it is highly imperative to treat the wastewater containing Cr(VI) before its discharge. At present work, the rate of biosorption was studied under a variety of conditions, including initial Cr(VI) concentration (5-50 mg/L), amount of biosorbent (0.5-3 g/100 mL), pH (1-8), temperature (298-318 K) and contact time (30-120 min). Biosorption of Cr(VI) is in all cases pH-dependent showing a maximum at equilibrium pH values between 2 and 3. The biosorption data fitted well with Langmuir and Freundlich isotherms. The biosorption capacity calculated from the Langmuir isotherm was $q = 33.58$ mg Cr(VI)/g of dry seeds (at 303 K). Biosorption kinetics data well fitted using pseudo-second-order. Thermodynamic studies confirmed that biosorption of Cr(VI) ions by mucilaginous seeds of *Cydonia oblonga* was spontaneous and endothermic nature.

Key words: *Cydonia oblonga*, chromium removal, mucilaginous seeds, biosorption

1. Introduction

Heavy metals are commonly found in various industrial wastewaters and can cause serious water pollution and threaten the environment. Among the heavy metals, chromium is being one of the important heavy metal pollutants present in the environment. Chromium and its compounds are extensively used in industry, with the most usual and important sources coming from the alloy reparation, metal cleaning and processing, leather tanning, wood preservation, ore processing, and petroleum refining processes (Acosta *et al.*, 2004; Hamadi *et al.*, 2001). In the effluents from these industries, chromium is present primarily as hexavalent chromium (Cr(VI)) and trivalent chromium (Cr(III)). Nevertheless, hexavalent form is five hundred times more toxic than the trivalent one (Mohan *et al.*, 2005). Cr(VI) has been classified as a Group I human carcinogen by International Agency for Research on Cancer (IARC) and as a Group A inhalation carcinogen by US Environmental Protection Agency (EPA) (Hamadi *et al.*, 2001). Cr(VI) is considered as a common teratogenic,

mutagenic, and carcinogenic chemicals and the presence of Cr(VI) ions in the environment is posing serious problems and causing great public concern, which significantly motivates the investigation and development of new and improved materials to address the problems (Wang *et al.*, 2011; Zhou *et al.*, 2008). In addition, a long-term exposure of Cr(VI) to mankind may cause severe physical disorders, such as dermatitis and the malfunctioning of the liver, kidney, circulatory and nervous systems (Dubey and Gopal, 2007).

The US EPA requires 0.05 and 0.1 mg/L of Cr(VI) in drinking water and surface waters, respectively. Furthermore, the permissible limit of Cr(VI) for industrial effluents to be discharged to the surface water is 0.1 mg/L and for potable water it is 0.05 mg/L by World Health Organization. Consequently, chromium containing wastewaters must be treated to lower Cr(VI) levels to allowable limits before discharging into the environment (Altun and Pehlivan, 2012; WHO, 2006). Various processes have been used for treating Cr(VI) containing wastewater, including electrochemical precipitation, lime coagulation, oxidation/reduction, ion exchange, membrane ultrafiltration, solvent extraction, and adsorption (Olmez, 2009; Bazrafshan *et al.*, 2008; Alguacil *et al.*, 2004).

Nevertheless, these techniques can be inefficient and normally not cost-effective. During the last decades, a new technique of biosorption has been proposed and considered to remove but also recover many metals including chromium (Pachero *et al.*, 2011). The removal of metallic ions from an aqueous solution through binding to various biomasses has been referred to as biosorption. Biosorption is considered as a promising technology for toxic metal elimination, thanks to the low-cost and easily available biosorbents, regeneration ability and the high eliminating efficiency for a variety of heavy metals (Hou *et al.*, 2012).

Various materials have been suggested for biosorption process including, algae, oysters, bacteria, yeast and various plants (Pachero *et al.*, 2011; Bazrafshan *et al.*, 2012; Bazrafshan *et al.*, 2013a; Bazrafshan *et al.*, 2013b). In

addition, removal of chromium by using various naturally available biomaterials such as seeds of *Ocimum americanum* (Lakshmanraj *et al.*, 2009), eucalyptus bark (Sarin and Pant, 2006) and saw dust, sugar cane bagasse and sugar beet pulp (Sharma and Foster, 1994) have been studied for the removal of Cr(VI) ions from water/wastewater.

