

Biosorption of Cr (VI) from aqueous solutions by biomass of *Agaricus bisporus*

N. Ertugay*, Y.K. Bayhan

Department of Environmental Engineering, Faculty of Engineering, Atatürk University, 25240 Erzurum, Turkey

Received 14 November 2006; received in revised form 16 May 2007; accepted 12 October 2007

Available online 26 October 2007

Abstract

In this study, biosorption of Cr (VI) ion was investigated by using biomass of *Agaricus bisporus* (a species of mushroom) in a temperature and shaking speed controlled shaker. The effect of shaking speed, biomass concentration, initial metal ion concentration and initial pH on biosorption yield was determined and the fitness of biosorption data for Freundlich and Langmuir adsorption models was investigated. Optimum biosorption conditions were found to be pH 1, $C_0 = 50$ mg/l, $m = 10$ g/l, shaking speed = 150 rpm, $T = 20$ °C Cr (VI), respectively. It was found that biosorption of Cr (VI) ions onto biomass of *A. bisporus* was better suitable to Freundlich adsorption model than Langmuir adsorption model. The correlation coefficients for the second-order kinetic model obtained were found to be 0.999 for all concentrations. These indicate that the biosorption system studied belongs to the second-order kinetic model.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Biosorption; *Agaricus bisporus*; Chromium; Kinetic modeling; Biosorption isotherms

1. Introduction

The toxic heavy metals contaminants in wastewater due to discharge of metal containing effluents into water bodies is one of the most environmental issues of this century. Heavy metals are discharged in small quantities into environment through numerous industrial activities. The heavy metal pollution represents a significant environmental problem arising from its toxic effects and accumulation throughout the food chain. Heavy metals such as chromium, nickel, lead, copper, etc., in wastewater are hazardous to environment and health [1]. The removal and recovery of heavy metals from wastewater is significant in the protection of the environment and human health [2].

The maximum levels permitted in wastewater are 5 mg/l for trivalent and 0.05 mg/l for hexavalent chromium. When low levels are present in the environment, trivalent chromium apparently plays an essential role in plant and animal metabolism, while hexavalent chromium directly toxic to bacteria, plants and animals [3]. The main sources of chromium pollution are mining, leather tanning and cement industries, use in dyes,

electroplating, production of steel and other metal alloys, photographic material and corrosive paints [4].

The removal of heavy metal contaminated wastewater is generally accomplished by conventional methods such as chemical precipitation, membrane separations, evaporation, resin ion exchange, electrowinning and reverse osmosis have major disadvantages such as high energy requirements, incomplete metal removal and large quantity of toxic waste sludge. However, these technologies are most suitable in situations where the concentrations of heavy metal ions are relatively high [2]. To compare with conventional processes, new methods must be economically viable as well as successful in contaminant removal [5]. Biosorption or biosorption to materials of biological origin has been proposed as an alternative to conventional methods for the economic removal of suspended solids, dissolved nutrients, pathogens and metals from wastewaters [6].

Biosorption has gained important credibility during recent years because of its ecofriendly nature, excellent performance, and low cost domestic technique for remediating even heavily metal loaded waste water [7]. Cr (VI) compounds are being used in a wide variety of commercial processes and unregulated disposal of the chromium containing effluent in both developing and developed countries has led to the contamination of soil, sediment, surface and ground waters [8]. Cr (VI) was selected

* Corresponding author. Fax: +90 442 2360957.

E-mail address: nertugay@atauni.edu.tr (N. Ertugay).

for biosorption studies by many researchers employing *Mucor hiemalis* [9], *Bacillus thuringiensis* [10], *Pinus sylvestris* [11], *Rhizopus* [12], peat moss [13] and modified saw dust [14], lignin [15], algae [16]. But, no study was carried out about *Agaricus bisporus* which is a member of that group of organisms known as fungi.

The objective of this study was to investigate the possible use *A. bisporus* as an alternative biosorbent material for removal of Cr (VI) ions from aqueous solutions. The dynamic behavior of the adsorption was investigated on the effect of initial metal ion concentration, temperature, biosorbent mass, agitating speed, Fourier transform infrared spectroscopy (FTIR) analysis and pH of solution. The thermodynamic parameters were also evaluated from the biosorption measurements.

2. Materials and methods

2.1. Preparation of biomass

Fresh fungal biomass of *A. bisporus* which was purchased from a commercial company was used in this investigation as an adsorbent. The chemical characteristic of *A. bisporus* was shown in Table 1. Before use, it was washed with distilled water to remove dirt. After this, the biomass was dried at 80 °C for 24 h, and ground in a mortar to a very fine powder. Then, it was sieved through a 140-mesh copper sieve.

2.2. Preparation of Cr (VI) solutions

Cr (VI) solutions were prepared by using $K_2Cr_2O_7$. Stock solution (500 mg/l) of Cr (VI) was prepared by dissolving required quantity of $K_2Cr_2O_7$ in deionized distilled water. For biosorption experiments, Cr (VI) solution having 25–125 mg/l was prepared and used. The pH of the solution was adjusted with H_2SO_4 and NaOH solutions after addition of the biosorbent.

2.3. Batch biosorption experiments

The batch biosorption experiments were carried out in 250 ml erlenmeyer flasks containing 100 ml Cr (VI), on a rotary shaker at 150 rpm and 20 °C. The samples were taken at definite time intervals (3, 5, 10, 20, 30, 45, 60 min) and were filtered immediately to remove biomass by filter paper (Whatman 42) and the Cr (VI) in the remaining solution was analyzed. The residual of Cr (VI) ions in the biosorption was determined spectrophotometrically at 540 nm using diphenyl carbazide reagent in acid solution as the complexing agent for Cr (VI) [18], zeta potentials were measured with a zeta meter (Zeta-meter 3.0+ 542, USA). All the experiments were carried out at least twice. The values

used in calculations were mostly the arithmetic average of the experimental data.

