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RESEARCH ARTICLE

Biosorption of chromium(III) by *Sargassum* sp. biomass

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Chromium is present in different types of industrial effluents, being responsible for environmental pollution. Traditionally, the chromium removal is made by chemical precipitation. However, this method is not completely feasible to reduce the chromium concentration to levels as low as required by environmental legislation. Biosorption is a process in which solids of natural origin are employed for binding heavy metals. It is a promising alternative method to treat industrial effluents, mainly because of its low cost and high metal binding capacity. In this work the chromium biosorption process by *Sargassum* sp. seaweed biomass is studied. *Sargassum* sp. seaweed, which is abundant in the Brazilian coast, has been utilized with and without milling. The work considered the determination of chromium-biomass equilibrium data in batch system. These studies were carried out in order to determine some operational parameters of chromium sorption such as the time required for the metal-biosorbent equilibrium, the effects of biomass size, pH and temperature. The results showed that pH has an important effect on chromium biosorption capacity. The biosorbent size did not affect chromium biosorption rate and capacity.

Mining activities, agricultural run off, industrial and domestic effluents are mainly responsible for the increase of the metallic species released into the environment.

Contrary to toxic organics, that in many cases can be degraded, the metallic species that are released into the environment tend to persist indefinitely, accumulating in living tissues throughout the food chain.

A complete understanding about noxious effects caused by the release of toxic metals into the environment and the emergence of more severe environmental protection laws, have encouraged studies about removal/recovery of heavy metals from aqueous solutions using biosorption.

Conventional methods as precipitation, oxidation/reduction, ion exchange, filtration, membranes and evaporation are extremely expensive or inefficient for metal removal from diluted solutions containing from 1 to 100 mg/L of dissolved metal. In this context, the biosorption process has been recently evaluated (Volesky, 1990).

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Although biosorption is promising, its mechanism is not well elucidated. This knowledge is essential for understanding the process and it serves as a basis for quantitative stoichiometric considerations, which are fundamental for mathematical modelling and scale-up (Volesky, 1986).

Table 1. Biomass and resin with their metal-binding capacities.

Type of biomass	Biosorbent capacity (meq/g)
Sargassum sp.	2 – 2.3
Ascophyllum sp.	2 – 2.5
Eclonia radiata	1.8 – 2.4
Rhizopus arrhizus	1.1
Peat moss	4.5 – 5.0
Commercial resins	0.35 – 5.0

Source: Kratochvil and Volesky, 1998.

The mechanisms by which microorganisms remove metals from solutions are: (i) extracellular accumulation/precipitation; (ii) cell-surface sorption or complexation; (iii) intracellular accumulation (Muraleedharan et al. 1991). Among these mechanisms, process (i) may be facilitated by using viable microorganisms, process (ii) can occur with alive or dead microorganisms, while the process (iii) requires microbial activity.

Although living and dead cells are capable of metal accumulation, there are differences in the mechanisms involved, depending on the extent of metabolic dependence (Gadd, 1990).

The physiological state of the organism, the age of the cells, the availability of micronutrients during their growth and the environmental conditions during the biosorption process (such as pH, temperature, and presence of certain co-ions), are important parameters that affect the performance of a living biosorbent. The efficiency of metal concentration on the biosorbent is also influenced by metal solution chemical features (Volesky, 1990).

There are potent biosorbents easily available in all the three groups: algae, fungi and bacteria. A source of low cost biomass produced in great quantities, are marine macroalgae. Recent studies about biosorption of toxic metals by algae are focused on toxicological aspects, metal accumulation, and pollution indicators by living (metabolically active) biomass.

Table 1 lists some of the species having metal-binding capacity comparable with commercial synthetic cation-exchange resins.

Studies about the technological aspects of the metal removal by algae are scarce (Volesky and Holan, 1995). In this sense, the aim of this work is to determine the potential of chromium uptake, a highly toxic metal present in several industrial effluents, by the inactive biomass of the marine alga *Sargassum* sp., abundant on Brazilian coast.

Materials and Methods

Biomass

Brown marine alga *Sargassum* sp. from Brazilian coast was washed with distilled water and dried at 60ºC for 24 hours. The experiments were made with two biomass sizes: biomass in its natural size (with leafs and thallus) and milled biomass. Dry natural biomass was chopped and sieved by using a Tyler Standard Sieve Series. The milled particles with 0.625 mm of average diameter were used for sorption experiments. Dry weight of biomass was obtained after drying at 105ºC for 24 hours.

