Heavy Metal Sorption by Calcium Alginate Beads from *Sargassum filipendula*

Sirlei Jaiana Kleinübing, Frederico Gaia Costa da Silva, Caroline Bertagnolli and
Meuris Gurgel Carlos da Silva

School of Chemical Engineering, State University of Campinas, CEP 13081-970,
Campinas, SP, Brazil

Alginate extracted from *Sargassum filipendula* was evaluated for Cu^{2+} and Pb^{2+} sorption in the form of calcium cross-linked beads. The obtained maximum adsorption capacities were 0.79 and 1.26 mmol g^{-1}, for Cu^{2+} and Pb^{2+}, respectively. FTIR spectroscopy technique confirms that extraction was efficient. For *Sargassum filipendula* algae, the carboxylic, alcoholic, sulfonate and amino groups were observed. For alginate extracte, only the carboxylic and alcoholic groups were observed.

1. Introduction

Studies on the treatment of effluents containing heavy metals have shown adsorption to be a highly effective technique for the removal of heavy metals from diluted aqueous metal solutions. Additionally, adsorption has been found to be superior to other techniques for water re-usage in terms of its initial cost, design simplicity, and operational easiness (Papageorgiou et al. 2008). Seaweed has proven to be one of the most effective heavy metal sorbents and has been proposed to be used in industrial applications (low-cost biosorbents). Brazilian coasts offer a number of different algal biomass that could be used for metal biosorption, especially brown algae.

Alginates are polysaccharides found in brown seaweeds and are composed mainly of linear polymers of β-(1→4)-D-mannuronic (M) and α-L-guluronic (G) acids differing in terms of their proportions and linear arrangements. Different species of algae contain different percentages of mannuronic acid (M) and guluronic acid (G). Because of the differences in conformation of the two different residues, gellation with divalent cations can be attributed mainly to the G residue (especially to the pure polyguluronic (GG) chains), while the M residue contributes mainly to the cation exchange capacity of this naturally occurring polymer. However, hydroxyl groups have been found to play an important role not only in cation exchange capacity but also in the affinity of the material towards different metal ions (Davis et al. 2003).

The aim of this work is to investigate the potential use of sodium alginate derived from *Sargassum filipendula* for the removal of copper and lead ions from diluted aqueous solutions.

2. Materials and Methods

2.1 Extraction and purification of alginate

Sargassum filipendula marine algae were collected in São Paulo seashore (São Sebastião, Brazil) by the Biology Institute of São Paulo University (CebiMar). Alga samples were dried at 60°C overnight, and stored in a dry cabinet. The method

described by Percival and McDowell (1967) was used for extracting the alginate. The dry algae were soaked in formaldehyde for 24 h at 60 ºC, washed with water and dropped into an HCl solution (0.2 mol L^{-1}) for 24 h. After this time, the samples were washed again in distilled water before extraction in 2 % sodium carbonate solution. Alginate extraction was carried out at 60 ºC by soaking for 3 h. The alginate samples were then obtained from the crude extract by precipitation with ethanol. The precipitate was washed twice with acetone and freeze-dried.

2.2 Alginate bead preparation

Solutions of 2% sodium alginate (w/v) were prepared with ultrapure water by stirring for 24 h. The solution was left to rest for 12 h to degas and the alginate solution was added drop-wise into CaCl$_2$ solution (4%) at 50 rpm. Ca-alginate gel beads were formed upon contact with the cross linker solution and were left overnight to stabilize. The beads were washed and dried at room temperature for three days. The average particle size was approximately 1.02 mm±0.75.

2.3 Fourier transforms infrared spectroscopy (FT-IR)

FT-IR spectroscopy was used to confirm the presence of functional groups in samples of *Sargassum filipendula* and alginate extracted from seaweed. Infrared spectra were recorded in the 4000-600 cm^{-1} region using a Thermo Nicolet instrument, model IR-200. The ATR (attenuated total reflection) device allows for the obtainment of information about the surface.

2.2 Metal binding batch experiments

Cu^{2+} and Pb^{2+} solutions were prepared from copper (Cu(NO$_3$)$_2$.3H$_2$O) and lead (Pb(NO$_3$)$_2$) nitrate salts. Metal ion concentration was determined by atomic absorption spectrometry (Perkin Elmer AA Analyst 100 with air-acetylene oxidizing flame). Kinetic experiments were performed in continuously stirred beakers containing 500 mL of 4.0 mmol L^{-1} heavy metals solution (pH 4.5) and 1.0 g biosorbent.

