Simple and Competitive Adsorption Study of Nickel(II) and Chromium(III) on the Surface of the Brown Algae *Durvillaea antarctica* Biomass

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**ABSTRACT:** In this work Ni(II) and Cr(III) adsorption on *Durvillaea antarctica* surface were studied, optimal condition of pH, adsorption time is achieved for pH 5.0, with contact times of 240 and 420 minutes for a maximum adsorption capacity of 32.85 and 102.72 mg g⁻¹ for Ni(II) and Cr(III), respectively. The changes in the vibration intensity of the functional groups detected in the starting material by Fourier transform infrared spectroscopy and the opening of the cavities after the biosorption process detected by scanning electron microscopy images suggested the interaction of the metal ions with the surface and the changes in the chemical behavior of the solid. The heavy metal adsorption equilibrium data fitted well to the Sips model. The effect of competitive ions on adsorption equilibrium was also evaluated, and the results showed that the two metals compete for the same active sites of the biosorbent; the increase of the Ni(II) initial concentration increases its adsorption capacity but decreases the adsorption capacity of Cr(III).

1. **INTRODUCTION**

Heavy metal pollution has become a major worldwide problem,¹–¹² the high toxicity of these pollutants at low concentrations, also their capacity to accumulate in soil and water, hence their bioaccumulation in plant and animal tissues² and their capacity to accumulate in soil and surface hardness, discharge a significant amount of heavy metals into the environment.¹ Chrome plating and nickel plating are techniques of electroplating to produce a thin layer of chromium and nickel onto a surface, respectively. The uncontrolled release of effluents with high concentrations of these metals as a by-product of this activity commonly used in the industry has been reported.⁴

As mentioned earlier, among the discharges contaminated by heavy metals are those from electroplating, specifically with nickel and chrome; these ion metals are the Ni(II), Cr(III),⁴,⁵ and Cr(VI)⁵ ions, and the maximum permissible limits for industrial discharge are 3.0,¹ 1.0, and 0.1 mg L⁻¹,⁷ respectively. The permissible limit of Ni(II) and Cr(VI) in drinking water is 0.5 and 0.05 mg L⁻¹, respectively. The maximum concentration of total chromium in drinking water established by the Environmental Protection Agency is 100 µg L⁻¹.¹⁰,¹¹

A high concentration of nickel in water for human consumption, affects human health, causing kidney and lung disorders, dermatitis and gastrointestinal damage. Chromium causes skin diseases, lung carcinoma, among others,⁵ mainly when they accumulate in living tissues,⁶ Cr(III) is less toxic than Cr(VI) and acts as an essential microelement in mammals. Toxicity of Cr(VI) is associated with its high redox potential and mobility, also the ability to penetrate biological membranes.¹¹ In addition, nickel and chromium are mutagenic and carcinogenic.¹²

To mitigate the effects of this problem, industries have installed different water purification systems, including ion exchange, membrane filtration, precipitation, oxidation, and electrochemical treatments. Unfortunately, the use of other reagents and the energy cost of these processes increase the cost-efficiency ratio,⁴ promotes the formation of harmful byproducts,⁵ and their application is limited to a low concentration range (1–100 mg L⁻¹) of the metal ion.¹² An alternative to replace these water treatment methods is the...
adsorption using natural adsorbents in a process called biosorption.\textsuperscript{12} Biosorption is an environmental remediation method that uses living or dead biomass to reduce the amount of toxic components present in aqueous solution.\textsuperscript{3} This technique has gained interest because of its high efficiency,\textsuperscript{12} low cost, for being an environmentally friendly process,\textsuperscript{12,13} short reaction time, does not generate sludge, easy regeneration of the biosorbents, does not require nutrients (nonliving biomass), and the metal can be recovered.\textsuperscript{8} A wide variety of biomass has been used for biosorption, including aquatic plants such as Hydrilla, Cabomba, waste tea factories, fungal biomass, and algae.\textsuperscript{4}

One of the most promising biomass to be used as biosorbents is the algae, the biosorption capacity of algae biomass relies on its chemical structure, the functional groups present can interact with metal ions. Therefore, different adsorption mechanisms can occur, including electrostatic attraction, cation exchange, formation of superficial metal complexes, hydrogen bond, and microprecipitation.\textsuperscript{5} Another important aspect is its high abundance and availability in the oceans and its physical and chemical stability over long periods of time.\textsuperscript{14} There are three types of macroalgae: red (Rhophyta), green (Chlorophyta), and brown (Phaeophyceae),\textsuperscript{5,13} all have cell walls consisting of complex networks of biopolymers, cellulose as skeleton, fibrous parts, and a matrix of specific polysaccharides such as sulfated mucopolysaccharides (fucoidan), proteoglycans, alginates (mannuronic and guluronic acids) complexed with metal ions of alkali and alkali-terrous such as K(I), Na(I), Mg(II), and Ca(II) and other molecular components that depend of the type of algae.\textsuperscript{5,13} Of the three types of algae mentioned above, it has been shown that brown algae are the most efficient in biosorption of heavy metals, alginates have a high affinity for divalent cations and sulfated polysaccharides give account of the uptake of trivalent cations.\textsuperscript{14,15} Also, algal biomass has been used to adsorb organic pollutants such as phenanthrene, phenol and nonylphenol,\textsuperscript{13} colorants, and polyaromatic hydrocarbons.\textsuperscript{5} The efficacy of biosorption to remove different pollutants depends on solution pH, effluent composition, biosorbent concentration, temperature, and reaction kinetics.\textsuperscript{5,3,5}

