Adsorption of metal ions in red marine algae *Lithothamnium calcareum* in the treatment of industrial effluents

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ABSTRACT

This study investigated the adsorption capacity of the elements Chromium (Cr), Manganese (Mn) and Zinc (Zn) to marine algae *Lithothamnium calcareum* by means of adsorption kinetics and batch adsorption tests, with a view to the development of a simple technique for the treatment of effluents that have a high concentration of metal ions. The algae was sieved, washed and subjected to treatment. In the adsorption kinetics, 0.2 g of algae was weighed, an amount transferred to 125 mL Erlenmeyer flasks, to which was added 15 mL of solution with a concentration of 5 mg L^{-1} of the metal ion. The flasks were stirred at 60 rpm for 240 minutes. In batch adsorption, 0.2 g of algae was weighed, amount transferred to 125 mL Erlenmeyer flasks, to which was added 15 mL of solution with concentrations of 5, 10, 20, 50, 100, 250 e 500 mg L^{-1} of the metal ion. The flasks were stirred at 60 rpm for 24 hours. In the two tests, the supernatant solutions collected were centrifuged at 2000 rpm for 5 minutes and the equilibrium concentrations of metal ions were determined by atomic absorption spectrometry. It was found that, in 240 minutes of contact, the *Lithothamnium calcareum* removed 15.5% of Cr, 33.0% of Mn and 8.0% of Zn in solution; and that in 24 hours of contact, at a concentration of 5 mg L^{-1}, it removed 0.4% of Cr, 52.5% of Mn and 92.6% of Zn; and, at a concentration of 500 mg L^{-1}, it removed 20.0% of Cr, 22.6% of Mn and 40.8% of Zn. The results showed that the *Lithothamnium calcareum* submitted to thermochemical treatment presented potential for use in the adsorption of Cr, Mn and Zn.

Keywords: biosorbent, isotherm, kinetics, trace elements.

Adsorção de íons metálicos em alga marinha vermelha *Lithothamnium calcareum* no tratamento de efluentes industriais

RESUMO

Objetivou-se investigar a capacidade adsortiva dos elementos Cromo (Cr), Manganês (Mn) e Zinco (Zn) à alga marinha *Lithothamnium calcareum* por meio de ensaios de cinética de

adsorção e adsorção em batelada, tendo em vista o desenvolvimento de uma técnica simples para o tratamento de efluentes que apresentam elevada concentração de íons metálicos. A alga foi peneirada, lavada e submetida a tratamento. Na cinética de adsorção, pesou-se 0,2 g de alga, quantidade transferida para frascos Erlenmeyer de 125 mL, aos quais adicionou-se 15 mL de solução em concentração de 5 mg L^{-1} do íon metálico. Os frascos foram agitados a 60 rpm, por 240 minutos. Na adsorção em batelada, pesou-se 0,2 g de alga, quantidade transferida para frascos Erlenmeyer de 125 mL, aos quais adicionou-se 15 mL de solução em concentrações de 5, 10, 20, 50, 100, 250 e 500 mg L^{-1} do íon metálico. Os frascos foram agitados a 60 rpm, por 24 horas. Nos dois ensaios, as soluções sobrenadantes coletadas foram centrifugadas a 2000 rpm, por 5 minutos, e as concentrações de equilíbrio dos íons metálicos foram determinadas por espectrometria de absorção atômica. Verificou-se que, em 240 minutos de contato, a *Lithothamnium calcareum* removeu 15,5% do Cr, 33,0% do Mn e 8,0% do Zn em solução, e que, em 24 horas de contato, em concentração de 5 mg L^{-1}, removeu 0,4% de Cr, 52,5% de Mn e 92,6% de Zn, e, em concentração de 500 mg L^{-1}, removeu 20,0% de Cr, 22,6% de Mn e 40,8% de Zn. Os resultados mostraram que a *Lithothamnium calcareum* submetida ao tratamento termoquímico apresentou potencial de uso na adsorção de Cr, Mn e Zn.