Metal solution

Chromium solutions with different initial concentrations were prepared by dissolving $CrK(SO_4)_2.12H_2O$ in deionized water.

Biosorption experiments

Experiments to determine the contact time required for equilibrium sorption experiments were performed in Erlenmeyer flasks, using 1 L of metal solution and approximately 1 gram of biomass (dry matter). The flasks were maintained at 30ºC under constant agitation in a rotatory shaker. Samples (1 mL) were removed at different time intervals, membrane filtered (Millipore 0.45 μm pore size) and analysed for chromium by atomic absorption spectroscopy (AAS) (Varian SpectrAA-10 plus).

Batch equilibrium sorption experiments were carried out in 125 mL Erlenmeyer flasks for 6 hours (0.10-0.25 g of milled biomass, 50 mL of metal solution) in a rotary shaker. These experiments were done at pH 2.0, 3.0 and 4.0, at 20, 30 and 40ºC. Solutions of NaOH and H_2SO_4 were used to adjust the pH and this control was made every hour. After the sorption equilibrium was reached (6 hours), the solution was separated from the biomass by membrane filtration (Millipore 0.45 mm pore size).

The initial and equilibrium chromium concentrations in each flask were determined by AAS.

Data evaluation

The chromium biosorption coefficient (q) the construction of sorption isotherms was calculated from the initial concentration (C_i) and the final or equilibrium concentration (C_f) in every flask, as follows:

$$q = \frac{V\left(C_i - C_f\right)}{M} \qquad [1]$$

where, V is the volume of the chromium solution in the flask and M is the dry mass of biosorbent.

Two models were used to fit the experimental data: the Langmuir model and the Freundlich model.

The Langmuir sorption model was chosen for the estimation of maximum metal biosorption by the biosorbent. The Langmuir isotherm can be expressed as:

$$q = \frac{q_{\max} b C_f}{\left(1 + bC_f\right)} \qquad [2]$$

where b is a constant related to the adsorption/desorption energy, and q_{max} is the maximum biosorption upon complete saturation of the surface.

The Freundlich model is represented by the Equation [3].

$$q = kC_f^{(1/n)} \qquad [3]$$

where k and n are constants.

Results and Discussion

Chromium biosorption kinetics

The purpose of this experiment was the determination of the contact time required to reach the equilibrium between dissolved and solid-bound sorbate (*i.e.* ions).

Equilibrium time is a function of many factors, such as type of biomass (number and kind of biosorption sites), size and form of biomass, physiological state of biomass (active or inactive, free or immobilized), as well as the metal involved in the biosorption system. Reported values for equilibrium time are in the range from 15 minutes (Aksu and Kutsal, 1991) to ten days (Nourbakhsh et al. 1994).

Figure 1 presents the results obtained with the milled biomass at two different initial concentrations of chromium. A contact time of six hours was enough for the system to reach the equilibrium. So, this time was used to obtain the isotherms.

Figure 2 shows the evolution of chromium removal (percentage) by plotting 1 - ((C_t - C_{eq})/(C_0 - C_{eq})) as a function of time, where C_{eq} is the chromium concentration at six hours. This figure indicates more clearly that sorption can be divided into two stages: one in which the sorption rate is very high (60% of biomass saturation capacity was reached in a contact time of 10 minutes), followed by a second stage with a much lower sorption rate. This behavior has often been reported by other researches. Crist et al. 1988 and Crist et al. 1990, observed that proton uptake by algal cells consists of two processes, a fast surface reaction and a slow diffusion of protons into the cells.

Influence of biosorbent size on chromium biosorption

The influence of biosorbent size on chromium biosorption can be evaluated from Figure 3. The experimental results indicate that the biosorbent size did not influence the capacity and rate of chromium biosorption.

Although this is contrary to expected for an intraparticle diffusion controlled process, it is necessary to point out that the two sizes of biomass are actually of the same thickness (dimension which determines the diffusion distance). This is so because size grading of ground biomass particle by standard sieves works on the length and width dimensions.

This behavior has been reported by others (Kuyucak and Volesky, 1989; Yang and Volesky, 1999), although Leusch et al. 1995 showed that larger biomass particles of *Sargassum fluitans* and *Ascophylum nodosum* had higher metal uptake than smaller particles in the case of cadmium, copper, nickel, lead and zinc.