3. Results and discussion

3.1. Effect of pH on Cr (VI) uptake

Earlier studies have indicated that solution pH is an important parameter affecting biosorption of heavy metal ions [19]. In order to establish the effect of pH on the biosorption of Cr (VI) ions onto *A. bisporus*, the batch adsorption studies at different pH values were carried out in the range of 1.0, 2.0, 3.0, 5.0 and 7.0. As seen in Fig. 1, the maximum adsorption of Cr (VI) ions were observed at pH 1.0 and significantly decreased by reducing the pH values to 7.0. pH of solution affects both metal chemistry in water and zones which have bound metal in cell surface. In a study, the predominant Cr (VI) species are $HCrO_4^-$ and CrO_4^{2-} . Below pH 4.0, the $HCrO_4^-$ complex is the major form, while at pH above 9.0, the most abundant species is CrO_4^{2-} [4]. Another in a study, at still lower pH values $Cr_3O_{10}^{2-}$ and $Cr_4O_{13}^{2-}$ species are formed. In summary, decreasing of the pH results in the formation of more polymerized chromium oxide species [14].

Uptake of Cr (VI) increased markedly with decreasing solution pH. At pH 1 and 7 corresponding uptake yield values was found to be 92.4 and 28.8%, respectively. The highest uptake yield of Cr (VI) at pH 1.0 was found to be 92.4% and thereafter decreased with further increased in pH (Fig. 1). It is well-known that the dominant form of Cr (VI) at this pH value is the acid chromate ion species ($HCrO_4^-$) and increasing the pH will shift the concentration of $HCrO_4^-$ to other forms, CrO_4^{2-} and $Cr_2O_7^{2-}$. As the pH is lowered, however, the overall surface charge on the cells will become positive, which will inhibit the approach of positively charged metal cations. The Cr (VI) ions being in the anionic form of $HCrO_4^-$ in the aqua solution will interact with the cell surface in this case [20]. This can be explained related to the nature of the biosorbent at different pH in metal biosorption. Similar results were also obtained in the other studies [11,20,21].

Zeta potential states the electrical potential on the surface of a particle and it can also be stated as a measurement of charge

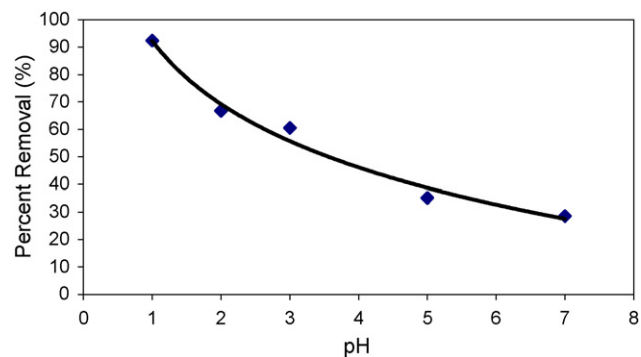


Fig. 1. Effect of initial pH on sorption of Cr (VI) by *A. bisporus* (initial Cr (VI) conc. = 50 mg/l, biosorbent conc. = 10 g/l, temperature = 20 °C, agitating rate = 150 rpm, contact time = 60 min).

Table 1
The chemical characteristics^a of *Agaricus bisporus* [17]

Water	Protein	Carbohydrate	Oil	Cellulose	Ash
90.8	2.76	2.85	0.24	0.90	1.00

^a The values were expressed as %.

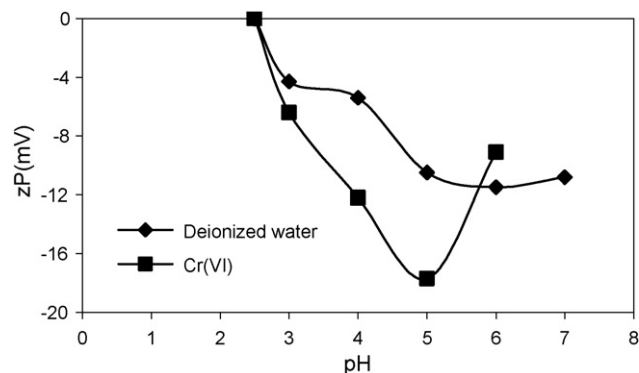


Fig. 2. The effect of pH on the zeta potential (initial Cr (VI) conc. = 50 mg/l, biosorbent conc. = 0.5 g/l, temperature = 20 °C, agitating rate = 150 rpm, contact time = 60 min).

of particles in the electrical field [22]. The surface charges and efficiency of biosorbents used for removal of metal ions can be determined by using zeta potential. Zeta potential values were measured by adding of *A. bisporus* to solution of Cr (VI) which was prepared by deionized water, and the zeta potential value was found to be negative.

As shown in Fig. 2, the zeta potential of *A. bisporus* approaches to zero as the pH decreases. At pH < 3.0, the zeta potential values was not able to measure due to ionic strength of medium. Since Cr (VI) has a negative charge at pH 1.0, more metal ions have been hold around particle due to positive charge of zeta potential of particle measured in this range. Therefore, the highest uptake yield was obtained at pH 1.0.