Palavras-chave: biossorvente, cinética, elementos traço, isoterma.

1. INTRODUCTION

Increasing technological and industrial expansion has intensified the contamination of water bodies with metal ions (Kobielska *et al.*, 2018; Calderón *et al.*, 2020). Various production processes generate effluents with a high concentration of trace elements such as Cadmium (Cd), Lead (Pb), Copper (Cu), Chromium (Cr), Nickel (Ni) and Zinc (Zn) (Akpomie *et al.*, 2018; Cheng *et al.*, 2019). These elements are toxic and present risks to the environment and human health (Lin *et al.*, 2016; Novaes *et al.*, 2018).

Metal ions are hardly removed by conventional methods of effluent treatment, they usually show resistance to biological degradation methods and are usually not removed effectively by physicochemical treatment methods such as chemical precipitation, coagulation, among others (Chigare *et al.*, 2019; Salama *et al.*, 2019). There is a clear need for the development of new treatment technologies for the removal of these elements present in effluents from industrial activities.

The adsorption process, the focus of this study, consists of the interaction between the adsorbent, a material capable of retaining ions or molecules of contaminants on its surface (Lakherwal, 2014; Chen *et al.*, 2016), and adsorbate, a substance present in the effluent, as trace elements, and which is retained on the surface of the adsorbent material (Qian, 2019).

The study of adsorption kinetics makes it possible to predict the speed with which the adsorbate will be removed from the solution and the time for the balance between the amount of solute in solution and adsorbed on the surface of the adsorbent (Petter *et al.*, 2016), which enables the proper projection of the effluent treatment plant (Wei *et al.*, 2017).

Another way to analyze the adsorption process is through the use of adsorption isotherms, which represent the distribution, in equilibrium, of the adsorbate molecules between the solid phase and the liquid phase, which allows us to identify how and how much of the contaminants the adsorbent will effectively adsorb (Nayak *et al.*, 2017).

The process of biosorption is similar to that of adsorption, differing only by the fact that the removal of compounds occurs using as adsorbent a biomaterial, such as algae biomass (He and Chen, 2014; Anastopoulos and Kyzas, 2015). Biosorption offers flexibility of operation, being recognized as an effective method for the treatment of effluents containing elements harmful to the environment (Beni and Esmaeili, 2020; Bulgariu and Bulgariu, 2020).

The red marine algae (*Lithothamnium calcareum*), whose main feature includes the presence of calcium carbonate in its cell walls, has a high adsorptive potential for metal ions (Veneu *et al.*, 2016; 2018). In addition to having a porous structure, which gives it a high specific surface and suggests its application in the adsorption of metal ions of industrial effluents, advantages such as wide availability, low cost and the possibility of reuse of biomass have been attributed to *Lithothamnium calcareum* (Bilal *et al.*, 2018; Cheng *et al.*, 2019).

Veneu *et al.* (2016) applied *Lithothamnium calcareum* in the treatment of aqueous solutions containing Cr and obtained 99.9% removal of the element. Ibrahim *et al.* (2016) evaluated the adsorption of Cd, Cr and Cu to marine algae *Ulva lactuta* and confirmed the potential use of the algae in the removal of trace elements from aqueous solutions. Mahmood *et al.* (2017) employed algae *Sargassum* sp. in Cd and Zn removal of synthetic wastewater and managed to get 95.3% and 90.1% removal.

Using marine algae *Jania rubens*, *Sinous Colpomenia* and *Ulva lactuca* as adsorbents, Ibrahim *et al.* (2018) achieved, respectively, 91.0%, 89.0% and 85.0% removal of metal ions from synthetic wastewater. The work attested to the use of algae *Jania Rubens* as an economical and efficient alternative technology for the removal of metal ions from wastewater.

