Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.20560

78 (2017) 183–191
June

Biosorption of chromium(VI) from water onto the heat-treated biomass of *Saccharomyces cerevisiae*

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Received 2 October 2016; Accepted 2 February 2017

ABSTRACT

Biosorption characteristics of Cr(VI) from aqueous solution by heat-treated *Saccharomyces cerevisiae* were investigated in a batch system. The influence of solution pH, initial Cr(VI) concentration, biomass concentration, co-existing ions, contact time and temperature on biosorption was explored. The biosorption was highly pH-dependent, and the optimum pH for biosorption was found to be 2.0. Adsorption capacity of Cr(VI) onto biomass decreased with a rise in biosorbent dosage and increased with the increasing initial Cr(VI) concentration. It was indicated that an increase in temperature would be favorable to Cr(VI) adsorption onto *Saccharomyces cerevisiae* in the range of 20°C–40°C. The biosorption process better followed the pseudo-second-order kinetic model, and the correlation coefficients obtained from the pseudo-second-order model were all higher than 0.99. The Langmuir and Freundlich isotherm models were applied to experimental equilibrium data. The Langmuir model better described the adsorption equilibrium than the Freundlich model. According to the Arrhenius equation, the activation energy of adsorption of chromium(VI) ions was determined as 18.37 kJ/mol. The calculated thermodynamic parameters indicated that Cr(VI) biosorption onto *Saccharomyces cerevisiae* was spontaneous and endothermic under studied experimental conditions. The results suggest that the biomass of *Saccharomyces cerevisiae* is a promising biosorbent for removal of chromium(VI) ions from the wastewater.

Keywords: Biosorption; Cr(VI); *Saccharomyces cerevisiae*; Kinetics; Thermodynamic; Isotherm

1. Introduction

The industries such as mining, alloy making, battery, metal finishing and electroplating discharge effluents containing high level of heavy metals into water bodies [1,2]. The discharge of heavy metals will cause serious environmental impact and has been one of the most important environment issues [3,4]. Heavy metal pollution poses a serious threat to living organisms and human beings, due to their acute toxicity, non-biodegradable nature, persistence in nature and accumulation throughout the food chain that brings about serious ecological and health risks [5,6]. Heavy metals such as chromium, cadmium, nickel, mercury and lead are very toxic for living beings, even at low concentrations [7,8]. Chromium exists primarily as Cr(III) and Cr(VI), and Cr(VI) is more soluble and toxic than Cr(III). Cr(VI) was reported to cause cancer in the digestive tract and lungs of human beings [9]. Hence, the removal of Cr(VI) from wastewaters was extremely important.

Many conventional techniques for removal of heavy metals, including chemical precipitation, lime coagulation, solvent extraction, ion exchange and reverse osmosis, have been developed to remove heavy metals from wastewaters. However, most of these techniques have certain major disadvantages such as incomplete metal removal, high energy requirements and secondary pollution of toxic waste sludge due to heavy metal treatments [10–14]. Biosorption using microbial biomass as the adsorbent is emerging and potential alternative technique for metals removal [15]. The biological materials for the removal and recovery of toxic or precious metals from wastewaters usually include living and non-living microorganisms. The removal of metal ions by non-living cells can be

defined as biosorption. The metal biosorption onto non-living cell of biomass is a physico-chemical reaction whose mechanism is not metabolically controlled. Bioaccumulation is the preferred term in the case that living organisms are used. The main advantages of biosorption by using dead biomass are low operating, short operation time, reusability of biomass, no production of secondary toxic compounds and no continuous supply of nutrient required in the solution [16–19].

Cr(VI) biosorption by various biomaterials such as algae [3], bacteria [8], fungi [14], industrial wastes and agricultural wastes [12,17,20] has been carried out by many researchers. The biosorption mechanisms depend on the type of functional groups on the surface of the biomass, the nature of the metal and the characteristics of the matrix around the biosorbent species. The cell wall contained many functional groups such as amino group, carboxyl, hydroxyl, sulfhydryl and phosphate group of lipid, playing an important role in metal binding [21,22]. However, the exact adsorption mechanism is not well understood yet.

Yeast biomass, especially *Saccharomyces cerevisiae*, is a readily available by-product in substantial quantities from traditional fermentation industries such as beer, alcohol and pharmacy manufacturing, which could serve as economical and constant supply sources of biomass for metal ions adsorption. The aim of the present work is to assess the mechanism and potential of heat-treated *Saccharomyces cerevisiae* biomass for the biosorption of hexavalent chromium. The study provides the basic data on the effect of external environmental parameters such as solution pH, contact time, metal concentration, co-existing ions, biomass concentration and temperature. In order to investigate the mechanism of Cr(VI) biosorption, the characteristic constants of uptake were calculated using pseudo-first-order and pseudo-second-order kinetics models, respectively. The Langmuir and Freundlich isotherm models were used to describe adsorption equilibrium data. The Cr(VI) biosorption mechanism onto heat-treated biomass of *Saccharomyces cerevisiae* was also evaluated according to thermodynamics and kinetics.