3.2. Effect of impeller speed on Cr (VI) biosorption

Biosorption studies of Cr (VI) with *A. bisporus* biomass was carried out in a shaker working at pH 1.0 using a Cr (VI) solution of 50 mg/l. The four different impeller speeds as 60, 100, 150 and 200 rpm were selected for biosorption of Cr (VI) on *A. bisporus* biomass.

The alteration in speed affected biosorption of Cr (VI). The uptake yield increased in the range from 60 to 150 rpm, but, it decreased after 150 rpm. The maximum uptake yield of Cr (VI) was obtained at 150 rpm; indicating impeller speed of 150 rpm was suitable for chromium ion removal by *A. bisporus* biomass under these experimental conditions (Fig. 3). The uptake yield decreases due to higher liquid film thickness around particle at lower impeller speeds while the film diffusion rate increases throughout pore diffusion point which is a factor for limiting the rate at higher impeller speeds. Besides, decreasing uptake yield at further speeds indicates more mechanisms than one in removal of Cr (VI). These results are similar to data obtained with other biomass, where more than one mechanism is involved in biosorption of metal ions [23].

3.3. Effect of biosorbent concentration on biosorption of Cr (VI)

The biosorbent concentrations ranging from 3 to 15 g/l were used for determining the effect of biosorbent concentrations on

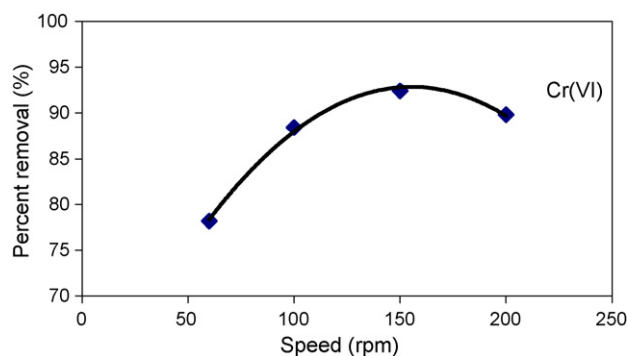


Fig. 3. Effect of impeller speeds on biosorption of Cr (VI) (initial Cr (VI) conc. = 50 mg/l, biosorbent conc. = 10 g/l, pH 1, temperature = 20 °C, contact time = 60 min).

the biosorption by *A. bisporus* biomass. The adsorbed metal ion amount per unit weight of biosorbent (q_e) decreased as the biosorbent concentration increased (Fig. 4). The decrease in q_e with increase in biosorbent concentration may be due to complex interactions of various factors. However, the biomass can undergo different modifications depending on the experimental conditions such as pH, ionic strength, temperature, metal ion in solution and its same biomass concentration level: for example, the aggregates formed during biosorption may reduce the effective biosorption area [24]. More quantity of biosorbent results in increasing of surface area and biosorption regions which causes removal of more chromium. The removal of metal increased until biosorbent concentration Cr (VI) of 10 g/l, and then, it decreased at further biosorbent concentrations due to occurring aggregation. The highest uptake yield was obtained at biosorbent concentration of 10 g/l.

3.4. Effect of initial Cr (VI) concentration dependent temperature

The initial concentration provides a significant driving force to overcome all mass transfer resistance of metal ion between the aqueous and solid phases. Hence, a higher initial concentration of Cr (VI) increases the biosorption rate [25]. Cr (VI) biosorption capacities of *A. bisporus* were presented as a contact time in Fig. 5.

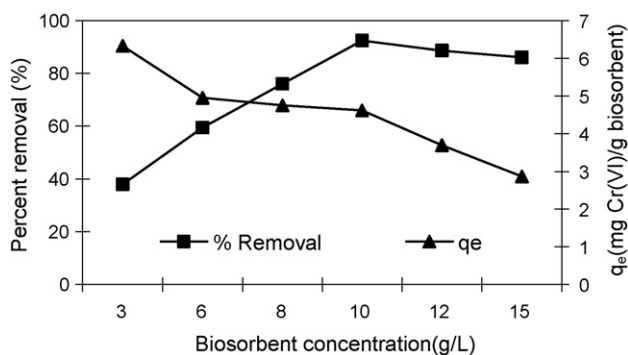


Fig. 4. The effect of *A. bisporus* conc. on biosorption of Cr (VI) ions (initial Cr (VI) conc. = 50 mg/l, pH 1, temperature = 20 °C, agitating rate = 150 rpm, contact time = 60 min).

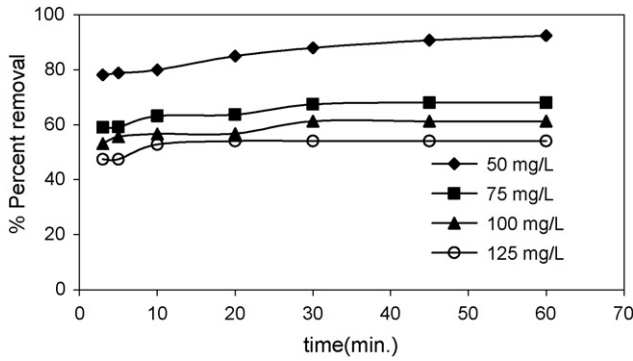


Fig. 5. Effect of contact time on the removal of Cr(VI) (biosorbent conc. = 10 g/l, temperature = 20 °C, agitating rate = 150 rpm, pH 1.0).

As shown in Fig. 5, the uptake of 80% was obtained at first 10 min in which Cr(VI) ions contacted with cell surface and then, the equilibrium was established relatively. A second equilibrium was established at 45 min following the first equilibrium step while the biomass has adsorbed Cr(VI) ions, and then adsorption ended. The results indicate that the metal sorption was very efficient in the first few minutes of the process. This is probably due to the availability of active sites around or inside the cells. In the second stage, with the gradual occupancy of active sites [26].