In the present study the biosorption of Cr(VI) on to mucilaginous seeds of *Cydonia oblonga* was investigated. The effects initial pH, reaction time and Cr(VI) concentration on the binding of chromium to the *Cydonia oblonga* was investigated as well as the capacity of the biosorbent for Cr(VI) at different temperatures. The thermodynamics of the binding process were investigated, which included determining the ΔG , ΔH , and ΔS . The kinetics of the sorption process was studied at temperatures of 298-318 K. In addition, adsorption isotherms were studied at various temperatures. The isotherm provides a relationship between the concentration of Cr(VI) in solution and the amount of Cr(VI) adsorbed on the solid phase when both phases are in equilibrium.

2. Experimental

2.1. Biosorbent preparation

The seeds of *Cydonia oblonga* used in this study were obtained from local area. The seeds are washed with distilled water to remove dirt and other particulate matter. The washing procedure was continued till the wash water contained no color. The seed contains a thin outer layer having larger capacity of hydration. After soaking in distilled water, the outer layer of seeds swells which appear as a white gel. The dry seeds were black in color and ovoid in shape with mean size approximately 2 mm length and 1.5 mm width. When the seeds were soaked in water, they swelled and sorbed more water. The average size of swollen seeds was 4-5 mm. The swollen part was white mucilage composed.

The required quantity of seeds was taken in a test tube (60 mL) containing two third volume of water and allowed to swell for about 40 min. The mouth of the test tube was tightly plugged (for any probable leakage). The test tube was then placed in a boiling water bath for 60 min. After boiling, the water-seed suspension was passed through sieves to drain the excess water. The mucilaginous seeds were washed in fresh distilled water. After that they were directly used as an adsorbent. A fresh biosorbent was prepared by following the above procedure for daily experiments.

2.2. Preparation of stock solution (absorbate)

All chemicals and reagents used were of analytical grade. Standard stock Cr(VI) solution (1000 mg/L) was prepared by dissolving $K_2Cr_2O_7$ salt in deionized water and desired solutions were prepared by dilution of the stock solution. The pH was adjusted using 1N H_2SO_4 and 1N NaOH. Fresh dilutions were used for each study.

2.3. Analysis

The residual concentration of Cr(VI) was determined spectrophotometrically (Hach digital UV-Vis spectrophotometer, model DR/5000) at 540 nm using the diphenyl carbazide reagent (Sen and Ghosh Dastidar, 2007). A standard graph of absorbance vs concentration was obtained for known chromium concentrations. The absorbance value of sample was used to determine the unknown concentration.

2.4. Batch sorption experiments

The adsorption isotherm experiments were conducted at laboratory temperature (23 ± 2 °C) by varying the concentrations from 5 to 50 mg/L. Aliquots of 100 mL chromium solution at different concentrations were taken in 250 mL conical flasks and pH was adjusted to 2 using 1N H_2SO_4 and 1N NaOH. The boiled swollen mucilaginous seeds of *Cydonia oblonga* (after grinding) equivalent to 1.0 g dry weight were added to each conical flask. Then, the flasks were placed in a rotary shaker maintained at 150 rpm for 24 h.

The amount of Cr(VI) adsorbed per unit mass of biosorbent q_e (mg/g) was calculated as follows:

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations of Cr(VI) (mg/L), respectively. V is the volume of chromium solution (L) and M is the mass of adsorbent used (g). Adsorption isotherms were performed at temperatures of 298, 303, 308, 313 and 318 K, respectively. The flasks were shaken to ensure that the sorption process reached equilibrium.

To express the percent of Cr(VI) removal, the following equation was used:

$$\text{Efficiency, (\%)} = \frac{(C_i - C_f)}{C_i} \times 100 \quad (2)$$

where C_i and C_f represent the initial and final (after sorption) Cr(VI) concentrations, respectively.

2.4.1. Effect of pH on Cr(VI) uptake/sorption

The effect of pH on Cr(VI) sorption was studied by varying the pH from 2 to 8. The initial concentration of Cr(VI) solution used for this study was 15 mg/L. The biosorbent dosage was equivalent to 1.0 g dry weight of boiled mucilaginous seeds. Flasks were agitated on a rotary shaker at 150 rpm for 90 min. The suspensions were then filtered through Whatman 42 filter paper and the concentration of Cr(VI) in the filtrates was analyzed. The above procedure was repeated three times and the average value was taken.

