

Recovery of Copper from Leached-Tailing Solutions by Biosorption

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Abstract

Mining is one of the main economic activities of several developing countries as Chile. Due to the progressive fall of the ore grades and the increasingly refractory composition of minerals, concentrating plants have increased that has led to an increase in the generation of tailings. Tailings, especially those obtained in the past, have remaining copper and other valuable species in quantities that can potentially be recovered, such as gold, silver, vanadium and rare earth elements. This transforms this abundant waste into a potential source of precious or strategic metals for secondary mining. One of the techniques of solid-liquid separation that allows the processing of solutions with low concentrations of metals corresponds to the adsorption, and more recently the biosorption, which is based on the use of biological matrices that do not constitute an environmental liability after application. Biosorption occurs as a consequence of the wide variety of active functional groups present in the different types of biomass. Bacterial, fungal, plant and algal biomasses have been described as biosorbents, mainly for the treatment of diluted and simple solutions. This work aims to recover copper from leached tailings using biomass of the red algae *Gracilaria chilensis* as a biosorbent. The tailing samples were taken from an abandoned deposit in the north of Chile and after an acid leaching copper was biosorbed, for which the kinetics of adsorption and the equilibrium isotherms were studied, applying the Freundlich and Langmuir models. Operational parameters such as adsorbent dose, pH and initial metal concentration were studied.

Keywords: biosorption; copper; algae; tailings; mine waste

1. Introduction

It is well known that Chile is a country that supports much of its economy in mining activity, representing a contribution of 13% to its GDP. Among the minerals in which Chile occupies a leading position are copper, lithium, iodine, silver and molybdenum. In the case of copper, 31% of the metal traded in the world comes from Chile (5,700,000 Mt), and half of this amount is obtained from the region of Antofagasta, which makes it a strategic region for the country development (COCHILCO, 2017; US Geological Survey (USGS), 2015).

In the current context, the copper ore grades are increasingly low, and in more refractory forms, therefore mining operations have increased the amount of processed material, producing larger volumes of unprocessed low-grade ores that are below cut-grade. Additionally, the installation of new concentrating plants or expansion of the existing ones has increased the generation of tailings. According to the latest cadastre, there are 740 tailings deposits in Chile and 51 in Antofagasta (Figure 1), of which 72% are inactive or abandoned and with an estimated amount of 520 Mt (SERNAGEOMIN, 2018).

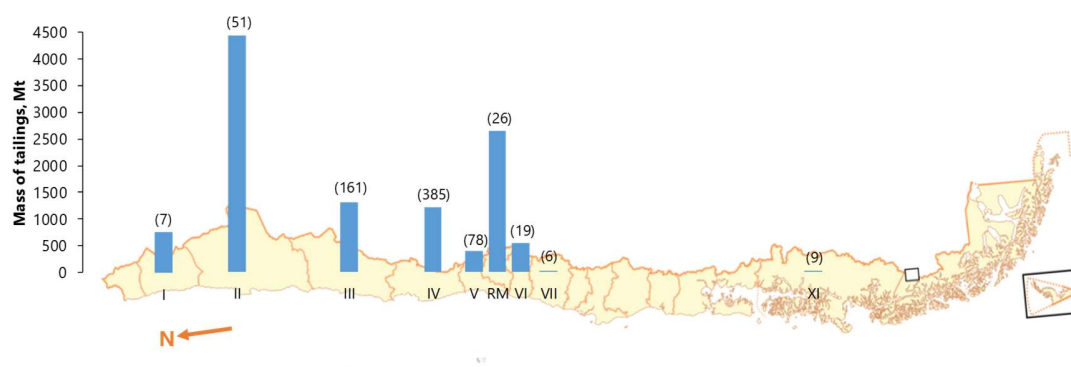


Figure 1. Discarded tailings in Chile are significantly predominant in the northern. The numbers in parenthesis denote the quantity of tailing deposits in each region of Chile (SERNAGEOMIN, 2018).

The prosperity of Chile, as in every mining-based country, is closely linked to the availability of exploited resources, their demand and international prices. Thus, the decrease of the so-called copper price super-cycle results in a considerable drop in the national incomes and, therefore, opens space for the development of new technologies that improve yields and reduce production costs, as well as the evaluation to process new mineral resources as the wastes (tailings and low-grade ores) produced extensively by the mining operations. Although tailings are depleted in the element extracted during the flotation, they still have many other valuable species that potentially can be recovered, transforming this discarded resource in an interesting secondary raw material. In Chile, the processing of tailings for the extraction of minerals is incipient, but with an emerging potential, since chemical and mineralogical analyses of some tailing deposits have detected the presence of valuable metals in quantities that would eventually allow their extraction and with attractive prices for their processing, such as copper, zinc, vanadium, strontium, silver and, even, rare earths as lanthanum and yttrium (CORFO, 2013; Rojas, 2003; SERNAGEOMIN, 2018).

On the other hand, macroalgae represent a diverse group of eukaryotic, photosynthetic marine organisms widely distributed throughout the world's oceans that are classified into three divisions based on their pigmentation: brown (Phaeophyta), red (Rhodophyta) and green (Chlorophyta). The colour is given by the predominance of one pigment on the others; thus, for example in the case of the brown algae the presence of fucoxanthin, a pigment that protects from sunlight, masks the colour of chlorophylls a and c, betacarotenes and other

xanthophylls. As reserve substances, the seaweeds have high molecular weight polysaccharides, being the principal laminarins, alginates, fucanoids, carrageenans and agars. The walls of the macroalgae cells are composed of cellulose and alginic acid (Gómez-Ordóñez et al., 2010).

The seaweeds are used as food since ancient times, mainly by China, Japan and the Republic of Korea. Additionally, other of the relevant uses of the seaweeds are the extraction of the phycocolloids: alginate, agar and carrageenan, which are used as thickening and gelling agents that have a broad spectrum of industrial applications in pharmaceuticals, cosmetic, food industry and agriculture (Gómez-Ordóñez et al., 2010). Approximately 1 Mt of fresh seaweed is now annually harvested to extract 55,000 t of these phycocolloids valued at US\$585 million. Particularly, the production of alginate (US\$ 213 million) and agar (US\$ 132) is made from extracts of brown and red algae, respectively (McHugh, 2002). Chile is one of the first agar producers in the world, supplying 10% of the global biomass for agar and alginates (Bixler and Porse, 2011; Vásquez et al., 2012).

