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APPLICATION OF ALGINATE EXTRACTION RESIDUE FOR AL(III) IONS BIOSORPTION: A COMPLETE BATCH SYSTEM EVALUATION

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ABSTRACT

The residue derived from the alginate extraction from *S. filipendula* was applied for the biosorption of aluminum from aqueous medium. The adsorptive capacity of the residue (RES) was completely evaluated in batch mode. The effect of pH, contact time, initial concentration and temperature was assessed through kinetic, equilibrium and thermodynamic studies. The biosorbent was characterized prior and post-Al biosorption by N₂ physisorption, Hg porosimetry, He picnometry and thermogravimetry analyses. Equilibrium was achieved in 60 minutes. Kinetics obeys pseudo-second order model at aluminum higher concentrations. Isotherms followed Freundlich model at low temperature (293.15 K) and D-R or Langmuir model at higher temperatures (303 and 313 K). Data modeling indicated the occurrence of both chemical and physical interactions in the aluminum adsorption mechanism using RES. The maximum adsorption capacity obtained was of 1.431 mmol/g at 293 K. The biosorption showed a spontaneous, favorable and exotherm character. A simplified batch design was performed, indicating that the residue is a viable biosorbent, achieving high percentages of removal using low biomass dosage.

Keywords: Aluminum; biosorption; residue; brown algae; batch design; water treatment.

AUTHOR CONTRIBUTIONS

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Literature search and data analysis: Heloisa Pereira de Sá Costa

Writing - original draft preparation: Heloisa Pereira de Sá Costa

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DECLARATIONS

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1. INTRODUCTION

Toxic metals can be widely found in effluents derived from several industrial sectors. They are non-degradable chemical species and have a strong tendency to bioaccumulate, which makes these metals potentially dangerous to living organisms. Aluminum is classified as a toxic metal and remarkable concentrations of this metal have been reported in effluents from several industries, e.g., mining, smelting, metallurgy and electroplating (Vijayaraghavan et al. 2012; Boeris et al. 2016). Another significant source of effluents contaminated by aluminum are water treatment plants, due to the use of chemicals composed of aluminum (aluminum sulfate and polyaluminium chloride) in the flocculation process, often high concentrations of the metal are found in effluents from this treatment step (Merian et al. 2004; Stephens and Jolliff 2015).

Several studies report that aluminum contamination can cause harmful effects on different organisms. In plants, excessive Al^{3+} ions in soils mainly affect the roots and can trigger deficiency in the absorption and transport of nutrients, loss of biomass and genotype changes (Skibniewska and Skibniewski 2019). In fishes, it can induce oxidative stress, in addition to cause fatal damages to the nervous and respiratory system (Freda 1991; Gensemer and Playle 1999; Walton 2011). In humans, the bioaccumulation of this metal is mainly associated with the potential development of neurological diseases such as Alzheimer's and the development of bone diseases related to inhibition of bone cell growth and activity and bone mineralization (Dermience et al. 2015). For this reason, the maximum amount of aluminum present in industrial effluents discharged in water bodies is monitored by environmental pollution control authorities in several countries.

Amidst the diverse procedures for removing toxic metals in aqueous media like precipitation, adsorption, ion exchange using resins and membrane processes, biosorption is a promising technology also applied for the treatment of effluents. This process presents several advantages mainly for being ecofriendly and having low cost. These factors are associated with the fact that in this process, unconventional materials are used as adsorbents, usually wastes.

Plenty of materials have been investigated as a biosorbent for Al (III) removal, including biomass derived from fungi, bacteria, algae and agro-industrial residues (Lee et al. 2004; Ozdemir and Baysal 2004; Sari and Tuzen 2009; Tassist et al. 2010; Rajamohan et al. 2014; El Houda Larbi et al. 2019; Titah et al. 2019). Among them, algae stand out because they are cheap, have high availability in addition to having high affinity with toxic metals, the latter being directly related to the composition of algae cell wall. Alginate is a biopolymer that composes the structure of brown algae and is considered to play a major role on the uptake of metals by biosorption (Davis et al. 2003). This compound has commercial value since it is used extensively in the cosmetics, food and pharmaceutical industry due to characteristics such as its viscosity and its stabilizing properties. The alginate extraction process produces a fibrous residue with no added commercial value.

Costa et al. (2016) found that the process of alginate obtainment using the brown algae *Sargassum filipendula* generates a residue that still preserves several functional groups identical to those found in raw alga and directly linked to the ion exchange mechanism of the biosorption process. Several studies point to this residue as a promising biosorbent in the uptake of toxic and precious metals, in addition to being also efficient in removing emerging pollutants (Freitas et al. 2018; Cardoso et al. 2020; Coelho et al. 2020; Moino et al. 2020). Furthermore, the use of waste as an adsorbent material has less environmental impact compared to traditional adsorbents like activated carbon (Nishikawa et al. 2018). Costa et al. (2020) also examined the application of the residue for removal of metals present in real industrial effluents and found a remarkable removal of aluminum, revealing a great affinity between this metal and the biosorbent. However, in-depth studies investigating aluminum biosorption using this biomass have not been found in the literature.

In view of this, the aim of this work is to investigate the innovative application of the residue from the alginate extraction from the *Sargassum filipendula* algae as a low-cost adsorbent for the biosorption of Al³⁺ ions. This manuscript aimed to elucidate the

mechanisms involved in the process through kinetic, equilibrium and thermodynamic assays. Biosorbent characterizations prior and post the biosorption were carried out, offering significant information regarding the biomaterial characteristics. In addition, this work also intended to aggregate the elucidation of mechanisms and interactions involved in the biosorption of aluminum in broad-spectrum, expecting to contribute to the minimization of impacts caused by this hazardous component on the ecosystem.