Different materials are used as adsorbents for the removal of single metal ions, but multicomponent metal systems make it difficult to perform biosorption studies. Therefore, the mechanism of biosorption in the presence of two or more metals is complex and difficult to understand. This system depends on the pH, temperature, number of solutes and their concentrations, the type of interaction between the ions of different metals, and the anchoring sites of each ion on the surface of the biosorbent.\textsuperscript{1,5} This research has the objective of studying the simple biosorption of Ni(II) and Cr(III) ions and competitive between Ni(II)–Cr (III) and Ni(II)–Cr(VI) ions on the surface of the brown algae Durvillaea antarctica.

2. EXPERIMENTAL SECTION

2.1. Biomass and Preparation. A fresh D. antarctica brown algae sample was washed with distilled water to remove salt and impurities, and then was dried at 40 °C in an oven (Memmert, Germany) for 72 h. The dry material was then cut into small pieces before being ground using a hammer mill. Dry ground biomass was sieved at 500–1000 μm of particle size, and the material was used for all the experiments.

2.2. Physicochemical Characterization of Biomass. 2.2.1. Thermogravimetric Analysis. The thermal behavior of the starting biomass was evaluated by Thermogravimetric analysis (TGA)—DTG between 30 and 900 °C with a heating rate of 10 °C min\textsuperscript{−1}, under an atmosphere of N\textsubscript{2} (Cryogas) with a flow rate of 100 cm\textsuperscript{3} min\textsuperscript{−1}. A thermogravimetric analyzer (Hitachi TGA/SDTA model 7200) was used. TGA was also used to determine the maximum rate of mass loss of organic compounds, moisture, and ash.\textsuperscript{16}

2.2.2. Textural Properties. The porous structure of the biomass was determined by the nitrogen adsorption–desorption isotherms at −196 °C using an IQ\textsubscript{5} (Quantachrome Instruments, Miami, FL, USA) and its software to calculate the textural characteristics: BET area and pore size distribution by BET and Dubinin–Astakhov models.\textsuperscript{35,30} Prior to measurements, the biomass was degassed at 70 °C in an inert atmosphere for 6 h to remove moisture or contaminants preadsorbed on the biomass.\textsuperscript{17}

2.2.3. Boehm Titration Method. Biomass surface chemistry was characterized by the titration method, and the content of acidic and basic surface functional groups can be quantified by the analysis of acid-basic titrations. Then, 0.500 g of biomass was put in contact with 50 mL of 0.1 M basic solutions of different strength, NaOH, Na\textsubscript{2}CO\textsubscript{3}, or NaHCO\textsubscript{3} (Sigma-Aldrich), in different containers. Similarly, 50 mL of 0.1 M HCl was added to determine the total basicity. The mixtures were kept at 25 °C with constant stirring for 48 h. Subsequently, 10 mL of each solution was titrated with 0.1 M standard solutions of HCl or NaOH for basic and acidic group determination, respectively.\textsuperscript{18}

2.3. Determination of Optimum pH. In order to investigate the effect of pH on Ni(II) and Cr(III) ion biosorption, solutions of 50 mg L\textsuperscript{−1} Ni(II) and Cr(III) from their respective precursors NiCl\textsubscript{2} (Sigma-Aldrich) and Cr\textsubscript{2}(SO\textsubscript{4})\textsubscript{3} (Sigma-Aldrich) at different initial pH values (2, 3, 4, 5, and 5.5) were prepared. The pH was adjusted with 0.1 M NaOH or 0.1 M HCl, and 50 mL of each solution at different pH was prepared and 50 mg of biomass was added. The flask were shaken for 7 h at 160 rpm at room temperature (20 ± 1 °C) with a shaker (Lab-Line Instruments, Mistral Multi Mixer, India). Then each solution was filtered with a polyvinylidene difluoride (PVDF) 0.45 μm membrane and was poured into a propylene tube. The samples were analyzed by atomic absorption spectrometry (AAS) (PerkinElmer, Analyst 300, EE.UU.).\textsuperscript{1} The metal adsorption capacity in equilibrium was calculated according to eq 1

\[
q_e = \frac{V(C_i - C_e)}{m}
\]  

where V is the volume of the metal solution (mL), C\textsubscript{i} and C\textsubscript{e} are the initial and equilibrium concentration of metal in solution (mg L\textsuperscript{−1}), and m is the amount of biomass (g).

