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# Nickel biosorption using *Gracilaria caudata* and *Sargassum muticum*

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ABSTRACT

Two seaweeds (*Sargassum muticum*, *S.m.* and *Gracilaria caudata*, *G.c.*) collected on the coasts of Cuba have been tested and compared for nickel biosorption. The metal was efficiently bound to the biomass at pH 3 for *S.m.* and pH 5 for *G.c.* Sorption isotherms, at the optimum pH, showed that *S.m.* is more efficient than *G.c.*: maximum sorption capacity reached about 70 mg Ni $g^{-1}$ and 45 mg Ni $g^{-1}$ for *S.m.* and *G.c.*, respectively. The isotherms were modeled using the Langmuir equation (which fits better experimental data than the Freundlich and Temkin equations). Sorption kinetics were also carried out varying metal concentration, sorbent dosage particle size and temperature. The kinetics were modeled using the pseudo-second order rate equation and the intraparticle diffusion equation.

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## 1. Introduction

The regulations concerning the discharge of contaminants to the environment are becoming more and more stringent. For example, metal ions may induce strong impact on the quality of water bodies, on wild and domestic life, and consequently on human health. Additionally, in many countries the discharge of a waste material in landfill is only authorized when the user has proved that the material cannot be valorized or recycled. These constraints have motivated a number of processes for recovering metals from effluents or waste materials. For example, recycling and metal recovery from spent batteries has retained a great attention in the research community for the last decade, based on the evolution of discharge regulations [1].

A number of processes exist for the treatment of metal-bearing solutions, including sorption on mineral sorbents [2], on ion exchange and chelating resins [3–5], on extractant impregnated resin [6,7], chemical precipitation [1,8], or membranes processes [9]. However, these processes frequently meet limiting criteria that make their application uncompetitive. Technical limitations (concentrations reached by the process), economical constraints (cost of the materials for large-size applications, energy consumption), environmental criteria (production of highly contaminated sludge or sorbent, poorly recyclable or difficultly valorizable) are some of the issues that may explain the need for alternative treatment processes. Biosorption has been widely investigated for the last decades, being considered a promising alternative to conventional processes [10]. Biosorption consists in using a biomass (produced from microorganisms, agriculture waste, biopolymers) for the binding of metal ions [11], dyes [12], organic compounds through a wide range of physico-chemical mechanisms, including ion exchange, chelation, complexation, precipitation. A great diversity of biosorbents has been carried out for metal binding. For example, bacterial cells [13,14], fungal biomass [15,16], algal biomass [17–23], stabilized anaerobic sludge [24,25], agriculture waste [26], crab shell [27–29], biopolymers [30–34] have been tested for nickel biosorption.

Algal material has a strong affinity for divalent cations. The binding efficiency is commonly explained by the presence of several polysaccharides in their cell walls: alginate [34–39] and fucoidan [40]. A numerous literature exists on metal interactions with alginate. It is commonly accepted that divalent metal cations interact with guluronic and mannuronic acids (the units constituting alginate biopolymer) through the "egg box" mechanism. Metal cations interact with carboxylic groups to form a dense network. Actually, this interaction can be also used for the ionotropic gelation of alginate to prepare hydrogels.

This study investigates the potential of two seaweeds, *Gracilaria caudata* and *Sargassum muticum*, endemic macroalgae from Cuban coasts (but also invasive in several countries over the world, including Europe) for biosorption. These biosorbents were tested for Ni(II) sorption. Nickel is known for having allergic effects (contact allergy through skin sensitivity causing dermatitis) at low concentration, while high-level exposure can induce lung and nasal sinus cancers

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depending on the administration mode (carcinogenesis effects). Nickel causes oxidative stress and may induce nausea, dizziness and diarrhea. EPA sets the admissible levels in drinking water to 0.04 mg $L^{-1}$ [41]. The WHO guideline value was fixed to 0.07 mg $L^{-1}$ [42].

The first part of the study checks the impact of pH on sorption performance (and acid–base/charge characteristics of the biosorbents). The sorption isotherms are established at the optimum pH and at different temperatures in order to evaluate the thermodynamics of the systems. The last part carries out the uptake kinetics varying sorbent dosage, sorbent particle size, temperature and metal concentration in order to evaluate the contribution of resistance to intraparticle diffusion on the control of sorption kinetics.

## 2. Materials and methods

### 2.1. Biomass

Two different algal biomass were tested: *Sargassum muticum* (*S.m.*), a brown algae collected on the north coast of Cuba (Caibarién beach), and *Gracilaria caudata* (*G.c.*), a red algae collected on the south coast of Cuba (close to Cienfuegos). After being collected, the biomass was repeatedly washed with demineralized water to remove impurities and cations such as $Ca^{2+}$ and $Na^{+}$, dried in an oven (at 60 °C) and stored in desiccators. In order to investigate the impact of particle size, the biomass was grinded and sieved into three fractions: 125–250 μm, 250–500 μm and 710–1000 μm.

### 2.2. Characterization of biosorbents

The water content of the biosorbent was evaluated by weight loss at 60 °C overnight (higher temperature could induce a partial degradation of the biomass); the drying time was sufficient to reach constant weight.

The analysis of biosorbent charge was performed by titration using the method of pH derivation (pH of zero charge). The biomass (i.e., 50 mg) was added to a water solution (i.e., 100 mL), which pH was adjusted to target values (i.e., between pH 3 and 11) using 0.1 M solutions of HCl or NaOH. The suspension was maintained under agitation (at 150 rpm) for 48 h. The pH of zero charge ($pH_{pzc}$) was determined as the pH corresponding to the crossing of the curve $pH_{eq} = f(pH_i)$ with the first bisector ($pH_{eq} = pH_i$).