Pseudo-first order, pseudo-second order and intraparticle diffusion models were used to fit the experimental data. The equations are represented as follow, as Eq. (1), Eq. (2) and Eq. (3), respectively:

$$\frac{dq_t}{dt} = k_1 (q - q_t) \tag{1}$$

$$\frac{dq_t}{dt} = k_2 (q - q_t)^2 \tag{2}$$

$$q_t = k_p t^{\frac{1}{2}} \tag{3}$$

Where: q represents the amount of adsorbate retained in the solid at equilibrium, q_t represents the amount of adsorbate retained at time t, k_1, k_2 and k_p are the rate constants for the reaction of pseudo-first order (min^{-1}), pseudo- second order (g mmol^{-1} min^{-1}) and intraparticle diffusion (mmol g^{-1} min$^{-1/2}$), respectively.

For equilibrium studies, the heavy metal solution concentrations varied from 0.3 to 4.0 mmol L^{-1} and the amount of biosorbent used was 2 g L^{-1}. During the reaction process, the pH was maintained constant at 4.5 by hourly addition of 0.1 mol L^{-1} HNO$_3$.

These results were adjusted to the Langmuir model, which can be expressed as:

$$q_t = \frac{q_{max}bC}{1+bC}$$

(4)

Where: q_t is the metal uptake at equilibrium (mmol g^{-1}); q_{max} is the maximum Langmuir uptake (mmol g^{-1}); C is the final metal concentration at equilibrium (mmol L^{-1}); b is the Langmuir affinity constant (L g^{-1}).

3. Results and Discussion

3.1 FTIR

The FT-IR spectrum of *Sargassum filipendula* and alginate extracted of *Sargassum filipendula* is shown in Figures 1 and 2, respectively. The biosorption capability of algae has been attributed mainly to the cell wall, which is composed of a fiber-like structure and an amorphous embedding matrix of various polysaccharides. Alginates and sulfated polysaccharides such as fucoidan are important components in cell walls of brown algae. For the *Sargassum filipendula* algae (Figure 1), it was clear that carboxylate ions gave rise to two bands: a strong asymmetrical stretching band at 1633,2 cm^{-1} and a weaker symmetrical stretching band at 1409,14 cm^{-1}. Carboxylate ion double bands were identical for alginate extracted of algae (Figure 2), at 1618,3 and 1516,7 cm^{-1}, respectively. For *Sargassum* algae, there were clear band of amino groups (NH) at 1537,2 cm^{-1}. The bands at 1237 cm^{-1} representing –SO$_3$ stretching were mainly present in sulfonic acids of polysaccharides, such as fucoidan. These bands were not observed in alginate extracted from algae. The results indicate that the alginate extracting process was effective. The FT-IR analyses showed that the main chemical groups involved in the biosorption for *Sargassum filipendula* algae were carboxylic, alcoholic, sulfonate and amino groups (Kleinübing et al., 2010).
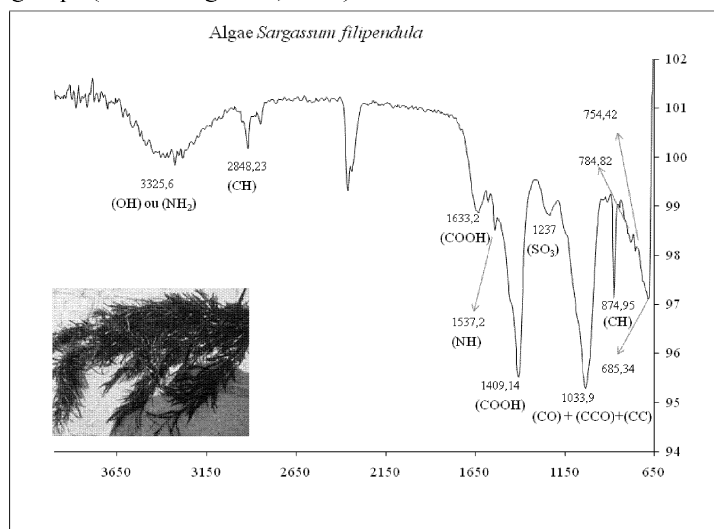