2.4. Determination of Equilibrium Time. Fifty milligrams of biomass were added in 50 mL of 50 mg L\textsuperscript{−1} Ni(II) or Cr(III) solutions, and the pH of the solutions was adjusted according to the optimum value obtained in Section 2.3. Flasks were shaken at 160 rpm at room temperature (20 ± 1 °C). Samples were taken at 5, 10, 30, 60, 120, and 240 min.

2.5. Biosorption Experiments. The biosorption experiments were carried out in 50 mL polypropylene flasks containing 50 mL of Ni(II) or Cr(III) metal ion solutions at different concentrations whose concentration ranged from 7.5 to 300 mg L\textsuperscript{−1} at pH 5, and 50 mg of algae biomass. The
solutions were maintained in agitation at 160 rpm during the time required to reach the equilibrium (previously determined as described in Section 2.4) at 20 ± 1 °C, which was 240 and 420 min for Ni(II) and Cr(III), respectively. After reaching the equilibrium, the solutions were filtered through a 0.45 μm PVDF membrane. The filtrate was analyzed to determine the final concentration at the end of the process by AAS.

The equilibrium data were adjusted to Langmuir, Freundlich, Redlich–Peterson, Sips, and Toth isotherm models to describe the biosorption phenomena on the *D. antarctica* surface.

### 2.6. Biomass Analysis Postbiosorption

#### 2.6.1. SEM Analysis

Scanning electron microscopy (SEM) micrographs were obtained on a JEOL model 6490-LV microscope. The procedure consists of placing small fragments of the sample on a metallic surface to obtain the maximum contrast in the photograph. The sample is transferred to the SEM chamber, and an acceleration voltage of 5 kV is observed at different magnification (between 100 and 10 000×).

#### 2.6.2. Calorimetric Experiments

Determination of immersion enthalpies were performed using a homemade heat conduction calorimeter (Calvet type). The immersion liquids used for the calorimetric characterization were water and nickel and chromium solutions (300 mg·L⁻¹). To determine the immersion enthalpies, a 0.050 g of biomass was weighed in a glass bulb and then it was attached to the calorimetric cell. Then, 8 mL of the desired solvent was added to the calorimetric cell and the calorimeter was assembled and left then cứ to reach the equilibrium enthalpies, a 0.050 g of biomass was weighed in a glass bulb and then it was attached to the calorimetric cell. The procedure consists of placing small fragments of the sample on a metallic surface to obtain the maximum contrast in the photograph. The sample is transferred to the SEM chamber, and an acceleration voltage of 5 kV is observed at different magnification (between 100 and 10 000×).

#### 2.6.3. Infrared Spectroscopy

The identification of surface groups on the solid was examined by infrared spectroscopy in a Nicolet Impact 410 Fourier transform infrared spectroscopy (FTIR). The sample was pulverized with KBr, and a pellet was formed.

#### 2.7. Adsorption Models

Because of the availability of the software, the linearization of the equilibrium data is used to estimate the parameters of the nonlinear models; however, the transformation of linear nonlinear equations increases the error of the analysis by altering the distribution of the data. The nonlinear regression method is more complex and is recommended for estimation of model parameters.

#### 2.7.1. Freundlich Model

The Freundlich model is described by an empirical equation used for systems with a high degree of heterogeneity. In this model it is assumed that adsorption occurs on a heterogeneous site and also has three parameters taken from the theory of these models, and also has three parameters taken from the theory of these models. The Freundlich isotherm constant can be determined by linearization of the equilibrium data, which is to be evaluated in the adsorption favorability. The values of *n* between 2 and 10 indicate a high adsorption capacity, while values between 1 and 2 indicate moderate adsorption capacity, and values lower than 1 indicate poor adsorption capacity.

The Freundlich isotherm model is described by eq 3

$$Q_e = \frac{q_m K_F C_e^{1/n}}{1 + K_f C_e}$$

where *Q*ₐ is the maximum adsorption capacity of the metal by brown *D. antarctica* algae in equilibrium, *C*ₑ is the concentration of the metal in equilibrium, *K*ᵢ is the Freundlich isotherm constant representing the maximum capacity of biosorption intensity, respectively. The Freundlich constant (*n*₁) depends on the adsorption capacity and is used to evaluate the adsorption favorability. The values of *n*₂ between 2 and 10 indicate a high adsorption capacity, while values between 1 and 2 indicate moderate adsorption capacity, and values lower than 1 indicate poor adsorption capacity.