The global catches of seaweeds for phycocolloids production are led by Chile, with 51.3% (McHugh, 2003, 2002; Rebours et al., 2014). The extensive Chilean coast provides a wide diversity of brown and red algae species, being the most relevant in order of economic importance: *Gracilaria chilensis* (Pelillo), *Lessonia nigrescens* (Black Huiro), *Lessonia traberculata* (Huiro palo) and *Macrocystis pyrifera* (Huiro) (Buschmann et al., 2004; Santelices, 1989). According to FAO (2011), Chile was the world's largest producer of seaweed outside Asia. In 2016, the total of brown and red algae collected in Chile was about 260,000 t (SERNAPESCA, 2016).

Although the use of activated carbon as adsorbent has demonstrated to be the best method for the recovery of metals, its high cost and difficult to regenerate results in an unpractical application for the treatment of large volumes or diluted effluents, in this context, biosorption emerges as a cost-effective and efficient alternative for removal of heavy metals from wastewaters. Living and dead biomass of microorganisms, fungi, micro and macroalgae and plant extracts have been used as biosorbent for the recovery of metals from industrial effluents such as lead, cadmium, zinc, copper, chromium, gold and silver (Cui and Zhang, 2008; Michalak et al., 2013).

Biosorption is a rapid and reversible ion-binding process due to is independent of cellular metabolism; therefore dead biomass can be used (Vijayaraghavan and Yun, 2008; Volesky, 2007). Some of the advantages of biosorption are the possibility to store the adsorbents for an extended period of time, no toxicity effects by high metal concentrations, have no nutrient limitations, the metals captured can be readily desorbed, the application can be performed over a wide range of pH (3-9) and temperature (4-90°C) (Baysal et al., 2009; Gadd, 2009; Sathishkumar et al., 2010; Selatnia et al., 2004). Other advantages of this process that is a clean and simple alternative for the recovery of metals in non-concentrated solutions, low capital investment costs and that these biological materials are renewable, cheap and

can be obtained from agriculture, aquaculture or industrial waste (Davis et al., 2003; Kuyucak, 1990).

Among the studied biosorbents, macroalgae are a promising group since the complex mucilaginous polysaccharides on their cell walls (alginates and fucoidans) have a high affinity for di and trivalent cations (Figure 2) (Figueira et al., 1999; Fourest et al., 1994; Khoo and Ting, 2001). The most abundant functional groups related to the interaction with metals by macroalgae are carboxyl, amino, phosphate, hydroxyl, sulfhydryl and sulfonate (Raize et al., 2004; Volesky, 2007). The use of seaweeds for the biosorption has been validated mainly for wastewater treatment, preferably from diluted or pure solutions (Mata et al., 2009, 2008; Romera et al., 2007; Volesky, 2007). Plaza Cazón et al. (2012) used *Macrocystis pyrifera* to remove zinc and cadmium from wastewater, demonstrating its good uptake capacity and similar to other macroalgae species such as *Sargassum filipendula*, *Gymnogongrus torulosus* and *Fucus vesiculosus*, which are reported in previous works (Luna et al., 2010; Mata et al., 2008). The same group evaluated the use of *M. pyrifera* and *Undaria pinnatifida* for the chromium and mercury biosorption from aqueous solutions, demonstrating that the carboxylic and amino groups are strongly involved in chromium binding, while amino and sulfhydryl for mercury uptake (Plaza Cazón et al., 2012b, 2011).

An important aspect to consider is that biosorption is a surface process and the metal biosorbent interaction mechanism may be physical by electrostatic interactions and Van der Waals forces, or chemical by ion exchange, proton shift, complexation and chelation (Crist et al., 1999; Davis et al., 2003; Raize et al., 2004; Volesky, 1990). The factors that have an influence on the biosorption and that are related to the physicochemical properties of metals are concentration, molecular weight, ionic radius and oxidation state. Moreover, other properties of the biosorbents and the operational conditions such as pH, temperature and biosorbent concentration also have importance on the process performance. Among all the influencing factors, pH is one of the most important due to controls the ionic dissociation and speciation of sites and metals in the solution (Esposito et al., 2002; Gavrilescu, 2004; Yang and Volesky, 1999). The wide variety of active functional groups in algae biomass would result in a diverse range of adsorption mechanisms, for this reason, different metals and quantities of metals can be obtained with different biosorbents (Goyal et al., 2003).

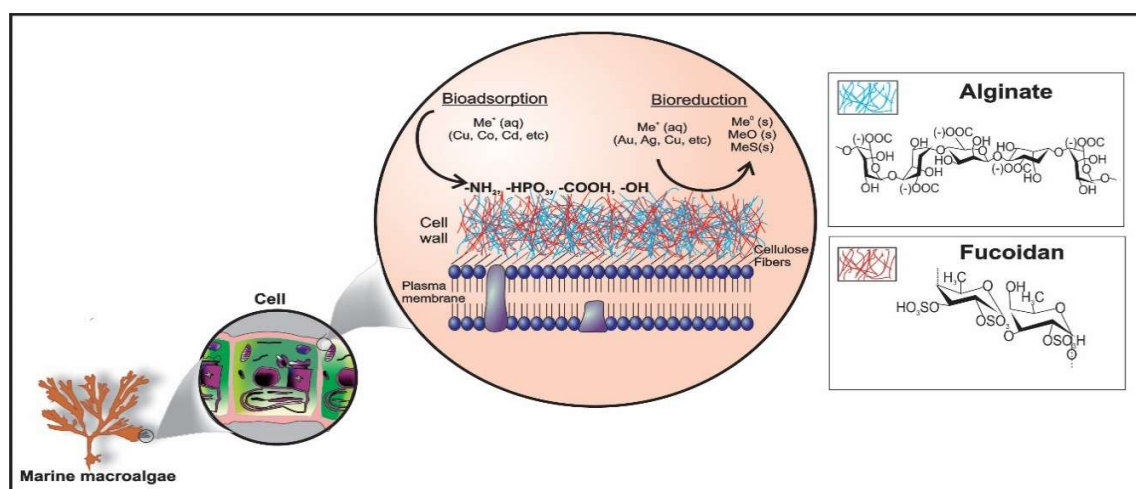


Figure 2. Most abundant polysaccharides containing brown and red algae: alginate and fucoidan, which are related to the metal biosorption process.

