Kinetic Adsorption of Copper Ions by the Residue of Alginate Extraction from the Seaweed *Sargassum filipendula*

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This study focuses on the removal of Cu^{2+} ions present in low concentration in aqueous solutions using residue of alginate extraction as bioadsorbent from the brown seaweed *Sargassum filipendula*. Bioadsorption kinetic experiments were carried out at room temperature (25 ºC) and at different initial metal ion concentration (1.0, 1.5 and 2.0 mmol/L). Experimental data were described using pseudo-first-order and pseudo-second-order models. Bioadsorption mechanisms were investigated using intraparticle diffusion and Boyd models. It was observed that an average time of 60 minutes was required to reach equilibrium when the initial copper concentration was 1.0 and 1.5 mmol/L, whereas for the initial concentration of 2.0 mmol/L an average time of 120 minutes was required. Besides that, it was observed that the higher the initial concentration of copper in solution, the greater the adsorbed amount of copper. Pseudo-first-order and pseudo-second-order models fitted adequately the experimental data. Intraparticle diffusion and Boyd models showed that external diffusion is the controlling step.

1. Introduction

The degradation of water resources is one of the major environmental problems. Different pollutants can alter the quality of aquatic systems, such as toxic metals. Copper is a toxic metal found in wastewater from many industries, such as electroplating and petroleum refining industries. At low concentration, this metal does not have any negative effect to human beings. However, it can cause many problems related to health such as vomiting, nausea and headache, when it is present in high concentration (Alloway, 2010; Silva *et al.*, 2015).

Once the inadequate disposal of this metal results in environmental damages, several technologies have been studied to remove it from effluents, such as chemical precipitation, reverse osmosis and ion exchange. However, these processes are considered expensive and inefficient when it involves pollutants in low concentration, but still hazardous to human beings. Thus, alternative methods have been used to remove metal ions in diluted effluents, such as adsorption and, specifically, bioadsorption (Freitas *et al.*, 2017).

Bioadsorption can be defined as a process which involves removal of toxic metals through a mechanism that does not require metabolic activity (Davis *et al.*, 2003). This process has several advantages, such as lower operating cost, high efficiency, no nutrient requirements and less generation of chemical or biological sludge to be disposed of. These advantages have encouraged the use of this process in order to reduce the pollutant load caused by toxic metals, like copper (Silva *et al.*, 2016).

The solid material used in the bioadsorption process is called bioadsorbent. Different bioadsorbents are used to remove toxic metals in industrial effluents, such as brown seaweed *Sargassum* (Kleinübing *et al.*, 2013) and alginate extraction from the brown seaweed *Sargassum* (Bertagnolli *et al.*, 2014). This brown seaweed is used as bioadsorbent due to the composition of its cell wall, which contains functional groups that allow electrostatic attraction and complexation of metal ions in aqueous solutions. Besides that, some biochemical compounds can be found in the cell wall of these algae, such as alginate (Volesky and Holan, 1995).

Alginate is a biopolymer used as thickening and gelling agent in the food industry. When alginate is extracted from the brown seaweed, a residue is generated containing functional groups that would be responsible for the bioadsorption process (Aderhold *et al.*, 1996). The residue of alginate extraction is usually used in the production of animal food, but with a new application as bioadsorbent, this residue is going to have a higher added value (Cardoso *et al.*, 2016; Costa *et al.*, 2016).

Therefore, the main objective of this work is to evaluate the kinetic of copper bioadsorption using residue of alginate extraction as bioadsorbent from the brown seaweed *Sargassum filipendula*. Furthermore, kinetic models were used to describe the experimental data and the mechanism involved.

2. Materials and methods

The brown seaweed *Sargassum filipendula* was collected at Cigarras Beach, in São Sebastião (north coast of São Paulo), during the summer, and transported to Campinas under refrigeration. After that, the brown seaweed was rinsed with distilled water, dried in an oven at 60 °C for 24h. Then, it was grinded and sieved into fractions smaller than 1 mm diameter.

