Batch and column removal of nickel from aqueous solutions using the Sargassum filipendula brown marine macroalgae

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ABSTRACT. The nickel(II) biosorption capacity of the Sargassum filipendula brown marine algae was studied in the batch mode. The biosorption study involved the determination of equilibrium data of the nickel-biomass system, considering the influence of the pre-treatment, particle size and agitation speed on the biosorption process. The equilibrium data obtained for the batch and column systems were adjusted by means of the Langmuir isotherm. The results showed that the column system presents a larger capacity of nickel removal from the aqueous solutions, compared to the batch system. The biosorption equilibrium was obtained in approximately four hours of experiment. The biomass size, agitation speed and the pre-treatment of algae did not affect nickel biosorption rate and biosorption capacity.

Key words: Sargassum filipendula, biosorption, nickel.

RESUMO. Remoção de níquel de soluções aquosas em batelada e em coluna utilizando a alga marinha marrom Sargassum filipendula. Neste trabalho foi estudada a capacidade de biossorção de níquel(II) pela alga marinha marrom Sargassum filipendula em sistema batelada. O estudo da biossorção envolveu a determinação dos dados de equilíbrio do sistema níquel-biomassa, considerando a influência do pré-tratamento, tamanho de partícula e velocidade de agitação no processo de biossorção. Os dados de equilíbrio obtidos para os sistemas em batelada e em coluna foram ajustados por meio da isoterma de Langmuir. Os resultados mostraram que o sistema em coluna apresentou maior capacidade de remoção de níquel comparado ao sistema em batelada. O equilíbrio de biossorção foi obtido em aproximadamente quatro horas de ensaio. O tamanho da partícula, a velocidade de agitação e o pré-tratamento da biomassa não afetaram significativamente a taxa de biossorção de níquel nem sua capacidade de remoção.

Palavras-chave: Sargassum filipendula, biossorção, níquel.

Introduction

The contamination of wastewater by toxic heavy metallic cations is a worldwide environmental problem (Kalyani et al., 2004). Contrary to toxic organics, which 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 (Cossich, 2000).

Biosorption is a popular technique that utilizes inactive/dead biological materials for the removal of heavy metals. Various biomaterials have been examined for their biosorptive properties and different types of biomass have shown different levels of metal uptake (Holan and Volesky, 1994). Among the most promising biomaterials studied, seaweeds were found to be very efficient and bind to a variety of metals (Volesky and Holan, 1995). The presence of key functional groups on the algal cell walls is responsible for their outstanding metal-sorbing properties (Davis et al., 2003). In recent years, research on the mechanisms of biosorption has been intensified since biomass can be employed to sequester heavy metals from industrial effluents or to recover precious metals from processing solutions (Davis et al., 2003). Compared with other methods for removing toxic metals from industrial effluents, the biosorption process offers the advantages of a high purity of effluent treated and the low operating cost (Shiever and Volesky, 1995).

Because of many intrinsic problems to maintain active microbial populations under highly variable conditions of wastewaters, living systems are often unreliable. The algae are harvested or cultivated in

many parts of the world, and are, therefore, readily available in large quantities for the development of highly effective biosorbent materials (Feng and Aldrich, 2004).

Nickel is one of the toxic heavy metals that are common pollutants of the environment. In humans, nickel can cause serious problems, such as dermatitis, allergic sensitization, and damage to lungs and the nervous system. It is also a known carcinogen (Axtell et al., 2003). According to the World Health Organization (WHO) guidelines for drinking water, the permissible level Ni^{2+} is 5 ppm. Nickel is present in raw wastewater streams from industries such as electroplating, nonferrous metals mineral processing, dye industries, porcelain enameling and steam-electric power plants (Yu and Kaewsarn, 2000). This work was developed with the objective of evaluating the nickel biosorption process by means of the biomass of the *Sargassum filipendula* seaweed, considering the determination parameters of nickel sorption, such as the time required for the metal-biomass equilibrium, the effects of biomass size, agitation speed, the pre-treatment of the in-nature algae, and evaluating the biosorption capacity in batch and in continuous system.