Then, the influence of biosorbent size on metal uptake seems to be a function of both the type of biomass and the metal ion.

Effect of pH

It is now well established that heavy metals are taken up from water predominantly by ion exchange. Carboxyl and sulphate groups have been identified as the main metal-sequestering sites in seaweed and, as these groups are acids, its availability is pH dependent. At pH in the range 3.5-5.5 these groups generate a negatively charged surface, and electrostatic interactions between cationic species and this surface can be responsible for metal biosorption.

Figure 4 shows the effect of pH on the biosorption capacity of the marine alga *Sargassum* sp. at different temperatures. As shown, pH is an important parameter for the sorption process, especially in the temperature range from 30ºC to 40ºC. The chromium biosorption capacity was at all temperatures higher at pH 4.0 (at pH 5.0 a chromium precipitate was observed).

This pH dependence suggests a competition of metallic ions and protons by the same binding sites, since in this pH range chromium ion is present as a cation.

The effect of pH on metal biosorption have been studied by many researches, and the results demonstrated the increasing cation uptake with increasing pH values, as fungi biomass (Tsezos and Volesky, 1981; Guibal et al. 1992) as algae biomass (Darnall et al. 1986; Kuyucak and Volesky,

1989; Aksu and Kutsal, 1991; Garnham et al. 1993; Holan et al. 1993; Holan and Volesky, 1994; Kratochvil et al. 1998).

After a certain contact time, a pH increase was observed during the flask experiments. After the first hour the pH decreased in those experiments at high values of initial chromium concentrations (> 200 mg/L).

Similar effects were observed by Kuyucak and Volesky, 1989 when studying cobalt biosorption using several types of marine algae, including the brown alga *Sargassum natans*. According to these authors, an increase of pH could be the result of dissolution of some cytoplasmic components or ions, such as carbonates, released into the solution.

The hypothesis of dissolution of cell components seems to be viable for the present study, because of some difficulties of filtration at pH 4.0 and for solutions which showed an increase of pH.

The decrease of pH can be attributed to the chemical features of the chromium(III) solution rather than to the sorption mechanism (Kuyucak and Volesky, 1989; Kratochvil et al. 1998). Chromium(III) in water can undergo hydrolysis and/or complexation reactions. The extension of these reactions depends primarily on the total chromium(III) concentration, pH and the type of anions in the solution. The hydrolysis reaction generates divalent cations $Cr(OH)^{2+}$ and protons which contribute to the increase of acidity of the chromium(III) solutions (Kratochvil et al. 1998).

Effect of temperature

Temperature has not been studied as a relevant variable in biosorption experiments. The tests are usually performed at approximately 25-30ºC. However, Tsezos and Volesky, 1981; Kuyucak and Volesky, 1989; and Aksu and Kutsal, 1991 reported a slight increase in cation uptake by seaweed in the range of 4 to 55ºC.

The effect of temperature on chromium biosorption by *Sargassum* sp. was not as pronounced as the effect of pH. This fact can be observed on Figure 5.

At pH 3.0 an increase of temperature from 30ºC to 40ºC, produced a definite increase on biosorption capacity, which was not observed when the temperature increased from 20ºC to 30ºC.

At pH 4.0 and at high equilibrium concentrations, biosorption capacity increase significantly with temperature, which was not the case at low equilibrium concentrations.

The fact that chromium uptake is strongly affected by pH and increases with temperature is in agreement with the ion-exchange hypothesis.

Adjustment of experimental data

Langmuir and Freundlich isotherms were used to adjust the experimental data obtained for a particular condition. These isotherms have been frequently used to fit experimental data (Holan et al. 1993; Holan and Volesky, 1994; Leusch et al. 1995; Costa and França, 1996) in studies with different metals and biomass. In general, the results are in good agreement with the experimental data.

For continuous removal of chromium(III) in fixed-bed reactors, the use of whole (not ground) biomass is to be preferred to decrease or avoid an excessive compression of the bed.

The best results of chromium uptake by *Sargassum* sp. biomass were obtained at pH 4.0. As the chromium uptake was not affected by temperature at low equilibrium concentrations, it was decided to work at temperature of 30ºC, which is close to environment in Brazil.