2. MATERIAL AND METHODS

2.1. Biosorbent preparation

Sargassum filipendula was obtained at Cigarras' beach, on the northern coast of São Paulo, Brazil. The seaweed was washed with deionized water and dried at 313.15 K for 24 h. After this process, the alga was milled and sieved in particles with size inferior to 1 mm. For the alginate extraction, McHugh's methodology (1987) was employed. This process originates sodium alginate as its main product and a solid alginate free biomass as waste, here termed as residue (RES). Initially 15 g of dried biomass were added to 500 mL of formaldehyde solution (0.4% v/v) for 30 minutes with constant agitation. This step aims to clarify and remove phenolic compounds present in the seaweed. In order to remove the remaining phenolic compounds, the biomass was washed with deionized water and put in agitation within 500 mL of 0.1 mol/L hydrochloric acid solution for 2 hours. Finally, the extraction of alginate was carried out, the washed algae biomass was added to 350 mL of sodium carbonate solution (2% w/v) in constant stirring at 333.15 K for 5 h. As a result of this step a viscous mixture was obtained, it was first manually filtered using a polypropylene filter.

Then, the retained (residue) was washed exhaustively and vacuum filtered, in order to ensure that all the alginate was effectively extracted. After this step, the residue obtained was dried at 333.15 K for 24 h. For the biosorption experiments, RES was also milled and sieved into an average diameter of 0.737 mm.

2.2. Evaluation of pH effect

In order to evaluate the impact of pH on the biosorption of aluminum ions using the adsorbent residue, tests were conducted in a finite bath system with aluminum initial concentration of 1 mmol/L, biosorbent dosage of 2 g/L, agitation and temperature of 200 rpm and 298.15 K, respectively. The pH values tested were defined based on the metallic

speciation of the aluminum, aiming the non-precipitation of the metal. The biosorption capacity (q) and total aluminum removal percentage (%Rem) were calculated using Equation 1 and 2, respectively.

$$q(t) = \frac{(C_0 - C(t))V}{m} \quad (1)$$

$$\%Rem = \left(\frac{C_0 - C_{eq}}{C_0} \right) \cdot 100 \quad (2)$$

The initial concentration, the metal ions concentration at time t (min) and solute concentration in equilibrium are respectively represented for C_0 , C_t and C_{eq} (mmol/L); w represents the RES dry weight (g); and V is the volume of solution (L).

2.3. Kinetic study

Kinetic assays were performed at room temperature (298.15 K), in batch mode, with different initial aluminum concentrations (1, 2 and 3 mmol/L). The dosage of 2 g/L of RES was put in contact with the metallic solution, in continuous agitation of 250 rpm. Aliquots were collected at pre-set times and the remaining aluminum concentration was evaluated through atomic absorption spectroscopy, AAS (model AA-7000, Shimadzu, Japan). The system pH was maintained at 4 using a HNO_3 solution (0.1 mol/L). Equation 1 was applied to obtain the adsorbent's adsorption capacity (q).

The mechanisms involved in Al(III) biosorption were investigated through different kinetic models that were adjusted to the experimental data: pseudo-first order (PFO) (Lagergren 1898), pseudo-second order (PSO) (Ho and McKay 1999), intraparticle diffusion (ID) (Weber and Morris 1963), Boyd (Boyd et al. 1947) and external mass transfer resistance (EMTR) (Puranik et al. 1999). Origin 8.0 and Maple® 20 software were employed for data analysis. PFO, PSO and ID models are represented in Equations. 3, 4 and 5, respectively.

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

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

$$q(t) = k_i t^{0.5} + c \quad (5)$$

Where $q(t)$ is the amount of metal removed in relation to time t (mg/g), q_{eq} is the quantity of metal adsorbed in the equilibrium (mg/g), k_1 is the constant of the PFO model (min^{-1}), k_2 is the constant of the biosorption rate of the P-SO model (g/mg.min), k_i is the ID model constant ($\text{mmol/g.min}^{0.5}$) and c is a parameter that is related to the thickness of the boundary layer.

Represented by Equations 6 and 7, the Boyd equation allows to detect the controlling rate step of the process by plotting B_t vs time, when the graph line crosses the origin, the intraparticle diffusion is the rate-controlling step; in any other way, the external diffusion is the predominant step.

$$F = \frac{q(t)}{q_{eq}} = 1 - \left(\frac{6}{\pi^2}\right)\exp(-B_t) \quad (6)$$

$$B_t = -0.4977 - \ln(1 - F) \quad (7)$$

Using the particles radius (r), the diffusion rate, D_i (cm/s^2), can be determined from Equation 8.

$$D_i = \frac{r^2 B}{\pi^2} \quad (8)$$

The External Film Mass Transfer Resistance model (EMTR) (Equation 9) presumes that the equilibrium of solute adsorbed with the boundary layer, i.e., the interface between the liquid phase and the film involving the biosorbent surface, is the process rate-controlling step.

$$\frac{dC_p}{dt} = \frac{k_{MT}V}{wq_{max}K_L} \left(1 + C_p(t)\right)^2 \cdot (C(t) - C_p(t)) \quad (9)$$

In equilibrium conditions, $C(t)$ is the metal solution concentration at time t and C_p corresponds to the adsorbate concentration in sorbent-solution interface (mmol/L), k_{MT} stands for the model constant (1/min), K_L is the constant obtained from the Langmuir isotherm model (L/mmol) and q_{max} represents the maximum biosorption capacity (mmol/g).

2.4. Equilibrium study

The biosorption equilibrium study was performed with 50 mL of Al (III) solutions, with initial concentration values range from 0.2-20 mmol/L, at pH 4, with 0.1 g of RES, in a

shaker with temperature control (Jeio Tech, SI-600R, Korea) with continuous agitation (250 rpm). Three temperatures were studied (293.15, 303.15 and 313.15 K). The pH was established at 4 and controlled with HNO₃ solutions (0.1 and 0.5 mol/L). The initial and final Al (III) concentration was measured by AAS. The amount of adsorbed metal was calculated using Eq. 1.

