



# Biosorption of nickel(II) and copper(II) ions in batch and fixed-bed columns by free and immobilized marine algae *Sargassum* sp.



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## ABSTRACT

In this study, the brown algae harvested in the State of Pernambuco - Brazil, *Sargassum* species, and the commercial sodium alginate were used as free and immobilized biosorbents for the removal of nickel and copper ions in batch and continuous experiments from aqueous solutions. The alginate beads and immobilized biosorbent were produced from the ionic polymerization using the drip method in calcium chloride solution. Equilibrium data show that the calcium alginate matrix increased the maximum biosorption capacity in immobilization, and both biosorbent materials presented greater affinity and uptake capacity for copper ions than for nickel ions. The experimental results were better fitted to the Langmuir model than to the Freundlich model, obtaining favorable type isotherms. Continuous systems showed a different equilibrium condition, once the experiments carried out in fixed-bed columns presented higher biosorption capacity than those performed in batch experiments, also suggesting that the bed packed with immobilized biosorbent was not affected by the low porosity. The immobilized biosorbent also had easy packing.

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## 1. Introduction

Heavy metals are metallic elements that have density over 5.0 g cm<sup>3</sup>, such as nickel and copper, are very important for global development (Järup, 2003). Many activities use heavy metals in their manufacturing process or product. Nickel is intensely used in its pure form as coating of metal pieces, because it presents great resistance to corrosion and oxidation. Copper is an excellent conductor of heat and electricity, it is used in different areas, such as electrical industry, construction, galvanization, agricultural products, among others (de-Bashan and Bashan, 2010). However, heavy metals can represent a significant pollution source. Although these metals are essential for living beings, some species and high concentrations can be highly toxic, persistent in the environment (non-biodegradable), and bioaccumulative in food chain (He and Chen, 2014).

Treatment technologies for removal of metals from industrial effluents include chemical precipitation, electrochemical, membranes filtration, ion exchange, adsorption and evaporation. However, these methods are usually expensive or inappropriate for

treating highly diluted solutions (Mata et al., 2009). As an alternative, biosorption is a process that uses inexpensive biomass in order to remove metal ions from complex and highly diluted solutions. According to Naja and Volesky (2011), biosorption is a complex process that can involve mechanisms of ion exchange, physical adsorption, chemical adsorption, including complexation/chelation, and precipitation. There are several biomass evaluated for removal of metals, such as bacteria, fungi, algae and agro-industrial residues (Gadd, 2009; Wang and Chen, 2009). Marine algae are identified as a promising biosorbents due to their high biosorption capacities, low cost, renewability and abundance in many regions of the world (He and Chen, 2014). Among the diverse species of marine algae, brown algae has been attracting attention because it presents polysaccharides alginate and fucoidan, which are active in ion exchange processes (Davis et al., 2003; Romera et al., 2006).

Biosorption as a technology for the removal and recovery of metals will only be competitive when utilized in continuous systems to treat large volumes, such as the fixed-bed columns (Cossich et al., 2004). Fixed-bed column is easy to operate, it requires small space, ensures high concentration gradient, and allows the treatment of large volumes of metal solutions (Da Silva et al., 2002). In scaling up the biosorption process, the use of free particulate

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biosorbents has some drawbacks including small particle size, low mechanical strength, strong densification and poor distribution in bed. These disadvantages cause problems in columns, such as the decrease of the process efficiency, difficulties in separation process, poor regeneration/reuse (Fomina and Gadd, 2014). Biomass immobilization in polymeric matrices (as alginate) can then improve the bed packing, producing biosorbent with particle size, mechanical resistance, and rigidity adequate for use in fixed-bed column. Alginate is a polymer that occurs in all brown algae and have the property of reacting with polyvalent cations such as calcium, producing strong gels (Romera et al., 2006).

Abu Al-Rub et al. (2004) analyzed *Chlorella vulgaris* immobilized in alginate beads in nickel removal. They have observed that the immobilization enhanced the biosorption ability and enabled the use of the biosorbent in various sorption/desorption cycles with the same removal potential. Other studies also have evaluated the immobilization of seaweed (Mata et al., 2009), fungus (Hanif et al., 2015), and agricultural wastes (Kausar et al., 2016) biomass in alginate matrix; however, all these studies were carried out in batch experiments.

Therefore, the objective of this work was to evaluate seaweed *Sargassum* sp. immobilized in alginate for the removal of copper and nickel through a fixed-bed column system.

## 2. Materials and methods

### 2.1. Materials

Seaweed *Sargassum* sp., purchased from algae collectors cooperative of Pernambuco State – Brazil, was washed with distilled water, dried at 60 °C, mashed in blender, separated in sieve from Tyler's series and stored in closed recipients. Particles with an average diameter of 1.5 mm were used in batch experiments; particles with an average diameter of 2.2 mm were used in column experiments, and particles with diameter smaller than 150 μm were used in the immobilization. Commercial sodium alginate (Êxodo Científica, Brazil) was used for biomass immobilization.