The Langmuir's model constants, q_{max} and b, were calculated by the Maximum Likelihood Method (Valkó and Vagda, 1987). The values obtained were q_{max} = 68.94 mg chromium/g biomass and b = 0.0482 L/mg chromium; the Freundlich's model constants, k and n, were calculated by Simplex method, and the values obtained were k = 10.782 and n = 3.04. The experimental isotherm (pH = 4.0; T = 30ºC) and the isotherms obtained by the Langmuir and Freundlich models are presented in the Figure 6.

The Langmuir model predicts the formation of an adsorbed solute monolayer, with no side interactions between the adsorbed ions. It also assumes that the interactions takes place by adsorption of one ion per binding site, and that the sorbent surface is homogeneous and contains only one type of binding site. The Freundlich model does not predict surface saturation. It considers the existence of a multilayered structure.

The results presented in Figure 6 indicate that both models, Langmuir and Freundlich, fit reasonably well the experimental data: medium differences between the experimental and predicted values are 3.0 and 3.4%, respectively. This is acceptable if the complex structure of the alga surface is considered, where many chemical groups can contribute on the biosorption process, which none of the tested models takes into account.

Concluding Remarks

The biomass of the marine alga *Sargassum* sp. demonstrated a good capacity of chromium biosorption, highlighting its potential for effluent treatment processes.

The kinetics of chromium biosorption by inactive biomass of the marine alga *Sargassum* sp. was fast, reaching 60% of the total biosorption capacity in ten minutes.

The biosorbent size had no influence on chromium biosorption rate.

pH had a strong effect on chromium biosorption capacity.

The capacity of chromium biosorption by biomass increased with pH and was higher at pH 4.0.

Within the range tested, the effect of temperature on the chromium biosorption capacity was mild.

Langmuir and Freundlich sorption models were in good agreement with experimental results.

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Appendix

Figures

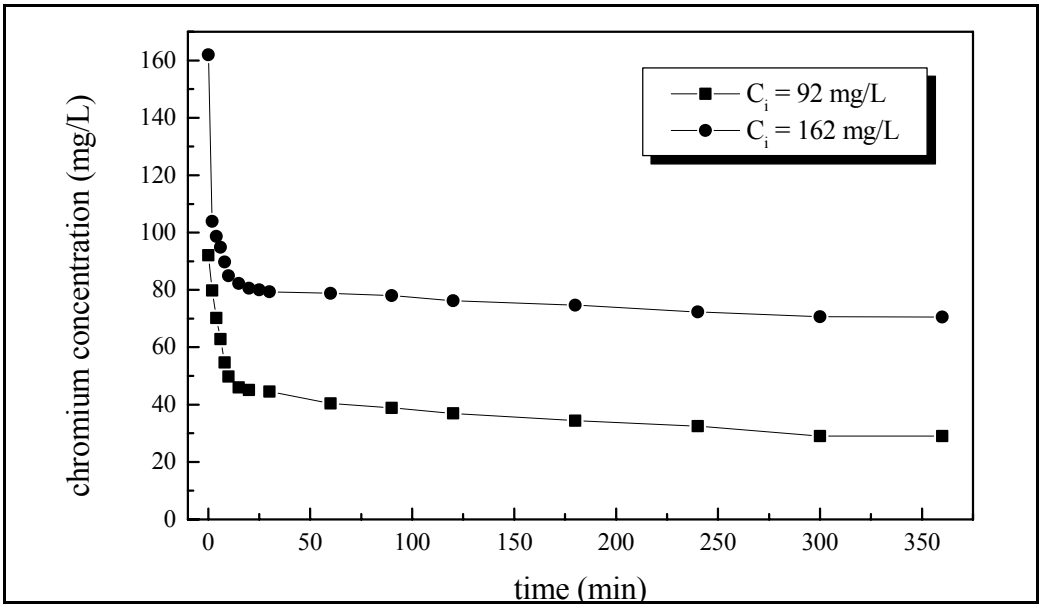

Figure 1. Chromium biosorption kinetics at two different initial concentrations. Biomass concentration = 1 g/L; pH = 4.0; T = 30ºC.