Langmuir (Equation 10) (Langmuir 1918), Freundlich (Equation 11) (Freundlich 1907) and Dubinin-Radushkevich (D-R) (Equation 12) (Dubinin and Radushkevitch 1947) models were applied to represent the sorption isotherm data:

$$q_{eq} = \frac{q_{max} K_L C_{eq}}{1 + K_L C_{eq}} \quad (10)$$

$$q_{eq} = K_F (C_{eq})^{1/n} \quad (11)$$

$$q_{eq} = q_{max} \exp \left(-k \left(RT \ln \left(1 + \frac{1}{C_{eq}} \right) \right)^2 \right) \quad (12)$$

Wherein, K_F is the Freundlich model constant, related to the solid's biosorption capacity, (mmol/g); n is a dimensionless number linked to biosorption intensity; k (mol²/J²) represents a parameter associated to the sorption energy, E (kJ/mol) (Equation 13); R is the constant of the ideal gas law (J/mol.K) and T is the temperature (K).

$$E = \frac{1}{\sqrt{2k}} \quad (13)$$

2.5. Thermodynamic and isosteric heat

The thermodynamic parameters are essential to evaluate important information of the biosorption system. Variation of Gibbs energy (ΔG°, kJ/mol) reveals if the biosorption is spontaneous (ΔG° < 0) or not (ΔG° > 0), variation of enthalpy (ΔH°, kJ/mol) helps to identify if the nature of the process is endothermic (ΔH° > 0) or exothermic (ΔH° < 0). The variation of entropy (ΔS°, J/mol/K) values can be related to randomness in metallic solution-biosorbent interface. Such parameters are determined by the combination of Equations 14 and 15, which provides the Van't Hoff equation (Equation 16), where K_c is the thermodynamic equilibrium constant.

$$\Delta G^\circ = -RT \ln K_c \quad (14)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (15)$$

$$\ln K_C = \frac{-\Delta H^\circ}{R} \frac{1}{T} + \frac{\Delta S^\circ}{R} \quad (16)$$

In this study, K_C was obtained from Henry's constant (K_H , g/L) by multiplying its value by 1000 (Equation 17), in way to consider the dimensionality (Milonjic 2007), therefore:

$$K_C = 1,000 K_H = 1,000 \left(\frac{q_e}{C_e} \right) \quad (17)$$

The isosteric heat of an adsorption system (ΔH_{is} , J/mol) can be defined as the energy released when a constant amount of adsorbate (q_{eq}) is attached to the solid surface of the adsorbent. This variable is linked to the process temperature, as well as to the equilibrium concentration (C_{eq}). The analysis of this parameter can provide information about the thermodynamic behavior of the adsorbed phase and the heterogeneity of the adsorbent surface (Hartzog and Sircar 1995; Santos et al. 2020). ΔH_{is} can be determined by the Clausius – Clapeyron equation (Equation 18) and its integrated form becomes Equation 19 (Srivastava et al. 2007).

$$\Delta H_{is} = R \frac{d \ln C_{eq}}{d(1/T)} \quad (18)$$

$$\ln C_e = \frac{\Delta H_{is}}{R} \frac{1}{T} + constant \quad (19)$$

The angular coefficient obtained from plot of $\ln C_e$ in function of $1/T$, for a fixed q_e , provides the values of ΔH_{is} .

2.6. Error analysis

All model adjustments were evaluated according to the correlation coefficients (R^2), Relative Mean Deviations (RMD) (Equation 20) and the corrected Akaike information criteria (AICc) (Equation 21).

$$RMD = \frac{1}{N} \sum_{i=1}^N \left| \frac{q_{exp} - q_{pred}}{q_{exp}} \right| \times 100 \quad (20)$$

$$AICc = N \cdot \ln \left(\frac{\sum_{i=1}^N (q_{exp} - q_{pred})^2}{N} \right) + 2p + \frac{2p(p+1)}{N-p-1} \quad \text{when } \frac{N}{p} < 40 \quad (21)$$

The predicted and experimental points are represented by q_{exp} and q_{pred} , respectively, N is the number of experimental points and p is the number of model parameters. In cases where two or more models present appropriate adjustments to the experimental data, the calculation of Akaike weight (w_a) in Equation 22 may help to select which one is more suitable by its representativity.

$$w_a = \frac{\exp\left(-\frac{1}{2}(AICc_i - AICc_{\min})\right)}{\sum_{i=1}^r \exp\left(-\frac{1}{2}(AICc_i - AICc_{\min})\right)} \quad (22)$$

In this Equation, r denotes the number of models; $AICc_i$ represents the corrected Akaike information criteria from each model; and $AICc_{\min}$ is the lowest value of $AICc$ obtained among all fittings.

2.7. Simplified batch design

This methodology is generally applied to predict the amount of biomass necessary to treat a given volume of solution and achieve the desired level of removal of the contaminant (Aravindhnan et al. 2007). It is reasoned on the molar balance represented in Equation 1, at equilibrium conditions and replacing q_{eq} for Langmuir parameters (q_{max} and K_L), Equation 1 can be rewritten as Equation 23 for the calculation of the required amount (w) to treat volumes of Al(III) solutions achieving a desired removal percentage. In this study, the estimations were performed with initial metal concentration of 1 mmol/L, for volumes varying from 1 to 10 with 40, 60 and 90% for desirable removal.

$$w = \frac{V(C_0 - C_{\text{eq}})}{\frac{K_L q_{\text{max}} C_{\text{eq}}}{1 + K_L C_{\text{eq}}}} \quad (23)$$