Studies in order to know the adsorptive potential of marine algae are important, since they make it possible to predict the removal of a certain contaminant as a function of time, enabling the optimization of the process so that the desired concentration at the end of the treatment is obtained effectively (Zeraatkar *et al.*, 2016; Mazur *et al.*, 2018; Rangabhashiyam and Balasubramanian, 2019; Ameri *et al.*, 2020).

Given the above, this study investigated the adsorption capacity of the elements Chromium (Cr), Manganese (Mn) and Zinc (Zn) to *Lithothamnium calcareum* by means of adsorption kinetics and batch adsorption tests, with a view to the development of a simple technique for the treatment of effluents that have a high concentration of metal ions.

2. MATERIAL AND METHODS

The marine algae used in the present study (Figure 1) was provided by a company for the extraction and processing of products derived from the *Lithothamnium calcareum*, comprising the residue of these activities.

Figure 1. Marine algae used in the study.

The ability of *Lithothamnium calcareum* in adsorbing the elements Cr, Mn and Zn was evaluated by assays of adsorption kinetics and batch adsorption, according to the adaptation of the procedure performed by Oliveira *et al.* (2014).

The tests were carried out in the Water Quality Laboratory of the Environmental and

Sanitary Engineering Nucleus, belonging to the Departmet of Environmental Engineering (DAM) of the Federal University of Lavras (UFLA) and in the Biomaterials Laboratory, belonging to the Engineering Department (DEG) of UFLA.

2.1. Treatment of marine algae *Lithothamnium calcareum*

Initially, the marine algae was sieved in a 0.5 mm sieve and the material retained in the sieve was washed with distilled water until the observation of the stabilization of the electrical conductivity of the washing water. After this step, the algae was subjected to heat treatment.

The thermochemical treatment of the algae consisted of weighing, in a Petri dish, 50 g of the previously sieved and washed algae placed in a stove at a temperature of 100ºC for a period of 24 hours. After this step, the algae was cooled to room temperature and subjected to agitation in a solution of 1 L of citric acid 0.001 Molar, with the aid of a magnetic stirrer for the period of 1 hour, as performed by Almeida (2018).

This treatment aimed to remove the outer layer of the algae by citric acid, leaving its cavities exposed, as verified by Almeida (2018) in scanning electron microscopy. In addition, the author found, by infrared spectroscopy with Fourier transform, that the treatment, although mild, was sufficient to promote the opening of new pores and increase the surface area for adsorption, since he observed an increase of 3.0478 $mg^2 \, g^{-1}$ on its specific surface.

The apparent specific mass (1.20 $g \, cm^{-3}$) and the specific mass of particles (2.15 $g \, cm^{-3}$) of the algae were obtained by the tube and pycnometer methods, respectively, according to Teixeira *et al.* (2017) and, in possession of these values, its total porosity was determined (0.4419 $cm^3 \, cm^{-3}$).

2.2. Adsorption kinetics

In the adsorption kinetics assay, 0.2 g of treated marine algae were weighed on an analytical balance, an amount that was transferred to 125 mL Erlenmeyer flasks, to which 15 mL of solution was added at a concentration corresponding to 5 mg L^{-1} of the metal ion under study. For this purpose, these salts were used: Potassium Chromate (K_2CrO_4), Manganese Chloride ($MnCl_2$) and Zinc Chloride ($ZnCl_2$). The concentration applied in the study was based on Resolution No. 430 of the National Environment Council (Conama, 2011), which establishes maximum levels of contaminants for the disposal of industrial effluents.

The solutions were individually subjected to contact with marine algae. During the test, the temperature and pH of the solutions were measured using, respectively, an infrared thermometer and a bench pH meter. The tests were conducted at mean temperature of 25.0ºC ± 1.0ºC and mean pH of 7.5 ± 1.0.

The Erlenmeyer flasks containing the solutions and marine algae were stirred at 60 rpm on a stirring table for 2, 5, 10, 20, 60, 120, 180 and 240 minutes, in triplicate for each stirring time. The collected supernatant solutions were centrifuged at 2000 rpm for 5 minutes and the supernatants were packaged in glass vials.