The metal solutions were prepared from the dissolution of nickel sulfate (NiSO<sub>4</sub>·6H<sub>2</sub>O, Synth, Brazil) and copper sulfate (CuSO<sub>4</sub>·5H<sub>2</sub>O, Synth, Brazil) in distilled water.

### 2.2. Biomass immobilizations

Immobilized biosorbents were prepared in form of alginate beads by ionic polymerization in calcium chloride solution, according to the method used by Abu Al-Rub et al. (2004). An amount of up to 0.50% (w/v) of *Sargassum* sp. powdered was mixed in 2% sodium alginate solution. This mixture was then dropped into a 4% calcium chloride solution (CaCl<sub>2</sub>·2H<sub>2</sub>O, Êxodo Científica, Brazil) using a peristaltic pump. The beads were kept in the calcium solution for at least 4 h for complete gelation. After that, the beads were washed with distilled water to remove excess CaCl<sub>2</sub> and stored in sealed recipient at room temperature until next use. For Ca-alginate beads only, similar procedures were used, but without brown algae. The biosorbents moisture was determined in oven at 105 °C for at least 24 h.

Fig. 1 depicts the experimental apparatus used for immobilization, where a syringe was coupled into the tubing and dripping height was fixed at 20 cm.

### 2.3. Biosorption isotherm of Ni<sup>2+</sup> and Cu<sup>2+</sup> ions

Batch sorption experiments were carried out to obtain the mono-component equilibrium data. A series of solutions (75 mL) with different initial metal concentrations (0–7 mmol L<sup>-1</sup>) were

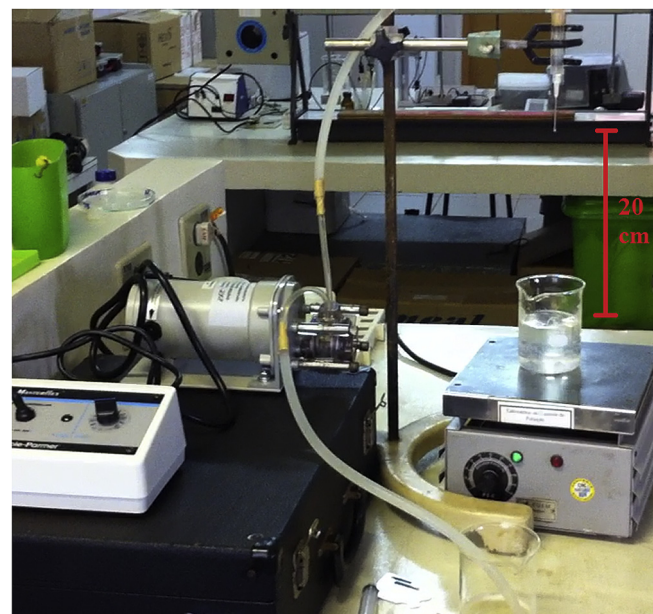


Fig. 1. Production of Ca-alginate beads by drip method.

placed in contact with 0.1 g of biosorbent (free biomass, immobilized algae in alginate beads and alginate beads) at a constant temperature of 30 °C, stirred at 150 rpm and pH 5.0, periodically adjusted with sulfuric acid. Assays duration was determined by biosorption kinetics carried out previously, obtaining 4 h for nickel and 6 h for copper. Initial and equilibrium concentrations were determined by atomic absorption spectroscopy (VARIAN - SpectrAA 50B). The amount of metal biosorbed was calculated using the equation:

$$q_e = \frac{(C_i - C_e)V}{m_s} \quad (1)$$

where  $q_e$  is the amount of metal uptake in equilibrium (mmol g<sup>-1</sup>),  $C_i$  e  $C_e$  are the initial and equilibrium metal concentrations in the solution (mmol L<sup>-1</sup>),  $V$  is the volume of the solution (L), and  $m_s$  is the biosorbent dry weight (g).

The Langmuir (Equation (2)) and Freundlich (Equation (3)) isotherms were fitted to equilibrium data by non-linear regression using the software Origin 7.0 (Langmuir, 1918; Freundlich, 1906; apud Wang and Chen, 2009).

$$q_e = \frac{Q_{max}bC_e}{1 + bC_e} \quad (2)$$

$$q_e = K_F C_e^{1/n} \quad (3)$$

In Langmuir model,  $Q_{max}$  (mmol g<sup>-1</sup>) is the maximum biosorption capacity (i.e., when the surface is completely covered with metal ions), and  $b$  (g mmol<sup>-1</sup>) is a Langmuir constant that represents the affinity between the biosorbent and the metal ion. While in Freundlich model,  $k_F$  ((L mmol<sup>-1</sup>)<sup>1/n</sup> (mmol g<sup>-1</sup>)) is Freundlich constant related to uptake capacity and  $n$  is Freundlich exponent known as biosorbent intensity (Akbari et al., 2015).

### 2.4. Continuous system – fixed bed-column

Continuous system experiments were carried out in a jacketed stainless steel column with an internal diameter of 2.8 cm and height of 50 cm. Bed height was fixed at 30.6 cm for all

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