2.8. Biosorbent characterization

The biosorbent was characterized prior (RES) and post (RES-Al) the process aiming to understand the interactions involved in the Al (III) removal. The true density (ρ_t) of raw and contaminated residue were analyzed by He pycnometry (Accupyc II 1340, Micrometrics). The apparent density (ρ_a) and the pore size distribution were determined using an Hg porosimeter (AutoPore IV, Micrometrics), applying a pressure range of 0.5-60000 psi. The biosorbent porosity (ϵ_p) was then calculated by Equation 24.

$$\varepsilon_p = 1 - \left(\frac{\rho_a}{\rho_t} \right) \quad (24)$$

Adsorption and desorption isotherms of N₂ physisorption for RES and RES-Al were obtained using BET (Brunauer, Emmett and Teller) method. The samples were dried for 24 hours at 333.15 K. Thermogravimetric analysis was performed in a dynamic nitrogen atmosphere (DTG 60, Shimadzu - Japan), with temperature range of 303.15 - 1223.15 K and gas outflow of 50 mL/min.

3. RESULTS AND DISCUSSION

3.1. Effect of pH

Biosorption systems are influenced by several factors. Temperature, pH, adsorbate initial concentration, adsorbent dosage and stirring are the most investigated parameters for biosorption process optimization (Ruthven 1984). At first, the influence of pH on the Al (III) biosorption was assessed. Moino et al. (2020) presented the isoelectric point of RES (pH_{zpc}) surface at 5.3, indicating that above this point the biosorbent surface is negatively charged, favoring cations adsorption (Zhu et al. 2015). Nevertheless, based on the metallic speciation, at pH values below 5 99.9% of aluminum present in aqueous media are in Al³⁺ form. After that point, the formation of precipitated species begins (Krewski et al. 2007; Walton 2011). Therefore, pH evaluation was conducted in pH 2, 3 and 4

The results presented in Fig. 1 demonstrate that pH 2 was the most unfavorable condition, within the pH range evaluated, with values of maximum removal percentage below 10 % and adsorption capacity of 0.127 mmol/g. This effect can be explained by the high concentration of H⁺ ions in low pH ranges, since these ions tend to compete with Al³⁺ ions for the sites in the adsorbent. At pH 4, removal percentages above 80% and biosorption capacity of 0.4255 mmol/g were reached, indicating the favoring of the system. This value agrees with other studies that carried out biosorption of aluminum in different biomasses as shown in Table 3 (section 3.3). Therefore, pH 4.0 was defined to accomplish Al³⁺ biosorption experiments.

279 **Fig 1** Effect of pH on Al^{3+} removal using RES

280

281 3.2. Kinetic study

282 Figure 2 displays biosorption kinetic curves of Al (III) ions onto RES. Analyzing the
 283 kinetic profiles, the system achieved the equilibrium in approximately 60 minutes. He
 284 and Chen (2014) pointed out that cationic metal biosorption systems using algae-derived
 285 biomass tend to be faster, where a remarkable removal occurs between 20 and 60 minutes,
 286 followed by a slower stage, reaching equilibrium generally between 2 and 6 hours, a
 287 behavior similar to that observed in the system of this work. The capacities of adsorption
 288 at equilibrium (q_{eq}) were 0.3825, 0.6152 and 1.0107 mmol/g equivalent to the percentages
 289 of 93.96, 61.87 and 72.03 % of removal for concentrations of 1, 2 and 3 mmol/L,
 290 respectively. The improvement in the adsorption capacity with the increasing in metal
 291 concentration in solution is associated to the intensification of the driving force for mass
 292 transfer. A similar behavior was observed in former biosorption studies of toxic metals
 293 employing the same biosorbent (Freitas et al. 2017; Nishikawa et al. 2018).

294 **Fig 2** Biosorption kinetics of Al^{3+} ions by RES for three different aluminum initial concentrations

295

296 Figures 1S to 3S (Supplementary Material) show the results of the adjustments of the
 297 models of pseudo-first order, pseudo-second order, intraparticle diffusion, Boyd and
 298 External Film Mass Transfer Resistance to the initial concentrations of 1, 2 and 3 mmol/L
 299 of Al^{3+} . The variables obtained from the models fitting, along with the adjustment
 300 evaluation parameters (R^2 , RMD and AICc) are presented in Table 1.

301 It can be noted that, among the phenomenological models, the PFO model demonstrated
 302 a better fit in the 1 mmol/L system, while the PSO model better described the 2 and 3
 303 mmol/L kinetics, with higher R^2 values, lower DMR and lower AICc. Since these
 304 parameters are very similar for pseudo-first and pseudo-second order models on 1
 305 mmol/L system, it can be said that the PSO model better represented the whole process.
 306 In general, it is widely reported that this model tends to better fit the kinetic data of
 307 biosorption of Al(III) and other toxic metals (Farooq et al. 2010; Tassist et al. 2010; He
 308 and Chen 2014; Naeemullah et al. 2017; El Houda Larbi et al. 2019). Among the reasons
 309 that stands out is the fact that the pseudo-first order model better describes the beginning
 310 of the process, while the PSO model better describes the system as a whole, so when
 311 equilibrium data are used in mathematical modeling applying these two models, k_2 values
 312 tends to be favored (Pagnanelli 2011; Daneshvar et al. 2017). It can also be directly related
 313 to the interactions occurring between the metal and the functional groups of the biosorbent
 314 (Bulgariu et al. 2015). The PSO model indicates that the rate-limiting stage its possibly
 315 related to a chemisorption mechanism, occurring via the electrons sharing between Al(III)

ions and the residue in the valence shell (Ho and McKay 1999). It can be observed that the constant k_2 tends to decrease with higher initial concentration, since it is a function of the process conditions (Foo and Hameed 2010).