2. Materials and methods

2.1. Preparation of biomass

Saccharomyces cerevisiae obtained from Angel Yeast Corporation, China, was firstly grown in bean sprouts extract medium using the shake-flask method. After 3 d growth, the biomass of *Saccharomyces cerevisiae* was harvested from the liquid medium by centrifugal separation of 5,000 rpm, washed with distilled water and autoclaved at 121°C for 20 min. Then the heat-treated biomass was stored at 4°C for later use. Before adsorption, the amount of moisture in the biomass was measured by drying desired amount of wet biomass samples at 70°C for 24 h. The growth medium was prepared by dissolving 30 g glucose in the 1 L bean sprouts extract obtained by boiling 100 g bean sprouts for 30 min in given volume of distilled water.

2.2. Biosorption experiments

A stock solution of Cr(VI) (1,000 mg/L) was obtained by dissolving 2.828 g of $K_2Cr_2O_7$ (Guarantee Reagent Grade) in the distilled water, and the other concentrations were prepared by diluting the stock solution with distilled water. The batch biosorption studies were explored at various pH (2–8), biosorbent concentration (0.4–2.4 g dry weight per liter), initial Cr(VI) concentration (10–100 mg/L), contact time (0–300 min) and temperature (20°C–40°C) with 50 mL Cr(VI) ions solution in an orbital shaker. Each kind of ions Na^+, K^+, Ca^{2+}, Mg^{2+}, NO_3^-, Cl^- and SO_4^{2-} stock solutions (1,000 mg/L) was obtained by dissolving required quantity of NaCl, KCl, $CaCl_2$ $MgCl_2$, $NaNO_3$, NaCl and Na_2SO_4 in the distilled water. Each kind of ions in Cr(VI) solutions was prepared by diluting the stock solution with required Cr(VI) solutions. Before mixing with the biomass, the pH of solutions was adjusted to desired values with 0.1 M HCl or NaOH solution.

Batch biosorption experiments were conducted in 150 mL conical flask on a rotary shaker at 130 rpm. After biosorption equilibrium, the sample was centrifuged at 5,000 rpm for 10 min, and the supernatant liquid was analyzed for the remaining Cr(VI) ions concentration. The residual of Cr(VI) ions in the solution was determined spectrophotometrically at 540 nm using diphenylcarbazide reagent in acid solution as the complexing agent for Cr(VI) ions. Chemicals used in this study were of analytical reagent grade. All the batch biosorption experiments were carried out in triplicate, and the average results were presented. The Cr(VI) removal efficiency (%) and adsorption capacity, q_e (mg/g), were calculated by using the following equations:

$$\text{Removal efficiency}(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (2)$$

where q_e is the amount of Cr(VI) biosorbed onto the unit amount of the biomass (mg/g) at equilibrium. C_0 is initial concentration of Cr(VI) in liquid phase (mg/L). C_e represents concentration of Cr(VI) in liquid phase at equilibrium (mg/L). V is the volume of solution (L), and M is the amount of biosorbent used (g, dry weight). The zeta potential measurement of biomass was conducted by using zeta potential meter (JS94H2, Shanghai Zhongchen Digital Technique & Equipment Co., Ltd., China).

3. Results and discussion

3.1. Zeta potential of Saccharomyces cerevisiae

The cell wall of *Saccharomyces cerevisiae* is composed of three layers, namely the outer mannan layer, the middle protein layer and the inner dextran layer. When the solution pH value is changed, the surface of the yeast will absorb or release a certain amount of H^+ and then be charged. Zeta potential measurement performed on biomass of *Saccharomyces cerevisiae* is shown in Fig. 1. Yeast cell surface typically contains abundant functional groups, such as –OH, $–NH_2$ and –COOH groups, which are known to be subject to protonation or dissociation depending on solution pH. It was observed that the value of zeta potential of *Saccharomyces*

cerevisiae decreased as the pH of the solution was increased. The isoelectric point of the yeast was in the range of pH 3–4 (about pH 3.43). Increasing the value of pH from 3 to 4, the value of zeta potential of *Saccharomyces cerevisiae* changed from positive to negative. At the pH value less than the point of zero charge, zeta potential of yeast was positive. As the pH value of the solution increased up to 5, the zeta potential decreased rapidly. While the pH value was greater than the isoelectric point, the value of zeta potential of yeast was negative and slowly decreased with the increase of pH from 5 to 8.

3.2. FTIR spectra analysis

The fourier transform infrared (FTIR) spectra of heat-treated *Saccharomyces cerevisiae* before and after Cr(VI) adsorption are shown in Fig. 2. It is observed from Fig. 2(a) that the broad and strong band in the region of 3,000–3,500 cm^{-1} is attributed to N–H and O–H stretching vibrations, suggesting the presence of hydroxyl and amine groups on cell of *Saccharomyces cerevisiae*. The peak observed at 2,928 cm^{-1} could be assigned to the stretching vibration of $–CH_2–$ bond of methylene groups. The peaks at 1,638 and 1,526 cm^{-1} show the stretching band of C=O from the amide I band, the bending band of N–H and stretching band of C–N from the amide II band. Those peaks are the characteristic absorption peaks of protein. The peaks at 1,406 and 1,250 cm^{-1} could be caused by the stretching vibration of C=O from carboxyl and carbonyl groups, respectively. Adsorption peak at 1,046 cm^{-1} could be attributed to the stretching band of C–N from the amide III and the stretching band of P–O–C [2,5,10].