2.4.2. Effect of sorbent dose

Batch biosorption experiments were done at a different concentrations of biosorbent from 0.5 g to 3.0 g in a 100 mL solution of 15 mg/L of Cr(VI) at pH 2.0, for a contact time of 90 min at 23 ± 2 °C. The samples were then agitated and filtered and the filtrates were analyzed as mentioned before.

2.4.3. Effect of contact time and initial concentration of Cr(VI)

Batch biosorption experiments were carried out at different contact times (30, 60, 90, 120 and 150 min) and different initial concentrations of Cr(VI) (5, 15, 25, 40 and 50 mg/L) at pH 2.0. The *Cydonia oblonga* dosage was 1.0 g in 100 mL solution in 250 mL conical flask at 23 ± 2 °C. The samples were then agitated (150 rpm) and filtered. The filtrates were analyzed as mentioned before.

2.4.4. Isotherm studies

Adsorption isotherm studies were carried out with different initial concentrations of Cr(VI) (5, 15, 25, 40 and 50 mg/L) and fixed doses of biosorbent at initial pH 2. The adsorbent dosage was equivalent to 1.0 g dry weight of boiled mucilaginous seeds. In order to study the adsorption isotherm, three equilibrium isotherms including Langmuir, Freundlich and Temkin were analyzed.

2.4.5. Effect of temperature on equilibrium studies

Thermodynamic parameters of the biosorption process were determined by carrying out batch mode experiments at various initial Cr(VI) concentration in the range 5-50 mg/L, with all other experimental conditions were kept constant. The temperatures chosen for this study were in the range 298-318 K. Furthermore, kinetic studies were also carried out at different time intervals and Cr(VI) concentration but at fixed biosorbent dose and pH.

3. Results and discussion

3.1. Effect of initial pH

The pH of solution plays a critical role in the biosorption process of metals. Generally, pH has a profound influence on sorption of metals. Consequently, in this study the role of pH in the maximum removal of Cr(VI) ions was examined over a pH range of 2-8, to find the optimum pH for the sorption process and also to see whether biosorbent shows good uptake over a broad pH range. Cr(VI) uptake was affected by the change in pH and maximum removal efficiency of Cr(VI) occurs at initial pH ranging from 2 to 4 (91.7-97.4%) and decreases at lower and higher pH values as depicted in (Fig. 1). The maximum biosorption capacity was found to be 14.61 mg/g for Cr(VI) at pH 2. In contrast, removal efficiency at pH 8.0 was only 49.1% and biosorption capacity was 7.36 mg/g. The optimum biosorption of Cr(VI) by seeds mucilaginous of *Cydonia oblonga* at low pH may be attributed to the presence of large amount of hydrogen ions (H^+) at such pH levels, which neutralize the negatively charged adsorbent surface and thus reduce hindrance to the diffusion of Cr(VI) anions. At high pH values, the abundance of hydroxide ions (OH^-) increases hindrance to diffusion of Cr(VI) anions, thereby reducing the removal efficiency (Rao *et al.*, 2002). On the other hand, in highly acidic media, the adsorbent surface might be highly protonated and favour the uptake of Cr(VI) in the anionic form $HCrO_4^-$. Maximum sorption at pH 2.0 indicates that it is the $HCrO_4^-$ form of Cr(VI) which is adsorbed preferentially on the adsorbents (Cimino *et al.*, 2000). Furthermore, the findings attribute that pH of

solution affects the solubility of metals and the ionization state of the functional groups like carboxylate, phosphate and amino groups of the cell walls of the biomaterial (Popuri *et al.*, 2007). Industrial effluents containing Cr(VI), generally has low pH. Consequently, no pH adjustments would be required prior to biosorption process, thereby reducing the cost of Cr(VI) biosorption process. Similar finding was reported by Lakshmanraj *et al.* (2009).

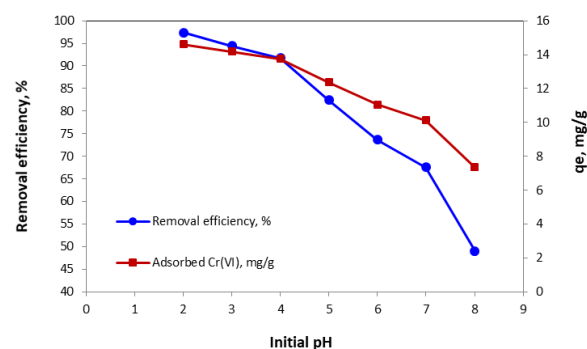


Figure 1. Effect of initial pH on Cr(VI) biosorption by seeds of *Cydonia oblonga* (Cr(VI) concentration = 15 mg/L, biosorbent dose = 1 g/100 ml, time = 90 min)