Table 1 Kinetic model adjustments for Al (III) biosorption with different initial concentrations

Model	Parameters	Concentration (mmol/L)		
		1	2	3
	q_{exp} (mmol/g)	0.3825	0.6152	1.0107
PFO	q_e (mmol/g)	0.3798	0.5874	0.9254
	k_1 (min^{-1})	0.0905	0.0746	0.1212
	R^2	0.9940	0.9716	0.9720
	RMD (%)	10.7	24.1	12.5
	AICc	-132.413	-91.1839	-83.0646
PSO	q_e (mmol/g)	0.4214	0.6561	1.0103
	k_2 (g/mmol.min)	0.2866	0.1543	0.1693
	R^2	0.9862	0.9902	0.9961
	RMD (%)	10.6	23.8	5.1
	AICc	-118.8427	-104.0165	-104.3081
ID	k_i (mmol/g.min ^{0.5})	0.2181	0.1731	0.4715
	c (mmol/g)	0.0216	0.0542	0.0614
	R^2	0.9806	0.9683	0.9787
Boyd	D_i (cm ² /min)	$3.8287 \cdot 10^{-5}$	$2.2316 \cdot 10^{-5}$	$1.4268 \cdot 10^{-5}$
	R^2	0.9799	0.9626	0.8636
EMTR	k_{MT} (m/s)	0.0840	0.04409	0.0799
	R^2	0.9971	0.9867	0.9880
	RMD (%)	7.6	6.4	12.2
	AICc	-135.911	-98.927	-84.102

For the models based on mass transfer resistance, it is possible to note the presence of all the steps described by the intraparticle diffusion model in all studied concentrations: an initial stage of rapid removal of Al (III) ions, referring to external adsorption; a second gradual stage referring to intraparticle diffusion, this being the controlling-rate step, and the third stage where diffusion is lower due to the low concentration of solute in the solution, representing the equilibrium of system (Chen et al. 2003). The linear adjustment of this model was obtained in the region of the second stage and the high values of R^2 , mainly for the 1 mmol/L concentration, indicates the possible relevance of intraparticle diffusion in the process kinetic rate. This result, however, is not in agreement with that observed in the fitting of Boyd model, where the linear coefficient of the line Bt vs. t in

all studied concentrations, although close, does not cross the origin, thus indicating that internal diffusion is not the predominant stage (Boyd et al. 1947). In addition to this, the D_i values in the order of 10^{-5} suggests that in this process the controlling step is the diffusion in external film (Singh et al. 2005).

Furthermore, it can be observed in Table 1 that the effective diffusion coefficients decrease as the concentration is increased, which corroborates with the results obtained in the intraparticle diffusion model, where there is an increase in the effect of the boundary layer (c) with the initial concentration, implying greater resistance to mass transfer and consequently less effective diffusion. This directly proportional relationship between the boundary layer and the initial concentration of the metallic solution, also observed by Freitas et al. (2018) in the removal of copper using the same biosorbent, which indicates that the increase in aluminum concentration is directly related to the increase in external resistance to mass transfer. The better adjustment of the EMTR model rather than the DI model to the kinetic data, for all concentrations tested, ratifies that the process is predominantly governed by diffusion in external film. This behavior is consistent with results found in the literature concerning the uptake of other toxic metals onto RES (Cardoso et al. 2017) as well as studies regarding the biosorption of Al(III) employing different biosorbents (Cayllahua and Torem 2010; Halim et al. 2012; Rosa et al. 2018).

3.3. Equilibrium study

Figure 3 depicts the equilibrium isotherms adjustments employing the Langmuir, Freundlich and Dubinin-Radushkevich (D-R) models at 293.15, 303.15 and 313.5 K. According to Giles et al. (1960) classification, the initial slope of the isotherms obtained is classified as H type, which suggests that the metal has elevated affinity for the biosorbent material. It is also possible to note the decrease in adsorptive capacity with the increase in temperature, a characteristic behavior of an exothermic system. A similar result was obtained by Freitas et al. (2020) and Nishikawa et al. (2018) for the biosorption of Ag(I) and Cd(II), respectively, using the same biomaterial as adsorbent. Cayllahua and Torem (2010) found the same behavior for aluminum biosorption using a bacterial biomass. This can be confirmed in Table 2, where the experimental q_{max} values decreases as the temperature increases. Although in most studies concerning the biosorption of Al(III) an endothermic behavior predominates, some authors like Yurtsever and Nalçak (2019) also found an exothermic process for Al(III) biosorption.

Fig 3 Langmuir, Freundlich and D-R models adjustment to biosorption isotherms of Al^{3+} removal using RES at a. 293.15 K; b. 303.15 K; c. 313.15 K

Table 2 shows the best fitting of Freundlich model at the lowest temperature (293.15 K) considering all adjustment parameters (R^2 , AICc, RMD and w_a). For higher temperatures (303.15 and 313.15 K), good adjustments were obtained with two models, Langmuir and D-R. In this case, the Akaike wight (Equation 22) was applied and the ratio between the w_a for both models were calculated. For 303.15 K the ratio of evidence was 1.059 for the Langmuir model, which indicates that this model is 1.059 times more representative than the D-R adjustment at this temperature. For 313.15 K, D-R model revealed to describe the equilibrium data 1.195 times better than Langmuir. However, according to Santos et al. (2019), such a low ratio of evidence is not significant, therefore, both models may be adequate to describe the system in 303.15 and 313.15 K. Although, Langmuir model assumes that the biosorbent surface is composed by active sites energetically homogeneous, whilst D-R and Freundlich describe adsorption in multilayers, i.e., on a heterogeneous surface. That said, considering the excellent fitting of Freundlich model to describe equilibrium data at 293.15 K, it can be considered that the surface of RES is

predominantly heterogeneous. The results analyzed for isosteric heat, further discussed in this section, helps to stand this hypothesis.