#### 2.7.2. Langmuir Model

The Langmuir model is based on the assumption that adsorption occurs on a homogeneous site, where each adsorbate molecule occupies an specific adsorption site, and the maximum adsorption occurs with the formation of the complete monolayer, in which, there is no migration of the adsorbate molecules on the adsorbent surface.

The Langmuir isotherm model is described by eq 4

$$Q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$$

where *Q*ₐ is the maximum adsorption capacity of the metal by brown *D. antarctica* algae in equilibrium, *C*ₑ is the concentration of the metal in equilibrium, *K*ₐ is the Langmuir related to the biosorption energy.

#### 2.7.3. Sips Model

The two previous isotherm models have been widely used to analyze the biosorption of various contaminants present in aqueous solutions. The Sips model simultaneously involves the Freundlich and Langmuir models, and also has three parameters taken from the theory of these models and has more capacity to describe the biosorption equilibrium.

The Sips isotherm model is described by eq 5

$$Q_e = \frac{K_{SP} C_e}{1 + a_{SP} C_e^g}$$

where *K*ₚ, (L·mg⁻¹), is the equilibrium Sips constant and *n*ₗ is the heterogeneity factor; a value of *n*₁ close to or equal to 1 occurs in biosorbents with homogeneous active sites, whereas a value of *n*₁ close to 0 occurs in biosorbents with heterogeneous active sites.

#### 2.7.4. Redlich–Peterson Model

Redlich and Peterson include the characteristics of both the Langmuir and Freundlich isotherms in a single equation.

The Redlich–Peterson isotherm model is described in eq 6

$$Q_e = \frac{K_{RP} C_e}{1 + a_{RP} C_e^g}$$

where *K*ₚ is the constant of the Peterson–Redlich model (L·g⁻¹) and *a*ₚ is another constant of the Peterson–Redlich model (mg·L⁻¹) and *g* is the exponent of this model and must be between 0 < *g* < 1.

When *g* = 1 the Redlich–Peterson equation becomes the Langmuir eq 6.

When *g* = 0, the equation of Redlich–Peterson becomes the law of Henry (eq 7).

$$Q_e = \frac{K_{RP} C_e}{1 + a_{RP}}$$

#### 2.7.5. Toth Model

The Toth model presents an asymmetric quasi-Gaussian energy distribution of the adsorption sites, where most sites have lower adsorption energy than the maximum adsorption energy peak. The Toth modifies the Langmuir equation in order to reduce the error between the
experimental data and the data modeled by the adsorption equilibrium. This model fits to heterogeneous systems in which adsorption occurs in multiple layers. The exponent of the Toth isotherm \((n_{T})\) is related to the heterogeneity of the surface, if \(n_{T}\) is equal to the unit, the Toth model is reduced to the Langmuir model; this suggests that the adsorption occurs on a homogeneous surface.\(^{22}\) This correlation is applied for liquid—solid adsorption.\(^{27}\)

The model of the Toth isotherm is reported in eq 8

\[
Q_{e} = Q_{m}C_{e}(b_{T} + C_{e}^{n_{T}})^{-1/n_{T}}
\]

\((8)\)

\(b_{T}\) and \(n_{T}\) are constants of the model.

3. RESULTS AND DISCUSSION

3.1. Physicochemical Characterization of \textit{D. antarctica}. TGA was used to assess the degradation of the biomass under increasing temperature, providing qualitative information on the composition, based on the temperature ranges in which it degraded. The present study applied TGA under N\(_{2}\) (i.e., pyrolysis) (Figure 1).

![Figure 1. TG-TGA of the brown algae \textit{D. antarctica} biomass.](image)

The brown algae \textit{D. antarctica} decomposition occurred in four stages as has been reported in the literature.\(^{16}\) There was an initial mass loss starting at 30 °C until 300 °C, the slope change was associated with a process of desorption of free and anchored water to the matrix of the algae \textit{D. antarctica} and the decomposition of protein, soluble carbohydrates, and hemicellulose. The second temperature interval ranged from 300 to 400 °C describes a strong loss of mass with three differentiated processes; these are related to the rapid decomposition of cellulose, lipids, and insoluble polysaccharides. Subsequently a mass loss was observed in the temperature range of 400–600 °C, the mass loss in this interval has been attributed mainly to decomposition of lignin and insoluble polysaccharide residues. Finally, in the temperature interval ranged from 600 to 800 °C inorganics and residual organics were decomposed. The ash contents of the algae \textit{D. antarctica} was 15% approximately.