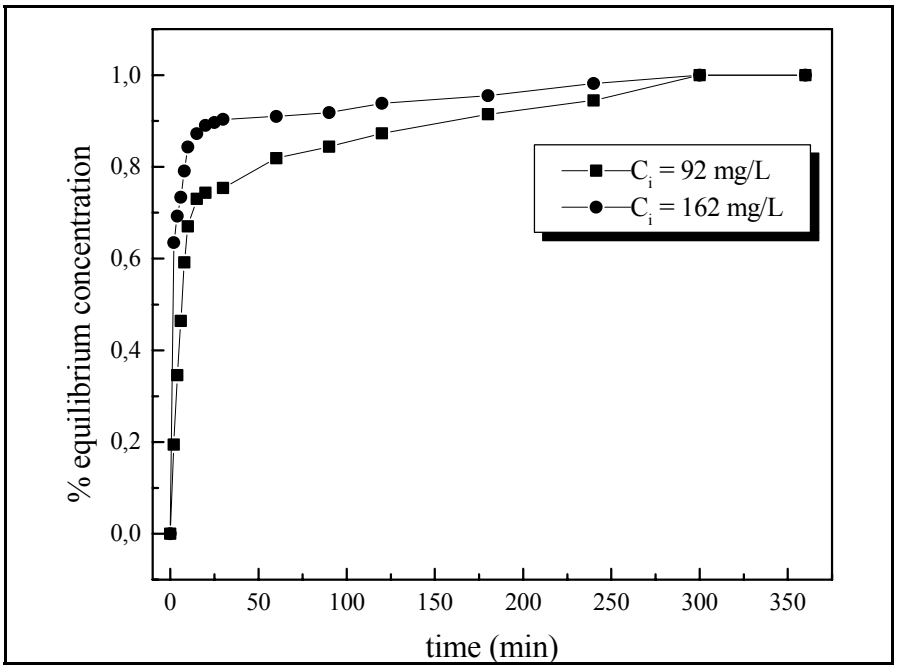

Figure 2. Percentage of chromium removal as a function of time for two different initial concentrations (data recalculated from those presented in Figure 1).

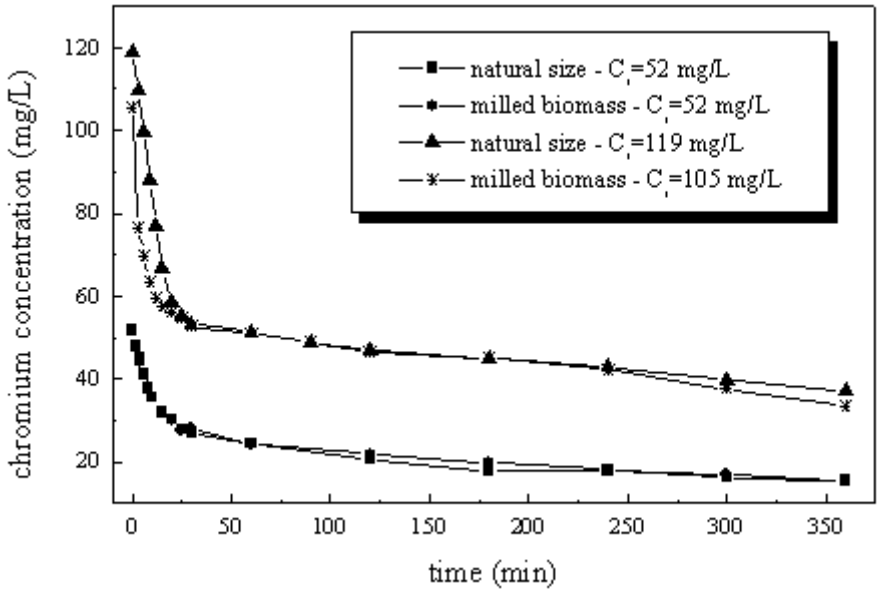

Figure 3. Effect of biosorbent size on chromium biosorption by *Sargassum* sp.