The stretching vibration at 3,438 cm^{-1} was shifted to 3,424 cm^{-1} after biosorption (Fig. 2(b)). The peaks of 1,638, 1,526, 1,406, 1,250 and 1,046 cm^{-1} were shifted to 1,630, 1,510, 1,390, 1,240 and 1,050 cm^{-1} after biosorption of Cr(VI), respectively. The shifts of the active groups suggest that hydroxyl, carboxyl, carbonyl and amine groups could be important binding sites during Cr(VI) biosorption onto *Saccharomyces cerevisiae*.

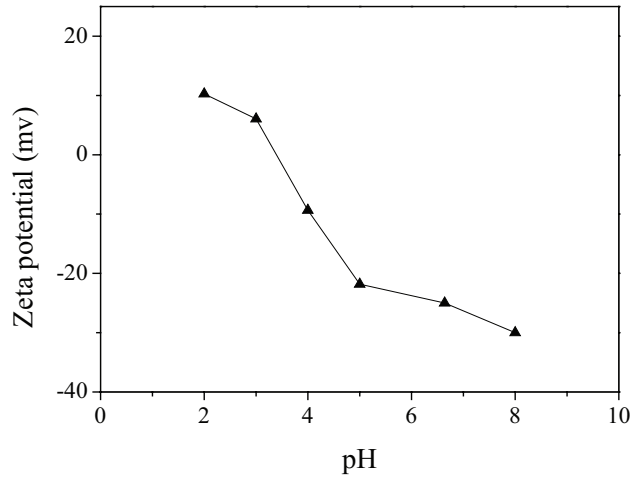

Fig. 1. Zeta potential of *Saccharomyces cerevisiae* at different pH.

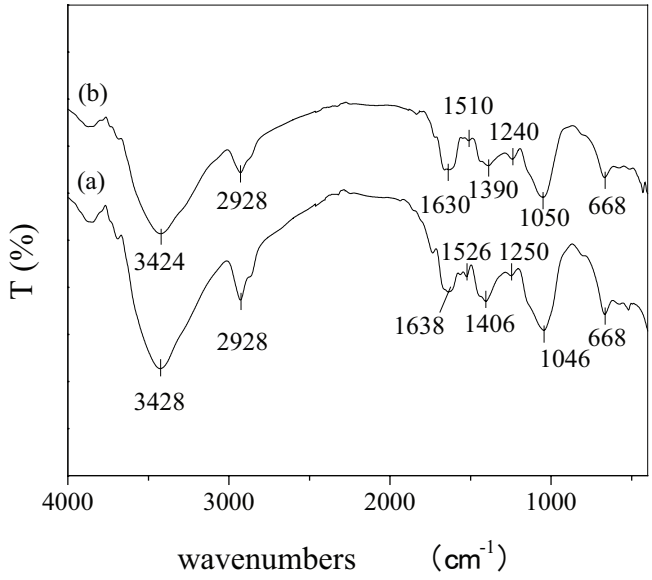

Fig. 2. FTIR spectra of heat-treated biomass of *Saccharomyces cerevisiae*: (a) before biosorption and (b) after biosorption.

3.3. Effect of solution pH

The initial pH of the solution is considered one of the most important factors affecting the adsorption process. Aqueous phase pH affects not only the speciation of metals but also the dissociation of active functional groups like carboxylate, phosphate and amino groups of the cell wall [23]. To determine the influence of pH on the biosorption of Cr(VI) ions onto *Saccharomyces cerevisiae*, the batch adsorption studies at different pH values were carried out at pH 2–8, and the results were presented in Fig. 3. The maximum biosorption capacity for Cr(VI) ions was observed at pH 2, and then decreased with increasing the pH values up to 8. The bind amount of Cr(VI) ions onto *Saccharomyces cerevisiae* decreased from 15.33 to 8.05 mg/g when solution pH increased from 2 to 8. This is attributed to the presence of Cr(VI) ions in the form of anions and change of surface charge of yeast biomass. At solution

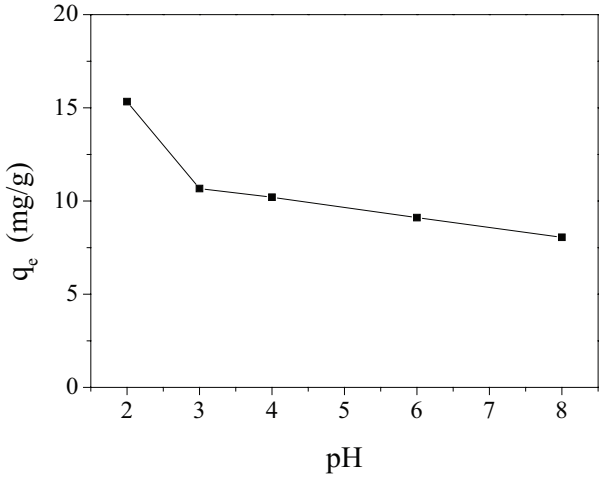

Fig. 3. Effect of solution pH (biosorbent dosage 0.6 g dry weight dry weight per liter; Cr(VI) concentration 20 mg/L; temperature 30°C; contact time 300 min).

