

THERMODYNAMIC STUDY OF CHROMIUM (VI) SORPTION ON TO BROWN ALGAE

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ABSTRACT

The aim of this research work is to investigate sorption characteristic of brown algae *Sargassum bevanom* (S.bevanom) for the removal of Cr(VI) ions from aqueous solutions. The sorption of Cr(VI) ions by batch method is carried out. The optimum conditions of biosorption were found to be: a biomass dose of 0.7 g in 100 ml of Cr(VI), contact time of 100 min, pH and temperature 3 and 40 °C respectively. It was found that temperature has a positive effect on the removal efficiency.

INTRODUCTION

Rapid industrialization over the years led to an increase and accumulation of hexavalent chromium in environment. Chromium exists in environment as trivalent [Cr(III)] and hexavalent [Cr(VI)] forms and Cr(VI) is considered highly toxic, carcinogenic and mutagenic. WHO (World Health Organization) recommended guideline value for chromium (as total chromium) in drinking water as 0.05 mg/L (desirable) with no relaxation on permissible limit [1,2]. Anthropogenic source of chromium is generally from various industrial processes like electroplating, leather tanning, wood preservations, manufacturing of dye, paint and paper [3]. The chemistry of Cr(VI) is greatly dependent on pH of the solution. At pH value below 1, the predominant species is H_2CrO_4 . Cr(VI) normally exists in the anionic form, as $\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^- or CrO_4^{2-} forms depending on pH and concentration (Table 1). In acidic media (pH 2–4) Cr(VI) exists mostly in the form of dichromate ($\text{Cr}_2\text{O}_7^{2-}$) ions. At pH between 2 and

6, $\text{Cr}_2\text{O}_7^{2-}$ and HCrO_4^- ions exist in equilibrium and under alkaline conditions (pH > 8) it exists predominantly as chromate anion [4]. Several physicochemical wastewater treatment processes have been developed and reported to remove hexavalent chromium. These include chemical reduction followed by precipitation [5,6], electrochemical precipitation [7], ion exchange [8], solvent extraction [9], evaporation, reverse osmosis, foam separation, adsorption, biosorption [10,11]. Several researchers investigated adsorption of chromium using certain easily available low cost materials such as rice bran, wool, sawdust, etc. [12–14].

Table 1

Composition of Cr(VI) solution as a function of pH

Ph	Predominant species
<1	H_2CrO_4
2–4	$\text{Cr}_2\text{O}_7^{2-}$
4–6	HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$
6–8	$\text{Cr}_2\text{O}_7^{2-}$, CrO_4^{2-}
> 8	CrO_4^{2-}

In this study, removal of Cr(VI) by *S.bevanom* is studied. The effects of dosage of *S.bevanom*, contact time, temperature, and pH value on biosorption of Cr(VI) are investigated in detail, also adsorption thermodynamic parameters is obtained.

Materials and methods

Collection of biomass

Biomass of *S. bevanom* was collected from the Persian Gulf (Bandar Boshehr, Iran). The biomass after collection was washed thoroughly with tap water. This was followed by washing three times with deionized water and finally by glass distilled water in order to get a clean biomass that is free from silt, sand, diatoms and other epiphytic organisms. After cleaning the biomass was dried and stored at room temperature. The acid-treated alga was prepared by transferring the BL into 0.5M HCl and then stirring the mixture at 200rpm for 8.0 h at room temperature. The BL was then centrifuged (Eppendorf Centrifuge model HM-150 IV, Korea), washed with the physiological saline solution and dried in an oven at 60 °C. Subsequently, it was ground on an agate stone pestle mortar and sieved, to select the particles between 200 and 300 mesh sizes for use.

Preparation of chromium solutions:

Stock solution of 30 ppm concentration of Cr(VI) were prepared using analytical grade $K_2Cr_2O_7$ provided by Merck Company and stored at room temperature. This stock solution was used to prepare dilute solutions of chromium ion by the dilution with double distilled water.

Batch adsorption experiments

The magnetic mixer was 300 rpm throughout the study. At the end of predetermined time intervals, the sorbate was filtered and the concentration of Cr(VI) ion was determined. All experiments were carried out twice and the adsorbed Cr(VI) ion concentrations given were the means of duplicate experimental results. Atomic absorption spectrometer (AAS) (Model 929, Unicam) was used to analyze the concentration of heavy metal ions.

Results and discussion

Effect of contact time

Figure 1 shows the effect of contact time on biosorption of Cr(VI) by *S. bevanom*. For Cr(VI), biosorption rate reaches up to 90.5% when contact

time is 60 min, and then little change of biosorption rate is observed. The biosorption rate is 90.5% when reacting for 60 min. and then it is become nearly constant.