Although the nitrogen adsorption isotherms (Figure 2a) are not a conventional method for characterizing algae-type biosorbents, it can be observed that the capacity of nitrogen adsorption is low and as expected has a low area, with a wider pore size distribution centered between 8 and 30 Å (Figure 2b),\(^{17}\) which indicates that the biosorption process will be determined by the establishment of specific interactions between the surface groups and the ions in solution.

The Boehm method is a chemical method to identify surface functional groups, is based on the neutralization of the acid groups present on the surface by using basic solutions of different strength,\(^{18}\) according to the results a concentration of acid groups associated with the presence of carboxylic acids and lactonic and phenolic groups is observed, these groups come from the main compounds of brown algal type \textit{D. antarctica} which include the sulfated polysaccharides, which consist mainly of galactose, methylated sugars, and anhydrides (Table 1).\(^{28,30}\) On the other hand, the most important saccharide structures found in the extracts of these organisms are fucoidans, laminarins, galactans, and alginates. Figure 3 shows some of the possible compounds already determined by other techniques and extraction of these algae, such as \(\pi\)-mannuronic and \(\pi\)-guluronic acids and fucodiphlorethol-EtbI.\(^{28−30}\)

These compounds consist of several functional groups, such as carboxyl, hydroxyl, sulfate, phosphate, and amino groups, which play a very important role in the metal biosorption process. The mechanism of interaction of metal ions and algae biomass will always be affected by the characteristics of the biomass, the species and ionic charges of the metal ions, and other external factors such as pH and temperature of the solution as will be discussed later. According to Boehm titration, the surface groups presented on the biomass surface are mainly acidic, among these the phenolic groups have the higher concentration (1241 \(\mu\text{mol g}^{-1}\)), coherently with the composition of the main structures as mentioned before.\(^{26,30}\)

As for the total basicity parameter (1819 \(\mu\text{mol g}^{-1}\)), it can be attributed to the electron density given by the delocalized \(\pi\) electrons located in the double bonds of the constituents of the algae, as well as to terpene-like structures.\(^{28}\) A higher concentration of weak acid groups with respect to the basic ones, is also related to the point of zero net proton charge reported in the literature for this biomass, which is 5.54.\(^{29}\)

![Figure 2. (a) N\(_{2}\) adsorption—desorption isotherm. (b) Pore size distribution.](image)
3.2. Determination of the Optimum pH for the Adsorption of Ni(II) and Cr(III).

In the pH diagram for the nickel species in aqueous solution presented in Figure 4a, it is observed that in nickel solutions whose pH values are below 8, the Ni(II) species predominates. In the range of pH 8−11, nickel is present in the form of Ni(OH)+. Above a pH of 8.5, a Ni(OH)2 precipitate forms and above pH 11, Ni(OH)3− and Ni(OH)42− anions are formed, which are formed by dissolving the Ni(OH)2 precipitate.31

In the pH diagram for the chromium species in aqueous solution (Figure 4b), it is observed that in a pH higher than 6 the Cr(III) species are hydroxylated and precipitate in the form of Cr(OH)3. In this speciation diagram of Cr(III), the molar distributions of the chromium species according to the pH value are distributed as follows: Cr3+ (∼90%), CrOH2+ (∼10%) at pH 3; Cr3+ (∼40%), CrOH2+ (∼60%) at pH 4; and Cr3+ (∼5%), Cr(OH)2+ (∼70%), and Cr(OH)3+ (∼20%) a pH 5.32,33

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The progressive increase in the adsorption capacity at acidic pH is associated with the surface charge of the biosorbent. At low pH there is a high positive charge density because of the high concentration of protons on the surface. This produces a high electrostatic repulsion during the adsorption of the metal ions, decreasing the adsorption capacity of these pollutants. By increasing the pH the electrostatic repulsion decreases because...
of the reduction of the positive charge density at the sorption sites, this can improve the adsorption of metal ions.\textsuperscript{36} This effect was observed in the two metal ions studied because they have similar physicochemical properties such as low electronegativity, close ionic radius, and positive electronic charge.

In this work, simple and competitive adsorption tests were performed on the ions; therefore, the subsequent adsorption tests were performed at a pH of 5 for both compounds [Ni(II) and Cr(III)], in order to obtain comparative results.

\textbf{3.3. Determination of the Equilibrium Time for the Bioadsorption of Ni(II) and Cr(III).} Figure 6a shows the progress of the Ni(II) adsorption process on the surface of \textit{D. antarctica} as a function of time; as expected, as the time elapses, \( Q_t \) increases until 120 min. \( Q_t \) obtained for the times of 120 and 240 min are significantly different, indicating that the adsorption equilibrium is reached at a time of 120 min and then a desorption process occurs. Figure 6b shows the change of \( Q_t \) for the Cr(III) ion as a function of time, in the first 240 minutes it is fast, subsequently it could be observed that the retention process continued but to a much lesser extent until 420 min; therefore, the subsequent experiments of adsorption of the Cr(III) and Cr(VI) ion were carried out for further 420 min.\textsuperscript{14}

\textbf{3.4. Bioadsorption Isotherms: Mechanisms and Theoretical Treatment of Data.} The starting and postbiosorption biomass were analyzed using FTIR, SEM, and immersion calorimetry in order to correlate the changes observed in the biomass and the possible mechanism by the biosorption process like it is discussed below.