### 2.3. Sorption experiments

A stock solution of Ni(II) was prepared at the concentration of 1 g $L^{-1}$ using $Ni(NO_3)\cdot 6H_2O$ in demineralized water (adding a drop of nitric acid to stabilize the solution). This stock solution was used for the preparation of test solutions by dilution (in the range 0–150 mg Ni $L^{-1}$, for sorption isotherms; at 10 mg Ni $L^{-1}$ for investigating the pH effect); the pH was controlled to target value using 0.1 M solutions of HCl or NaOH. The biomass was added to the solution (sorbent dosage: 0.5 g $L^{-1}$) and the suspension was maintained under agitation (at the velocity of 150 rpm) on a reciprocal shaker for 48 h. The pH was not controlled during the sorption process but the equilibrium pH was systematically measured. Samples were collected and filtrated on a cellulose filter membrane (pore size: 1–2 μm). A drop of concentrated acid was systematically added to stabilize the filtrate and for analytical purpose. Metal concentration was determined by ICP-AES (inductively coupled plasma atomic emission spectrometry) using a Jobin Yvon Activa M (Jobin-Yvon, Longjumeau, France). Full experimental conditions (sorbent dosage, pH, metal concentration, temperature, etc.) are reported in the caption of the figures. The sorption capacity ($q$, mg Ni $g^{-1}$, or mmol Ni $g^{-1}$) in the biomass is determined by the mass balance equation: $q = (C_0 - C_{eq}) \times V/m$; where $C_0$ and $C_{eq}$ are the initial and final concentrations of Ni(II) in the solution, $V$ (L) is the volume of solution and $m$ (g) is the sorbent amount. The sorption efficiency (SE: $100 \times (C_0 - C_{eq})/C_0$, %) was plotted versus equilibrium pH for pH optimization (SE versus $pH_{eq}$); while for sorption isotherms the sorption capacity was plotted versus equilibrium metal concentration in the solution ($q$ versus $C_{eq}$).

For uptake kinetics, a given amount of sorbent was added to a pre-stabilized solution (target metal concentration and pH), samples were collected at fixed contact times, filtrated using a filter membrane, acidified and finally analyzed using ICP-AES. Unless specified (for target experiments) the sorbent dosage was set to 0.5 g $L^{-1}$, the temperature was fixed to 20 °C. The standard particle size was 125–250 μm, and the agitation speed was set at 150 rpm. The final pH was measured. The relative concentration ($C(t)/C_0$) was plotted versus time for comparing kinetic profiles.

### 2.4. Modeling of sorption isotherms and uptake kinetics

Sorption isotherms represent the distribution of the solute at equilibrium between the solid phase (the sorbent) and the liquid phase (the solution). The plot of $q$ versus $C_{eq}$ can be modeled using a number of equations. Though the equations of Freundlich and Langmuir are the most commonly used, alternative equations such as the Langmuir–Freundlich and the Temkin equations have also been cited [43].

$$\text{Langmuir}: \quad q = \frac{q_m b C_{eq}}{1 + b C_{eq}} \tag{1}$$

with $q_m$ (mg Ni $g^{-1}$ or mmol Ni $g^{-1}$), $b$ (L $mg^{-1}$ or L $mmol^{-1}$) are the constants of the Langmuir equation that were determined by a non-linear regression correlation method.

$$\text{Freundlich}: \quad q = k_F C_{eq}^{1/n} \tag{2}$$

with $k_F$ ($mg^{1-1/n}\,L^{1/n}\,g^{-1}$ or $mmol^{1-1/n}\,L^{1/n}\,g^{-1}$) and $n$ are the constants of the Freundlich equation.

$$\text{Temkin} \quad q = \frac{RT}{b_{Te}} \ln(a_{Te} C_f) \tag{3}$$

with $a_{Te}$ (L $g^{-1}$) and $b_{Te}$ (J $mol^{-1}$) are the constants of the Temkin equation.

$$\text{Langmuir–Freundlich}: \quad q = \frac{q_{m,LF} b_{LF} C_{eq}^{\alpha}}{1 + b_{LF} C_{eq}^{\alpha}} \tag{4}$$

with $q_{m,LF}$ (mg Ni $g^{-1}$ or mmol Ni $g^{-1}$), $b_{LF}$ ($(L\,mg^{-1})^{1/\alpha}$ or $(L\,mmol^{-1})^{1/\alpha}$) and $\alpha$ are the constants of the Langmuir–Freundlich equation.

The modeled curves frequently meet difficulties for correctly modeling the curved section of the isotherms. They overestimate sorption capacity in the intermediary section of the curve. Escudero et al. used a bi-site Langmuir equation for the modeling of hexanol using alginate aerogels [44]. This behavior is typical of systems involving several types of sorption sites with different adsorption energies. Assuming that several sites could be involved in the binding, the Langmuir equation becomes:

$$q = \frac{q_{m,1} b_1 C_{eq}}{1 + b_1 C_{eq}} + \frac{q_{m,2} b_2 C_{eq}}{1 + b_2 C_{eq}} \tag{5}$$

where ($q_{m,1}$,$b_1$) and ($q_{m,2}$,$b_2$) are the parameters for the two types of sorption sites.

The affinity coefficients ($b_1$ and $b_2$) may be significantly different reflecting the differences in strength of the interaction of the solute with these different sorption sites. The same concept can be applied to systems where the reactive groups interact with different metal species for which they have different affinities. This is especially

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