It has also been described that biosorption can lead to metal bioreduction, where some of the compounds forming the cell walls react with metal ions and converts them to its elemental form, producing tiny particles of metal named as nanoparticles (Gamez et al., 2000; Gericke and Pinches, 2006; Torres et al., 2005). Metal nanoparticles have a great scientific and technological interest because they have unique optoelectrical and physicochemical properties, which are given by their crystallographic and morphological characteristics. The use of nanoparticles is playing an increasingly important role in the development of new key technologies applied to electronics, catalysis, drug release, cancer therapy, detection and gas monitoring (Castro et al., 2013; Mack et al., 2007; Mandal et al., 2005).

In this work, the biomass of the red algae *Gracilaria chilensis* was used as biosorbent to recover copper from leached mining tailings. The tailings samples were taken from an abandoned deposit in the north of Chile and after an acid leaching copper was adsorbed, for which the kinetics of adsorption and the equilibrium isotherms were studied, applying the Freundlich and Langmuir models. Operational parameters such as adsorbent dose, pH and initial metal concentration were also optimised.

2. Materials and methods

2.1 Tailings and biomass

Samples of tailings deposits located in the commune of Taltal, Antofagasta, Chile, were taken in two sampling campaigns. In the deposit, the first 15 cm of surface material was discarded to rule out potential noise in the composition. The granulometry of the tailings was characterized by sieving, using the 0.064-0.71 mm size fraction.

The samples were taken and conducted to dependencies of the University of Antofagasta, where it was homogenized, using a Jis shovel. A representative section of each sample was obtained and subsequently chemically and mineralogically analysed. The chemical analysis of the mineral was performed by ICP-MS and the mineralogical content was obtained by X-ray diffraction (XRD)

In this investigation, biomass of the red alga species, *Gracilaria chilensis* was used. The seaweed was collected from the coast of Mejillones, Antofagasta, Chile, from an experimental centre of repopulation of this marine species. This alga once collected was sun-dried for two days and subsequently washed with distilled water to eliminate adhering remains. The samples were left to dry in a stove at 60°C for 12 h.

For the characterization of the biomass infrared spectroscopy by Fourier transform (FT-IR) was used. The analysis showed the presence of ionisable functional groups (carboxyl, hydroxyl and amino) capable of interacting with protons or metal ions. Furthermore, the band assignments of the FTIR for typical functional groups present in biomass are illustrated in Table 1.

Table 1. Vibrational stretches of functional groups related to biosorption (He and Chen, 2014).

Functional groups	Formula	Wavenumber (cm ⁻¹)
Hydroxyl	-OH	3200-3600
Carboxyl	-COOH	1670-1760(C=O); 1000-1300(C-O)
Carboxylate	-COOM	1400-1650
Amine	-NH ₂ , -R ₂ NH	3200-3500 (-NH); 1500-1650(C-N and N-H)
Sulphur	-SO-	1000-1400; 1000-1300(-SO ₃)
Phosphorous	-PO-	1000-1400
Carbonyl	-HC=O, R ₂ C=O	1680-1750 (C=O)
Alcoholic	-R ₃ C-OH	1000-1200 (C-O)
Nitro	-NO-	400-700
Methyl, methylene	-CH ₃ , -CH ₂ -	2800-3000

2.2 Mineral leaching

For leaching of ore tailing, in a beaker, 500 mL of sulphuric acid 1 M is contacted with 16 g of tailings. The leaching was carried out in 4 h, on a mechanical stirrer at 500 rpm and the obtained solution (named as PLS) was used to leach a new load of fresh tailing ore under the same conditions. Five leaching-cycles of 4 h were carried out in order to increase the concentration of copper for the subsequent bioadsorption tests. Chemical analysis of copper and iron from solutions was performed by atomic absorption spectrometry (AAS).

In order to remove iron, which is the main interferent species in biosorption, the final PLS was treated by adding NaOH 2 M until reaching a pH 4, point where the iron precipitates as

$\text{Fe}(\text{OH})_3$ and the copper remains in the solution, according to the equilibrium curves of pH vs. Eh (Figure 3). The solution was decanted for 10 h, and the liquid fraction was recovered for the biosorption experiments. Samples for chemical analysis of copper and iron were taken before and after the precipitation.

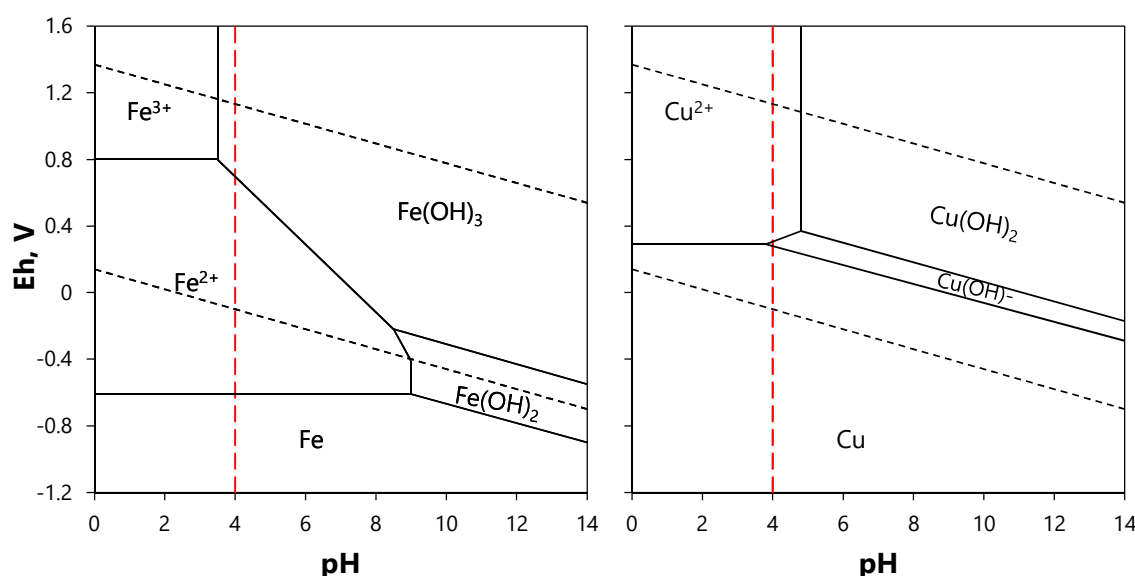


Figure 3. Pourbaix diagram for a) iron and b) copper at 25 °C. Vertical lines at pH 4 denotes the precipitating condition used in the treatment of PLS.

2.3 Batch bioadsorption procedure.

To pre-treat the biomass, 20 g of dried alga was suspended in 400 mL of CaCl_2 0.2 M with stirring at 150 rpm for 4 h. pH 5 was maintained with NaOH 0.1 M. The sample was washed several times with deionized water to remove excess calcium, filtered and dried for 12 h at 60°C.