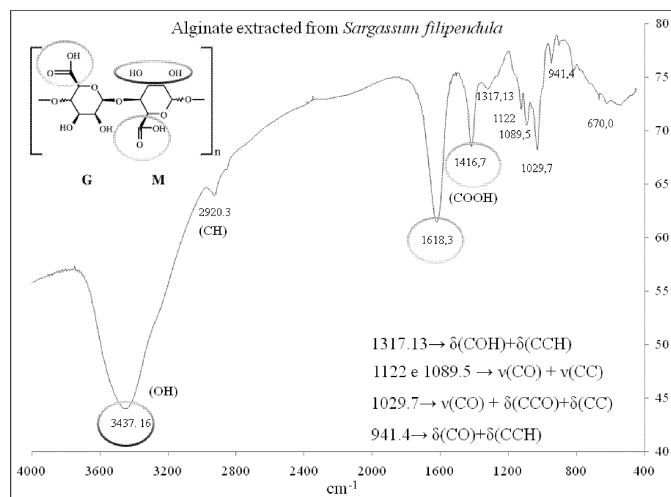*Figure 1: FTIR spectroscopy from Sargassum filipendula algae.*

Figure 2: FTIR spectroscopy from sodium alginate extracted.

3.2 Equilibrium studies

Langmuir isotherm was used to fit the experimental data. The results are shown in Figure 3. Langmuir parameters obtained were q_{max} of 0.79 and 1.26 mmol g^{-1} and b values of 1.10 and 1.84L $mmol^{-1}$ for Cu^{2+} and Pb^{2+}, respectively. The maximum amount adsorbed on a monolayer is represented by q_{max}, and b is the Langmuir association constant, which is related to the adsorption energy. The apparent Langmuir constant (b) is a measure of stability for the complex formed between metal ions and adsorptive surface layer of biosorbents under specified experimental conditions. For example, a small "b" value indicates that the metal ion has a high binding affinity with the biosorbent. The values of b and q_{max} indicate that calcium alginate beads have a greater affinity for Pb^{2+} than for Cu^{2+}. For *Sargassum filipendula* algae, the Langmuir parameters obtained for copper was q_{max} of 1.35 and b value of 3.42 $Lmmol^{-1}$ (Kleinübing et al., 2011). The result of q_{max} achieved in this study is smaller than value obtained for *Sargassum filipendula* algae. The capacity of brown marine algae to remove several metal species is due to the presence of important functional groups constituents on their cell wall. These cell walls are mainly composed of three types of biopolymers: alginate (heteropolymer constituted of guluronic acid and mannuronic acidic residues), fucoidan (heteropolymer constituted of sulfated esters of fucose and glucuronic acid moieties), and cellulose (Davis et al., 2003). The results indicate that not only alginate is important for copper removing. Functional groups present in other biopolymers are participating in the biosorption process.

3.3 Kinetic studies

Figure 4 presents Cu^{2+} and Pb^{2+} ion kinetic curves adjusted with the pseudo-first-order and pseudo-second-order models. Linear correlation coefficients and pseudo-first-order (k_1) and second-order (k_2) constants, as well as the equilibrium capacity obtained, are shown in Table 1. The value of correlation coefficient R^2 is relatively high (>0.98) for

both metals. Therefore, it can be concluded that the models describe the biosorption kinetics of metals over calcium alginate beads. The intraparticular diffusion model was also employed to assess adsorption mechanisms. The results are shown in Figure 5. This model assumed that the adsorption is controlled by three stages: the first sharper linear stage being a rapid external diffusion and surface adsorption; the second linear stage being a gradual adsorption stage, where intraparticle diffusion is rate limited; and the final stage being a final equilibrium stage, where the intraparticle diffusion starts to decrease due to low concentration in solution phase as well as less available adsorption sites.
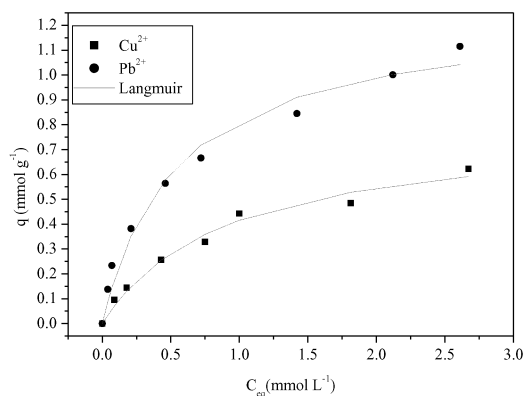