**Material and methods**

**Material**

The biomass used was the *Sargassum filipendula* brown seaweed, which was washed in water, rinsed with distilled water and dried in an oven at 60°C for 24 hours. The pre-treatment was made with part of this dry algae, immersing it into a solution of CaCl\(_2\) 0.2 M (of pH 5 after correction with HCl 1 N), under slow agitation for 24 hours, rinsed with distilled water and dried in an oven at 60°C for 24 hours. Dry biomass was chopped and sieved to different fraction sizes. Dry particles with an average diameter of 0.22 and 2.20 mm were used for sorption experiments in batch, and particles with an average diameter of 2.20 mm were used for the experiments in fixed bed column. The dry weight of biomass was obtained after drying it at 105°C for 24 hours. Nickel solutions with different initial concentrations were prepared by dissolving NiCl\(_2\) 6H\(_2\)O in deionized water.

**Methods**

Experiments to determine the contact time required for equilibrium sorption experiments were performed in Erlenmeyer flasks, using 1 L of metal solution and 1.5 g of biomass (dry matter). The flasks were maintained at 30°C under constant agitation in a rotatory shaker (200 rpm). Samples of 1.2 mL were removed at different time intervals, membrane filtered (Millipore 0.45 μm pore size), and the concentration of nickel was determined by atomic absorption spectroscopy (AAS) (Varian SpectrAA-10 plus). Experiments to evaluate the influence of the particle diameter, agitation, and pre-treatment of the algae were carried out under the same procedure with the smallest particle size (0.22 mm), agitation speed of 100 rpm and with *in nature* algae (without pre-treatment), respectively.

Experiments to evaluate the influence of the pH were done in 125 mL Erlenmeyers flasks for 4 hours, containing 75 mL of the metal solution, into which 0.125 g of dry biomass particles (with an average diameter of 2.2 mm) were added. The suspensions were agitated in a rotatory shaker at 200 rpm, 30°C and pH varying from 2 to 5.5. After 4 hours, the sorption equilibrium was reached; the solution was separated by vacuum filtration and the concentration of nickel was determined by AAS. Batch equilibrium sorption experiments were carried out with the same procedure, however, in pH 3. Solutions of HCl and NaOH were used to adjust the pH and this control was followed every hour. All experiments were carried out in duplicate.

The equilibrium concentration of metal ion (\(q_0\)) was calculated from the initial concentration (\(C_0\)) and the equilibrium concentration (\(C_{eq}\)), in each flask, using Equation 1:

\[
q_{eq} = \frac{V(C_0 - C_{eq})}{M}
\]

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

Continuous-flow sorption experiments were conducted in a steel column with a height of 50 cm and a diameter of 2.8 cm and with controlled temperature. The bed length used in these experiments was 30.6 cm. A peristaltic pump fed the nickel(II) solution (pH 3.0) to the bottom of the column with a flow rate of 6 mL min\(^{-1}\). The temperature of stream feeding solution and of the column was controlled at 30°C through a thermostatic bath. Liquid samples in the top of the column were collected at pre-defined time intervals. The total concentration of nickel(II) was determined by AAS.

When the system reaches equilibrium, the metal concentration in the fluid phase is constant throughout the column and equal to the feed concentration (\(C = C_{eq} = C_f\)). The biosorption
capacity of the nickel (II) was calculated from the experimental breakthrough curves, using the following equation:

\[ q_m = \frac{C_0 Q}{1000 M} \int \left( 1 - \frac{C}{C_q} \right) dt \]  

(2)

where Q is the flow rate and M is the biomass weight inside of the column.

The integral represented by Equation 2 was analytically solved by means of the polynomial approach of the term \( \left( 1 - \frac{C}{C_q} \right) \).