In a first approach, kinetic study for biosorption process were conducted using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ solutions at defined copper concentrations of {2, 20, 40, 100, 200 and 400} mg/L, 1 g/L biomass and pH 3. Subsequently, in a second stage, batch biosorption experiments for synthetic and actual leached-tailing solutions were carried out using 50 mL of solution (200 mg/L for synthetic solution and 150 mg/L for PLS solution). The pH 1.5 was adjusted for each solution with NaOH and H_2SO_4 0.1 M. Biomass dosage of 0.5 g/L was added, and agitated at 160 rpm in an orbital shaker for 8 h at room temperature. Finally, the solution was filtered, and chemically analysed by AAS for copper. The biosorption of metal, q , was calculated from the mass balance of the sorption system (Eq. 1).

$$q = \frac{V(C_i - C_f)}{W} \quad (1)$$

Where V is the volume of the solution (L), W is the amount of dry biomass (g), C_i and C_f are the initial and final concentrations of the metal (mmol/L), respectively.

2.4 Desorption

The biomass used in the biosorption experiments was filtered and added to an Erlenmeyer flask with 50 mL of desorbing agent: hydrochloric 0.1 M and sulphuric acid 0.05 M. Desorption was conducted for 90 and 180 minutes at 160 rpm in an orbital shaker. Finally, the treated biomass was washed with distilled water and calcium chloride to reactivate the biomass and reuse for another biosorption cycle.

The performance of the reused biomass in each adsorption-desorption cycle was evaluated calculating an effectivity rate (%DA) by Eq. (2).

$$\%DA = \frac{M_{des}}{M_{ads}} * 100 \quad (2)$$

where M_{des} and M_{ads} are the amount of metal ion in solution after desorption and the amount of metal initially biosorbed by biomass (mg or mmol), respectively.

2.5 Kinetics of the bioadsorption process.

The study of the kinetics of the biosorption process allows determining the time it takes for the system to reach equilibrium and the speed of union of the ions to the active external and internal centres of the biosorbent. Different physical and chemical models are used to study the biosorption equilibrium. These models relate the amount of metal adsorbed per unit mass of the adsorbent (q) with the remaining concentration of the metal in solution (C_e).

The most applied models in biosorption, due to their simplicity, predictive capacity and goodness of fit are the Freundlich and Langmuir expressions. The Freundlich model assumes that it adsorbs a single layer of solute onto the surface of the adsorbent being able to establish adjacent interactions between the molecules that are adsorbed and a heterogeneous distribution of the adsorption sites due to the diversity of the binding sites as well as the nature of the adsorbed metal ions. The Langmuir model, meanwhile, supposes a single layer of adsorption with a homogeneous distribution of both the adsorption sites and the adsorption energies without interaction between the adsorbed molecules. Freundlich equation is expressed through Eq. (3).

$$q = kC_e^{1/n} \quad (3)$$

Where k (L/g) and n are the Freundlich constants related to the adsorption capacity and the adsorption intensity of the biosorbent by the metal, respectively. A normal biosorption reaches values of $1/n$ below one. On the other hand, Langmuir equation is represented by Eq. (4).

$$q = \frac{q_{max}bC_{eq}}{1 + bC_{eq}} \quad (4)$$

Where q_{max} indicates the maximum adsorption capacity of the metal ion by the biosorbent (mmol/g), b indicates the affinity of the biosorbent for the metal (L/mmol).

In order to represent the biosorption results by the adsorption models, the kinetic parameters b , k , n were fitted by the least squared method. The differences between q_{exp} and q_{mod} were considered as denoted in Eq. (5). Where q_{exp} is the experimental metal uptake, q_{mod} is the modelled uptake and \bar{q}_{exp} correspond to the mean of experimental uptake.

$$R^2 = 1 - \frac{\sum (q_{exp} - q_{mod})^2}{\sum (q_{exp} - \bar{q}_{exp})^2} \quad (5)$$

3. Results and discussions

3.1 Characteristic of tailing sample

From the chemical analysis, the composition of main metal species is shown in Table 2, where aluminium and iron are the most abundant metal elements. The tailing has a copper concentration above 2400 mg/L, which is considered high for a residual waste. This is due to the used tailing comes from an old deposit and was produced by less efficient processes of ore flotation.

Table 2. Chemical composition of main metals in the ore tailing.

Major metals (%)							Minor metals (mg/L)						
Al	Fe	K	Ca	Mg	Na	Ti	Cu	Mn	P	Ba	Zn	Ce	Sr
8.4	6.0	4.1	2.8	2.3	1.3	0.4	2425	1520	1370	760	252	234	201

The mineralogical analysis suggests that the most abundant species in tailings samples correspond to quartz and other silicates, and copper is present in low quantity as oxidized species (Table 3).

Table 3. Mineral composition of the SOTRN tailing.

Mineral (crystalline phase)	Formula	%
Orthoclase	KAlSi ₃ O ₈	22.2
Chlorite (1MIIb)	(Mg ₅ Al)(Si,Al) ₄ O ₁₀ (OH) ₈	20.2
Albite	NaAlSi ₃ O ₈	17.7
Quartz	SiO ₂	14.0
Muscovite (1M)	KAl ₂ (Si ₃ Al)O ₁₀ (OH) ₂	5.7
Phlogopite	KMg ₃ (Si ₃ AlO ₁₀)(OH) ₂	5.4

Halite	NaCl	4.5
Calcite	CaCO ₃	2.5
Chalcoalumite	CuAl ₄ SO ₄ (OH) ₁₂ ·3H ₂ O	2.0
Magnetite	Fe ₃ O ₄	2.0
Gypsum	CaSO ₄ ·2H ₂ O	2.0
Others	-	<2.0

The particle size distribution is given in Figure 4, where it can be observed that around 50% of the mass is particles smaller than 94 μm , and 40% is smaller than 64 μm . This reflects that this tailing is a very fine material, and conducting the decision to treat it subsequently by agitated leaching.