2.1 Alginate extraction

The alginate extraction was performed according to the method described by McHugh (1987). In this method, 15 g of brown algae were brought into contact with 500 mL of formaldehyde solution (0.4% v/v) under constant agitation for 30 minutes, in order to clarify and remove phenolic compounds (Bertagnolli *et al*., 2014). The material is then washed thoroughly with deionized water and then brought into contact with 500 ml of hydrochloric acid solution (0.1 mmol/L) under constant agitation for 2 hours in order to remove the phenolic compounds still present. After this initial stage, the material was washed thoroughly with deionized water and then brought into contact with 350 ml of sodium carbonate solution (2% w/v) under constant agitation for 5 hours at 60 °C. The viscous mixture was vacuum filtered to separate the residue and the solution containing alginate. After that, an amount of ethanol was added in the ratio 1:1 (v/v) in order to precipitate the alginate, while the residue was washed and dried at 60 °C for 24 hours. The yield of material obtained (alginate and residue) was calculated according to Eq. (1):

$$\%yield(material) = \left(\frac{final\ dry\ matter\ of\ material)}{seaweed\ dry\ matter\ before\ extraction} \right) x100 \tag{1}$$

2.2 Metal speciation

The metal speciation of copper was simulated using the software MEDUSA (Make Equilibrium Diagrams Using Sophisticated Algorithms) and HYDRA (Hydrochemical Equilibrium – Constant Database) (Puigdomenech, 2004) with concentration of 2.0 mmol/L. The study of metal speciation is important to determine the value of pH during the experiments and avoid precipitation of the metal species.

2.3 Bioadsorption kinetics

Bioadsorption kinetics experiments were performed with 1 g of bioadsorbent added to 500 mL metallic solution of copper in a metallic ion initial concentration of 1.0, 1.5 and 2.0 mmol/L. Kinetic experiments are important to evaluate the rate of bioadsorption in relation to time. The metal adsorption capacity by the bioadsorbent was calculated according to Eq. (2).

$$q = \frac{(C_0 - C_f)V}{m_s} \tag{2}$$

where: q = metallic ion adsorption capacity (mmol/g); C_o = metallic ion initial concentration (mmol/L); C_f = metallic ion final concentration after equilibrium has been reached (mmol/L); V = solution volume (L); m_s = bioadsorbent dry mass (g).

Besides that, various models were used to describe the experimental data and the mechanisms involved, such as pseudo-first-order, pseudo-second-order, intraparticle diffusion and Boyd model. The study of kinetic modeling is relevant to investigate the mechanism of bioadsorption.

Pseudo-first-order model (Lagergren, 1898) considers that the predominant resistance to mass transfer is the external resistance. In this case, it is described through a pseudo-first-order relation, given by Eq. (3):

$$q(t) = q_{eq}(1 - e^{-k_1 t}) \tag{3}$$

where: q(t) = metallic ion adsorption capacity at time t (mmol/g); q_{eq} = metallic ion adsorption capacity at equilibrium (mmol/g); k_1 = adsorption rate constant of pseudo-first-order (min^{-1}); t = tempo (min).

Pseudo-second-order model (Ho and McKay, 1999) considers that mass transfer is controlled by external diffusion. This model is described through a pseudo-second-order relation, given by Eq. (4):

$$q(t) = \frac{q_{eq}^2 k_2 t}{q_{eq} k_2 t + 1} \tag{4}$$

where: k_2 = adsorption rate constant of pseudo-second-order (g.mmol.min^{-1}).

The intraparticle diffusion model considers that the predominant resistance is the resistance due the internal diffusion through the pore (Weber and Morris, 1963). This model is given by Eq. (5):

$$q(t) = k_i t^{0,5} + c \tag{5}$$

where: k_i = characteristic parameter of the process (mmol/(g.min$^{1/2}$)); c = constant that provides an approximation of the boundary layer thickness (mmol/g).