As shown in Fig. 5 the uptake yield decreases with increasing initial Cr(VI) concentration at different temperatures while the equilibrium sorption capacity of *A. bisporus* increases with increasing initial metal concentration due to driving force until onset of saturation at concentrations. The increases of loading capacity of *A. bisporus* with increasing initial Cr(VI) concentration may also be due to higher interaction between metal ion and biosorbent. As *A. bisporus* offered a finite number of surface binding sites, Cr(VI) biosorption showed a saturation trend at higher initial Cr(VI) concentration. Also, the rise in sorption capacity with temperature is because of rise in the kinetic energy of sorbent particles. Secondly, at high temperature due to bond rupture of functional groups on adsorbent surface there may be an increase in number of active sorption sites, which may also lead to enhanced sorption with the rise in temperature [27].

As seen in Fig. 6, at 20 °C, when the initial Cr(VI) ion concentration increased from 50 to 125 mg/l, the uptake capacity of *A. bisporus* increased from 4.62 to 6.75 mg/g. With the change in temperature from 20 to 40 °C, the uptake capacity and adsorption yield increased from 6.13 to 8.64 mg/g and from 61.3 to 86.4% at 100 mg/l initial Cr(VI) concentration, respectively. The increase of the biosorption yield and adsorption capacity at increased temperature indicated that the adsorption of Cr(VI) ions by *A. bisporus* may involve not only physical but also chemical sorption. This effect may be due to the fact that at higher temperature an increase in active sites occurs due to bond rupture [28].

3.5. Adsorption isotherms

One of the important aspects for the evaluation of sorption process as a unit operation is the equilibria of sorption [29].

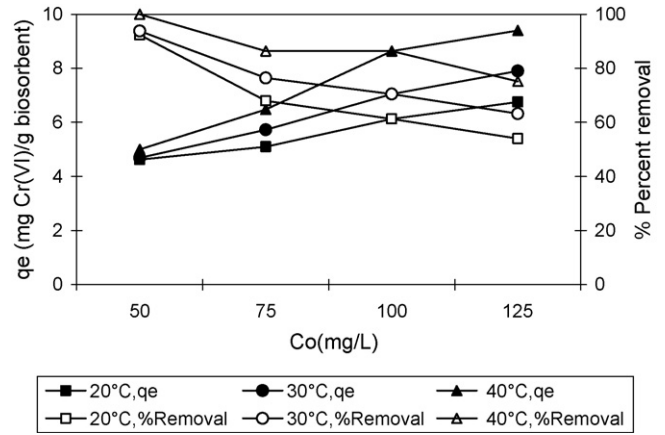


Fig. 6. Effect of initial Cr(VI) concentration on uptake capacity and removal for *A. bisporus* at different temperature (pH 1.0, biosorbent concentration = 10 g/l, agitating rate = 150 rpm, contact time = 60 min).

The equilibrium of biosorption of heavy metals is modeled using adsorption-type isotherms. The Langmuir and Freundlich isotherm models were used to describe the biosorption equilibrium of biomass. The Freundlich isotherm is a nonlinear sorption model. This model proposes a monolayer sorption with a heterogeneous energetic distribution of active sites, accompanied by interactions between adsorbed molecules. The general form of this model is

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

where K_F (mg/g) stands for adsorption capacity and n for adsorption intensity.

The logarithmic form of Eq. (1) is:

$$\log q_e = \log K_F + 1/n \log C_e \tag{2}$$

The Langmuir model represents one of the first theoretical treatments of nonlinear sorption and suggests that uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules. In addition, the model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate. The Langmuir isotherm is represented in the following equation:

$$q_e = \frac{Q_L b C_e}{1 + b C_e} \tag{3}$$

where Q_L (mg/g) and b are Langmuir constants related to adsorption capacity and the energy of biosorption, respectively. Eq. (3) is usually linearized to obtain the following form:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_L} + \frac{1}{b Q_L} \tag{4}$$

The linearized plot of C_e/q_e versus C_e for Cr(VI), respectively was analyzed, and the results obtained at the experimental temperatures are shown in Table 2.

In the Langmuir model the adsorption intensity (R_L) is expressed by the following equation:

$$R_L = \frac{1}{1 + b C_0} \tag{5}$$

Table 2
Model parameters for the biosorption of Cr (VI) on *A. bisporus* at different temperatures

Freundlich model				Langmuir model			
<i>T</i> (°C)	<i>K_F</i> (mg/g)	1/ <i>n</i>	<i>R</i> ²	<i>Q_L</i> (mg/g)	<i>b</i> (l/mg)	<i>R</i> ²	<i>R_L</i>
20	1.79	0.32	0.97	8.00	0.07	0.99	0.12
30	2.18	0.33	0.98	11.28	0.05	0.99	0.16
40	4.37	0.28	0.73	13.79	0.09	0.75	0.10

Table 3
Comparison between the Cr (VI) removal by *Agaricus bisporus* and other found in the literature

Adsorbent	<i>Q_L</i> (mg/g)	References
PAC	0.03	[32]
<i>Lyngbya putealis</i>	7.72	[33]
<i>Lentinus sajor-caju</i> (untreated)	22.10	[34]
Olive oil factory wastes	12.15	[27]
<i>Aspergillus niger</i>	20.9	[35]
<i>Rhizopus arrhizus</i>	23.92	[36]
<i>Aspergillus sydoni</i>	9.07	[37]
<i>Neurospora crassa</i> (AcOH pretreated)	15.85	[38]
<i>Agaricus bisporus</i>	8.00	This study

where *C*₀ (mg/l) is the initial concentration of the metal. If the average of the *R_L* values from the different initial concentrations used is between 0 and 1, it indicates favourable adsorption [30]. The average values of *R_L* for the different initial Cr (VI) concentrations at the respective temperature are shown in Table 2. Values of adsorption capacity of the other biosorbents are given in Table 3 for comparison.