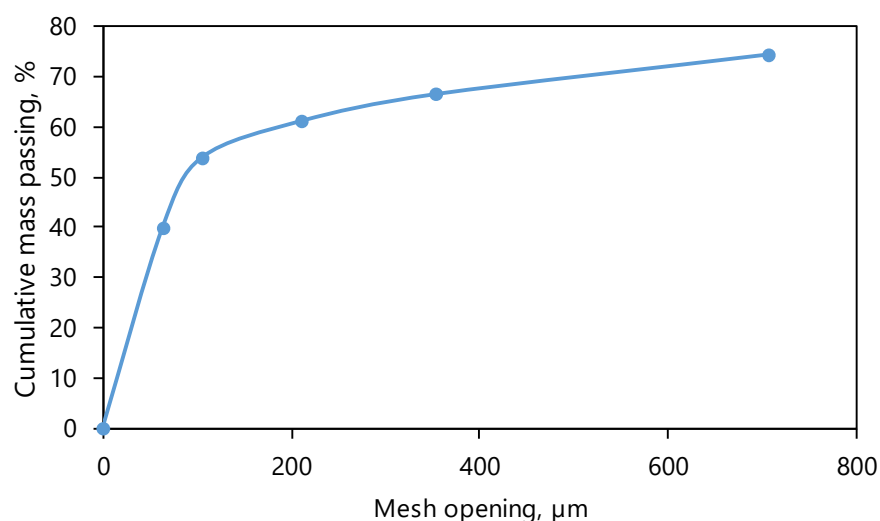


Figure 4. Particle size distribution of SOTRN tailing.

3.2 Leaching and treatment of tailings

The mineralogical profile of tailings suggests that leaching of tailing can be performed using only sulphuric acid, due to copper is as oxidised mineral (Chalcoalumite) and the ore is very fine, i.e. with a large surface area. The leaching was performed in a mechanically stirred vessel, at 500 rpm. The dissolution kinetics of copper resulted fast, with an almost complete recovery in a couple of hours, reaching a final concentration of 43 mg/L in 4 h. To concentrate the copper content in the solution, five 4 h-leaching cycles were performed, obtaining that copper increases its concentration in about 50 mg/L every cycle; at the final cycle, it was reached a concentration of 200 mg/L for copper and 700 mg/L for iron. There is an increase between the first and the fifth cycle of 5.4 and 4.1 times for copper and iron, respectively (Figure 5). In this context, the removal of the iron excess was addressed by precipitation, adding NaOH to increase the pH to 4.

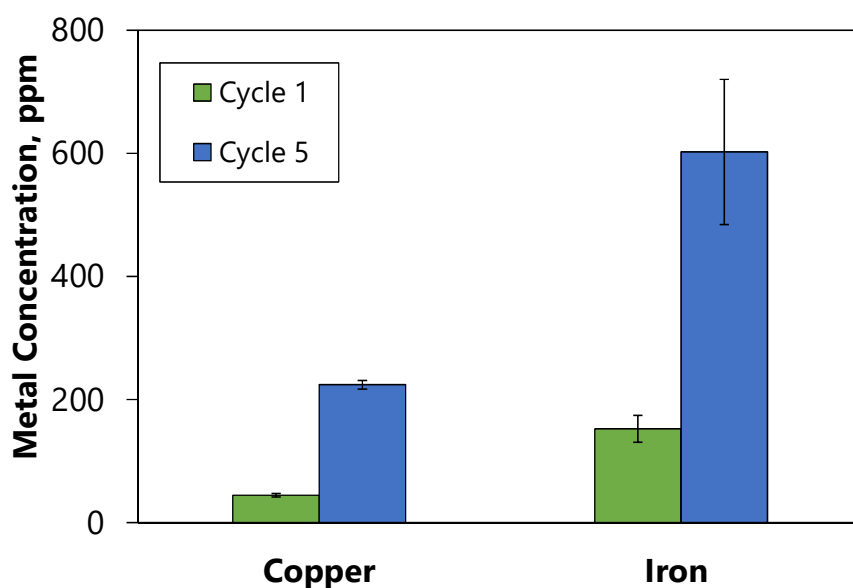


Figure 5. Leaching of tailing with different dissolution cycles. Contact time per cycle of 4 h and 500 rpm

In the iron precipitation, a significant removal was obtained, between 65-75%, but the losses of copper reached about 30%. Copper moved out preferably by entrainment and occlusion in the precipitated fraction. The precipitating treatment decreases the iron concentration from 700 to 200 mg/L and copper levels from 200 to 150 mg/L (Figure 6). After the treatment, the composition of copper and iron in the solution was similar.

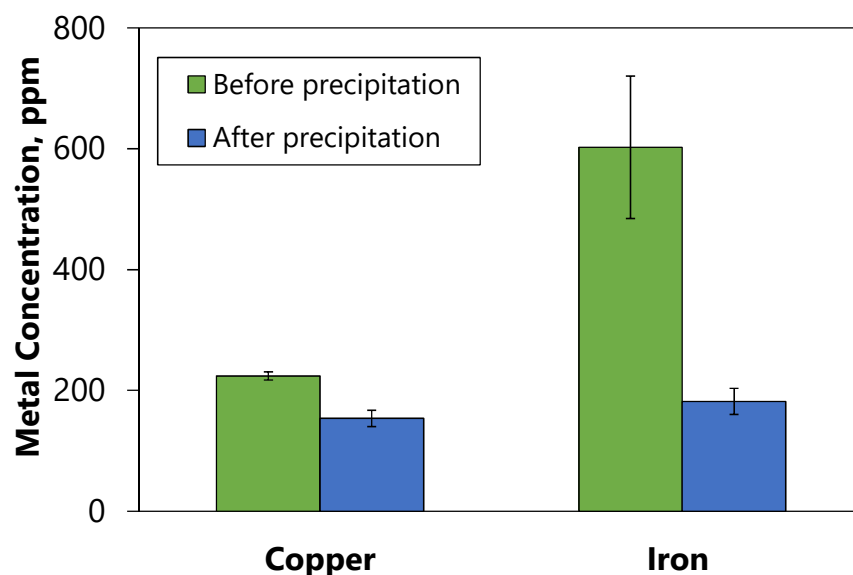


Figure 6. Effect of precipitation treatment on the removal of iron from PLS. Solution pH 4 after precipitation.

3.3 Biosorption from synthetic and leached tailing solutions

3.3.1 FTIR

Metal biosorption depends especially on the components of the cell wall. In this context, FTIR was realised in order to characterise the chemical groups that are present in the *Gracilaria chilensis* biomass and those involved in the biosorption process. The biomass used for biosorption experiment has chemical groups containing O-, N-, S-, and P-, which participated directly in the binding of metals, such as carboxyl, hydroxyl and sulphate groups. The groups present in the algal cell wall are as polysaccharides: fucoidan and alginate, which was also reported in other works (Lesmana et al., 2009; Wang and Chen, 2009).