The Boyd's kinetic expression (Boyd *et al.*, 1947) presents the effective diffusivity of the adsorbate in the bioadsorbent, being able to predict the current limiting step involved in the adsorption process. The Boyd model is given by Eq. (6):

$$B_t = -0,4977 - \ln(1 - F) \tag{6}$$

where: F = fractional attainment of equilibrium at time t; B_t = Boyd number.

Effective diffusion coefficient (D_i) was calculated using Eq. (7):

$$\alpha = \frac{\pi^2 . D_i}{r^2} \tag{7}$$

where: r = radius of the bioadsorbent particle; α = slope coefficient of the line B_t vs t.

To evaluate the adjustment of mathematical models to experimental data it was used the correlation of determination (R^2) and Mean Relative Deviation (MRD), represented by Eqs. (8) and (9), respectively.

$$R^2 = 1 - \frac{\sum_{i=1}^{N}(q^{exp} - q^{calc})^2}{\sum_{i=1}^{N}(q^{exp} - \bar{q})^2} \tag{8}$$

$$MRD = \frac{\sum_{i=1}^{N}\left(\frac{(q^{calc} - q^{exp})}{q^{exp}}\right)}{N} x100 \tag{9}$$

where: N = number of data; q^{exp} = experimental value; q^{calc} = value calculated by the model; $\bar{q}$ = average of the observed values.

3. Results and discussion

3.1 Alginate extraction

The extraction yield of alginate and residue from the brown seaweed *Sargassum filipendula* were 24.69 ± 4.01% and 46.18 ± 2.51%, respectively. The values obtained of extraction yield of alginate were in agreement with the range of alginate present in brown seaweed (10%-40%) (King, 1983). While the values obtained of extraction yield of residue were in agreement with Bertagnolli *et al.* (2014) that was about 39%.

3.2 Metal Speciation

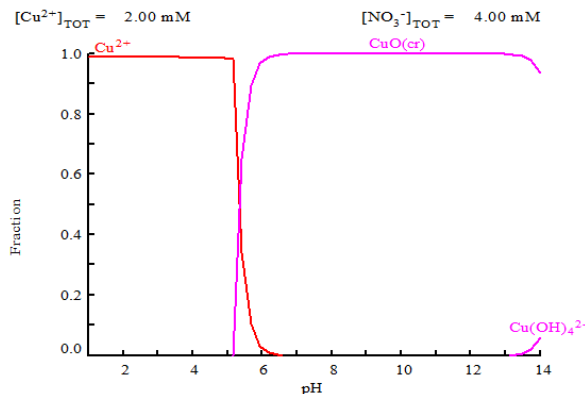The metallic speciation diagram was obtained by software HYDRA/MEDUSA and is shown in Figure 1:

Figure 1: Speciation diagram in aqueous solution of copper (Cu concentration = 2.0 mmol/L).

It is observed that the metal precipitation occurs with a pH above 5. Therefore, it was chosen a pH 5.0 for all kinetic experiments in order to avoid precipitation of copper.

3.3 Bioadsorption kinetics

Figure 2 shows the bioadsorption kinetic curves of different metallic ions concentration and the adjustments of the pseudo-first-order model and pseudo-second-order model, respectively.