Analyzing the variable E , associated to the energy of sorption, obtained through the D-R model, it is observed that the biosorption mechanisms in this system are predominantly physical in the entire temperature range studied. A similar result reported by Nishikawa et al. (2018) using the same biomaterial for the removal of cadmium. In addition, the values of parameter n of the Freundlich model, which represents the adsorption intensity, are greater than a unity, which suggests the favorability of the biosorption. Also, K_f increases proportional to the adsorption capacity since this parameter is related to electrostatic attraction force (Shaaban et al. 2017).

Table 2 Equilibrium model adjustments for Al (III) biosorption at different temperatures

Model	Parameters	Temperature (K)		
		293.15	303.15	313.5
Experimental	$q_{\max}$ (mmol/g)	1.4317	1.0337	0.6137
Langmuir	$q_{\max}$ (mmol/g)	1.1618	1.0164	0.6094
	K_L (L/mmol)	11.2876	11.6058	10.1475
	R^2	0.8576	0.9465	0.8186
	RMD (%)	31.89%	21.31%	41.69%
	AICc	-18.6639	-32.3661	-28.9440
	w_a	0.000	0.514	0.440
Freundlich	$K_F [(mmol/g).(L/mmol)^{1/n}]$	0.7776	0.6905	0.4366
	n	4.0099	5.2018	6.9881
	R^2	0.9762	0.8078	0.5311
	RMD (%)	23.10%	48.19%	56.16%
	AICc	-34.7619	-20.8533	-23.7930
	w_a	0.999	0.002	0.034
D-R	$q_{\max}$ (mmol/g)	1.1304	1.0009	0.6036
	E (kJ/mol)	5.5047	5.6249	5.5516
	R^2	0.8460	0.9458	0.7457
	RMD (%)	31.55%	21.13%	39.89%
	AICc	-17.9641	-32.2485	-29.3010
	w_a	0.000	0.485	0.526

Within the Langmuir model the K_L parameters indicates the affinity between Al (III) ions and the residue, its value tends to increase with $q_{\max}$ values. As expected, the highest K_L was found associated with the higher $q_{\max}$, at 293.15. The decrease in this parameter with the temperature increasement also reveals an exothermic pattern.

Table 3 presents a comparison between $q_{\max}$ values in aluminum biosorption using different types of algae and using the residue studied in this work. It is possible to observe that the waste has an interesting performance, and its maximum adsorptive capacity value is very close to the values presented for other biomasses. The main advantage of RES is that it is a waste, which is normally disposed and has no added value. Additionally, its raw material (*S. filipendula*) is found in abundance in nature, thus making it even more attractive for the biosorption process.

Table 3 Maximum adsorption capacity ($q_{\max}$) for Al^{3+} uptake by different algae biosorbents

Biosorbent	Experimental conditions	$q_{\max}$ (mmol/g)	Reference
Beach-cast seaweed	$C_0 = 0.18-18.5$; $D = 2.5$; $T = 298$; pH 4	0.833	(Lodeiro et al. 2010)
<i>Turbinaria conoides</i>	$C_0 = 18.3-36.6$; $D = 2$; $T = 295$; pH 4	2.592	(Vijayaraghavan et al. 2012)
<i>Gelidium latifolium</i>	$C_0 = 0.018-37.06$; $D = 1$; $T = 298$; pH 4	2.060	(Shaaban et al. 2017)
<i>Ulva lactuca</i>	$C_0 = 0.018-37.06$; $D = 1$; $T = 298$; pH 4	2.082	(Shaaban et al. 2017)
<i>Colpomenia sinuosa</i>	$C_0 = 0.018-37.06$; $D = 1$; $T = 298$; pH 4	2.116	(Shaaban et al. 2017)
<i>Padina pavonica</i>	$C_0 = 0.37-14.82$; $D = 8$; $T = 323$; pH 4.5	2.864	(Sari and Tuzen 2009)
RES	$C_0 = 0.2-20$; $D = 2$; $T = 293$; pH 4	1.431	This work

* C_0 = Initial concentration (mg/L); D = biosorbent dosage (g/L); T = temperature (K).

3.4. Thermodynamics analysis

Figure 4S (Supplementary Material) shows the graph of $\ln(K)$ versus $1/T$. The calculation of the K_d constant was performed in the region of infinite dilution of the isotherms for the three temperatures analyzed. The value of the coefficient for determining the linear regression of the graph was 0.9822, so its linear and angular coefficients were used to

calculate the thermodynamic parameters (ΔH and ΔS) according to Equation 16. The thermodynamics parameters obtained are given in Table 4.

Table 4 Thermodynamic parameters for Al (III) biosorption using RES

T (K)	ΔG (kJ.mol ⁻¹)	ΔH (kJ.mol ⁻¹)	ΔS (J.mol ⁻¹ .K ⁻¹)
293.15	-11.385		
303.15	-9.659	-61.991	-0.172
313.15	-7.932		

Negative values for ΔG demonstrate that Al(III) uptake using RES is a spontaneous process within the studied temperature range. Besides that, ΔG decreases with temperature increasement indicating that lower temperatures favor the process.

The negative value of ΔH confirms exothermicity of the process of biosorption of Al(III) using RES. The absolute value of ΔH can also assist in defining the nature of the process. In physisorption, absolute values of ΔH ranging from 2.1 to 20.9 kJ.mol⁻¹, while ΔH values in the range of 80-200 kJ.mol⁻¹ are configured as chemical processes (Saha and Chowdhury 2011). In this study, the value is in the range for chemical processes, which indicates that instead of being a purely physical process as pointed out by D-R model, chemical interactions may also be involved in its removal mechanism.

The negative ΔS value obtained reveals a decrease in the system disorder, that is, the adsorbate changes from a less organized state, in the liquid phase, to a more organized state when adsorbed to the surface of the biosorbent, decreasing the entropy variation, reflecting that the Al molecules were orderly adsorbed. In addition, negative entropy values also indicate that the process has associative mechanisms, that is, the system disorder tends to decrease and no considerable modification happens in the internal structure of the biomaterial.