Once detected the functional groups in the biomass, the FTIR spectrogram of original biomass was compared with biosorbed biomass, detecting changes associated with the influence of metal sorption (Figure 7). FTIR shows shifts of bands related to groups involved in the copper biosorption. The region between 3600 and 3200 cm^{-1} corresponds to hydroxyl stretches in several compounds, and amines and amides in amino acids. This band is broad due to it has a high number and large density of hydrogen bonds. The carbonyl stretching of carboxylic acids (C-O) appears near to 1700 cm^{-1} and the carboxylate stretching at 1650-1400 cm^{-1} (C=O). The carboxylic sites are deprotonated by the effect of Cu(II).

On the other hand, the band at 1100 cm^{-1} is assigned to antisymmetric stretching in sulfonate from fucoidan. Primary and secondary amides are observed by the peaks at 3500-3200 and 1650-1500 cm^{-1} , respectively, which are related to amino acids and peptide bonds in proteins and glycoproteins.

The acid treatment of algae can dissolve polysaccharide compounds in the outer layer of the cell wall to a certain extent, thus creating additional binding sites (usually amino groups), which can be associated to the decreasing of the intensity of nitro group at 700 cm^{-1} . In addition, the IR bands at around 600-650 cm^{-1} ascribed to the stretching vibration of Cu-O bond in monoclinic CuO, which was also observed in other works related to bioreduction of copper oxide nanoparticles on the cell wall of different species (Reddy, 2017; Usman et al., 2013).

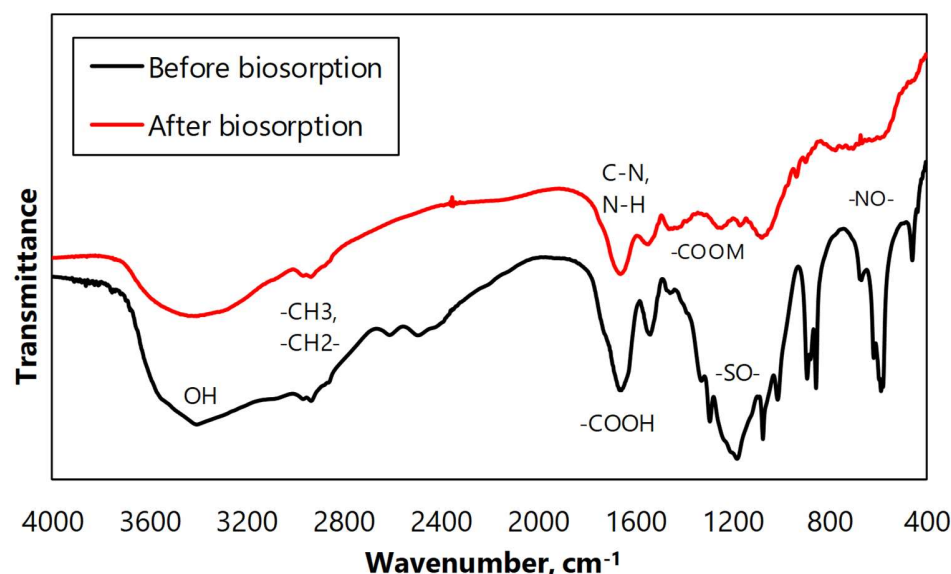


Figure 7. Vibrational stretches of functional groups. (a) Before and (b) after the synthetic biosorption.

3.3.2 Biosorption kinetics and desorption

In order to study the effect of contact time in the biosorption, the kinetic was studied for 120 min as the maximum time. The observed performance for synthetic- and leached tailing-solutions were compared, showing that copper uptake increases significantly with time until approximately 1 h. After, the biosorption capacity is reduced due to the saturation of functional groups. The metal uptake at the 120 min for synthetic and PLS solutions obtained a maximum metal uptake of 0.41 and 0.35 mmol/g, respectively (Figure 8). The presence of other ions that compete with Cu(II) in the PLS solution affects that lower biosorption capacity is obtained.

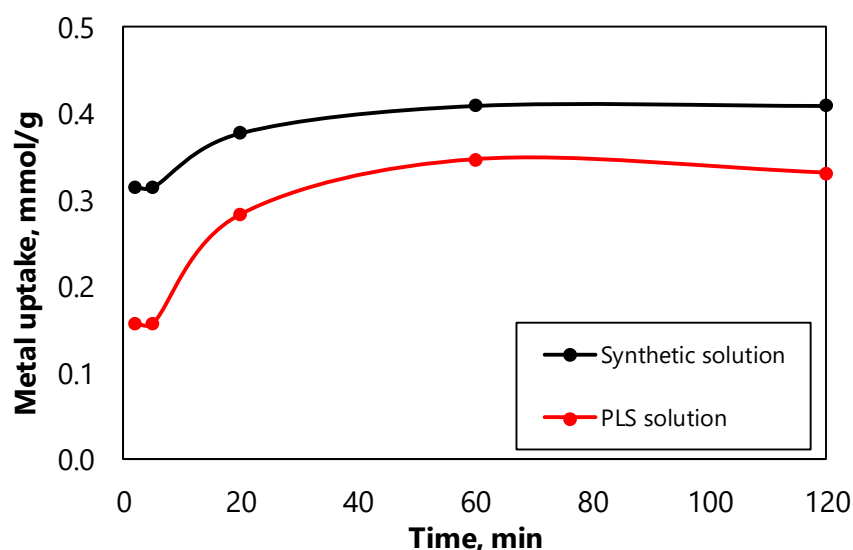


Figure 8. Copper biosorption kinetics by *Gracilaria chilensis*. (a) Synthetic solution and (b) PLS solution at pH 1.5 and biomass concentration of 0.5 g/L

Once bioadsorption finished, the desorption was studied by changing the properties of the surface through acidification of media. For this, H_2SO_4 and HCl as desorbing agent and two desorption periods: 90 and 180 min were tested. Results show that H_2SO_4 was the best desorption agent since for 90 and 180 min of desorption period, the desorption-adsorption effectivity resulted greater than for HCl , between 1.5 and 2 times (Figure 9). On the other hand, the desorption curves for H_2SO_4 show that no significant differences were obtained between 90 and 180 min, suggesting that a short desorption time is adequate for subsequent biosorption-desorption cycles. In the case of HCl , the time of desorption is critical due to the desorption effectivity increase almost twice.