**Fitting of the experimental data**

Two models were used to fit the experimental data: the Langmuir model and the Freundlich model. These models are the most frequently used isotherms in the literature describing the non-linear equilibrium between adsorbed pollutant on the cells and pollutant in solution at a constant temperature (Aksu and Dönmez, 2006). The Langmuir and Freundlich models are simple, give a good description of experimental behavior in a large range of operating conditions and are characterized by a limited number of adjustable parameters (Aksu and Dönmez, 2006). The Langmuir sorption model was chosen for the estimation of the maximum metal biosorption \( q_{\text{max}} \) by the biosorbent. The Langmuir isotherm can be expressed as:

\[ q_m = \frac{q_{\text{max}} b C_m}{(1 + b C_m)} \]  

(3)

where:

- \( q_m \) is the amount of metal ion bound to per gram of dried biomass at equilibrium and \( C_m \) is the residual (equilibrium) metal concentration left in solution after binding, respectively;
- \( q_{\text{max}} \) is the maximum amount of metal ion per unit weight of adsorbent to form a complete monolayer on the surface bound at high \( C_{eq} \);
- \( b \) is a constant related to the affinity of the binding sites.

The Freundlich isotherm model assumes neither homogeneous site energies nor limited levels of sorption. The Freundlich model is the earliest known empirical equation and is shown to be consistent with exponential distribution of active centers, characteristic of heterogeneous surfaces (Aksu and Dönmez, 2006).

Equation 4 represents the Freundlich model:

\[ q_m = K \frac{C_{eq}^{1/n}}{C_{eq}} \]  

(4)

where \( k \) and \( n \) are constants.

**Results and discussion**

**Nickel biosorption kinetics**

The purpose of these experiments was the determination of the contact time required to reach the equilibrium between dissolved and solid-bound sorbate. The determination of this time is very important because it will be used later to obtain the isotherms. Figure 1 presents the results obtained with biomass of 2.20 mm (mean diameter) at two different initial nickel concentrations (1.75 and 5.0 meq L\(^{-1}\)).

![Figure 1. Nickel biosorption kinetics at different initial concentrations (biomass concentration = 1.5 g L\(^{-1}\); \( D_p = 2.2 \) mm; agitation velocity = 200 rpm; \( pH = 3.0; \) \( T = 30^\circ C \))](image)

Figure 2 shows the behavior of nickel removal (percentage) by plotting 1-((\( C_t \)-\( C_{eq} \))/(\( C_0 \)-\( C_{eq} \))) as a function of time, where \( C_{eq} \) is the nickel concentration at 24 hours. Figure 2(a) shows the behavior of nickel removal during the whole experiment and Figure 2(b) shows the behavior of nickel removal in the first 30 minutes of experiment. Figure 2 clearly indicates that sorption can be divided into two stages: one in which the sorption rate is very high (70% of biomass saturation capacity was reached at a contact time of 15 minutes), followed by a second stage with a much lower sorption rate.

This behavior indicates that proton uptake by algal cells consists of two processes: a fast surface reaction and slow proton diffusion into the cells.

Many researchers have also investigated the performance of the algae for the removal of various heavy metals. Gupta *et al.* (2006) verified that the biosorption rate of Cu(II) by *Spirogyra species* was fast.
during the first 30 minutes of contact time and most of the removal takes place during this period.

![Figure 2](image-url)  
**Figure 2.** Behavior of nickel removal (percentage): (a) During whole experiment; (b) In the first 30 minutes of experiment.

**Influence of pre-treatment, biosorbent size, agitation and pH on nickel biosorption**

Figure 3 shows the effect of pre-treatment on the biosorption kinetics of the *Sargassum filipendula* marine algae. As shown, the pre-treatment did not influence the nickel biosorption, since it did not cause loss or increase in the biosorption capacity of the biomass, and the behavior of solutions in contact with the treated biomass was similar to that of the biomass without treatment.

The influence of biosorbent size on nickel biosorption can be evaluated from Figure 4. Figure 4 showed an increase of approximately 10% in the nickel biosorption with the smaller particle size. However, this small difference cannot be attributed to the particle size difference, as this variation may have been caused by experimental variation, caused mainly by biomass in homogeneity, as it is composed of stems and leaves.

Cossich (2000) reported that different sizes of *Sargassum* sp. biomass did not influence the capacity and rate of nickel biosorption.