As illustrated, the adsorption data obtained for biomass was found to be fitting more to the Langmuir isotherm than Freundlich isotherm. The magnitude of *K_F* and *n* constants indicated that *A. bisporus* had a high adsorption capacity for Cr (VI) ions. Besides, that 1/*n* values are of between 0.1 and 1.0 range indicates suitable Cr (VI) adsorption on anion exchange [31]. From Langmuir isotherm constants, the monolayer saturation capacities, *Q_L*, increased from 8.0 to 13.79 mg/g as the temperature of solution increased ranging from 20 to 40 °C.

3.6. Thermodynamic parameters

Thermodynamic parameters such as change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were determined using the following equations.

The apparent equilibrium constant (*K_C*) of the biosorption is defined as:

$$K_C = \frac{C_{ad,eq}}{C_{eq}} \quad (6)$$

where *C_{ad,eq}* and *C_{eq}* is the concentration of Cr (VI) on the adsorbent and residual Cr (VI) concentration at equilibrium, respectively. In this case the activity should be used instead of concentration in order to obtain the standard thermodynamic

Table 4
Thermodynamic parameters for the adsorption of Cr (VI) on *A. bisporus*

Temperature (°C)	ΔG° (kJ/mol)	ΔH° (J/mol)	<i>TΔS</i> [°] (kJ/mol)
20	−0.39		36.48
30	−1.36	36.18	37.72
40	−2.88		38.97

equilibrium constant (*K_C*) of the adsorption system.

$$\Delta G^\circ = -RT \ln K_C \quad (7)$$

where ΔG° is standard free energy change, *J*; *R* the universal gas constant, 8.314 J/(mol K) and the absolute temperature, *K* [27].

The Gibbs free energy change, ΔG° , can be represented as follows [39]:

$$\Delta G^\circ = \Delta H^\circ - \Delta S^\circ \quad (8)$$

As seen in Table 4, the negative value of ΔG° is due to the fact that the biosorption process is spontaneous with high affinity of Cr (VI) to *A. bisporus*. The standard enthalpy and entropy changes of biosorption determined from the ΔG° versus *T* (Fig. 7) were 36.18 and 0.124 J/mol, respectively. The positive value of ΔH° suggests the endothermic nature of Cr (VI) biosorption. The positive value of ΔS° confirms the increased randomness at the biosorbent–Cr (VI) solution interface during biosorption.

3.7. Kinetic studies

The several kinetic models are needed to determine the data to examine the mechanism of adsorption process such as mass transfer and chemical reaction [40]. One of them is the pseudo-first-order Lagergren model which considers that the rate of occupation of biosorption sites is proportional to the number of unoccupied sites [41]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (9)$$

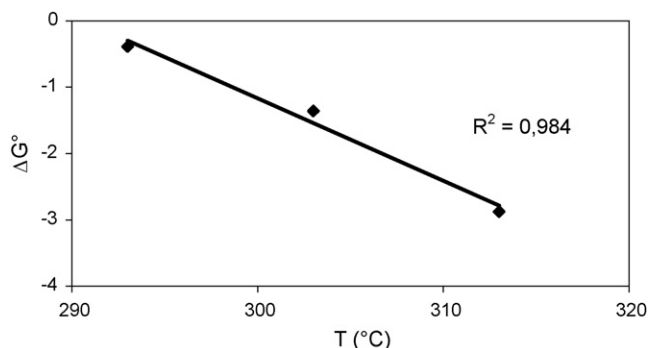


Fig. 7. Plot of ΔG° against *T* for Cr (VI) on *A. bisporus*.

Table 5

Comparison of the first and second-order biosorption, and calculated and experimental q_e values for different initial chromium concentrations (biosorbent conc. = 10 g/l, pH 1, temperature = 20 °C, agitating rate = 150 rpm, contact time = 60 min)

C_0 (mg/l)	$q_{e,exp}$ (mg/g)	First-order kinetic model			Second-order kinetic model			
		k_1 (1/min)	$q_{e,cal}$ (mg/g)	R^2	k_2 (g/mg min)	$q_{e,cal}$ (mg/g)	R^2	h (mg/g min)
50	4.620	0.052	0.942	0.981	0.160	4.679	0.999	3.502
75	5.100	0.095	1.061	0.865	0.220	5.175	0.999	5.891
100	6.130	0.028	0.731	0.608	0.191	6.218	0.999	7.384
125	6.760	0.253	2.196	0.923	0.340	6.825	0.999	15.837

Integrating Eq. (2) between limits, $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, Eq. (9) is obtained:

$$\log \left[\frac{q_e}{q_e - q_t} \right] = \frac{k_1}{2.303} t \quad (10)$$

Eq. (10) can be rearranged to obtain a linear form:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (11)$$

where q_e and q_t are the amounts of adsorbed Cr (VI) ions on the biosorbent at equilibrium and at time t (mg/g), respectively, and k_1 is the equilibrium rate constant of pseudo-first-order adsorption (1/min).

The slopes and intercepts of plot of $\log(q_e - q_t)$ versus t were used to obtain the first-order rate constant k_1 and equilibrium adsorption density q_e . The comparison of the results with the correlation coefficients was presented in Table 5. The correlation coefficients for the first-order kinetic model at all concentrations were low. Therefore, it can be concluded that this adsorption system was not a first-order reaction.