pH below the isoelectric point (<3.43), the surface function groups of yeast cell acquired positive charge by adsorbing H^+ to protonation. The positively charged cell surface favors the adsorption of Cr(VI) anions due to the electrostatic attraction, resulting in higher adsorption capacity. With the increase of solution pH from 4 to 8, the number of H^+ ions in solution reduced, and electrostatic attraction gradually weakened; thus, adsorption capacity of Cr(VI) anions decreased. At solution pH greater than isoelectric point, the number of negatively charged sites on cell increased by adsorbing OH^- ions to ionization. The negatively charged surface sites on yeast cell cause poor adsorption of Cr(VI) anions due to the electrostatic repulsion [21,24]. It was also found that Cr(VI) concentrations at equilibrium were equal to total Cr at equilibrium at pH 2–8, indicating that Cr(VI) in solution was not reduced to Cr(III) after adsorption in the studied pH range. All the succeeding experiments were performed at pH 2.

3.4. Effect of biosorbent concentration

The biosorbent concentration ranging from 0.4 to 2.4 g/L (dry weight) was used for determining the effect of biosorbent amount on the biosorption by yeast. Fig. 4 presents the biosorption of Cr(VI) anions onto biomass as a function of biomass concentration. The equilibrium capacity of Cr(VI) ions decreased with increasing biosorbent concentration. As the biomass concentration in the system increased from 0.4 to 2.4 g/L (dry weight), biosorption capacity decreased sharply from 20 to 10 mg/g dry weight. This could be attributed to interference between the binding sites at higher concentrations. Higher specific metal uptake at lower biosorbent concentrations could be due to an increased metal-to-adsorbent ratio, which decreased upon an increase in biosorbent concentration [25,26]. While the removal percentage of hexavalent chromium increased from 30.11% to 60% with increasing biomass dosage from 0.4 to 2.4 g dry weight per liter. The increase in the percentage of Cr(VI) removal with biosorbent amount could be attributed to an increase in the adsorbent surface area, rising in the number of binding sites available for biosorption.

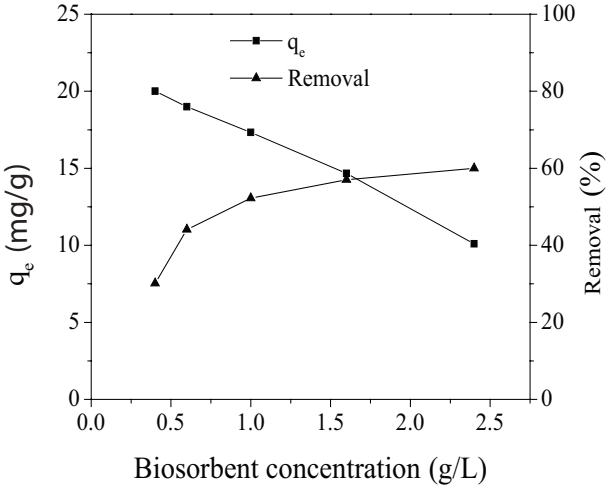

Fig. 4. Effect of biomass dosage (pH 2; Cr(VI) concentration 20 mg/L; temperature 30°C; contact time 300 min).

3.5. Effect of initial chromium(VI) concentration

Biosorption of Cr(VI) on the biomass of *Saccharomyces cerevisiae* was carried out at the concentrations in the range of 10–100 mg/L at temperatures varying from 20°C to 40°C. The results were given in Fig. 5. As seen in Fig. 5, the biosorption capacity of Cr(VI) was raised with an increase in the initial concentration. Initial Cr(VI) concentration provides an important driving force to overcome all mass transfer resistances of Cr(VI) ions between the aqueous and solid phase. Hence, a higher initial Cr(VI) concentration will enhance the adsorption amount [6,27]. The amount of Cr(VI) adsorption increased from 9.21 to 36.42 mg/g with rising initial concentration from 10 to 100 mg/L at 30°C. Fig. 3 also shows a rise in the Cr(VI) uptake with the increasing temperature from 20°C to 40°C. A larger biosorption capacity of Cr(VI) was also observed at a higher temperature range. The biosorption capacity increased from 28.92 mg/g at 20°C to 44.03 mg/g at 40°C for Cr(VI) concentration of 100 mg/L. It is suggested that the higher temperature favor Cr(VI) biosorption.

3.6. Effect of co-existing cations and anions

Heavy metal wastewater usually contains some kinds of light metal ions and anions such as Na^+, K^+, Ca^{2+}, Mg^{2+}, NO_3^-, Cl^- and SO_4^{2-}, which may impact Cr(VI) removal by biomass. Effect of different cations and anions at the concentration of 50 mg/L on removal of Cr(VI) was studied, and the results were presented in Fig. 6. It was found from Fig. 6(a) that the biosorption capacities of Cr(VI) without the presence of cations and with the cations were observed to be 16.50 mg/g without cations, and 16.50 mg/g with Na^+, 16.20 mg/g with K^+, 15.79 mg/g with Ca^{2+} and 16.48 mg/g with Mg^{2+}. The results indicated that the effect of each of the cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) at concentration of 50 mg/L on adsorption of Cr(VI) was no significant competition with Cr(VI) for the binding sites.