![Figure 3](image-url)  
**Figure 3.** Effect of pre-treatment on nickel biosorption kinetics by *Sargassum filipendula* marine algae (biomass concentration = 1.5 g L\(^{-1}\); \(D_p\) = 2.2 mm; agitation velocity = 200 rpm; pH = 3.0; T = 30°C)

![Figure 4](image-url)  
**Figure 4.** Influence of biosorbent size on nickel biosorption by *Sargassum filipendula* marine algae (biomass concentration = 1.5 g L\(^{-1}\); agitation velocity = 200 rpm; pH = 3.0; T = 30°C)

Figure 5 shows the nickel biosorption kinetics experiments by the *Sargassum filipendula* biomass without agitation and with agitation at two different speeds (100 and 200 rpm). It was noticed an accentuated variation in the beginning of the test at 200 rpm, although the final concentration for the two systems was similar. Malkok (2006) studied the effect of agitation speed on biosorption of Ni(II) by the cone biomass of *Thuja orientalis* and it was verified that with an agitation speed increase from 18 to 420 rpm, Ni(II) adsorption increased from 81 to 86.5%. Malkok (2006) suggested that the diffusion of nickel ions from the solution to the adsorbent surface and into the pores has increased with the increase of agitation rate.

According to Ko *et al.* (2001), batch adsorption had mass transfer resistances in the liquid film and intraparticle. This result can be explained, as larger agitation causes smaller resistance in the liquid film,
Removal of nickel by *Sargassum filipendula*

and faster adsorption takes place.

![Graph](image)

**Figure 5.** Influence of agitation on nickel biosorption by *Sargassum filipendula* marine algae (biomass concentration = 1.5 g L\(^{-1}\); \(D_p = 2.2\) mm; pH = 3.0; T = 30°C)

It is now well established that heavy metals are removed from water predominantly by ion exchange. Carboxyl and sulfate groups have been identified as the main metal-sequestering sites in seaweed, and as these are acid groups their availability is pH dependent. Thus, to verify the influence of pH on nickel biosorption tests were carried out in different pHs. The results are shown in Figure 6.

![Graph](image)

**Figure 6.** Influence of pH on nickel biosorption by marine alga *Sargassum filipendula* (biomass concentration = 1.7 g L\(^{-1}\); \(D_p = 2.2\) mm; agitation velocity = 200 rpm; \(C_0 = 100\) mg L\(^{-1}\); T = 30°C)

It can be observed that in pH 2 a removal smaller than 10 mg g\(^{-1}\) was reached, and it increased to 25 and 30 mg g\(^{-1}\) approximately in pHs 3 and 3.5, respectively. From pH 3.5 the biosorption capacity remained constant until pH 5.5. This behavior can be explained once an increase in pH produces a decrease in the H\(^+\) ion concentration which competes for the absorption sites. Consequently, an increase in pH leads to an increase in the biosorption for cationic species such as the nickel complexes.

Sheng *et al.* (2004) evaluated the sorption of lead, copper, cadmium, zinc and nickel for four types of marine algae, and it was verified that an increase of pH values provides an increase of metallic ions removal.

Gong *et al.* (2005) evaluated the lead biosorption and desorption of the Spirulina maxima pre-treated with CaCl\(_2\) and in *nature*. It was verified that the maximum biosorption was found at pH 5.5.

Hashim and Chu (2004) studied the biosorção of cadmium for brown, green and red marine algae, and it was observed that the equilibrium concentration of cadmium was similar for pHs from 3 to 5, but it decreased significantly when the solution pH was reduced to 2.

However, Schiever and Volesky (1995) *apud* Cossich (2000), report that high pH values can damage the material structure and can provoke an increase in the solubility of the metallic complexes. Moreover, high pH values can cause precipitation of the metallic complexes and they should be avoided during the sorption experiments, since the distinction between sorption and precipitation during metallic removal would be difficult.

**Fitting of the experimental data**

Langmuir and Freundlich isotherms were used to fit the experimental equilibrium data obtained at pH 3, 3.5 and 4, at 30°C. The experimental equilibrium data and the isotherms obtained by the Langmuir and Freundlich models are presented in Figure 7.

The values obtained for \(q_{\text{max}}\) and \(b\), \(n\) and \(K\) are shown in Table 1. The Langmuir model gave a better fit to the experimental data than the Freundlich model, as the correlation coefficient came closer to one and the variance was smaller. In addition, it was observed that the alga biosorption capacity increased with pH, from 1.47 meq g\(^{-1}\) at pH 3 to 1.72 meq g\(^{-1}\) at pH 4.