The equilibrium concentrations of the elements were determined by atomic absorption spectrometry, by direct acetylene air flame method, in the Laboratory of Foliar Analysis of the Department of Chemistry (DQI) of UFLA, according to APHA *et al.* (2012). The current of the hollow cathode lamps, the height of the burner and the wavelength used in the determination were: 6 mA, 9 cm and 357.9 nm for the Cr, 5 mA, 7 cm and 279.5 nm for the Mn and 5 mA, 7 cm and 213.9 nm for the Zn.

The adsorbed quantities were calculated using Equation 1. The removal percentages were obtained by applying Equation 2.

$$S = \left(C_i - C_f \right) \frac{Vol}{m} \tag{1}$$

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$$Remoção = \frac{(C_i - C_f)}{C_i} \times 100 \tag{2}$$

Where: S = concentration of the adsorbed element by adsorbent mass (mg g^{-1}); C_i e C_f = initial and final concentration of the element in solution (mg L^{-1}); m = mass of algae (g); Vol = volume of solution (L).

The results of the adsorption kinetics assay were adjusted by the models of Pseudo-first order (Equation 3), Pseudo-second order (Equation 4) and Elovich (Equation 5). To estimate the parameters, the method of minimizing the sum of the squares of the deviations was used, using the Solver® package of Microsoft Excel.

$$Q_t = Q_e(1 - e^{-K_1 t}) \tag{3}$$

$$Q_t = \frac{Q_e^2 K_2 t}{1 + Q_e K_2 t} \tag{4}$$

$$Q_t = \frac{1}{\beta} \ln \ln (1 + \alpha \beta t) \tag{5}$$

Where: Q_t = concentration of the adsorbed element by adsorbent mass in time (mg g^{-1}); Q_e = amount adsorbed on balance (mg g^{-1}); t = equilibrium time (minutes); K_1 (min^{-1}) and K_2 (mg g^{-1} min^{-1}) = constants of the models of Pseudo-first order and Pseudo-second order, respectively; α = initial adsorption rate (mg g^{-1} min^{-1}); β = desorption constant (mg g^{-1}).

2.3. Batch adsorption

In the adsorption kinetics assay, 0.2 g of treated marine algae was weighed on an analytical balance, an amount that was transferred to 125 mL Erlenmeyer flasks, to which 15 mL of solution was added at concentrations corresponding to 5, 10, 20, 50, 100, 250 and 500 mg L^{-1} of the metal ion under study. For this purpose, these salts were used: Potassium Chromate (K_2CrO_4), Manganese Chloride ($MnCl_2$) and Zinc Chloride ($ZnCl_2$).

The solutions were individually subjected to contact with marine algae. During the test, the temperature and pH of the solutions were measured using, respectively, an infrared thermometer and a bench pH meter. The tests were conducted at mean temperature of 25.0ºC ± 1.0ºC and mean pH of 7.5 ± 1.0.

The Erlenmeyer flasks containing the solutions and the marine algae were stirred at 60 rpm in a bench incubator with orbital stirring for 24 hours, in triplicate for each concentration. The collected supernatant solutions were centrifuged at 2000 rpm for 5 minutes and the supernatants were packaged in glass vials.

The equilibrium concentrations of the elements were determined by atomic absorption spectrometry, by direct acetylene air flame method, in the Laboratory of Foliar Analysis of the Department of Chemistry (DQI) of UFLA, according to APHA *et al.* (2012). The current of the hollow cathode lamps, the height of the burner and the wavelength used in the determination were: 6 mA, 9 cm and 357.9 nm for the Cr, 5 mA, 7 cm and 279.5 nm for the Mn and 5 mA, 7 cm and 213.9 nm for the Zn. The adsorbed quantities were calculated using Equation 1.