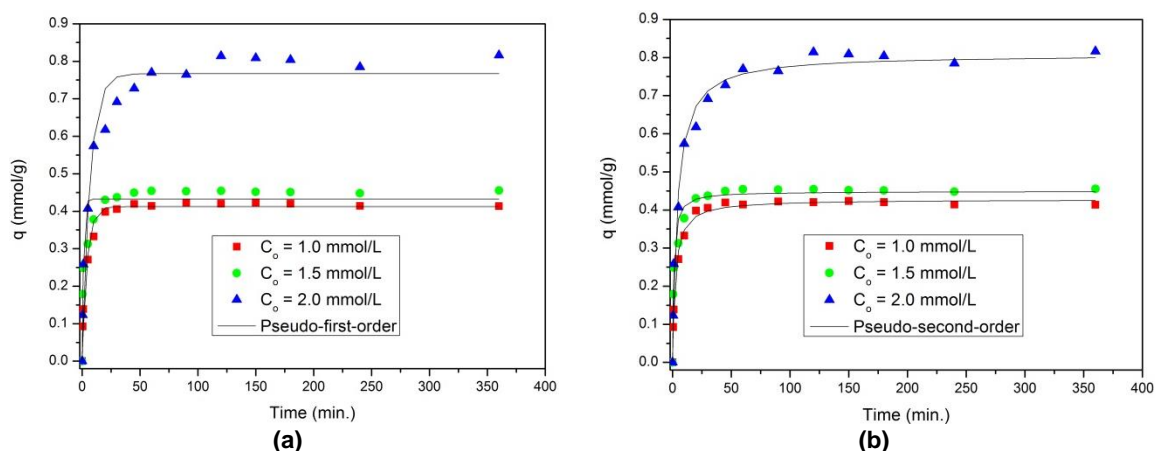<p align="center">(a)   (b)</p>

Figure 2: Adjustment of (a) the pseudo-first-order model and (b) the pseudo-second-order model to the experimental data of copper bioadsorption kinetics at different initial concentrations.

From Figure 2, it can be observed that an average time of 60 minutes was required to reach equilibrium when the initial copper concentration was 1.0 and 1.5 mmol/L, whereas for the initial concentration of 2.0 mmol/L an average time of 120 minutes was required. It is also observed that the higher the initial concentration of copper in solution, the greater the adsorbed amount of copper.

When the initial concentration of the toxic metal is low, the adsorption process is relatively fast. However, when the initial concentration is increased, the molecules settle on the surface of the solid material and over time they rearrange so that the surface can adsorb more molecules, which leads to a greater competition for active sites.

Besides that, it can be observed from the Figure 2 that the pseudo-first-order and pseudo-second-order models can adequately fit the experimental data. For these two models, their parameters, the determination coefficient R^2 and the Mean Relative Deviation (MRD) were determined, which allows to evaluate the adjustment to the experimental data. All these data can be found in Table 1.

Table 1: Parameters obtained from the pseudo-first-order and pseudo-second-order models.

Model	Parameter	Concentration of the copper solution		
		1.0 mmol/L	1.5 mmol/L	2.0 mmol/L
Experimental	q_{eq} (mmol/g)	0.421	0.451	0.802
Pseudo-first-order	q_{eq} (mmol/g)	0.413	0.433	0.767
	k_1 (min^{-1})	0.235	0.870	0.147
	R^2	0.974	0.922	0.947
	MRD (%)	8.656	7.352	12.641
Pseudo-second-order	q_{eq} (mmol/g)	0.428	0.449	0.808
	k_2 (min^{-1})	1.016	2.338	0.307
	R^2	0.994	0.974	0.982
	MRD (%)	3.842	4.626	7.428

In Table 1, it can be seen that the pseudo-second-order model presents a better adjustment compared to the pseudo-first-order model. This better adjustment of the pseudo-second-order model was expected because this model involves a chemisorption step being the rate controlling step.

Concerning the intraparticle diffusion model, shown in Figure 3, we can distinguish the three stages: at the beginning, the stage related to external diffusion, then the step referring to the intraparticle diffusion with gradual adsorption, and finally, the reference stage to equilibrium. The data of the second stage were adjusted linearly in order to describe the relevance of this step in the bioadsorption process. Table 2 shows the parameters of the intraparticle diffusion model, as well as the determination coefficient R^2 and the Mean Relative Deviation (MRD).
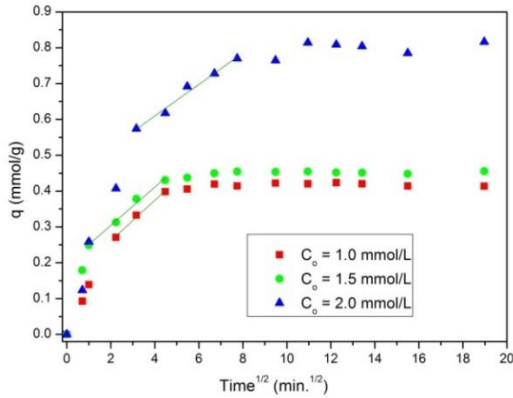
Figure 3: Adjustment of the intraparticle diffusion model to the experimental data of copper bioadsorption kinetics at 3 initial concentrations.