Figure 4 illustrates the isosteres (plots of $\ln C_e$ vs $1/T$) for the selected equilibrium capacities ($q_e = 0.96, 0.95, 0.93$ mmol/g), all plots were linear, with $R^2 > 0.9$. Isotheric heat was calculated from the angular coefficients. Table 5 summarizes the results obtained.

436 **Fig 4** Adsorption isosteres for Al^{3+} biosorption onto RES

437

438

439 **Table 5** Isotheric heat for different equilibrium capacities

$q_e \text{ (mmol/g)}$	$\Delta H_{st} \text{ (kJ/mol)}$	R^2
0.96	-7.11	0.9871
0.95	-7.27	0.9437
0.93	-8.51	0.9222

440

441 The values of ΔH_{st} vary proportionally with the values of q_e . This behavior can be
 442 associated with adsorbents with an energetically heterogeneous surface (Erbil 2009),
 443 suggesting that the surface of RES is composed of different energetically active sites.
 444 Relatively low values obtained for ΔH_{st} are directly linked to the low q_e range studied,
 445 since low q values imply strong sorbate-sorbate interactions which results in low isosteric
 446 heat. This also explains the proportional increase between ΔH_{st} and q , high q_e values
 447 implies increased sorbate-biosorbent interactions leading to higher ΔH_{st} (Saha and
 448 Chowdhury 2011). Some authors also attribute this change to the possible occurrence of
 449 side interactions between metal ions adsorbed on biosorbent surface (Srivastava et al.
 450 2007).

451 The magnitude of the isosteric value provides information on the nature of the adsorption
 452 mechanisms involved in the process, with ΔH_{st} values below 80 kJ/mol indicating the

occurrence of physisorption mechanisms, as in the case of this study. This result is also in line with the mean adsorption energy (E) values obtained through the D-R model, presented in the previous section. It is possible to conclude that in the RES-Al uptake occurs mainly by physical interactions with participation of chemisorption mechanisms such as ion exchange in the rate limiting step of the process, as shown in Section 3.2. This result is not uncommon considering the complex matrix of this biosorbent.

3.5. Simplified batch design

Figure 5 shows the amount of RES necessary to achieve removals of 40, 60 and 90% by volume ranging from 1 to 10 L for a solution with an initial concentration of 1.0 mmol/L Al. It is possible to observe that the amount of residue required increases with increasing volume and desired removal percentage. Despite this, to treat 10 L of solution with 90% removal, only 15 g of RES are needed. Comparatively, in the study performed by Moino et al. (2020) for the removal of Ni (II) using this same biosorbent, under the same conditions studied here, about 140 g of RES were taken to achieve 90% of removal in 10 L of 1 mmol/L Ni solution. In this work, the low amount of waste required to treat large volumes satisfactorily has a direct impact on the viability of the system, in addition to being an important feature for the process scale-up.

Fig 5 Simplified batch design for the RES amount required to obtain 40, 60 and 90 % removal of Al(III) at 1 mmol/L

3.6. Biosorbent characterization

3.6.1. Structural properties

Table 6 presents the results obtained in the characterization of the porous structure of the biosorbent by mercury porosimetry and helium gas pycnometry. It can be seen that the apparent density decreases slightly after the biosorption process. This may suggest that the metal is mostly adsorbed on the surface of the residue and not just in its pores, thus causing an increase in the volume of the material and a decrease in apparent density. The same behavior was also observed for the true density of RES, which value is slightly higher than those obtained for RES-Al. Worth mentioning that the apparent density is calculated through the relationship between the mass of the solid and the total volume, that is, the real volume of the adsorbent added to the volume occupied by Hg filling in the pores of the solid. The true density, on the other hand, is calculated using the real volume, that is, the total solid volume without the volume of empty pores. Thus, the increase in the total volume caused by the adsorption of metal ions on the surface of the material also leads to a decrease in its value.

Table 6 Structural properties of the biosorbent before (RES) and after (RES-Al) Al(III) biosorption

	RES	RES-Al
Apparent density (g/cm³)	0.9826	0.9783
True density (g/cm³)	1.4820	1.4500
Porosity (%)	33.70	32.53

Porosity, calculated using Equation 24, also showed a decrease in its value, being an indication of the possible filling of empty pores. However, as pointed out by Freitas et al. (2019), this low variation indicates that aluminum has no influence on the pore filling of the biosorbent.

In summary, it is possible to note that the values obtained for the residue prior and post the adsorption of Al (III), despite the decreasing in general, the variations were minimal, revealing that the filling of pores may not be part of the mechanism of Al(III) removal by RES. In fact, these results agree with that observed in the kinetic analysis (Section 3.2), showing that external diffusion is the controlling step of the biosorption process.

Mercury intrusion porosimetry also provides data regarding the pore size distribution, as illustrated in Figure 6.

Fig 6 Pore size distribution of raw biosorbent and Al-contaminated

The pore diameter range remained the same after the biosorption process, corroborating with the result of the low variation in the porosity of the adsorbent analyzed previously. In physisorption, IUPAC classifies adsorbents according to their pore size (Sing 1985; Thommes et al. 2015). According to this classification and analyzing the profile shown in Figure 6, the residue can be determined as a macroporous material. Despite this, the RES has several pores with diameter significantly larger than the minimum determined for macropores. In previous works Cardoso et al. (2020) and Moino et al. (2020) obtained similar results and associate that this much larger pore width range is linked to cavities caused by the extraction process alginate, which leads the residue to have a predominantly rough surface instead of macroporous.