\textbf{3.4.1. FTIR Analysis.} The starting and postbiosorption solids were analyzed using FTIR (Figure 7). The biomass spectrum before the biosorption process presented six predominant peaks, at 3510 cm\(^{-1}\) attributed to stretching vibrations of \( \text{−OH} \) and \( \text{−NH} \) groups, 2930 and 1335 cm\(^{-1}\) attributed to stretching and bending of methyl groups (\( \text{−CH}_3 \)), respectively. 1642 cm\(^{-1}\) attributed to stretching vibrations of \( \text{−COOH} \) groups, 1264 cm\(^{-1}\) attributed to stretching vibrations of the \( \text{−C−O−C} \) bonds and finally at 1053 cm\(^{-1}\) attributed to stretching vibrations of the bonds \( \text{−C−O} \) of aliphatic groups. The spectrum of the exhausted biomass (after the biosorption process) revealed a few changes in the intensities and frequencies of some peaks; this can suggest that these functional groups are involved in the interactions and mechanism of adsorption. For example, the peak at 3510 cm\(^{-1}\) shifted to lower frequencies in both cases (Ni(II) and Cr(III) biosorption), suggesting that \( \text{−OH} \) and \( \text{−NH} \) groups are involved in ion metal uptakes.\textsuperscript{37}

\textbf{3.4.2. SEM Analysis.} The starting and postbiosorption solids were analyzed by SEM–EDX (energy dispersive X-ray spectroscopy) with this technique high-resolution black and white images were obtained that make it possible to study the morphology and also the elemental analysis of the surface before and after the biosorption process. The SEM micrographs in Figure 8a–c show the images obtained for the raw solid, which has an irregular and rough surface with some cavities that provide the surface area for interaction with ions in solution. In contrast, SEM micrographs in Figure 8d–g show the Ni(II) and Cr(III) exhausted biomass, respectively, with considerable differences in the raw solid morphology, and it is possible to observe homogenous open cavities with a diameter of around 20 \( \mu \text{m} \). The change in the structure indicates that ions could interact with the surface and produce the opening of the cavities.\textsuperscript{37}

The changes on elemental composition can be evaluated by the EDX spectrum, and the biosorption process of chromium in the surface of this material can be evidenced given that in the analysis area there is a chromium percentage of 20.07%; in contrast, the EDX analysis of the algae micrograph submitted to the nickel biosorption process shows a percentage of 26.70%. The EDX was performed at the same magnification of the image of the biomass area.

\textbf{3.4.3. Immersion Calorimetric Experiments.} To study and understanding of biosorption process in a liquid–solid as in the case study interface one must know the texture and chemical properties of the adsorbent, it is also necessary to know how the solid behaves in a liquid medium considering that some changes may occur when the adsorbent is immersed in a pure liquid or a solution. For this reason, it is necessary to use special methods that provide direct information on the liquid–solid particular interactions; immersion microcalorimetry has been used for this purpose. The parameter that is evaluated by immersion microcalorimetry is the immersion

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Figure 6. Determination of the equilibrium time of bioadsorption of (a) Ni(II) and (b) Cr(III) on the surface of \textit{D. antarctica}. \( Q_t \) corresponds to the adsorption capacity of metals at different times 5, 10, 30, 60, 120, 240, and 420 min at optimum pH.

Figure 7. IR spectra of the biomass before and after the biosorption process of Ni(II) and Cr(III) on the surface.
enthalpy ($\Delta H_{imm}$). The enthalpy change describes the exchange of heat that occurs in every physical or chemical process; therefore, it is a fundamental thermodynamic quantity that describes the amount of heat released or absorbed during the course of the study process. Specifically in the adsorption process the enthalpy represents the total energy change in the whole process, which includes different stages related to the heat of wetting, the energy necessary for the desolvation of the sites, and the energy change after adsorbate bonding.

Figure 9 shows the comparison of the calorimetry peaks generated by immersing an inorganic solid such as granular activated carbon in benzene and biomass in a chromium solution of 300 mg L$^{-1}$. For granular carbon, a large peak originates and the equilibrium is reached again around 300 s, while the biomass releases less heat when it interacts with the chromium solution and the equilibrium is achieved after approximately 2100 s, this has been attributed to its chemical properties of a natural biosorbent, as is its increase in size when absorbing a liquid.