3.2. Effect of biosorbent dose on Cr(VI) biosorption

The dependence of Cr(VI) ions onto mucilaginous seeds of *Cydonia oblonga* as a biosorbent was conducted in various biosorbent dosages ranging from 0.5 to 3.0 g/L while keeping other parameters constant, such as pH (2), initial concentration (15 mg/L) and contact time (90 min) as constant. Fig. 2 shows the Cr(VI) concentration of the solution as a function of dosage of biosorbent. As it can be seen from Fig. 2, the removal efficiency of Cr(VI) increased with the increase in dosage of biosorbent, as expected. However, about 93-97% of the Cr(VI) ions were effectively removed at the biosorbent dosage of 0.5-1.0 g where as 97.93% removal was achieved at the dosage of 3 g with the initial Cr(VI) concentration of 15 mg/L. In fact, the uptake of the Cr(VI) increased rapidly with increased amount of biosorbent from 0.5 to 1.0 g and slowed down from 1.0 to 3.0 g. This result can be explained by the fact that the sorption sites remain unsaturated during the sorption; whereas the number of sites available for sorption site increases by increasing the adsorbent dosage.

In contrast, a steady decrease in biosorption capacity, q_e with increasing mass dose was observed for Cr(VI) ion as shown in Fig. 2. Reduction in metal uptake, q_e , by *Cydonia oblonga* with increasing biomass concentration was attributed to an insufficiency of metal ions in solution with respect to available binding sites (Fourest and Roux, 1992). Other studies having similar result have been reported (Bazrafshan *et al.*, 2016b, Bazrafshan *et al.*, 2013a). Higher specific uptake at lower dry mass concentrations has also been attributed to an increased metal-to-biosorbent ratio, which decreases upon an increase in dry mass concentration (Puranik and Pakniker, 1999).

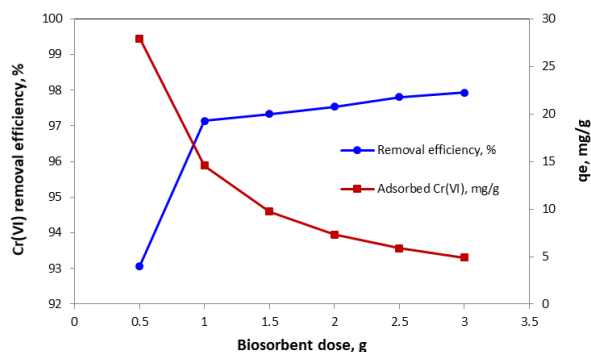


Figure 2. Effect of biosorbent dose on Cr(VI) biosorption by seeds of *Cydonia oblonga* (Cr(VI) concentration = 15 mg/L, initial pH = 2, time = 90 min)

3.3. Effect of contact time and initial concentration of chromium

The pollutant concentration and contact time between biosorbent and pollutant species play a significant role in the process of removal of pollutants from aqueous solutions by biosorption at a particular temperature and pH. The effects of initial Cr(VI) concentration and contact time on the removal rate of Cr(VI) by the *Cydonia oblonga* are shown in Fig. 3.

As it can be seen from Fig. 3, Cr(VI) removal is increased with increasing the contact time at all initial Cr(VI) concentrations. For the first 45 min, the biosorption uptake was rapid (43.7-79.6%), then it proceeds at a slower sorption rate and finally did not increase significantly up to 120 min. In the initial stages the removal efficiency of Cr(VI) at all concentrations increased rapidly due to the abundant availability of active binding sites on the biomass, and with gradual occupancy of these sites, the sorption became less efficient in the later stages (Costa and Leite, 1991). In fact, the biosorption kinetics of heavy metal ions consisted of two phases; an initial rapid phase where the biosorption was rapid and contributed significantly to the equilibrium biosorption, and a slower second phase whose contribution to the total metal biosorption was relatively small. The first phase of biosorption kinetics lasted for almost an hour. The trend of Cr(VI) biosorption was typical of metal binding to biomass by means of physicochemical interactions. Such particular behavior could have been due to the non-homogeneity of the biomass surface which possesses functional groups differing in dissociability and in Cr(VI) adsorption rates (Matheickal *et al.*, 1999).