Figure 7 presents the isotherms of adsorption and desorption of nitrogen realized by BET method for RES and RES-Al. According to IUPAC classification, isotherms for RES (Fig 7a) and for RES-Al (Fig 7b) are type II with a more gradual curvature. Type II isotherms are characteristics of nonporous or macroporous biosorbents, which corroborates with the results obtained from pore size distribution analysis. A minor curvature is related to overlap of monolayer coverage and the beginning of multilayer adsorption (Thommes et al. 2015).

Fig 7 N₂ adsorption and desorption isotherms for RES and RES-Al

3.5.4. Thermogravimetric analysis (TGA)

Thermogravimetric analyzes help to characterize the thermal resistance of the material. Figure 8 presents the TG, DTG (thermogravimetric analysis) and DTA (thermodifferential analysis) curves obtained for RES and RES-Al.

It can be seen from the TG curves for RES and RES-Al that the mass of the biosorbent decreases with heating. Both curves show a similar decay at the beginning of the process, this loss of initial mass is associated with dehydration of the material (Kalderis et al. 2008). The mass loss equilibrium is reached at 800 °C for RES and 600 °C for RES-Al. RES curve shows the first step between 250 and 350 °C, the loss of mass in this range is associated with the degradation of cellulosic compounds (330 °C) and the remaining alginic acid (200 °C). Alginate also usually presents another peak of degradation around 550 °C, but this behavior was not obtained for both RES and RES-Al (Soares et al. 1995, 2004). RES-Al curve presents a milder loss of mass profile, but a main point can be identified between 200 and 350 °C, as well as for RES, associated with the decomposition of cellulose and alginate present in the material structure. The total loss of mass for RES was of 91% and for the contaminated residue of 67.5%, which confirms the greater thermal stability of the latter.

541 **Fig 8** Thermal analysis curves for: (a) RES, and (b) RES-Al

542

543 All these factors reveal that the residue contaminated by aluminum has greater stability
 544 than the waste prior process. This indicates that the binding of Al (III) ions to the
 545 functional groups on the surface of the biosorbent increases the thermal stability of the
 546 intermediates formed by the heating process. Herewith, it can be concluded that the
 547 residue presents considerable stability when heated to temperatures around 150 °C, thus
 548 being able to be applied to processes that use higher temperatures. Despite this, as
 549 observed in the equilibrium study, higher temperatures disadvantage the uptake capacity
 550 for aluminum removal, so the application of this system at high temperatures would be
 551 unfeasible.

DTA curves identify the occurrence of endothermic and exothermic events. Endothermic peaks are observed at around 100 °C for both materials, these peaks are related to water evaporation. In RES it is possible to notice the presence of a peak related to an endothermic event (330 °C) and immediately afterwards an exothermic peak (350 °C), both are associated with the degradation of alginic compounds (Soares et al. 2004). Exothermic events between 200 and 400 °C also represent the decomposition of the protein fraction of the material and are related to a great loss of mass, which can be confirmed by observing the pattern of TG curves (Yu et al. 2008; Biswas et al. 2017). Above 400 °C exothermic events are linked to the occurrence of char formation. The endothermic peak observed at 380 °C for RES may be related to the depolymerization of cellulose.

For RES-Al, as in TG, a more attenuated DTA curve pattern, with less evident peaks, was obtained. Cardoso et al. (2020) obtained a similar behavior in the DTA curves obtained for the same residue contaminated with Zn ions, the authors associate this behavior with the presence of metal ions in the material. Although attenuated, the endothermic and exothermic peaks presented for RES-Al after 500°C may be related to the combustion of remaining metallic compounds (Do Nascimento et al. 2021).

4. CONCLUSIONS

This work evaluated the removal of aluminum ions through biosorption employing the waste originated from alginate extraction from *S. filipendula* algae. The pH presented significant influence in the process and pH 4 favored the uptake of Al(III) by RES. The kinetic study showed that the residue removes more than 90% of Al³⁺ ions in about 60 min of the process, in all concentrations tested. The PSO and EMTR models better described the kinetic behavior, demonstrating that the process is predominantly controlled by external diffusion. In equilibrium assays it was found that the increase in temperature decreases the biosorption capacity. In equilibrium data modeling, the 293.15 K isotherm was better described through the Freundlich model, whereas Langmuir and D-R models better fitted the isotherms at 303.15 and 313.15 K with the same representativity for both curves. The values of free adsorption energy, obtained by the DR model, indicates that the biosorption of aluminum by RES has characteristics of a physical process. The maximum adsorption capacity obtained was of 1.431 mmol/g at 293.15 K, a very encouraging value when comparing to other low-cost adsorbents. The biosorption of Al(III) is an exothermic and spontaneous process. The biosorbent surface is

heterogeneous with the occurrence of physical mechanisms during the removal process. The characterizations performed on the material prior (RES) and post aluminum biosorption (RES-Al) indicated that the residue has a macroporous structure, low porosity and considerable resistance to mass loss at temperatures up to 150 °C (423.15 K). The findings in this article demonstrate that the removal of aluminum using this biosorbent is a complex system, with the involvement of physisorption and chemisorption related mechanisms like ion exchange, which is for the most part associated to the nature and composition of the biomaterial.

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Figures

Figure 1

Effect of pH on Al^{3+} removal using RES

Figure 2

Biosorption kinetics of Al^{3+} ions by RES for three different aluminum initial concentrations

Figure 3

Langmuir, Freundlich and D-R models adjustment to biosorption isotherms of Al^{3+} removal using RES at a. 293.15 K; b. 303.15 K; c. 313.15 K

Figure 4

Adsorption isosteres for Al^{3+} biosorption onto RES

Figure 5

Simplified batch design for the RES amount required to obtain 40, 60 and 90 % removal of Al(III) at 1 mmol/L

Figure 6

Pore size distribution of raw biosorbent and Al-contaminated

Figure 7

N₂ adsorption and desorption isotherms for RES and RES-Al

Figure 8

Thermal analysis curves for: (a) RES, and (b) RES-Al

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