The adsorption kinetics may also be described by pseudo-second-order model [42]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (12)$$

Integrating between boundary conditions, Eq. (12) is obtained:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \quad (13)$$

Eq. (13) can be rearranged to obtain a linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (14)$$

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

The initial sorption rate is [43]:

$$h = k q_e^2 \quad (15)$$

The slopes and intercepts of plots t/q_t versus t were used to calculate the second-order rate constants k_2 and q_e . The straight lines obtained from plot of t/q_t versus t showed good fitness of experimental data with the second-order kinetic model for different initial chromium concentrations (Fig. 8).

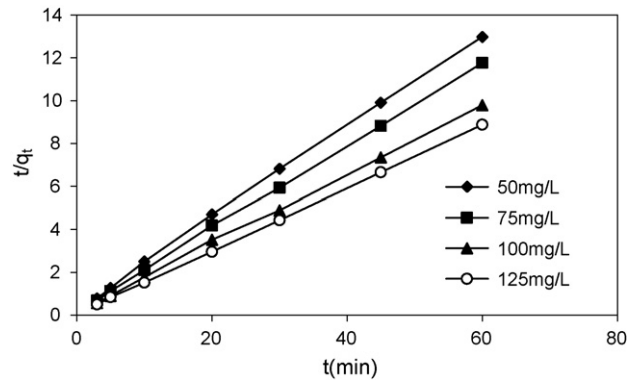


Fig. 8. The plot of the pseudo-order biosorption kinetics of chromium on *A. bisporus* biomass at different initial concentration (biosorbent conc. = 10 g/l, pH 1, temperature = 20 °C, agitating rate = 150 rpm, contact time = 60 min).

The correlation coefficients for the second-order kinetic model obtained were found to be 0.999 for all concentrations (Table 5). The calculated q_e values also agree very well with the experimental data. Therefore, it can be concluded that the adsorption system studied belongs to the second-order kinetic model.

3.8. Fourier transform infrared spectroscopy analysis

In order to determine the main functional groups of *A. bisporus* participate in Cr (VI) biosorption, it has recorded the natural and Cr (VI) binding FTIR spectrum of the *A. bisporus*. The FTIR spectra before and after adsorption of the *A. bisporus* are shown in Fig. 9.

Compared with the FTIR spectra before and after adsorption, there were clear band shifts and intensity decrease at four bands. These bands are the functional groups of *A. bisporus* participate in Cr (VI) biosorption [44,45] which are shown in Table 6.

Table 6

The FTIR spectral characteristics of *A. bisporus* before and after biosorption

IR peak	Absorption bands (cm ⁻¹)			Assignment
	Before ads.	After ads.	Differences	
1	2936	2925	-11	Aliphatic C–H group
2	1252	1243	-9	-SO ₃ stretching
3	928	927	-1	-C–C– group
4	717	609	-108	-CN stretching

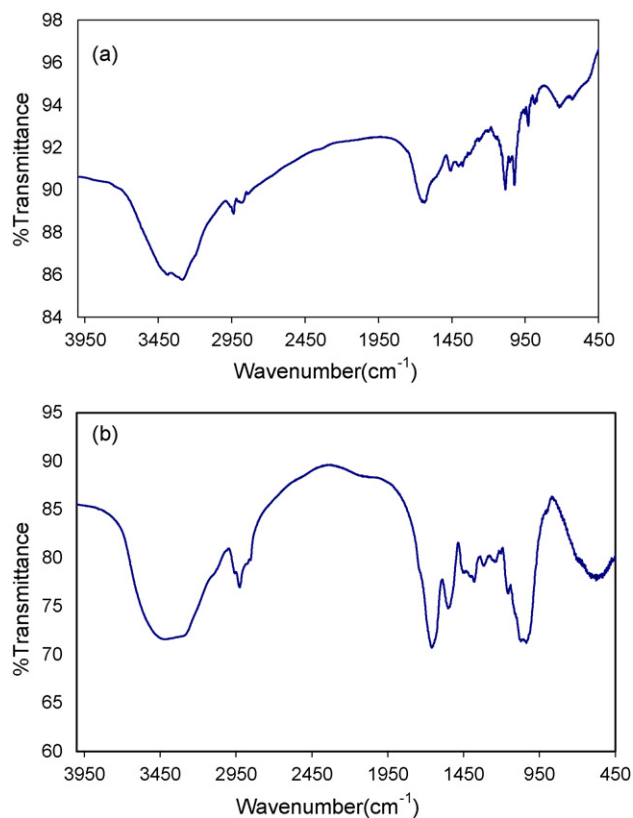


Fig. 9. (a) The FTIR spectra of *A. bisporus* before adsorption. (b) The FTIR spectra of *A. bisporus* after adsorption.

Among these functional groups especially aliphatic C–H group, $-\text{SO}_3$ stretching and $-\text{CN}$ stretching participate in Cr (VI) biosorption [27,46].

4. Conclusion

The aim of this work was to find the biosorption characteristics of *A. bisporus* for the removal of Cr (VI) ions. The maximum biosorption capacity was obtained pH 1.0. In this study, the results showed that high temperatures increased the biosorption capacity of Cr (VI) by *A. bisporus*. The biosorption capacity decreased as the biosorbent concentration increased.

The Freundlich and Langmuir biosorption models were used for the mathematical description of the biosorption equilibrium of Cr (VI) ions to *A. bisporus*. It was seen that the biosorption equilibrium data fitted well to the Langmuir.