The batch adsorption assay results were adjusted by the models of linear Freundlich (Equation 6), potential Freundlich (Equation 7), Langmuir (Equation 8) and Sips (Equation 9). To estimate the parameters, the method of minimizing the sum of the squares of the deviations was used, using the Solver® package of Microsoft Excel.

$$Q_e = K_d C_e \tag{6}$$

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$$Q_e = K_f C_e^{\frac{1}{n}}$$ (7)

$$Q_e = \frac{K_L C_e Q_m}{1 + K_L C_e}$$ (8)

$$Q_e = \frac{Q_m (K_S C_e)^{\frac{1}{ns}}}{1 + (K_S C_e)^{\frac{1}{ns}}}$$ (9)

Where: Q_e = amount of adsorbed solute (mg g^{-1}); C_e = equilibrium concentration in the supernatant (mg L^{-1}); K_d = Freundlich partition coefficient (L g^{-1}); K_f = Freundlich model constant potential (mg$^{1-1/n}$ kg^{-1} L$^{1/n}$); K_L = Langmuir model constant (L mg^{-1}); Q_m = maximum adsorption (mg g^{-1}); K_s = sips model constant (L mg^{-1})$^{1/n}$; n and ns = empirical coefficients of the models of potential Freundlich and Sips, respectively.
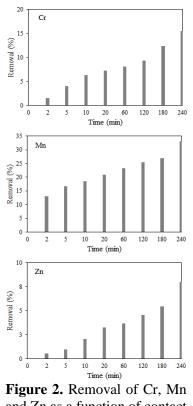
Based on the Freundlich partition coefficient (K_d), the determination of the retardation factors of the metal ion under study was carried out, applying Equation 10.

$$R = 1 + \frac{D_s}{P} K_d$$ (10)

Where: K_d = Freundlich partition coefficient (L g^{-1}); P = total porosity (0.4419 cm^3 cm^{-3}); D_s = apparent specific mass (1.20 g cm^{-3}).

3. RESULTS AND DISCUSSION

By analyzing the results of the adsorption kinetics test, an increase in the percentage of removal was found of Cr, Mn and Zn elements by marine algae *Lithothamnium calcareum* subjected to thermochemical treatment as a function of contact time (Figure 2).

Figure 2. Removal of Cr, Mn and Zn as a function of contact time with marine algae *Lithothamnium calcareum*.

In the first 2 minutes of contact, a high adsorption rate was observed of Mn to *Lithothamnium calcareum*, a situation represented by the high slope of the curve at the beginning of the process. Due to the high availability of active sites at the beginning of the adsorption process, the Mn ions in solution were able to interact with the marine algae, resulting in removal of 13.0% of the Mn ions in solution. After 5 minutes of contact, there was a reduction in the adsorption rate of Mn to the marine algae.

For the Cr and Zn elements, a high adsorption rate was observed in the first 10 minutes of contact to *Lithothamnium calcareum*, a situation represented by the high slope of the curve at the beginning of the process. Due to the high availability of active sites at the beginning of the adsorption process, the Cr and Zn ions in solution were able to interact with the marine algae, resulting in removal of 6.4% of the Cr ions and 2.0% of the Zn ions in solution. After 10 minutes of contact, the adsorption rate of Cr and Zn to marine algae was reduced.
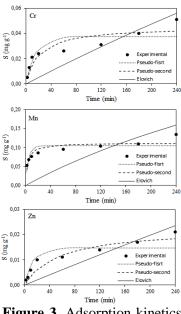
As the contact time progressed, the active sites present on the surface of the *Lithothamnium calcareum* were being occupied until its saturation, which resulted in a reduction in the adsorption rate of the ions Cr, Mn and Zn to marine algae.

According to Lin *et al.* (2020), in just 20 min of contact the algae can adsorb more than 90% of the metal ions in solution. The high adsorption rate in the initial minutes of contact can be attributed to the greater number of active sites available on the surface of the algae. Over time, due to the saturation of active sites, the adsorption rate decreases (Ibrahim *et al.*, 2016).