Fig. 6(b) shows the effect of each of the anions (NO_3^-, Cl^- and SO_4^{2-}) at the presence of 50 mg/L on biosorption of Cr(VI). Biosorption of Cr(VI) with the presence of any kind of

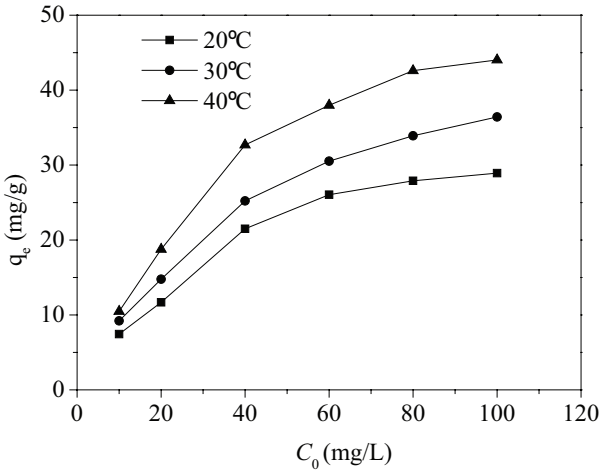

Fig. 5. Effect of initial chromium(VI) concentration on the biosorption of Cr(VI) onto biomass (pH 2; contact time 300 min; biomass dosage 0.6 g dry weight dry weight per liter).

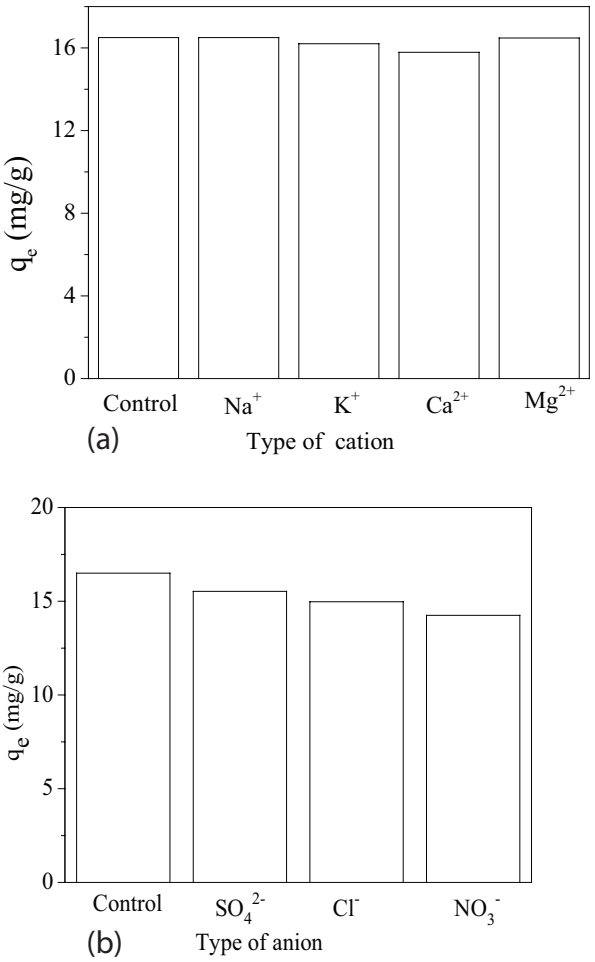

Fig. 6. Effect of co-existing cations (a) and anions (b) (pH 2; Cr(VI) concentration 20 mg/L; temperature 30°C; time 300 min; biomass dosage 0.6 g dry weight dry weight per liter, each kind of ions Na^+, K^+, Ca^{2+}, Mg^{2+}, NO_3^-, Cl^- and SO_4^{2-} concentration 50 mg/L).

anions NO_3^-, Cl^- or SO_4^{2-} in solution slightly decreased. The uptake of Cr(VI) with the presence of the studied anions at 50 mg/L dropped by 13.64 % with NO_3^-, 9.27 % with Cl^- and 5.88% with SO_4^{2-}, respectively. Experimental results reveal that the anions such as NO_3^-, Cl^- and SO_4^{2-} may interfere with the uptake of Cr(VI) by biomass. The slight drop in uptake of Cr(VI) with the presence of any studied anions NO_3^-, Cl^- or SO_4^{2-} in the solutions could be attributed to the additional anions to compete with Cr(VI) anions for definite binding sites on surface of biomass.

3.7. Effect of contact time and temperature

The effect of contact time on the adsorption of Cr(VI) onto *Saccharomyces cerevisiae* is presented in Fig. 7. The Cr(VI) adsorption by the biomass was a fast rate of biosorption process within the first 60 min of contact time at various temperatures (20°C–30°C), and the Cr(VI) uptake at 60 min was observed to be 12.05 mg/g at 20°C, 14.29 mg/g at 30°C and 15.27 mg/g at 40°C, respectively. The uptake of Cr(VI) gradually increased with increasing contact time and reached equilibrium in about 300 min. Initial higher rate of metal