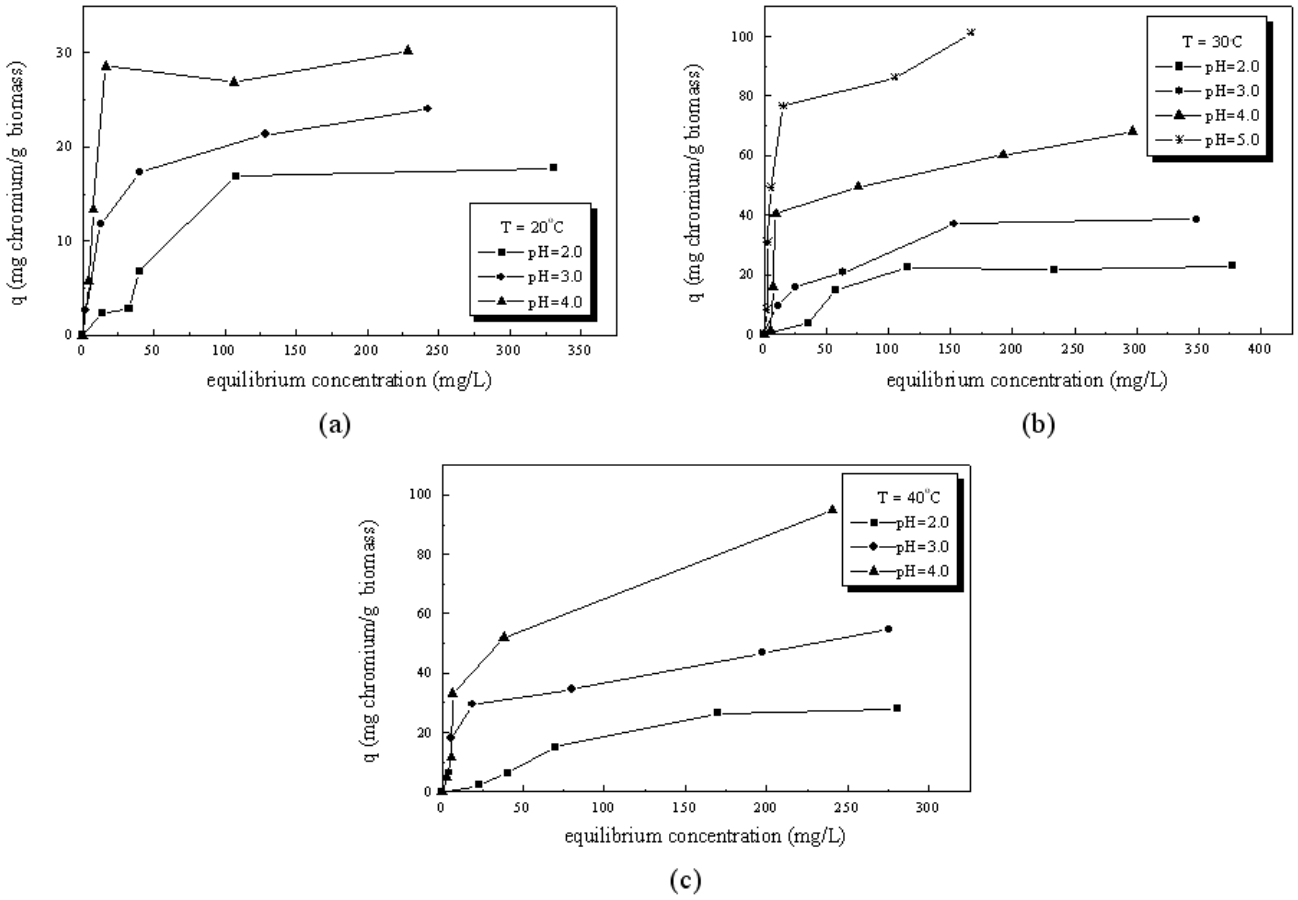

Figure 4. Effect of pH on the chromium biosorption by *Sargassum* sp.:
(a) temperature = 20ºC;
(b) temperature = 30ºC;
(c) temperature = 40ºC.