When the solution is put in contact with the algae, metal ions tend to flow from the aqueous medium to the surface of the algae until the solute concentration in the liquid phase remains constant. At this time, the adsorption rate reaches equilibrium (Ferreira *et al.*, 2017). The equilibrium time corresponds to a certain moment after which significant additional amounts of adsorbate will no longer be adsorbed.

Usually the adsorption rate reaches equilibrium after 3 hours of contact (Sari and Tuzen, 2009; Jacinto *et al.*, 2009). In general, it was observed that the adsorption of the elements Cr, Mn and Zn to *Lithothamnium calcareum* did not reach equilibrium, because, as seen in Figure 2, it was found that the percentages of removal of the elements continued increasing.

The models of Pseudo-first order, Pseudo-second order and Elovich were adjusted to the results obtained in the adsorption kinetics assays of Cr, Mn and Zn elements to marine algae *Lithothamnium calcareum* subjected to thermochemical treatment (Figure 3).

Figure 3. Adsorption kinetics of Cr, Mn and Zn elements to *Lithothamnium calcareum*.

Table 1 presents the adjustment parameters of the adsorption kinetics models for the elements under study.

Table 1. Setting parameters of adsorption kinetics models.

Element	Model					
	Pseudo-first order		Pseudo-second order		Elovich	
Chrome	Q_e	0.0376	Q_e	0.0455	β	3.8632
	K_1	0.0622	K_2	1.0541	α	0.0003
	R^2	0.7547	R^2	0.8401	R^2	0.8811
Manganese	Q_e	0.1051	Q_e	0.1120	β	3.8790
	K_1	0.2019	K_2	2.6231	α	0.0009
	R^2	0.6418	R^2	0.7870	R^2	0.8870
Zinc	Q_e	0.0146	Q_e	0.0225	β	3.8627
	K_1	0.0717	K_2	0.8220	α	0.0001
	R^2	0.8143	R^2	0.9326	R^2	0.8980

The Pseudo-second order model, which is based on the assumption that the adsorption capacity corresponds to the number of active sites available on the surface of the adsorbent (Vijayaraghavan *et al.*, 2017; Wang *et al.*, 2018), presented better adjustment for the Zn, with coefficient of determination equal to 0.9326.

The results obtained in the present study corroborate the results obtained in similar studies, in which the authors also observed that the Pseudo-second order model presented a better fit for the Zn (Table 2).

Table 2. Kinetic modeling of Zn adsorption in marine algae.

Seaweed	Contact time (min)	Q_e (mg g⁻¹)	K_2 (g mg⁻¹ min⁻¹)	R^2	Reference
Eucheuma denticulatum	120	1.22	0.0867	0.9999	Rahman and Sathasivam (2016)
Chara aculeolata *Nitella opaque*	360	4.60 2.98	0.1080 6.7930	1.0000 1.0000	Sooksawat *et al.* (2016)
Ulva sp.	120	7.55	0.0917	0.9998	Bădescu *et al.* (2017)
Chaetomorpha sp., *Polysiphonia sp.*, *Ulva sp.*, *Cystoseira* sp.	120	127.12	0.0006	0.9978	Deniz and Karabulut (2017)

Note: The differences between the adsorbed quantities in equilibrium are related to the different experimental conditions, such as the initial concentration of the studied element, the contact time, the stirring speed, the structure and the surface area of the adsorbent material, among others.