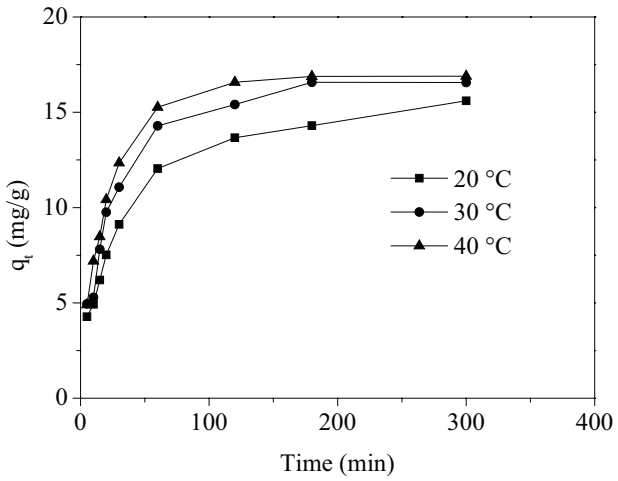

Fig. 7. Effect of contact time (pH 2; Cr(VI) concentration 20 mg/L; biomass dosage 0.6 g dry weight dry weight per liter).

biosorption could be attributed to availability of a large number of vacant active sites on adsorbent surface and the high concentration gradient during the initial period [28,29].

The influence of temperature on the biosorption of Cr(VI) onto *Saccharomyces cerevisiae* biomass is also shown in Fig. 3. Cr(VI) removal of biomass increased with the increase in temperature from 20°C to 40°C at contact time of 300 min. The Cr(VI) uptake by yeast biomass was 15.60 mg/g at 20°C, 16.56 mg/g at 30°C and 16.89 mg/g at 40°C, respectively. The result indicates this adsorption process is endothermic in nature. The increase in Cr(VI) uptake with increasing temperature may be due to either a rise in some new binding sites on the sorbent surface or the higher affinity of sites for metal at higher temperature [17,30].

3.8. Biosorption kinetics

In order to study the mechanism of Cr(VI) adsorption on biomass, two kinetic models were used to fit the experimental data. The linearized pseudo-first-order equation is expressed as [31]:

$$\ln(q_e - q_t) = \ln q_e - \frac{k_1}{2.303} t \tag{3}$$

where q_e and q_t (mg/g) are the amounts of Cr(VI) adsorbed at equilibrium and t (min), respectively. k_1 is the rate constant of the pseudo-first-order equation (1/min). q_e and k_1 were determined from the intercept and slope of the straight line of $\ln(q_e - q_t)$ vs. t (figure not shown).

The linearized pseudo-second-order kinetic model is given as [32]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

where k_2 is the rate constant of the pseudo-second-order equation (g/mg min). Values of q_e and k_2 were calculated from the slope and intercept of the plot of t/q_t vs. t (figure not shown).

The values of pseudo-first-order model constants (k_1 and q_e), the pseudo-second-order model constants (k_2 and q_e) and the corresponding linear regression correlation coefficients (R^2) of two kinetic models are given in Table 1. Table 1 shows that the correlation coefficients for the pseudo-second-order kinetics plots at the studied temperature are higher ($R^2 > 0.99$) than that of the pseudo-first-order model. The theoretical equilibrium biosorption capacity, q_{cal}, obtained from the pseudo-second-order model is closely in line with the experimental q_e values. The q_e and the second-order rate constant, k_2, increased with the increase in temperature. From these results, it can be easily concluded that the pseudo-second-order kinetic model is better than the pseudo-first-order model in this study. The similar results were reported for Cr(VI) adsorption by *Agaricus bisporus* [27].

The pseudo-second-order model can better describe the biosorption of Cr(VI) onto *Saccharomyces cerevisiae*. Therefore, activation energy of the biosorption process was calculated by using the rate constants (k_2) of the pseudo-second-order model according to the Arrhenius equation [33]:

$$\ln k_2 = \ln A - E_a/RT \tag{5}$$

where E_a, A, R and T are the activation energy (kJ/mol), the Arrhenius factor, the gas constant (8.314 J/mol K) and the temperature (K), respectively. The value of activation energy, E_a, could be determined from the slope of the plot of ln$k$ vs. 1/T. The magnitude of the activation energy gives information about the type of sorption on whether physical or chemical adsorption process is predominant. The physical adsorption process is rapid and easily reversible. The activation energy of physical adsorption is usually no more than 4.2 kJ/mol, because the forces involved are weak in the physical adsorption process. While chemical adsorption is specific, irreversible and involves forces much stronger than physisorption. The activation energy of chemisorption is of the same magnitude as the heat of chemical reactions. Chemisorptions can be subdivided into activated chemisorption and, less frequently, non-activated chemisorptions. Activated chemisorption implies that the adsorption rate varies with temperature according to finite activation energy (between 8.4 and 83.7 kJ/mol) in the Arrhenius equation (high E_a). However, non-activated chemisorption occurs very rapidly, and the activation energy is near zero [34].

According to the plot of ln$k$ vs. 1/T (figure not shown), the activation energy for Cr(VI) biosorption process was calculated and found to be 18.37 kJ/mol with a very high R^2 value of 0.9968. This value of E_a suggests that the Cr(VI) biosorption on heat-treated *Saccharomyces cerevisiae* is a chemical adorption process [35].