In addition, as shown in Fig. 3, when the initial Cr(VI) concentration is increased, the percent of Cr(VI) removal decreased. For example, the percentage removal decreases from 89.4% to 83.1% when Cr(VI) concentration increases from 5 to 50 mg/L with the same contact time and sorption temperature. In contrast when the initial Cr(VI) concentration is increased, the amounts of adsorbed Cr(VI) also increased, so the removal of Cr(VI) depends on its concentration in the solution. For example, when the initial Cr(VI) concentration increases from 5 to 50 mg/L (at contact time 15 min), the equilibrium sorption capacity of biosorbent increased from 0.286 to 2.359 mg/g. This

increase in the proportion of removed Cr(VI) may be probably due to equilibrium shift during sorption process. On the other hand, it may be due to an increase in the number of Cr(VI) ions for the fixed amount of biosorbent. The amount of Cr(VI) adsorbed per unit mass of biosorbent increases with increase in Cr(VI) concentration, may be due to the complete utilization of adsorption surface and active sites available which is not possible in low concentration. Similar findings were reported by Babu and Gupta (Babu and Gupta, 2008) on Cr(VI) removal by using activated Neem leaves and Ofomaja *et al.* on copper(II) biosorption onto pine cone powder (Ofomaja *et al.*, 2010).

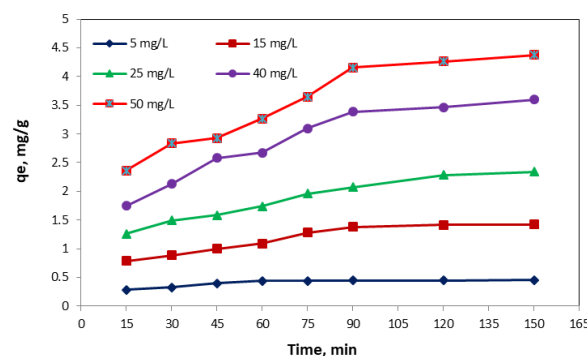


Figure 3. Effect of contact time on Cr(VI) biosorption by seeds of *Cydonia oblonga* (initial pH 2 and sorbent dose 10g/L)

3.4. Effect of temperature on Cr(VI) biosorption and thermodynamic studies

The biosorption of Cr(VI) ion on *Cydonia oblonga* was investigated as a function of temperature and the maximum removal of Cr(VI) ion was obtained at 318 K. The batch biosorption experiments were performed at different temperatures of 298, 303, 308, 313 and 318 °K for the initial Cr(VI) ion concentrations in the range of 5-50 mg/L at constant biosorbent concentration of 10 g/L and optimum pH value of 2. As presented in Fig. 4, biosorption of Cr(VI) increased from 82.9-91.9% to 91.4-94.7% with increase in temperature from 298-318 °K for different initial Cr(VI) concentrations (5-50 mg/L). Similar findings was reported by Ofomaja *et al.* on biosorption of copper(II) and lead(II) onto potassium hydroxide treated pine cone powder (Ofomaja *et al.*, 2010). In addition, a similar finding was reported by Sahu *et al.* on Cr(VI) removal from aqueous solution using Tamarind wood activated carbon (Sahu *et al.*, 2009). The increase in metal uptake with increasing temperature was attributed to either higher affinity of sites for metal or an increase in number of binding sites on activated carbon.

In order to determine the thermodynamic parameters, some experiments were carried out at different temperature 298-318 K for Cr(VI) biosorption. The Gibbs free energy of the sorption was calculated by the following equation:

$$\Delta G^0 = -RT \ln K_f \quad (3)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (4)$$

where R is universal gas constant (8.314 J/mol/K) and T is the absolute temperature in K. The thermodynamic parameter, Gibb's free energy change, ΔG^0 , is calculated using K_f obtained from Freundlich Eq. (7) and shown in Table 2. The values of enthalpy (ΔH^0) and entropy change (ΔS^0) can be obtained from the slope of the plot of ΔG^0 versus T. A plot of Gibb's free energy change, ΔG^0 , against temperature, T, was found to be linear (Figure 5).

The negative values of ΔG^0 confirm the feasibility of the process and also the spontaneous nature of biosorption with a high preference of Cr(VI) ions by *Cydonia oblonga*. Furthermore, the decrease in the negative value of ΔG^0 with an increase in temperature indicates that the adsorption process of Cr(VI) ions on *Cydonia oblonga* becomes more favorable at higher temperatures (Zaki *et al.*, 2000).