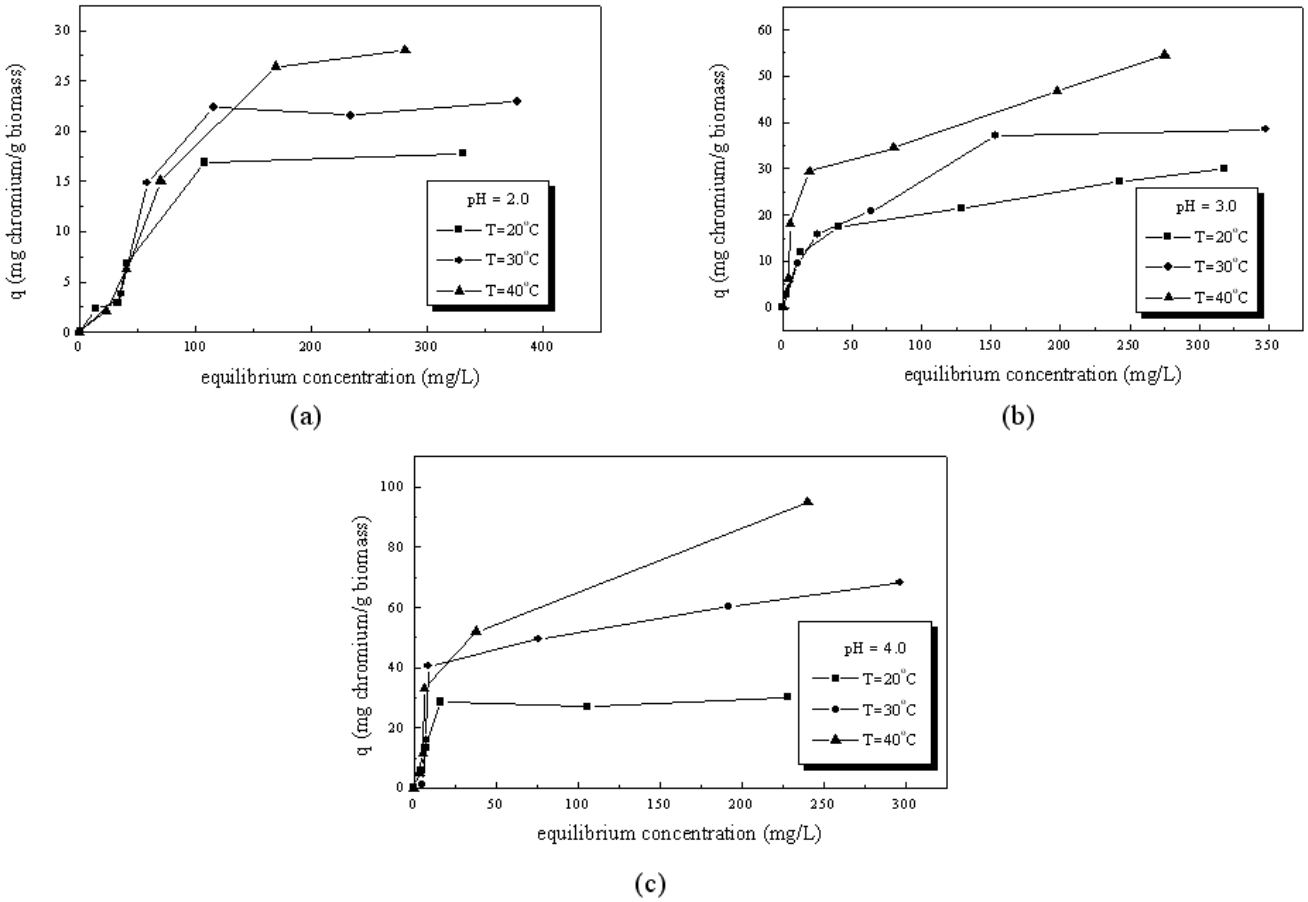

Figure 5. The effect of temperature on the chromium biosorption by *Sargassum* sp.:
(a) pH = 2;
(b) pH = 3;
(c) pH = 4.

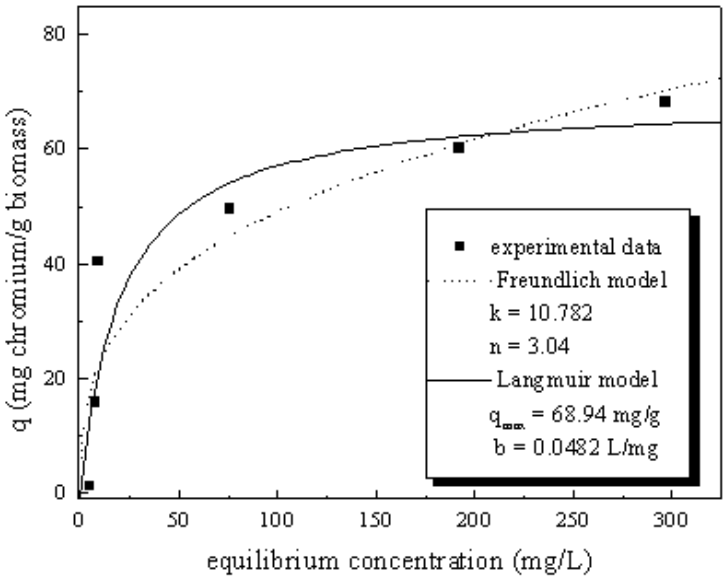

Figure 6. Experimental and adjusted isotherms.
pH = 4.0; T = 30ºC.