3.9. Biosorption isotherms

Langmuir and Freundlich isotherm models are the most frequently used models to describe the metal ion biosorption on the biomass. The linear form of the Langmuir model equation is given by [32,33]:

$$C_e/q_e = C_e/q_m + 1/bq_m \tag{6}$$

where C_e is equilibrium Cr(VI) concentration in solution (mg/L); q_e represents amounts of Cr(VI) adsorbed on biomass at equilibrium (mg/g); q_m shows the maximum adsorption capacity of chromium(VI) (mg/g); and b is Langmuir model constant (L/mg). The Langmuir constants, b and q_m, can be determined from the slope and intercept of the linear plot of C_e/q_e against C_e (Fig. 8(a)).

The Freundlich isotherm is expressed in the following equation [30,36]:

$$\lg q_e = (1/n)\lg C_e + \lg K_F \tag{7}$$

where K_F and n are indicative Freundlich isotherm parameters of adsorption capacity (mg/g) and intensity (L/mg), respectively. The Freundlich constants, K_F and n, can be determined from the linear plot of lnq_e against lnC_e (Fig. 8(b)).

The Langmuir and Freundlich constants along with the correlation coefficients (R^2) are given in Table 2. It is found that the values of correlation coefficients (R^2) for the Langmuir model are greater than 0.99 in the studied temperature range. These results indicate that the Langmuir model provides a good fit to the experimental data for the chromium(VI) biosorption in comparison with the Freundlich model. The 1/n value is between 0 and 1 indicating that the Cr(VI) biosorption is favorable at studied temperatures. Similar result was reported for the Cr(VI) biosorption onto *Marine macroalgae* and agricultural by-products [37].

3.10. Thermodynamic parameters

In order to determine the temperature dependence of the chromium(VI) biosorption process, thermodynamic parameters were analyzed. These thermodynamic parameters reflect the feasibility and spontaneous nature of the adsorption process. The value of $\Delta G°$ can be determined from the following equation [21,38]:

$$\Delta G° = -RT\ln K_c \tag{8}$$

Table 1
Kinetics parameters for Cr(VI) biosorption onto *Saccharomyces cerevisiae*

Temperature (°C)	q_e (mg/g)	First-order kinetic model			Second-order kinetic model		
		k_1 (1/min)	q_{cal} (mg/g)	R^2	k_2 (g/mg min)	q_{cal} (mg/g)	R^2
20	15.60	0.0119	10.72	0.9805	0.0026	16.56	0.9983
30	16.56	0.0207	11.32	0.9424	0.0033	17.66	0.9987
40	16.89	0.0316	12.71	0.9935	0.0043	17.82	0.9992

where K_c is the distribution coefficient, and T is absolute temperature. Relation between $\Delta G°$, $\Delta H°$ (enthalpy) and $\Delta S°$ (entropy) can be expressed by the following equation [21,38]:

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (9)$$

where the values of $\Delta S°$ and $\Delta H°$ can be determined from the intercept and slope of the plot between $\ln K_c$ vs. $1/T$ (figure not shown). The values of $\Delta G°$, $\Delta H°$ and $\Delta S°$ for the chromium(VI) biosorption onto *Saccharomyces cerevisiae* biomass at temperatures 20°C–40°C are given in Table 3.

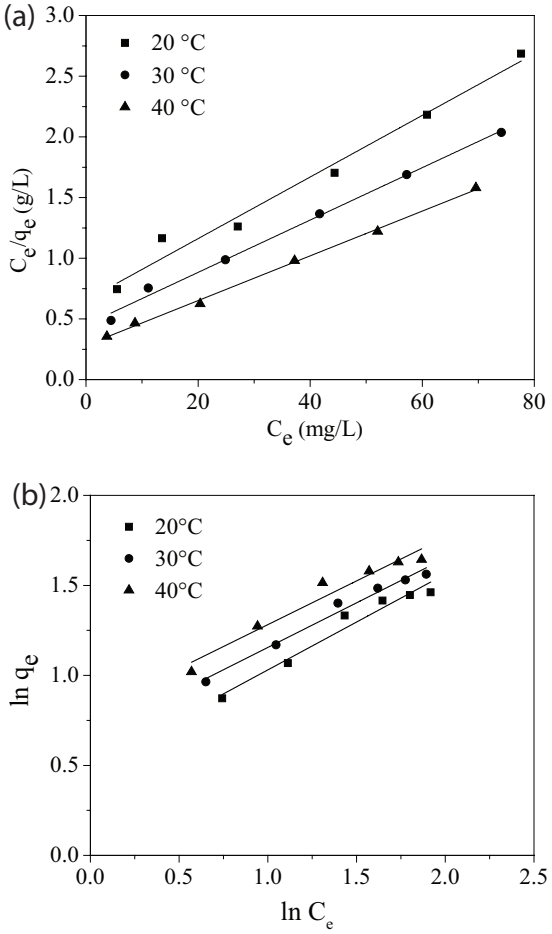

Fig. 8. (a) Langmuir and (b) Freundlich isotherms for chromium(VI) on *Saccharomyces cerevisiae* (pH 2; contact time 300 min; biomass dosage 0.6 g dry weight dry weight per liter).