Vijayaraghavan *et al.* (2006) studied the nickel uptake by the *Sargassum wightii* in different pH values and was verified that the uptake increased as the pH increases from 3.0 and reached maximum at pH 4.0. Further increase in pH resulted in decreased nickel uptake. This may be due to nature of binding sites in *Sargassum* biomass and their pKa values pH increases from 3.0 and reached maximum at pH 4.0 (Lodeiro *et al.*, 2004 *apud* Vijayaraghavan *et al.*, 2006).

Also, hydrogen ion competition at low pH and solution chemistry of metals are other important factors responsible for variation of metal uptake at different pH values (Volesky and Schiewer, 1999 *apud* Vijayaraghavan *et al.*, 2006).
Figure 8 presents the isotherms fitted by the Langmuir model at different pH values.

Table 1. Langmuir and Freundlich parameters.

<table>
<thead>
<tr>
<th>Model</th>
<th>pH 3 (meq g⁻¹)</th>
<th>pH 3.5 (meq g⁻¹)</th>
<th>pH 4 (meq g⁻¹)</th>
<th>Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir b (L mg⁻¹)</td>
<td>1.469 ± 0.004</td>
<td>1.569 ± 0.006</td>
<td>1.715 ± 0.008</td>
<td>0.985</td>
</tr>
<tr>
<td>Freundlich n</td>
<td>0.302 ± 0.001</td>
<td>0.642 ± 0.015</td>
<td>0.721 ± 0.023</td>
<td>0.905</td>
</tr>
</tbody>
</table>

The equilibrium data for nickel(II) biosorption by seaweed Sargassum filipendula (at pH 3.0, 30°C) and the Langmuir isotherm model curve obtained by fitting the experimental data obtained in the dynamic column are shown in Figure 9.

The values obtained for $q_{\text{max}}$ and $b$ in batch and in the continuous system were 2.496 (± 0.011) and 0.456 (± 0.002) with correlation coefficient as 0.890.

It can be observed that the biosorption capacity of the nickel(II) by Sargassum filipendula biomass in the column was larger than in batch system. The column system removes approximately 70% more nickel. This behavior was already reported by Silva (2000), which evaluated the cooper(II) removal capacity by seaweed Sargassum sp. and found $q_{\text{max}}$ values of 2.17 and 3.57 (meq g⁻¹) for batch and dynamic systems, respectively.

Vijayaraghavan et al. (2005) also compared the batch and column system for the cobalt(II) and nickel(II) biosorption and noticed an uptake (in batch) of 20.63 mg Co(II) g⁻¹ at pH 4.5 and 18.58 mg Ni(II) g⁻¹ at pH 4.0, while in column system there was an uptake of 50 mg Co(II) g⁻¹ and 39 mg Ni g⁻¹. This behavior probably results from the fact that in the batch system the ions released by the biosorbents are maintained in solution and acid
additions are made to maintain the pH constant, while in the column it is not possible to carry out the pH adjustments during the experiment.

**Conclusion**

The present study on biosorption of nickel(II) from aqueous solutions by *Sargassum filipendula* biomass presents the following conclusions:

- A contact time of four hours was enough for the system to reach equilibrium.
- The sorption kinetics of nickel(II) by *Sargassum filipendula* biomass can be divided into two stages: one in which the sorption rate is very high, followed by a second stage with a much lower sorption rate.
- The pre-treatment of biomass did not influence the Ni(II) biosorption.
- The biosorbents particle size did not influence the nickel biosorption.
- The agitation did not influence the biosorption capacity of Ni(II) by *Sargassum filipendula* biomass, although it showed influence on the biosorption behavior at the first hours of experiment.
- The pH was shown to be very significant in the biosorption process; the alga biosorption capacity increased with the pH.
- Langmuir sorption model was in good agreement with the experimental equilibrium data.
- Comparing the batch and the column experiments, the packed column effectively used the biomass metal binding capacity to a greater extent than the batch mode.

**References**


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