The suitability of the first- and second-order equations, kinetic model for the biosorption of Cr (VI) onto *A. bisporus* is also discussed. The pseudo-second-order kinetic model agrees very well with the dynamical behavior for the biosorption of Cr (VI) onto *A. bisporus*.

Thermodynamic constants were also evaluated using equilibrium constants changing with temperature. The negative value of ΔG° indicated the spontaneity and the positive values of ΔH° and ΔS° showed the endothermic nature and irreversibility of Cr (VI) biosorption, respectively.

Results obtained from this study showed that *A. bisporus* in a batch experiments were effective at removing Cr (VI) to very high concentrations from the aqueous solution.

References

- [1] Y.K. Bayhan, B. Keskinler, A. Cakıcı, M. Levent, G. Akay, Removal of divalent heavy metal mixtures from water by *Saccharomyces cerevisiae* using cross flow micro filtration, *Water Res.* 35 (9) (2001) 2191–2200.
- [2] P. Kaewsarn, Biosorption of copper (II) from aqueous solutions by pre-treated biomass of marine algae *Padina sp*, *Chemosphere* 47 (2002) 1081–1085.
- [3] F.C. Richard, A.C.M. Bourg, Aqueous geochemistry of chromium: a review, *Water Res.* (1991) 807–816.
- [4] R.L. Ramos, A.J. Martinez, R.M.G. Coronado, Adsorption of chromium(VI) from aqueous solutions on activated carbon, *Water Sci. Technol.* 30 (9) (1994) 191–197.
- [5] A.D. Sonia, M.T. Tobin, Uptake of chromium cations and anions by milled peat, *Resour. Conserv. Recycl.* 27 (1999) 151–156.
- [6] B. Volesky, *Biosorption of Heavy Metals*, CRC Press, Boca Raton, FL, 1989.
- [7] P. Kumari, P. Sharma, S. Srivastava, M.M. Srivastava, Biosorption studies on shelled *Moringa oleifera* Lamarck seed powder: removal and recovery of arsenic from aqueous system, *Int. J. Miner. Process.* 78 (2006) 131–139.
- [8] M.D. Szulczewski, P.A. Helmke, W.F. Bleam, Comparison of XANES analysis and extractions to determine chromium speciation in contaminated soils, *Environ. Sci. Technol.* 31 (10) (1997) 2954–2959.
- [9] N. Tewari, P. Vasudevan, B.K. Guha, Study on biosorption of Cr(VI) by *Mucor hiemalis*, *Biochem. Eng. J.* 23 (2) (2005) 185–192.
- [10] Y. Sahin, A. Ozturk, Biosorption of chromium (VI) ions from aqueous solution by the bacterium *Bacillus thuringiensis*, *Process Biochem.* 40 (5) (2005) 1895–1901.
- [11] H. Uzun, Y.K. Bayhan, Y. Kaya, A. Cakıcı, O.F. Algur, Biosorption of Cr(VI) from aqueous solution by cone biomass of *Pinus sylvestris*, *Bioresour. Technol.* 85 (2002) 155–158.
- [12] R.S. Bai, E. Abraham, Biosorption of Cr (VI) from aqueous solution by *Rhizopus nigricans*, *Bioresour. Technol.* 79 (2001) 73–81.
- [13] D.C. Sharma, C.F. Forster, Continuous adsorption and desorption of chromium ions by Sphagnum moss peat, *Process Biochem.* 30 (1995) 293–298.
- [14] C. Raji, T.S. Anirudhan, Batch Cr (VI) removal by polyacrylamide grafted sawdust: kinetics and thermodynamics, *Water Res.* 32 (12) (1998) 3772–3780.
- [15] S.K. Srivastava, R. Tyagi, N. Pant, N. Pal, Studies on the uptake of lead and zinc by lignin obtained from black liquor—a paper industry waste material, *Environ. Technol.* 15 (1994) 353–361.
- [16] Q. Yu, J.T. Matheickal, P. Yin, P. Kaewsarn, Heavy metal uptake capacities of common marine macro algal biomass, *Water Res.* 33 (1999) 1534–1537.
- [17] A. Günay, Mantar Yetiştiriciliği, İlke Kitabevi Yayınları No.:22, Ankara, ISBN 975-7923-15-X, p. 479.
- [18] A.D. Eaton, L.S. Clesceri, A.E. Greenberg, Standard Methods for the Examination of Water and Wastewater, American Public Health Association (APHA); AWWA, WPCF, Washington, DC, 1995, 4–23.
- [19] J.T. Matheickal, Q. Yu, Biosorption of lead from aqueous solutions by marine alga *Ecklonia radiata*, *Water Sci. Technol.* 34 (1996) 1–7.
- [20] Z. Aksu, U. Açikel, E. Kabasakal, S. Sezer, Equilibrium modeling of individual and simultaneous biosorption of Cr(VI) and nickel (II) onto dried activated sludge, *Water Res.* 36 (2002) 3063–3073.
- [21] E. Malkoç, Y. Nuhoğlu, The removal of Cr(VI) from synthetic wastewater by *Ulothrix zonata*, *Fresenius Environ. Bull.* 12 (4) (2003) 376–381.
- [22] V. Boonamnuayvitaya, C. Chaiya, W. Tanthaponichakoon, S. Jarudilokkul, Removal of heavy metals by adsorbent prepared from pyrolyzed coffee residues and clay, *Sep. Purif. Technol.* 35 (1) (2004) 11–12.
- [23] R.S. Prakasham, J.S. Merrie, R. Sheela, N. Saswathi, S.V. Ramakrishna, Biosorption of Cr (VI) by free and immobilized *Rhizopus arrhizus*, *Environ. Pollut.* 104 (1999) 421–427.