As the kinetic modeling showed that the experimental results were better described by the Pseudo-second order model, it is inferred that the adsorption of Zn to *Lithothamnium calcareum* involved, predominantly, mechanisms of chemical interactions between metal ions present in the solution and functional groups present on the surface of the seaweed.
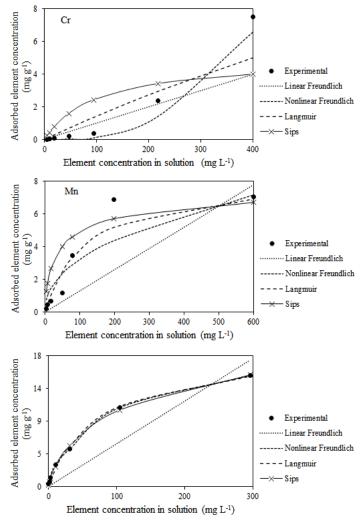
Thus, it was found that the adsorption of Zn to *Lithothamnium calcareum* occurred mainly by ion exchange. Similar behavior was reported by Ji *et al.* (2012) and Pozdniakova *et al.* (2016) in Zn adsorption studies in different marine algae.

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Elovich's model, which assumes that in an adsorption process, without taking into account the desorption, the adsorption rate decreases exponentially with the reduction of available active sites (Qiu *et al.*, 2011), presented better adjustment for Cr and Mn, with determination coefficients equal to 0.8811 and 0.8870, respectively. This indicates that over time, due to the increased coverage of the surface of the *Lithothamnium calcareum*, there was a decrease in the adsorption of Cr and Mn.

Many studies seeking to develop a theoretical basis for Elovich's model assume that adsorption occurs on the surface of highly heterogeneous adsorbents (Piasecki and Rudziński, 2007), this being one of the most used models to describe chemical adsorption (Lim and Lee, 2015; Largitte and Pasquier, 2016).

The Freundlich linear, Freundlich potential, Langmuir and sips models were adjusted to the results obtained in batch adsorption tests of Cr, Mn and Zn elements to marine algae *Lithothamnium calcareum* subjected to thermochemical treatment (Figure 4).

Figure 4. Adsorption isotherms of the elements Cr, Mn and Zn to *Lithothamnium calcareum*.

The initial concentration of the compound plays an important role in the adsorption process, since at high concentrations large amounts of metal ions are available to compete for binding sites (Al-Homaidan *et al.*, 2014).

By increasing the initial concentration of the metal ions under study, the adsorption rate per marine algae mass increased. This was because the increase in the initial concentration of the metal ions increased the mass transfer force, thereby increasing the rate at which the metal

ions were adsorbed (Rangabhashiyam *et al.*, 2016; Bădescu *et al.*, 2017).

However, although the adsorption rate increases with the increase in the concentration of metal ions, due to the saturation of the *Lithothamnium calcareum*, the adsorption showed greater efficiency in lower concentrations of metal ions Mn and Zn, corroborating with the result obtained by Tangjuank *et al.* (2009).

In a similar study, Ghasemi *et al.* (2016) found that the increase in the initial concentration of the compound resulted in a reduction in the efficiency of Mn removal by the marine algae used, *Sargassum hystrixalgae*. The author concluded that, due to the probable saturation of the active sites present on the surface of the alga, the percentage of Mn removal was reduced.

Table 3 presents the adjustment parameters of the adsorption isotherm models for the elements under study.

Table 3. Setting parameters of adsorption kinetics models.

Element	Model							
	Freundlich		Freundlich potential		Langmuir		Sips	
Chrome	K_d	0.0100	K_f	0.4500	Q_m	30.0000	Q_m	5.0000
			n	0.7500	K_L	0.0005	K_s	0.0100
	R^2	0.9415	R^2	0.9905	R^2	0.9176	ns	1.0000
							R^2	0.6557
Manganese	K_d	0.0129	K_f	0.4104	Q_m	8.3007	Q_m	8.0000
			n	2.2378	K_L	0.0085	K_s	0.0200
	R^2	0.6832	R^2	0.8574	R^2	0.9292	ns	1.5000
							R^2	0.8639
Zinc	K_d	0.0588	K_f	1.0000	Q_m	19.1232	Q_m	24.5867
			n	1.0000	K_L	0.0130	K_s	0.0066
	R^2	0.8811	R^2	1.0000	R^2	0.9966	ns	1.2973
							R^2	0.9979