Table 2 summarizes the results obtained from immersion calorimetry in water and in chromium and nickel solutions, the concentrations correspond to the highest concentration studied in the biosorption isotherms.
Table 3. Adjustment Parameters to the Models of the Freundlich, Langmuir, Redlich–Peterson, Sips, and Toth Isotherms for the Adsorption of Ni(II) and Cr(III) on the Surface of D. antarctica

| models              | parameter | nickel   | chromium |
|---------------------|-----------|----------|----------|
| Freundlich          | $K_f$     | 1.289    | 24.95    |
|                     | $n_f$     | 1.597    | 3.236    |
|                     | $R^2$     | 0.941    | 0.871    |
| Langmuir            | $Q_m$     | 51.28    | 100.2    |
|                     | $K$       | 0.009    | 0.169    |
|                     | $R^2$     | 0.942    | 0.962    |
| Redlich–Peterson    | $K_{SP}$  | 0.542    | 10.24    |
|                     | $a_{SP}$  | 0.029    | 0.023    |
|                     | $G$       | 0.816    | 1.352    |
|                     | $R^2$     | 0.943    | 0.983    |
| Sips                | $Q_m$     | 0.001    | 12.33    |
|                     | $K_f$     | 3522     | 157.0    |
|                     | $n_f$     | 0.505    | 0.651    |
|                     | $R^2$     | 0.955    | 0.984    |
| Toth                | $Q_m$     | 110.8    | 90.58    |
|                     | $b_{T0}$  | 14.57    | 75.70    |
|                     | $n_T$     | 0.531    | 2.045    |
|                     | $R^2$     | 0.943    | 0.974    |

From the Langmuir model it is possible to estimate the maximum metal uptake values; these were 51.3 and 100.2 mg g$^{-1}$ for Ni(II) and Cr(III), respectively. The capacity of adsorption can be affected by the physicochemical characteristics of the ions in this case a higher density of positive charge and lower ionic radius of chromium (0.69 Å) favors the adsorption on an ion such as nickel with an ionic radius of 0.78 Å. The coefficient related to the affinity between the biosorbents and the ion (K) is also studied in the Freundlich model, for K high values indicate a high affinity for the biosorbents and the ion metal and show a steep initial slope in the isotherm plot, as in the case of the chromium isotherm. 22

Table 4 it is observed that the Sips model has the best fit to the Ni(II) and Cr(III) biosorption data. The $R^2$ obtained for this model was 0.955 and 0.984 for Ni(II) and Cr(III), respectively. This model is based on the assumption that each
adsorption site interacts with a single molecule or ion of the adsorbate.\textsuperscript{39} It is also known that this model adjusts to low and high concentrations of metal ions where the interactions of the metal with the adsorbent are different and as their concentration decreases the interaction with the surface of the biomass also decreases. Indicating that the biosorption on the surface of the algae \textit{D. antartica} occurs in the interaction sites distributed heterogeneously. The \( n \) parameter of the Sips model obtained with the Ni(II) adsorption data is 0.505 and 0.651 for Cr(III) isotherm because this mean value is between zero and one, and it can be said that the degree of homogeneity/heterogeneity of the adsorption sites describes a greater concentration of groups superficial with the same capacity of adsorption in terms of energy.

### Table 4. Comparison of the Capacity of Adsorption of Ni(II), Cr(III), and Cr(VI) on the Surface of the Dead Biomass

| sample                  | specie (°C) | competitive system | pH  | \( Q_e \) (mg g\(^{-1}\)) | refs   |
|-------------------------|-------------|--------------------|-----|--------------------------|--------|
| Sargassum ilicifolium   | Ni(II)      | Zn(II) Cu(II)      | 5.0 | 133.8                    | 1      |
| living plants of        | Cr(VI)      |                    | 6.0 | 109.2                    | 2      |
| Salvinia minima         | Cr(VI)      |                    | 6.0 | 124.8                    | 2      |
| fern Asplenium nidus L. | Ni(II)      |                    | 9.2 | 4                        | 4      |
| Hydrilla verticillata   | Ni(II)      |                    | 29.4| 6                        | 6      |
| Salvinia auriculata s   | Cr(VI)      |                    | 4.4 | 2                        | 7      |
| Typha domingensis       | Ni(II)      |                    | 6.0 | 4.51                     | 8      |
| Fenton modified         | Ni(II)      |                    | 4.0 | 87.18                    | 12     |
| Hydrilla verticillata   | Ni(II)      | Ni(II)–Cr(III)     | 5.0 | 51.28                    | Present work |
| D. antarctica biomass   | Cr(VI)      | Ni(II) Ni(II)–Cr(III) | 100.2 |                        |        |
|                         | Cr(VI)      | Ni(III)–Cr(VI)     | 100.2 |                        |        |

Figure 11. (a) Competitive adsorption between Ni(II) and Cr(III) at a pH of 5 and a time of 420 min (b) competitive adsorption between Ni(II) and Cr(VI) at a pH of 5 and a time of 420 min. For both isotherms the concentration of Ni (II) was in the range between 7.5 and 300 ppm, while the concentration of Cr(VI) and Cr(III) remained constant at a value of 100 ppm.