Table 2: Parameters obtained from the intraparticle diffusion model.

Model	Parameter	Concentration of the copper solution		
		1.0 mmol/L	1.5 mmol/L	2.0 mmol/L
Intraparticle diffusion	k_i (mmol/g.min)	0.057	0.054	0.044
	c (mmol/g)	0.148	0.197	0.434
	R^2	0.993	0.989	0.981
	MRD (%)	1.383	1.785	1.097

According to Table 2, the intraparticle diffusion model presented a good fit to the experimental data. It is observed that the constant c, which represents the thickness of the boundary layer, increases with increasing initial concentration. In this case, the increase in the concentration of copper ions may have increased the external resistance.

The Boyd model, observed in Figure 4, shows that the linear adjustment for the three initial concentrations does not cross the axis at the origin, indicating that external diffusion is the controlling step. For this model, it was calculated the effective diffusion coefficient and it was settled the determination coefficient R^2. These values are shown in Table 3.
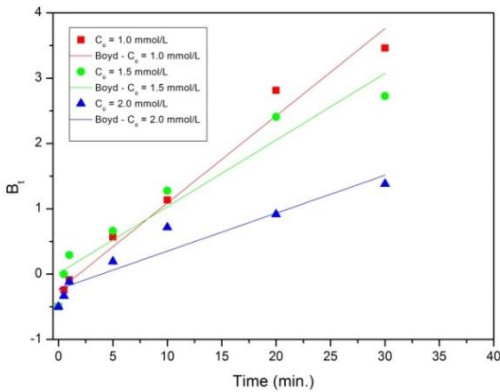

Figure 4: Adjustment of the Boyd model to the experimental data of copper bioadsorption kinetics in concentration of 1.0, 1.5 and 2.0 mmol/L.

Table 3: Parameters obtained from the Boyd model.

Model	Parameter	Concentration of the copper solution		
		1.0 mmol/L	1.5 mmol/L	2.0 mmol/L
Boyd	D_i (cm²/s)	3.1.E-07	2.3.E-07	1.3.E-07
	R^2	0.973	0.916	0.894

According to Table 3, the Boyd model presented a good fit to the experimental data. It is observed that the effective diffusion coefficient decreased with increasing initial concentration. In this case, it indicates that the external diffusion have influence in the process of mass transfer. The values of D_i are in agreement with

values found in the literature, which range is between 10^{-6} and 10^{-8} cm²/s for copper adsorption (Freitas *et al.*, 2017; Teixeira *et al.*, 2013).

4. Conclusions

The results of the kinetic biosorption experiments of copper at different initial concentrations (1.0, 1.5 and 2.0 mmol/L) indicated that the bioadsorption is dependent of the initial concentration, once the higher the initial concentration in solution, the greater the bioadsorption capacity of the material in equilibrium. The pseudo-second-order model presented a better adjustment than the first-pseudo-order model due to the higher values obtained for R² and the smaller deviations between the predicted and calculated experimental biosorption capacities. The intraparticle diffusion model and Boyd model indicated that the external mass transfer control the process. Finally, the material proved to be efficient and has the potential to be applied as bioadsorbent in the removal of copper in diluted aqueous solutions, once it showed very fast bioadsorption kinetics, which the adsorption equilibrium was reached in 2 hours for the higher concentration.

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