- [24] A. Esposito, F. Pagnanelli, A. Lodi, C. Solisio, F. Veglio, Biosorption of heavy metals by *Sphaerotilus natans*: an equilibrium study at different pH and biomass concentrations, *Hydrometallurgy* 60 (2001) 129–141.
- [25] G. Dönmez, Z. Aksu, Removal of Cr (VI) from saline wastewaters by *Dunaliella* species, *Process Biochem.* 38 (2002) 751–762.
- [26] S. Singh, B.N. Rai, L.C. Rai, Ni (II) and Cr (VI) sorption kinetics by microcystis in single and multi metallic system, *Process Biochem.* 36 (2001) 1205–1213.
- [27] E. Malkoç, Y. Nuhoglu, Y.M. Dunder, Adsorption of chromium (VI) on pomace-An olive oil industry waste: batch and column studies, *J. Hazard. Mater.* 138 (1–2) (2006) 142–151.
- [28] Z. Aksu, Determination of the equilibrium, kinetic and thermodynamic parameters of the batch biosorption of nickel (II) ions onto *Chlorella vulgaris*, *Process Biochem.* 38 (2002) 89–99.
- [29] P. Sharma, P. Kumari, M.M. Srivastava, S. Srivastava, Ternary biosorption studies of Cd (II) Cr (III) and Ni (II) on shelled Moringa oleifera seeds, *Bioresour. Technol.* 98 (2007) 474–477.
- [30] J. Romero-González, J.R. Peralta-Videa, E. Rodríguez, M. Delgado, J.L. Gardea-Torresdey, Potential of Agave lechuguilla biomass for Cr(III) removal from aqueous solutions: thermodynamic studies, *Bioresour. Technol.* 97 (2006) 178–182.
- [31] G. McKay, H.S. Blair, C.R. Garden, Adsorption of dyes on chitin I. Equilibrium studies, *J. Appl. Polym. Sci.* 27 (1982) 3043–3057.
- [32] M. Rao, A.V. Parwate, A.G. Bhole, Removal of Cr⁶⁺ and Ni²⁺ from aqueous solution using bagasse and fly ash, *Waste Manage.* 22 (2002) 821–830.
- [33] B. Kiran, A. Kaushik, C.P. Kaushik, Response surface methodological approach for optimizing removal of Cr (VI) from aqueous solution using immobilized cyanobacterium, *Chem. Eng. J.* 126 (2–3) (2007) 147–153.
- [34] G. Bayramoğlu, G. Çelik, E. Yalçın, M. Yılmaz, M.Y. Arica, Modification of surface properties of *Lentinus sajor-caju* mycelia by physical and chemical methods: evaluation of their Cr⁶⁺ removal efficiencies from aqueous medium, *J. Hazard. Mater.* 119 (1–3) (2005) 219–229.
- [35] D.P. Mungasavalli, T. Viraraghavan, Y.C. Jin, Biosorption of chromium from aqueous solutions by pretreated *Aspergillus niger*: batch and column studies, *Colloids Surf. A: Physicochem. Eng. Aspects* 301 (1–3) (2007) 214–223.
- [36] B. Preetha, T. Viruthagiri, Batch and continuous biosorption of chromium (VI) by *Rhizopus arrhizus*, *Sep. Purif. Technol.* 578 (1) (2007) 126–133.
- [37] R. Kumar, N.R. Bishnoi, G. Bishnoi, K. Bishnoi, Biosorption of chromium (VI) from aqueous solution and electroplating wastewater using fungal biomass, *Chem. Eng. J.*, in press.
- [38] S. Tunalı, I. Kiran, T. Akar, Chromium (VI) biosorption characteristics of *Neurospora crassa* fungal biomass, *Miner. Eng.* 18 (7) (2005) 681–689.
- [39] E. Malkoç, Y. Nuhoglu, Investigations of nickel (II) removal from aqueous solutions using tea factory waste, *J. Hazard. Mater.* 127 (1–3) (2005) 120–128.
- [40] M. Özacar, Equilibrium and kinetic modeling of adsorption of phosphorus on calcined alunite, *Adsorption* 9 (2003) 125–132.
- [41] C.C.V. Cruz, A.C. Da Costa, C.A. Henryques, A.S. Luna, Kinetic modeling and equilibrium studies during cadmium biosorption by dead *Sargassum* sp, *Biomass. Bioresour. Technol.* 91 (2004) 249–257.
- [42] M.S. Chiou, H.Y. Li, Equilibrium and kinetic modeling of adsorption of reactive dyes on cross-linked chitosan beads, *J. Hazard. Mater.* 93 (2002) 233–248.
- [43] Y.S. Ho, G. McKay, Sorption of dye from aqueous solution by peat, *Chem. Eng. J.* 70 (1998) 115–124.
- [44] D. Park, S.-Y. Yun, J.M. Park, Studies on hexavalent chromium biosorption by chemically treated biomass of *Ecklonia* sp., *Chemosphere* 60 (2005) 1356–1364.
- [45] E. Malkoç, Y. Nuhoglu, Y. Abali, Cr (VI) adsorption by waste acorn of *Quercus ithaburensis* in fixed beds: prediction of breakthrough curves, *Chem. Eng. J.* 119 (2006) 61–68.
- [46] E. Malkoç, Y. Nuhoglu, Potential of tea factory waste for chromium(VI) removal from aqueous solutions: thermodynamic and kinetic studies, *Sep. Purif. Technol.* 54 (2007) 291–298.