Next, the effect of a competitive ion is evaluated, in Figure 11a the results obtained when performing the competitive adsorption tests between Ni(II) and Cr(III) are presented. This figure shows the effect on the \( Q_e \) of chromium on the algae \textit{D. antarctica} as the concentration of Ni(II) increases. At low concentrations of Ni(II) the \( Q_e \) of this ion is low and there is a high adsorption of Cr(III), as the concentration of Ni(II) increases, the \( Q_e \) of Cr(III) decreases and increases the \( Q_e \) of Ni(II). Considering that the interaction of the functional groups of \textit{D. antarctica} is influenced by the concentration of the metal ions present in the aqueous solution. As noted above, the adsorption behavior of the cations of these metals on \textit{D. antarctica} is not similar because of the differences in their physicochemical properties, such as electronegativity, ionic radius, and electronic charge. The Sips model presents the best fit to the data obtained in nickel competitive adsorption, the \( R^2 \) value when applying this model was 0.971.

Figure 11b shows the results of the competitive adsorption between Ni(II) and Cr(VI). In this experiment, it was found that the adsorption of nickel is favored by the presence of the Cr(VI) ion because the \( Q_e \) value of Ni(II) in this experiment is greater than the value obtained in the simple adsorption. On the other hand, the \( Q_e \) of Cr(VI) reached small values even when the initial concentration of Ni(II) was below 7.5 ppm and decreased as the concentration of Ni(II) increased to 300 ppm (Figure 11b). The interactions of the functional groups present on the surface of the algae \textit{D. antarctica} with the metal ions favor the adsorption of the Ni\textsuperscript{2+} ion. The Sips model presents the best fit to the data obtained from Ni(II) adsorption, with a \( R^2 \) value of 0.997.

For all the isotherms, it is observed that when the initial concentration of the ion increases between 7.5 and 300 mg L\(^{-1}\) the capacity of adsorption increases because of the progressive occupation of the adsorption sites until the complete saturation of the adsorbent. According to the above observation, it can be concluded that dynamic equilibrium are influenced by the initial concentration. This behavior is explained by the increase in the driving force of the concentration gradient.\textsuperscript{43}

The Sips model presented the best fit to the data obtained in the simple adsorption of Ni(II) and Cr(III) and in the
competitive adsorption of the Ni(II) ion with Cr(III) and/or Cr(VI). The model of this isotherm incorporates the characteristics of Langmuir and Freundlich models. At low concentrations, the Sips model is reduced to the Freundlich isotherm, indicating that the adsorption of Ni(II) on the surface of D. antarctica was heterogeneous, while, at higher concentrations, this model predicts adsorption in the monolayer characteristic of the Langmuir isotherm. This model is valid when working at low and high concentrations of Ni(II).

3.6. Mechanisms of Bioadsorption. As mention above, the cell wall of brown algae is majorly composed of cellulose—hemicellulose and alginic acids in polymers structures which interact with alkali and alkali-terreous ions and other polysaccharides such as fucoidans and phlorotannins. Figure 12 illustrates the biosorption of Ni(II), Cr(III), and Cr(VI) metal ions which involve different mechanisms including: electrostatic attraction, cation exchange, formation of superficial metal complexes and hydrogen bond with alginates and phlorotannins, and microprecipitation. In general, it can be said that the Ni(II), Cr(III), and Cr(VI) adsorption data obtained experimentally in the present study show a good agreement with the data found in the literature (Table 4).

4. CONCLUSIONS

In this work, it was found that D. antarctica is an excellent biosorbent of Ni(II) and Cr(III). It was determined that the optimal conditions for carrying out the adsorption of metals is given at a pH of 5 and at a time of 240 and 420 min for Ni(II) and Cr(III), respectively. Under these conditions, the Q value for Ni(II) and Cr(III) was 32.85 and 102.7 mg g$^{-1}$, respectively. The change in the adsorption of ions in competitive systems showed that both Ni(II) and Cr(III) compete for the same adsorption sites on the surface of D. antarctica; although the physicochemical properties of Ni(II) and Cr(III) are similar, the adsorption of the ions favors the increase of its concentration and a lower ionic radius, while the Ni(II) and Cr(VI) ions present significant differences in their physicochemical properties, favoring the adsorption of Ni(II) independent of its concentration.

Figure 12. Schematic illustration of the main biosorption mechanism of Ni(II), Cr(III), and Cr(VI).

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Notes
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