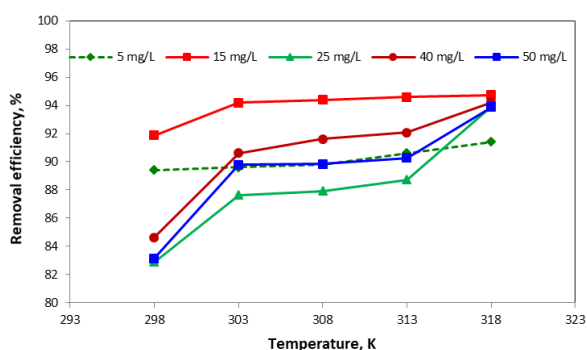


Figure 4. Effect of temperature on Cr(VI) ions biosorption onto seeds of *Cydonia oblonga* (pH=2, sorbent dose=10g/L and contact time =90 min)

Adsorption process can be classified as physical adsorption and chemisorption by the magnitude of the enthalpy (ΔH^0) change. It is accepted that if magnitude of enthalpy change is less 84 kJ/mol, adsorption is physical. However chemisorption takes place range from 84 to 420 kJ/mol (Errais *et al.*, 2011; Bazrafshan *et al.*, 2016a; Bazrafshan *et al.*, 2014). From these results (Table 1) it is clear that physisorption is much more favorable for the biosorption of Cr(VI) ions.

Table 1. Thermodynamics parameters for Cr(VI) ions biosorption onto seeds of *Cydonia oblonga*.

Temperature, K	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol/K)
298	0.374		
303	-0.123		
308	-0.221	17.71	0.058
313	-0.364		
318	-0.964		

Also, the positive value of ΔH^0 indicates that the sorption reaction is endothermic. Entropy (ΔS^0) has been defined as the degree of chaos of a system. The positive value of ΔS^0 suggests that some structural changes occur on the

adsorbent and the randomness at the solid/liquid interface in the adsorption system increases during the adsorption process (Gupta, 1998).

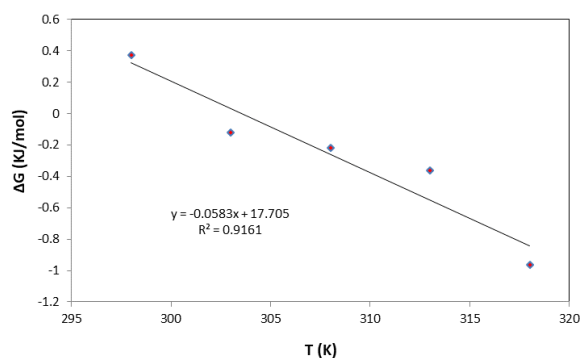


Figure 5. Plot of Gibbs free energy change, ΔG^0 , vs. temperature, T

3.5. Equilibrium isotherm

An important physiochemical aspect in terms of the evaluation of sorption processes is the sorption equilibrium. In fact, the isotherm provides a relationship between the concentration of sorbate in solution and its amount adsorbed on the solid phase when both phases are in equilibrium. In order to investigate the adsorption isotherm, three equilibrium isotherms were analyzed: the Langmuir, Freundlich and Temkin isotherm.

3.5.1. Langmuir isotherm

This isotherm model is valid for monolayer adsorption onto surface containing finite number of identical sorption sites. The saturated monolayer isotherm can be represented as:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (5)$$

where q_e is the amount of metal adsorbed per unit mass of adsorbent (mg/g), C_e is equilibrium concentration of the solution (mg/L), and q_m is the maximum amount of metal ions required to form a monolayer (mg/g). The Langmuir equation can be rearranged to linear form for the convenience of plotting and determining the Langmuir constants (K_L) and maximum monolayer adsorption capacity of biosorbent (q_m). The values of q_m and K_L can be determined from the linear plot of $1/q_e$ versus $1/C_e$:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L} \frac{1}{C_e} \quad (6)$$

3.5.2. Freundlich isotherm

The Freundlich equation is purely empirical based on sorption on heterogeneous surface, which is commonly described by the following equation:

$$q_e = K_f C_e^{\frac{1}{n}} \quad (7)$$

where, K_f and $1/n$ are the Freundlich constants characteristics of the system, indicating the biosorption

capacity and biosorption intensity, respectively. The Freundlich equilibrium constants were evaluated from the intercept and the slope, respectively of the linear plot of $\log q_e$ versus $\log C_e$ based on experimental data.