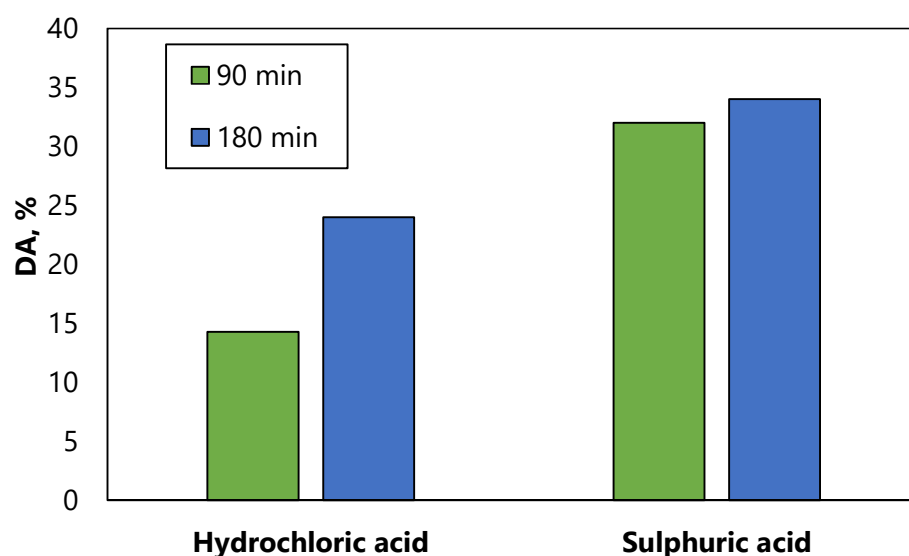


Figure 9. Desorption-adsorption effectivity of copper by two desorbing agents: HCl and H_2SO_4 for two different desorption periods: 90 and 180 minutes.

3.3.3 Equilibrium isotherms

The metal uptake was analyzed, and the experimental response was simulated by the Langmuir and Freundlich models. The uptake is controlled by the concentration at the equilibrium, which explains the gradual diminution in the variation of q at high C_e . Regarding the models, Langmuir as a hyperbolic expression appears to be more suitable for representing the whole biosorption, while Freundlich resulted in the best simulation at high concentrations, but with an overall fitting quality less than Langmuir one (Figure 10).

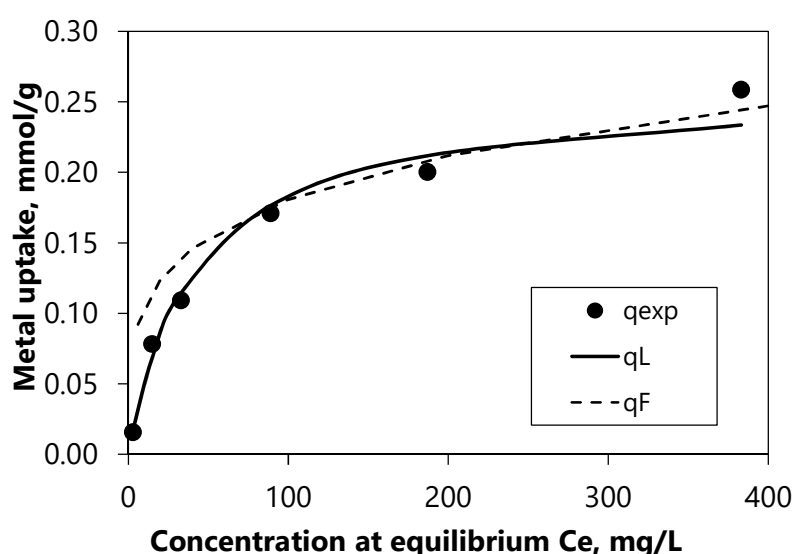


Figure 10. Equilibrium isotherm of copper biosorption at different concentrations of synthetic solution for 10 h. Biomass concentration of 1 g/L and pH 3. q_{exp} denotes the experimental metal uptake, q_L and q_F represent the Langmuir- and Freundlich-simulated metal uptakes.

The fitting parameters of Langmuir expression were the maximum metal uptake (q_m) and the metal affinity (b), which was determined by transforming the Langmuir equation into linear form, Eq. (5).

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{q_{max}b} \frac{1}{C_e} \quad (5)$$

In the case of the Freundlich model, the adsorption capacity (k) and the adsorption intensity (n) were determined by log-linearization of the model, Eq. (6).

$$\log q_e = \log k + \frac{1}{n} \log C_e \quad (6)$$

The linear least-squares method and the linearly transformed equations were applied to correlate the sorption data, and the determination coefficient was used as an indicator of quality adjustment (Table 4). According to the results, the biosorption process was best represented by the Langmuir isotherm, where biosorption occurs at sites located on a surface and each are can retain a single molecule adsorbed to form a monolayer; the

adsorption energy is the same in all the binding sites, and there is no interaction between other adsorbed species. The desired adsorption process is when high values of q_{max} and b are obtained. A high value of b indicates high affinity that reflects a strong initial slope in the system. The Freundlich isotherm is an empirical equation; it assumes that the energy of adsorption on the surface is heterogeneous, that is to say that the energy is not the same at all points on the surface of the adsorbent, in addition there may be some interactions between the adsorbed molecules. The success of the model depends on the shape of the isotherm when the coefficient n is greater than one, the isotherm is favourable.

Table 4. Fitting of adsorption parameters used in Langmuir and Freundlich models.

Parameter	Langmuir model	Freundlich model
q_{max} (mmol/g)	0.311	0.247
b (L/mmol)	9.149	-
k (L/g)	-	0.069
n	-	4.667
R^2	0.972	0.771

The physical meaning of the parameters and the values reached suggest that *G. chilensis* is a good biosorbent for copper, with magnitude levels comparable with other biosorbents; the kinetic parameters are in the range of the most common values obtained for non-lead biosorption processes, according to the literature, where it is noted high relative frequencies of q_{max} and b for copper around 0.25-0.50 mmol/g (55%) and 5-10 L/mmol (70%), respectively (Pagnanelli, 2011).

One of the mathematical models more cited in the literature is the Langmuir model that provides a quantification of the biosorption phenomenon, such as the case for algae used as biosorbents. The maximum sorption uptake and the equilibrium constant or affinity degree of the biomass for the adsorbate can be derived from that model. The equilibrium constant represents a fundamental tool in order to define the chemical equilibria in this type of systems. From the knowledge of those constants, it is possible to predict the behaviour of different biomass with a given metal. Therefore, this could be a useful tool in order to make the right choice between different biosorbents for each occasion.