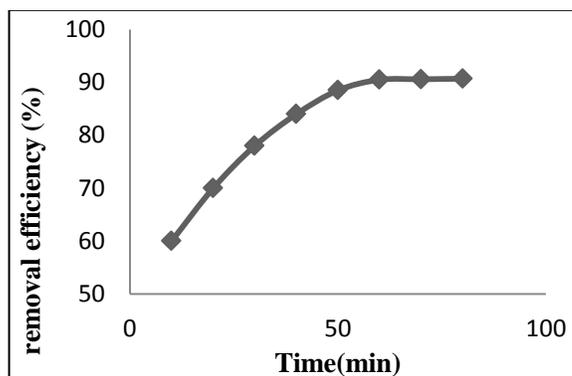


Figure 1

The effect of contact time on the removal efficiency

3.2. Effect of pH on Cr(VI) sorption

Earlier studies on heavy metal biosorption have showed that pH is an important parameter affecting the biosorption process [15]. The adsorption characteristics of Cr(VI) with various pH in the range of 2-10 were studied. The biosorption of Cr(VI) decreased with pH and then declined with further increase in pH. As seen from the Figure 2, the Cr(VI) equilibrium uptakes by BL increase with the pH values increase from 2.0 to 3.0. This increase in chromium uptake could be due to the ionization of carboxyl groups present in the seaweeds at this pH, which can result in higher interaction with chromium. For $pH > 4$ the reduction of Cr(VI) is considerable. The cell wall of BL contains a large number of surface functional groups, in which carboxyl is generally the most abundant acidic functional group. The pH dependence of metal adsorption can largely be related to type and ionic state of these functional groups and also on the metal chemistry in solution [16, 17]. Cr(VI) and some other metals such as arsenic, depending on the pH, are known to exist as anions. At low pH values, cell wall ligands are protonated and compete significantly with metal binding. With increasing pH, more ligands such as amino and carboxyl groups, would be exposed leading to attraction between these negative charges and the metals and hence increases in biosorption on to the cell surface [18]. As the pH increased further, the overall surface

charge on the cells could become negative and biosorption decreased [19, 20].

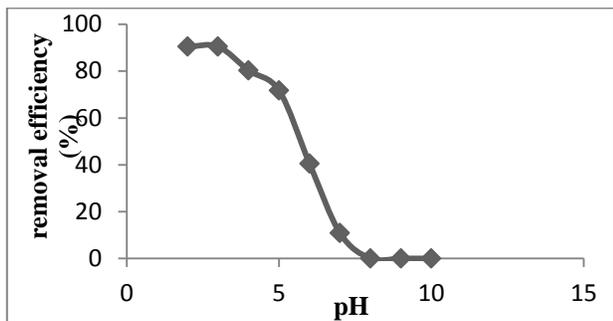


Figure 2

The effect of the pH on the removal efficiency

Effect of initial concentration of Cr(VI) on the adsorption

To investigate the effect of initial Cr(VI) concentration on Cr(VI) adsorption onto *S.bevanom*, batch mode experiments were performed at ambient temperature (20 ± 2 °C). The initial concentration of Cr(VI) solution was varied from 10mg/L to 300mg/L with optimum adsorbent dose, contact time and pH (Figure 3). It is evident from the result that the percentage removal of Cr(VI) decreased from 87.1% to 51.5% for initial Cr(VI) concentration of 100–300mg/L. The results indicate that there is a reduction in nitrate adsorption, owing to the lack of available active sites required for the high initial concentration of Cr(VI). The higher uptake of Cr(VI) at low concentration may be attributed to the availability of more active sites on the surface of the adsorbent for lesser number of adsorbate species.

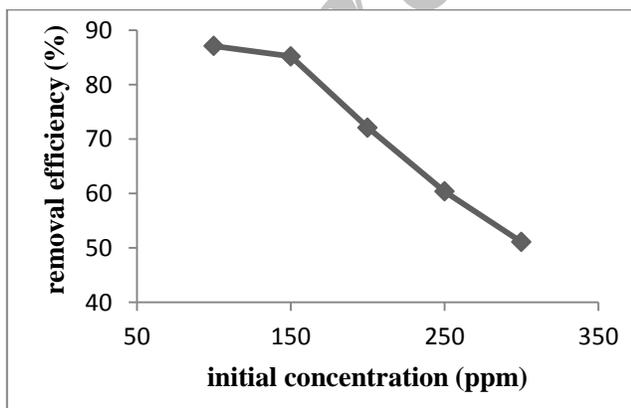


Figure 3

The effect of initial concentration on the removal efficiency

Effect of dosage of *S.bevanom* on biosorption of Cr(VI)

The effect of *S.bevanom* dose was studied for a by varying the dose between 0.1 g and 0.9 g in 100 ml aqueous. These tests were conducted at a temperature of 20 °C, with optimum pH value for Cr (VI). The initial metal ion concentration was 100 mg/L. It was observed that the adsorption percentage of Cr (VI) onto the *S.bevanom* increased rapidly with the increasing of adsorbent concentration (Figure 4). This result is expected because the increase of adsorbent dose leads to greater surface area. When the adsorbent concentration was increased from 0.1 g to 0.7g, the percentage of Cr(VI) ions adsorption increased from 58.24 to 87.1%. At higher concentrations, the equilibrium uptake of Cr (VI) did not increase significantly with increasing *S.bevanom*. For subsequent studies, a dose of 0.7g of *S.bevanom* into 100 ml aqueous solution was selected.