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (8)$$

3.5.3. Temkin isotherm

The Temkin isotherm, assumes that the fall in the heat of sorption is linear and the distribution of binding energies as uniform (up to some maximum binding energy). This model takes into account the presence of indirect adsorbate/adsorbent interactions and suggests that because of these interactions the heat of adsorption of all molecules in the layer would decrease linearly with coverage. The Temkin isotherm has generally been applied in the following form:

$$q_e = B \ln K_T + B \ln C_e \quad (9)$$

The constant K_T and B_1 can be calculated using a linear plot of q_e versus $\ln C_e$. K_T is the equilibrium binding constant (L/mg) corresponding to maximum binding energy and constant B_1 is related to heat of adsorption.

As presented at Table 2, the experimental data well fitted with all studied isotherm models. Nevertheless, equilibrium studies showed that the Freundlich isotherm gave a better fit for the equilibrium data.

The Langmuir capacity from this study was compared with those obtained by other biosorbents (Table 3). In comparison with other costly and low cost adsorbents, the results of the present study indicate that biosorbent prepared from *Cydonia oblonga* has a good sorption capacity.

Table 2. Isotherm parameters for Cr(VI) biosorption by seeds of *Cydonia oblonga* at various temperatures.

	298 K	303 K	308 K	313 K	318 K
Langmuir isotherm					
qm (mg/g)	10.21	33.58	25.97	29.59	4.68
k_L (L/mg)	0.09	0.03	0.04	0.04	0.22
R²	0.9654	0.8909	0.8850	0.9036	0.9506
Freundlich isotherm					
k_f	0.86	1.05	1.09	1.15	1.44
n	1.36	1.15	1.14	1.14	0.88
R²	0.943	0.9033	0.8946	0.9058	0.9685
Temkin isotherm					
K_T (L/mg)	0.3868	0.2781	0.2612	0.2313	0.1393
B	0.742	0.5707	0.5620	0.5650	0.4570
R²	0.903	0.8769	0.8730	0.8805	0.9609

Table 3. Maximum adsorption capacity of various adsorbents for Cr(VI) removal from aqueous solutions

Adsorbent	q _e , mg/g	Optimum pH	References
Leaf mould	25.9	2.5	(Sharma and Forster, 1996)
Coconut husk fiber	29	2.05	(Tan <i>et al.</i> , 1993)
Palm pressed-fibers	15	2	(Tan <i>et al.</i> , 1993)
Sugar cane bagasse	13.4	2	(Sharma and Foster, 1994)
Seeds of Ocimum americanum	32	1.5	(Lakshmanraj <i>et al.</i> , 2009)
Neem leaves	62.97	2	(Babu and Gupta, 2008)
Pine needles	21.5	2	(Dakiky <i>et al.</i> , 2002)
Cactus	7.08	2	(Dakiky <i>et al.</i> , 2002)
Eucalyptus bark	45	2	(Sarin and Pant, 2006)
Activated carbon	69.3	3.2	(Hu <i>et al.</i> , 2003)
Ocimum americanum L. seed pods	83.33	1.5	(Levankumar <i>et al.</i> , 2009)
<i>Cydonia oblonga</i>	33.58	2	Current study

3.6. Adsorption kinetics

Several kinetic models are in use to explain the mechanism of the sorption processes. In order to evaluate the kinetics of the sorption process, data from the kinetic studies were fitted into the pseudo-first-order and pseudo-second-order models. Kinetic sorption of heavy metals from wastewater has been studied using mostly pseudo-first-order and pseudo-second-order models. The first kinetic model

evaluated was the pseudo-first-order Lagergren's equation, shown in Eq. (10);

$$\log(q_e - q_t) = \log q_e - k_1 t / 2.303 \quad (10)$$

Thus, a plot of $\log(q_e - q_t)$ versus t provides the kinetic parameters k_1 and $\log q_e$ from the slope and intercept, respectively.

The second-order kinetic model (Bazrafshan *et al.*, 2015) is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (11)$$

where k_2 is the pseudo-second-order rate constant (g/mg/min); q_e the quantity of metal ions sorbed at equilibrium (mg/g); q_t the quantity of metal ions sorbed at time t (mg/g) and t is the time (min).