It is evident from Table 3 that the values of $\Delta G°$ are all negative at temperature of 20°C–40°C and decrease with the increase in temperature. The negative values of $\Delta G°$ indicate that the Cr(VI) biosorption process is spontaneous in nature and confirm the affinity of yeast biomass toward the Cr(VI) ions. The value of enthalpy change is positive, indicating the Cr(VI) biosorption process is endothermic. The positive value of $\Delta S°$ suggests an increase in the randomness at the solid–liquid interface during the Cr(VI) biosorption onto *Saccharomyces cerevisiae* [39,40].

3.11. Elution of Cr(VI)

Reusability of biosorbent is of importance in industrial practice for heavy metal removal from wastewater. Fig. 9 illustrates percentage elution efficiency of chromium(VI) from chromium(VI)-loaded *Saccharomyces cerevisiae* by eluant of 0.1 M NaOH at 30°C. It was observed that the elution efficiency of Cr(VI) increased with increasing contact time. A larger amount of Cr(VI) ions was eluted from chromium(VI)-loaded biomass in the first 20 min, and then the desorption rate slowly decreased. Equilibrium was established in 40 min, and no more Cr(VI) was desorbed afterward. At time of 10 min, the elution efficiency was already 59.81%, and then increased up to 88.11% at 40 min. The chromium(VI)-desorbed biomass of *Saccharomyces cerevisiae* was reused by adsorbing Cr(VI). The result showed that the uptake of Cr(VI) was found to be 14.58 mg/g, slightly dropped by 4.89% contrast to that of fresh biomass. These results indicate that the heat-treated biomass of *Saccharomyces cerevisiae* exhibited the good potential for application in the treatment of Cr(VI) wastewater.

4. Conclusions

The chromium(VI) biosorption onto heat-treated *Saccharomyces cerevisiae* was investigated in this study. The biosorption capacity decreased significantly with an increase in solution pH 2–8, and the maximum Cr(VI) adsorption capacity of Cr(VI) anions onto biomass was found to be 15.33 mg/g at pH 2. The equilibrium capacity of Cr(VI) ions decreased with

Table 3
Thermodynamic parameters for Cr(VI) biosorption by *Saccharomyces cerevisiae*

Temperature (°C)	$\Delta G°$ (kJ/mol)	$\Delta S°$ (J/mol K)	$\Delta H°$ (kJ/mol)
20	–1.07		
30	–2.08	221.82	66.17
40	–3.29		

Table 2
Parameters of Freundlich and Langmuir isotherms for Cr(VI) biosorption by *Saccharomyces cerevisiae*

Temperature (°C)	Langmuir isotherm model			Freundlich isotherm model		
	b (L/mg)	q_m (mg/g)	R^2	K_F (mg/g)	n (L/mg)	R^2
20	0.0383	40.00	0.9820	3.15	1.88	0.9615
30	0.0472	47.62	0.9917	4.57	2.02	0.9827
40	0.0638	55.56	0.9978	6.25	2.06	0.9544

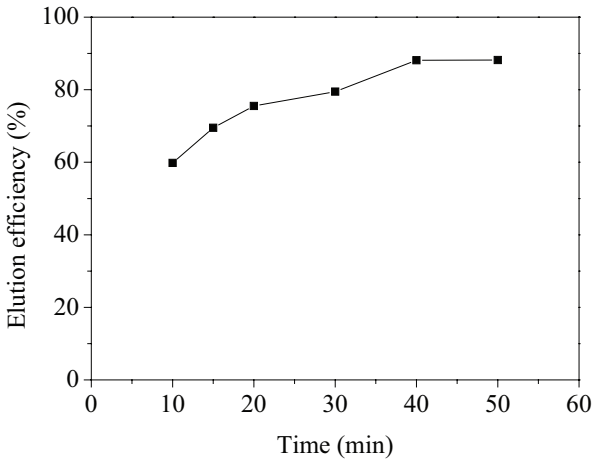

Fig. 9. Elution efficiency of Cr(VI) by 0.1 M NaOH.

increasing biosorbent concentration. Chromium(VI) uptake was increased with the increasing temperature from 20°C to 40°C, suggesting that the biosorption between the biosorbent and chromium(VI) ions was an endothermic process. The presence of each of anions NO_3^-, Cl^- and SO_4^{2-} may interfere with the Cr(VI) adsorption onto the biomass. The Cr(VI) uptake was observed to increase with increasing initial Cr(VI) concentrations. The biosorption process could be well described by the pseudo-second-order kinetic model. According to the value of activation energy of Cr(VI) biosorption, it is indicated that the Cr(VI) uptake onto *Saccharomyces cerevisiae* is chemical adsorption. The Langmuir isotherm provides good correlation for the biosorption process. According to FTIR spectra, hydroxyl, carboxyl, carbonyl and amine groups are the main binding sites for Cr(VI). Thermodynamic parameters $\Delta G°$, $\Delta H°$ and $\Delta S°$ were also calculated. The negative values of $\Delta G°$ indicate the spontaneity. The positive values of $\Delta H°$ and $\Delta S°$ show the endothermic nature of chromium(VI) biosorption and an increase in randomness at the solid–liquid interface. The results demonstrate that the biomass of *Saccharomyces cerevisiae* could be used as effective biosorbent for the removal chromium(VI) ions from aqueous solutions.

Acknowledgment

The author is grateful for the financial support of Open Research Fund of Key Laboratory of Wastewater Treatment Technology of Liaoning Province (No. 4771004kfs39).

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