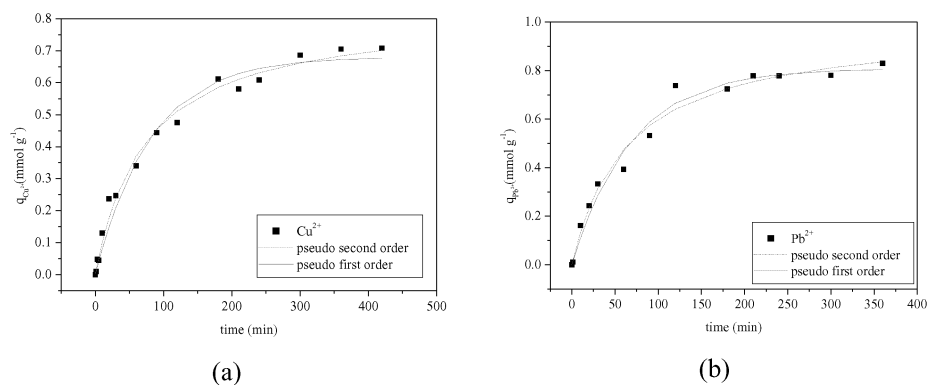*Figure 3: Langmuir isotherm for Cu^{2+} and Pb^{2+} biosorption.*

(a)   (b)

Figure 4: Pseudo-first and pseudo-second-order kinetic models for Cu^{2+} and Pb^{2+} biosorption.

As shown in Figure 5, adsorption has three stages. The first stage is completed in approximately 20 min. The second stage in the cases demonstrate a linear relationship, between 20 to 120 min and 20 to 180 min for Pb^{2+} and Cu^{2+}, respectively. The third stage is a slow process, due to the low concentration gradient. The k_d values (Figure 5) were calculated only for the region in second stages. Higher linear regression coefficients are obtained, which indicates the importance of intraparticle diffusion in the second stage.

Table 1: *Pseudo-first-order and second-order* Cu^{2+} *and* Pb^{2+} *adsorption rate coefficients models on calcium alginate bead.*

Metals	Pseudo-first order			Pseudo-second order		
	q_t	k_1	R^2	q_t	k_2	R^2
Cu^{2+}	0.680	0.0122	0.98	0.882	0.0167	0.99
Pb^{2+}	0.808	0.0144	0.98	0.986	0.0160	0.98
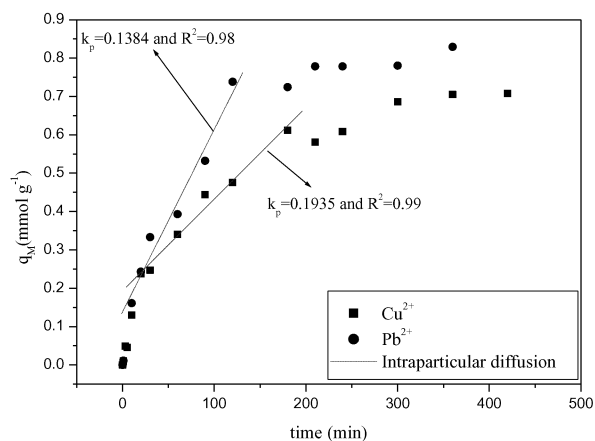
Figure 5: Kinetic intraparticular diffusion model for Cu^{2+} *and* Pb^{2+} *uptake.*

Acknowledgements

References

Davis, T. A., Volesky, B. and Mucci, A., 2003. A review of the biochemistry of heavy metal biosorption by brown algae. Water Research 37, 4311-4330.

Kleinübing, S. J., Vieira, R. S., Beppu, M., Guibal, E., da Silva, M. G. C., 2010. Characterization and Evaluation of Copper and Nickel Biosorption on Acidic Algae *Sargassum filipendula*. Advanced Materials Research, 13(4), 1-10.

Kleinübing, S. J., da Silva, E. A., da Silva, M. G. C., Guibal, E., 2011. Equilibrium of Cu(II) and Ni(II) biosorption by marine alga *Sargassum filipendula* in a dynamic system: Competitiveness and selectivity. Bioresource Technology, 102, 4610–4617.

Papageorgiou, S. K., Katsaros, F. K., Kouvelos, E. P., Nolan, J. W., Le Deit, H. and Kanellopoulos, N. K., 2006. Heavy metal sorption by calcium alginate beads from *Laminaria digitata*. Journal of Hazardous Materials 137, 1765-1772.