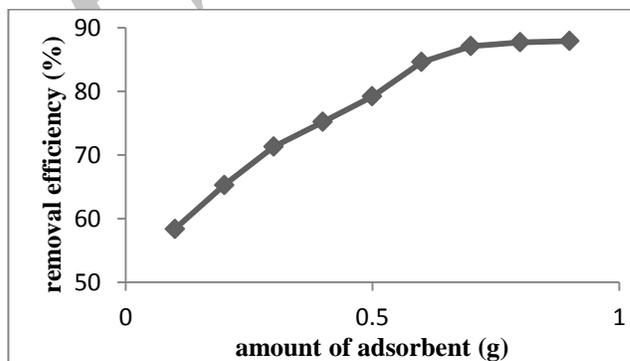


Figure 4

The effect of dosage on the removal efficiency

Thermodynamic study

Effect of temperature on adsorption of Cr(VI)

To study the effect of temperature adsorption experiments are carried out at 20–40 °C at optimum pH value of materials and adsorbent dosage level of 0.7g in to 100ml of solutions. The equilibrium contact time for adsorption was maintained at 120 min. The percentage of adsorption increases with rise of temperature from 20 to 40 °C. The results were shown in Table 2 and it revealed the endothermic nature of the adsorption process which later utilized for determination of changes in Gibbs free energy (ΔG), heat of adsorption (ΔH) and entropy (ΔS) of the adsorption of Cr(VI) from

aqueous solutions. The increase in adsorption with rise in temperature may be due to the strengthening of adsorptive forces between the active sites of the adsorbents and adsorbate species and between the adjacent molecules of the adsorbed phase.

Table 2

The effect of temperature on the removal efficiency

Temperature °C	Removal efficiency of Cr(VI) (%)
20	87.12
30	89.35
40	93.43

Effect of temperature on thermodynamics parameter on adsorption of Cr(VI)

To study the thermodynamics of adsorption of Cr(VI) on S.bevanom, thermodynamic constants such as enthalpy change ΔH , free energy change ΔG and entropy change ΔS were calculated using equations (1-3). The values of these parameters are given in Table 4. Thermodynamic parameter ΔH , ΔS and ΔG for Cr(VI) ions–S.bevanom system were calculated using the following equations:

$$K_c = \frac{F_e}{(1-F_e)} \quad (1)$$

$$\log K_c = \left(\frac{-\Delta H}{2.303RT} \right) + \left(\frac{\Delta S}{2.303R} \right) \quad (2)$$

$$\Delta G = -RT \ln(K_c) \quad (3)$$

where F_e is the fraction of Cr(VI) ions sorbed at equilibrium. A perusal of Table 3 indicated that the enthalpy change ΔH is positive (endothermic) due to increase in adsorption on successive increase in temperature. The negative ΔG values indicated thermodynamically feasible and spontaneous nature of the sorption. The positive value of ΔS reveals the increased randomness at the solid–solution interface during the fixation of the ion on the surface of the sorbent. Also, at all temperatures $\Delta H > T\Delta S$, indicating that the Cr(VI) ions adsorption onto S.bevanom is dominated by enthalpic rather than entropic changes.

Table 4

Thermodynamic parameter for Cr(VI) adsorption onto S.bevanom

	ΔH (kJ/kmol)	ΔS (kJ/kmol)	T °C	ΔG (kJ/mol)	r^2
			20	-4.65	
Cr(VI)	28.213	0.111	30	-5.35	5
			40	-6.91	

Conclusion

The S.bevanom showed considerable potential for the removal of Cr(VI) from aqueous solutions. The optimum conditions of sorption were found to be: a sorbent dose of 0.7 g in 100 ml of solution. Contact time of 120 min and pH=3. The results show the endothermic nature of the adsorption. The negative ΔG values indicated thermodynamically feasible and spontaneous nature of the sorption. The positive value of ΔS reveals the increased randomness at the solid–solution interface during the fixation of the ion on the active sites of the sorbent. The effect of Cr(VI) initial concentration was investigated, it was found that increasing the initial concentration reduce the removal efficiency.

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