The potential Freundlich model, which assumes the heterogeneity of the surface of the adsorbent and provides for an exponential distribution of several adsorption sites with different energies (Barquilla *et al.*, 2017), presented better adjustment for Cr and Zn, with determination coefficients equal to 0.9905 and 1.0000, respectively. This indicates that the adsorption of Cr and Zn to *Lithothamnium calcareum* occurred with the formation of multilayers on a heterogeneous surface, corroborating with the results obtained by Akpomie *et al.* (2018).

The results obtained in the present study corroborate the results obtained in similar works, in which the authors also observed that the model of Freundlich potential presented better fit for Cr (Rangabhashiyam *et al.*, 2016) and to the Zn (Rahman and Sathasivam, 2016).

The Langmuir model, which considers that adsorption sites on the surface of the adsorbent is finite, presented a better fit for the Mn, with coefficient of determination equal to 0.9292. This indicates that the Mn ions in solution did not undergo mutual interaction and did not change from one active site to another, and that the adsorption of the Mn to *Lithothamnium calcareum* ceased when all active sites were occupied by Mn ions, promoting the formation of a monolayer on the surface of the algae, corroborating the result obtained by Ghasemi *et al.* (2016).

The determination of the retardation factors (R) allowed us to infer on the adsorption of the metal ions evaluated by the values obtained: Cr 1.0272, Mn 1.0350 and Zn 1.1597. A predominance of adsorption of the bivalent elements was verified and an order of preference in

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the adsorption of the elements: Zn > Mn > Cr. was observed. The Freundlich partition coefficient (K_d) (Table 3), which expressed the binding energy between the metal ions studied and the active sites present on the surface of the *Lithothamnium calcareum* (Nascimento *et al.*, 2014), was a determining factor in this sequence.

By the results obtained in the present study, it was found that the removal of the elements Cr, Mn and Zn occurred mainly by ion exchange. The active sites present on the surface of the *Lithothamnium calcareum* were occupied by cations such as Ca^{2+} and Mg^{2+} (Ahmad *et al.*, 2018); however, when in contact with the solutions containing Cr, Mn and Zn, the alkaline earth metals were exchanged for the transition metals, being these adsorbed to the surface of the *Lithothamnium calcareum.*

In view of the results obtained in the present study and in the studies consulted, it was found that marine algae has been shown to be a good adsorbent material, presenting high adsorption capacity of metal ions, suggesting its use in the treatment of effluents that have a high concentration of these elements.

It is emphasized that factors such as algae treatment, pH, temperature and contact time can be modified to maximize the adsorption capacity of metal ions by seaweed.

4. CONCLUSIONS

The adjustment models identified in this study as having the best representation of the observed data were, for the most part, the same models verified in the literature related to the subject of this study.

In 240 minutes of contact, the marine algae *Lithothamnium calcareum* subjected to thermochemical treatment was able to remove 15.5% of Cr, 33.0% of Mn and 8.0% of Zn in solution.

In 24 hours of contact, the marine algae *Lithothamnium calcareum* subjected to thermochemical treatment was able to remove, in concentration of 5 mg L^{-1}, 0.4% Cr, 52.5% Mn and 92.6% Zn, and, at a concentration of 500 mg L^{-1}, 20.0% Cr, 22.6% Mn and 40.8% Zn.

The results showed that marine algae *Lithothamnium calcareum* submitted to thermochemical treatment presented potential for use in the adsorption of Cr, Mn and Zn, indicating its application in the treatment of effluents that have a high concentration of metal ions.

It is recommended that further studies be conducted in different experimental conditions, since it is important to observe the variation in the adsorption capacity of marine algae *Lithothamnium calcareum* depending on the variation of pH, temperature, contact time and other factors that may interfere with the adsorption process.

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