Evaluation of Metal Affinity of Ag^+, Cd^{2+}, Cr^{3+}, Cu^{2+}, Ni^{2+}, Zn^{2+} and Pb^{2+} in Residue of Double Alginate Extraction from Sargassum filipendula Seaweed

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The continuous population growth and technological development are contributing factors to the increased contamination of effluents with toxic metals. The removal of such metals from effluents has become an important subject for scientific research. Among the most used methods, adsorption has shown good potential to treat such effluents. In this work we investigated the metals affinity with the residue of alginate extraction from the seaweed *Sargassum filipendula*. The alginate residue has shown good results in the removal of metal contaminated industrial effluent and is an interesting subject of research. The experimental tests were performed using different metal solutions with concentration of 1.0 mmol.L^{-1}, at 180 rpm in room temperature 25 °C for a period of 24 h under controlled pH 3.5. The alginate residue can be used as a bioadsorbent in the treatment of metals contaminated effluents with good results. The first and second extractions residue has shown similar ability of ion removal.

1. Introduction

Metals can be found naturally in aquatic environments due to weathering of rocks and soil leaching. However, any metals can be labelled toxic since the level of toxicity is a function of the metallic ions concentration in aqueous media. At low concentration, metals are essential to living beings and play a major role in some biological functions. Chromium, for instance, takes part on sugar metabolism in mammals. Zinc and Copper act as cofactors for enzymes (Guilherme et al., 2005). In another hand, cadmium is not considered an essential element, being harmful to human beings and the environment (Muskett et al., 1979). When present, toxic metals can affect the body in different ways, leading to the development of several diseases, such as skin irritation to the development of some kinds of cancer (Miretzky and Cirelli, 2010). In Brazil, the discharge limits for cadmium, lead, copper, chromium, nickel, silver and zinc are respectively: 0.1; 0.2; 0.5; 1.0; 1.0; 2.0 and 5.0 mg.L^{-1}.

Numerous studies have been carried out in search of methods to solve and/or mitigate environmental issues. There are several techniques for the removal of metal ions in industrial effluents, such as chemical precipitation, ion exchange (Lu et al., 2015), and ultrafiltration (González-Muñoz et al., 2006). However, these methods are inefficient and expensive when the pollutants are present in low concentration. Alternative methods such as bio-adsorption offer the possibility of selective and efficient treatment in diluted effluent with the advantage of low cost (Lima, et. al., 2014). Industrial effluents from electroplating, leather tanning, pigments, (He et al., 2009), besides pesticides, fertilizer industries, paper production and batteries are the main sources of this type of contamination, either directly or indirectly (Fu and Wang, 2011).

The brown algae stands out as an effective alternative in the removal of toxic metals and may have similar performance to commercial adsorbents, are abundant, inexpensive and natural (Cechinel et al., 2016).

The adsorptive biomass capacity is directly related to the cell wall, which is mainly composed by biopolymer alginate that holds 70 % of the active sites of macroalgae (Davis et al., 2003). The extraction of alginate residue from seaweed, is commonly used in the production of animal feed, it also has high potential for application as bioadsorbent, but is not well known as an alternative bioadsorbent (Bertagnolli et al., 2014). Therefore, this study aims to evaluate the alginate extraction residue affinity with metal ions Ag (I), Cd (II), Cr (III), Cu (II), Mg (II), Ni (II), Pb (II) and Zn (II) in order to explore its biomaterial characteristics.

2. Materials and Methods

2.1 Preparation of algae and extraction of alginate
The seaweed *Sargassum filipendula* was collected in the São Paulo coast at Cigarras' beach in April 2015, and transported under refrigeration. The seaweed was then washed with distilled water, dried in an oven at 60 °C for 24 h, milled and sieved into fractions smaller than 1 mm diameter (0.737 mm).
The extraction was performed according the method described by McHugh (1987), based on the conversion of insoluble alginate present in a soluble form in the algal cell wall, typically sodium alginate (Larsen et al., 2003). 15 g of *Sargassum filipendula* seaweed were placed in contact with 500 mL of formaldehyde solution (0.4 % w/w) under constant stirring for 30 min, washed with deionized water and mixed with 500 mL of hydrochloric acid solution (0.1 mol.L^{-1}) for 2 hours. According Bertagnolli et al. (2014), the wash treatments are necessary to remove phenolic compounds and clarify the biomaterial. The alginate extraction was carried out with sodium carbonate solution (2 % w/w) at 60 °C for 5 h under constant stirring. The viscous mixture was vacuum filtered to separate the alginate solution from the process residue. The alginate was then precipitated in ethanol (1:1 v/v) and dried at 60 °C for 24 h. The residue was washed with deionized water and dried also at 60 °C for 24 h milled and sieved to achieve smaller than 1 mm particles. A double extraction was accomplished in order to verify if the residue with less alginate still maintains the ability of ions removal. The same methods with proportional quantities of sodium carbonated were used by second extraction.