If second-order kinetics is applicable, a plot of t/q_t versus t should show a linear correlation and the rate constant of the second-order adsorption k_2 and q_e can be calculated from the slope and intercept of this plot, respectively. This model is more likely to predict the behavior over the whole range of adsorption and is in agreement with chemical sorption being the rate-controlling step. The rate constants and the correlation coefficients are also summarized in Table 4. Figure 6 shows the plot of $\log(q_e - q_t)$ versus time for the experimental data obtained under the optimized conditions (pH 6, contact time 120 min and mixing rate 150 rpm). It can be seen that a linear relationship of $\log(q_e - q_t)$ against time was observed during the initial 120 min of biosorption, and then deviates from linearity from 120 min onwards. Therefore, the attachment of Cr(VI) ions to the biosorbent surface controlled the initial sorption of pollutants. However, when the biosorption time was 120 min and greater the experimental data fitted very well with the pseudo-second-order kinetics reaction (Figure 7).

Table 4. Kinetic parameters for the biosorption of Cr(VI) by seeds of *Cydonia oblonga* for different initial Cr(VI) concentrations at pH 2 (Time=150 min).

Cr(VI) concentration, mg/L	Pseudo-first-order kinetics			Pseudo-second-order kinetics		
	k_1 (1/min)	q_e , mg/g	R^2	k_2 (g/mg/min)	q_e , mg/g	R^2
5	0.0011	23.96	0.0034	21.07	2.042	0.9971
15	0.0061	1.88	0.1403	14.63	0.5979	0.9871
25	0.0042	1.046	0.2037	9.699	0.3688	0.9865
40	0.0052	1.58	0.3389	6.5203	0.2350	0.9913
50	0.006	2.01	0.3736	5.0872	0.1960	0.9834

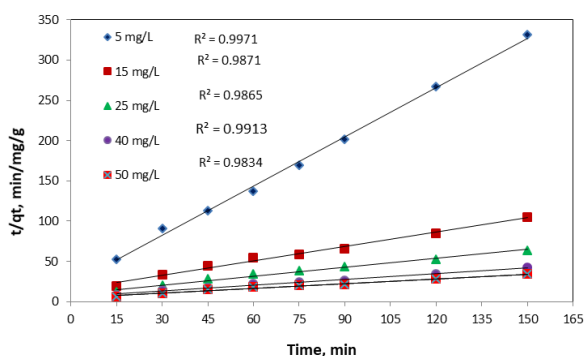


Figure 7. Pseudo-second-order reaction of the biosorption of the Cr(VI) by seeds of *Cydonia oblonga* at the optimized conditions (pH 2 and sorbent dose 10 g/L)

4. Conclusions

Hexavalent chromium is one of the most toxic heavy metals in aqueous solutions. Biosorption of Cr(VI) ions on to

Similar kinetic results were reported in the treatment of biodiesel wastewater by sorption with commercial chitosan flakes.

Analysis of the experimental data with the pseudo-second order kinetic model shows good agreement of the sets of data, which is reflected in the extremely high correlation coefficient of determination, obtained (Table 4 and Figure 7). Similar findings were reported by Babu and Gupta (2008) on adsorption of Cr(VI) by using activated neem leaves.

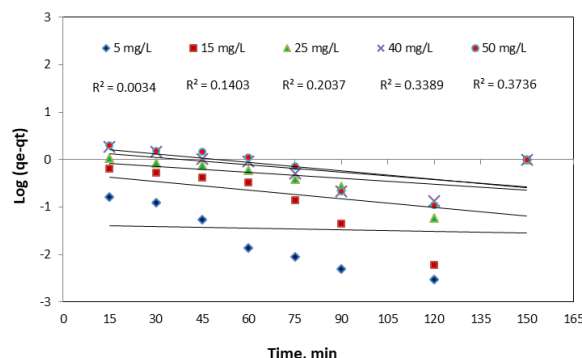


Figure 6. Pseudo-first-order reaction of the biosorption of the Cr(VI) by seeds of *Cydonia oblonga* at the optimized conditions (pH 2 and sorbent dose 10 g/L)

Cydonia oblonga has been studied. Biosorption capacity of the Cr(VI) ions was shown to be dependent on initial solution pH. Both the pseudo-first and pseudo-second order kinetic models were applied to analyze the biosorption kinetics. Biosorption kinetics data well fitted using pseudo-second-order. Thermodynamic studies confirmed that biosorption of Cr(VI) ions by mucilaginous seeds of *Cydonia oblonga* was spontaneous and endothermic nature. Finally, the results demonstrated the technical feasibility of biosorption by *Cydonia oblonga* as a reliable technique for removal of Cr(VI) from aqueous solutions.

Conflicts of Interest

This study did not have any conflict of interest statement.

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