The parameters of Langmuir, q_{max} and b , obtained for the biosorption of copper by different types of algae: brown, red and green have been previously studied and listed in Table 5 (Romera et al., 2007). The brown algae present the highest sorption uptakes followed by red algae, especially those with carragenates in their cell walls (*Chondrus crispus*), and the lowest sorption uptakes correspond to green algae, which are poor in fucoids. The presence of alginates in cell walls of brown algae, like carragenates in red algae, is responsible for the binding of metal on the biomass. Although that is the case for most of the studies reported in the literature, the values of q_{max} for brown algae are higher than for other kinds of algae (Romera and Ballester, 2006).

According to the reference values, the alga of the present study, *G. chilensis*, showed a biosorption behavior within the range observed by similar macroalgae. A high affinity coefficient for copper was reached but a limitation in the biosorption maximal capacity, denoting that the type of chemical groups on the biomass surface are adequate for a preferential copper uptaking but may be in deficient quantity.

One of the criteria that should be considered when choosing a bioadsorbent with industrial application is the availability. In this sense, although *G. chilensis* proved to be no better than brown algal biomass, which generally involve species that are overexploited around the world and that must be protected. Thus, as a beneficial aspect is that *G. chilensis* is an alga that has been cultivated and therefore can be produced in adapted marine farms.

Table 5. Values of Langmuir constants for copper biosorption by different macroalgae types (Romera et al., 2007).

Alga	Type	b (L/mmol)	q_{max} (mmol/g)
<i>Codium vermilara</i>	Green	8.920	0.266
<i>Spirogyra insignis</i>	Green	5.510	0.304
<i>Asparagopsis armata</i>	Red	8.370	0.335
<i>Chondrus crispus</i>	Red	2.470	0.637
<i>Gracilaria chilensis</i> *	Red	9.149	0.311
<i>Ascophyllum nodosum</i>	Brown	10.870	0.925
<i>Fucus spiralis</i>	Brown	10.390	1.116

* This study

On the other hand, a considerable number of bacteria, fungi and algae have been investigated for their biosorbent metal properties. The efficiency of the process will depend on the biomass chemical composition, which varies significantly for different species within the same genus or order (Gadd, 2009). In a compilation of different authors studying biosorbents, such as fungi, bacteria and algae, to make a comparison with this study, it shows that fungi work at low concentrations and their uptake by metal does not exceed 0.24 mmol/g. On the other hand, studies with bacterial biosorbents have a wider range of concentrations, and metal uptakes below 0.87 mmol/g, while algae show better biosorption by copper metals, working with large concentration values and obtaining in some cases for brown algae uptake over 1.10 mmol/g (Figure 11).

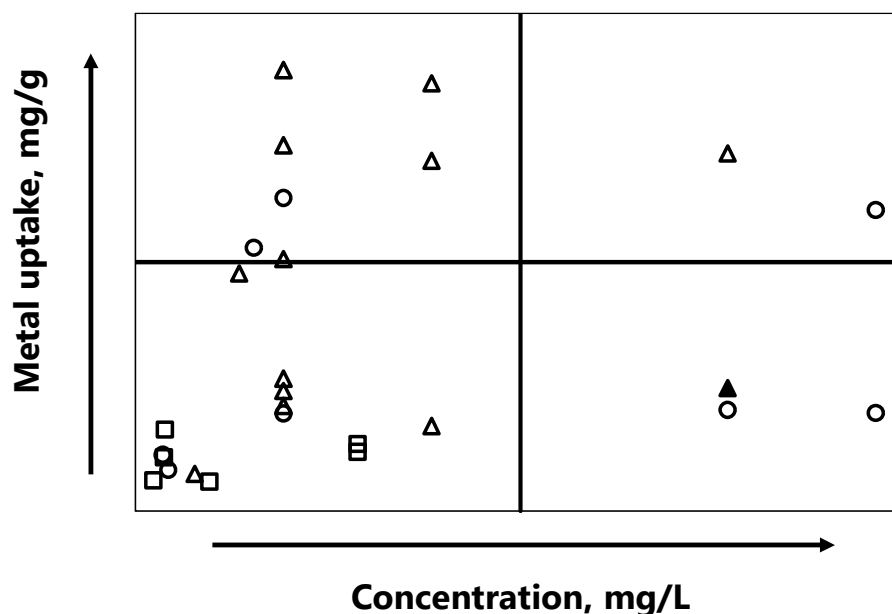


Figure 11. Metal uptake for different types of biomass; (□) Fungi, (○) Bacteria, (Δ) Alga and (▲) *G. chilensis* (this study).

In recent years, there has been an increasing interest in the use of new sorbent and very efficient biomaterials. At present, the various bibliographic revisions on the sorption uptake by different biomass do not allow to assert which one is more effective due to the many determining factors involved. The comparison of these biosorbent suggests that algae, in general, are promising biosorbents for heavy metals. Furthermore, algae are natural products collected in large amounts, especially the marine and brown ones. In addition, most algae are innocuous and easily welcomed by the public and environmental agencies for its biotechnological use since they do not generate toxic or non-removable by-products (Cuizano and Navarro, 2008).

4. Conclusions

The red seaweed *Gracilaria chilensis* was used as biosorbent of copper in batch system for synthetic and PLS solutions. Interactions between metal ions and functional groups on the biomass cell wall surface were identified by FTIR. Results propose that chemical groups involved in the copper biosorption were carboxyl, hydroxyl and amino.

Parameters influencing biosorption such as the initial metal concentration, the amount of biomass and the pH of the solution were examined. The biosorption kinetic for synthetic and tailing PLS found that the optimal contact time for the biosorbent was 60 min. The uptake capacity of Cu(II) by the biomass was reduced by the presence of other metallic species in the solution. Experimental biosorption data was represented by the Langmuir and Freundlich isotherms. Langmuir reached the best fitting ($R^2=0.972$), indicating that the copper biosorption on the *Gracilaria* biomass showed a monolayer adsorption trend on the active

sites of the biomass surface. Kinetic parameters are comparable with other reported values for the biosorption of other brown and red algae.

Two desorbent agents were tested, from which the sulphuric acid was able to release more copper from the biomass in a period of 90 minutes. HCl was less efficient and require more time.

Finally, *Gracilaria* biomass has a good copper uptake, working with conditions of pH 1.5, biomass concentration of 0.5 g/L and initial copper concentration of 200 mg/L. The copper concentration in the tested tailing PLS reached levels that allow its biosorption by 5-cycle leaching. Subsequent studies about the optimal conditions of biosorption and the feasibility to recover copper from a continuous columnar system are projected as the next tasks to face.

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