2.2 Metal speciation
The metal speciation study was simulated with the help of the software Visual MINTEQ 3.0 with concentration 1.0 mmol.L^{-1}. The obtained distribution diagrams of the metal species were in function of pH.

2.3 Affinity test
Affinity tests were performed with the toxic metals Ag (I), Cd (II), Cr (III), Cu (II), Mg (II), Ni (II), Pb (II) and Zn (II) and the alginate residues from the first and second extractions. For the tests, 50 mL of metal solution with 1.0 mmol.L^{-1} concentration were mixed with 0.5 g of bioadsorbent under agitation (180 rpm), at room temperature (25 °C) for 24 hours. The pH was maintained at 3.5 with nitric acid 0.1 mol.L^{-1}, according to metal speciation, in order to avoid the precipitation of metals as hydroxides. The tests were performed in a shaker to ensure homogeneity and the contact between solution and bioadsorbent. A centrifuge was used to separate the liquid phase. The initial and final concentrations of each test were determined by atomic absorption spectroscopy. The percentage removal and adsorption capacity were calculated as shown by Eqs(1) and (2):

$$\%Rm = \left(\frac{C_0 - C_{eq}}{C_0}\right) \times 100 \tag{1}$$

$$q = \frac{(C_0 - C_{eq})V}{m} \tag{2}$$

Where:
C$_0$: initial concentration of the metal ion (mmol.L^{-1});
C$_{eq}$: final concentration of metal ion after equilibrium (mmol.L^{-1});
m: bioadsorbent dry mass (g);
q: adsorption capacity of the metal ion (mmol.g^{-1});
V: solution volume (L);

3. Results and discussion

3.1 Metallic Speciation
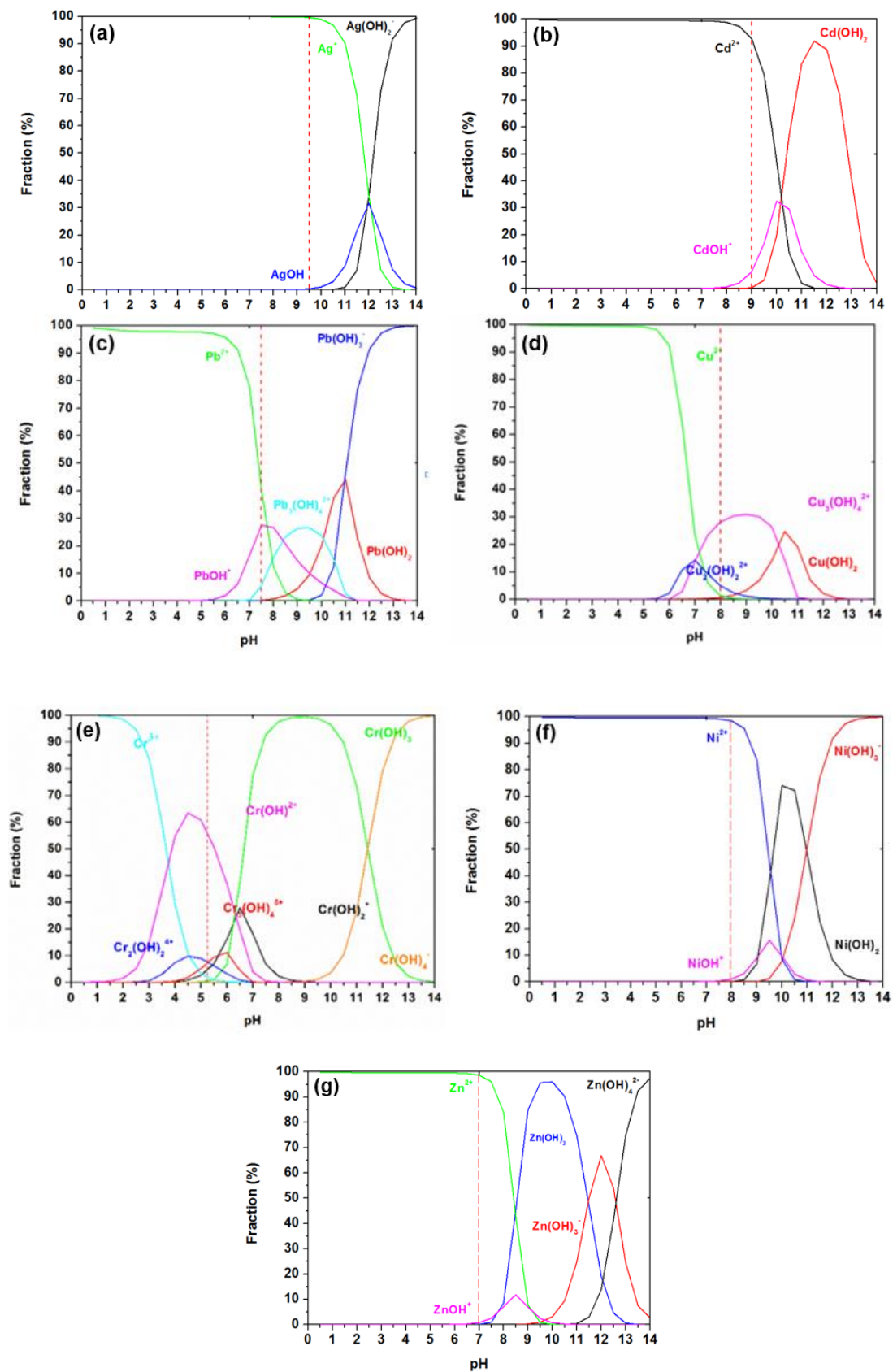The metallic speciation diagrams obtained by Visual MINTEQ software (version 3.0) are shown in Figure 1:

Figure 1: Speciation diagrams in aqueous solution: (a) Ag⁺; (b) Cd²⁺; (c) Pb²⁺; (d) Cu²⁺; (e) Cr³⁺; (f) Ni²⁺; (g) Zn²⁺.

In Figure 1 it is observed the pH range where metal precipitation occurs, the Chromium ion had the least working range, being that the metal precipitation occurs with a pH above 5. The other ions form insoluble compounds in pH values above 6. Therefore, we chose a pH 3.5 for all metallic solutions, so not to precipitate the metal ions and the possibility of performing tests in multicomponent solutions.

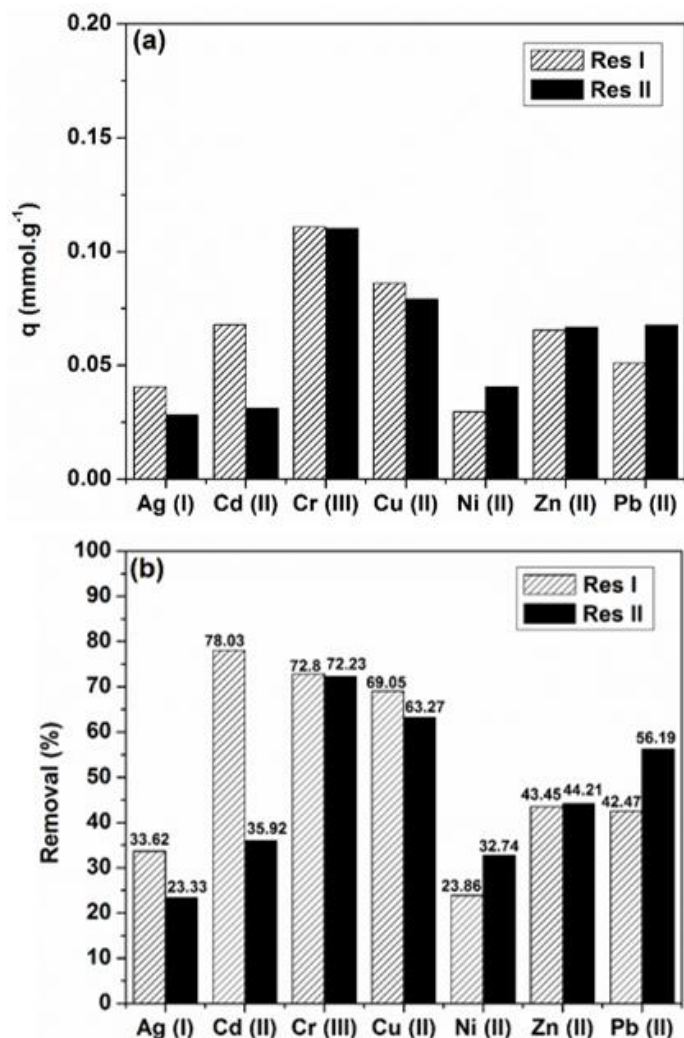### 3.2 Affinity tests
The affinity results are shown in Figure 2.

Figure 2: Affinity of metal ions Ag+, Cd2+, Cu2+, Cr3+, Ni2+, Zn2+ e Pb2+ by biomaterials expressed in percentage of removal (a) and capacity of adsorption (b) (mmol.g-1).

It is noted that both residues have similar adsorption capacity for chromium and zinc and an increase in nickel and lead, despite the lower amount of alginate and its constituents present in the residue from the second extraction. These results may be related to the sulphate groups present in fucoidan and that can also influence in the removal of some metals by biomaterial (Yang and Chen, 2008). It is also observed that the metal ions studied have the following affinity orders for adsorption capacity in two materials: $Cr^{3+}> Cu^{2+}>$ $Cd^{2+}> Pb^{2+}> Zn^{2+}> Ag^+> Ni^{2+}$ (residue I) and $Cr^{3+}> Cu^{2+}> Zn^{2+}> Pb^{2+}> Ni^{2+} > Ag^+$ (residue II). Lima (2015) evaluated the affinity of chromium, copper, cadmium, lead, zinc and nickel ions by macrophytes *Salvinia natans*, *Pistia stratiotes* and *Salvinia cucullata,* at room temperature, pH 4.0, and concentration of 1.0 mmol.L-1. Chromium showed the higher affinity between the three biomaterials, with adsorption capacity close to 0.40 mmol.g-1, followed by lead, copper, cadmium, nickel and zinc. Therefore, the result obtained in this work is satisfactory, since most of the constituents responsible for ensuring high adsorption capacity to biosorbents were removed by the alginate extraction process.

Factors such as hydrated ionic radius, electronegativity, and charge/ionic radius may affect the affinity sequence. The metal affinity order may be explained by the theory of strong/weak acids and bases such as strong acids are associated with strong bases. The Chromium ions presented a higher affinity with both residues since it is considered a strong acid. Ni^{2+}, Cu^{2+}, Zn^{2+} and Pb^{2+} ions are considered intermediate acids. The low adsorption observed for the Ag^+ ions might be related to the fact that it is a weak acid.

This theory does not apply to cadmium ion, even though it is a weak acid, a high adsorption capacity was obtained, and this can be explained by the high electronegativity (1.69) and a high load /ionic radius value which facilitate the adsorption by the adsorbent (Tobin et al., 1984).

The percentage removal presented different affinity sequences. The cadmium presented highest removal percentage followed by chromium, copper, zinc, lead, silver and nickel. In the residue II the chromium showed higher affinity followed by copper, lead, zinc, cadmium, nickel and silver.

With the exception of lead and nickel ions, the other ions showed better results in terms of percentage removal as well as higher adsorption capacity to the residue of first alginate extraction cycle, this is explained by the higher affinity that these ions have with the extracted material - alginate (Davis et al., 2003).

4. Conclusions

Analyzing the results obtained for the affinity tests, it can be concluded that the residue of the extraction of alginate in seaweed *Sargassum filipendula* presented, in general, good removal capacity for all metal ions investigated. The extraction residue has shown greater affinity for the ions Cr (III), Cu (II) and Cd (II). It is also observed that the Cd (II), Cu (II), Cr (III) and Ag (I) ions showed more affinity for the residue of the first extraction and the Pb (II), Zn (II) and Ni (II) ions for the residue of the second extraction.

This material proved to be efficient and it can be a good alternative as a bioadsorbent in the removal of toxic metals. This material is interesting from an economic point of view, such as low cost, renewable, and abundant and also adds value to waste of extraction process of alginate. Moreover, its high affinity for silver enables their use in the recovery of precious metals.

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