An evaluation of copper biosorption by a brown seaweed under optimized conditions

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A basic investigation into the removal of copper ions from aqueous solutions by *Sargassum* sp. was conducted in batch conditions. The influence of different experimental parameters such as initial pH, shaking rate, sorption time, temperature, equilibrium conditions and initial concentrations of copper ions on copper uptake was evaluated. Results indicated that for shaking rates higher than 100 rpm no significant changes in copper accumulation were observed, as well as for pH values between 3.0 and 5.0. No marked effect on the biosorption of copper was detected for temperatures between 298 and 328K. The Langmuir model better represented the sorption process, in comparison to the model of Freundlich. The process followed a second-order kinetics and its calculated activation energy was 5.2 kcal/mol. Due to its outstanding copper uptake capacity (1.48 mmol/g biomass) *Sargassum* sp. proved to be an excellent biomaterial for accumulating and recovering copper from industrial solutions.

The increased use of metals and chemicals in the process industries has resulted in the generation of large quantities of aqueous effluents that contain high levels of heavy metals, creating serious environmental disposal problems. Additionally, mining, mineral processing and extractive metallurgical operations generate huge volumes of toxic liquid waste (Modak and Natarajan, 1995). Since copper is a widely used material, there are many actual or potential sources of copper pollution. Copper may be found as a contaminant in food, especially shellfish, liver, mushroom,

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nuts, and chocolate. Briefly, any processing or container using copper material may contaminate the product, such as food, water or drink. Copper is essential to human life and health but, like all heavy metals, is potentially toxic as well (Nuhoglu et al. 2002).

A number of methods exist for the removal of heavy metal pollutants from liquid wastes when they are present in high concentrations. These include methods such as precipitation, evaporation, electroplating, ion-exchange and membrane processes (Matheickal and Yu, 1999). These processes are expensive, and also have other shortcomings, such as incomplete removal of metals, limited tolerance to pH change, moderate or no metal selectivity, very high or low working levels of metals, and production of toxic sludge or other waste products that also need disposal (Bunke et al. 1999; Eccles, 1999).

Biosorption of heavy metals from aqueous solution can be considered as an alternative technology in industrial wastewaters treatment (Veglió and Beolchini, 1997). It is based on the ability of biological materials to accumulate heavy metals from wastewater by either metabolically mediated, or physico-chemical pathways of uptake (Fourest and Roux, 1992). This innovative depurative process uses biomaterials which are either abundant in nature such as marine algae (Schiewer and Volesky, 1995) or wastes coming from industrial production (Gallagher and Moo-Young, 1998) and biological processes such as fermentation (Tianwei and Peng, 2000) and water treatment (Leung et al. 2000).

Brown seaweeds (*Phaeophyceae*) constitute an algal group containing the characteristic pigment fucoxantine, responsible for their brown color. Floating masses of *Sargassum* constitute the Sargasso Sea, being also very common in the Brazilian Coast. All *Sargassum* species contain floating bubbles, responsible for their decreased density, thus contributing for their presence in the marine environment. Quantitatively, the most abundant polysaccharide in the cell wall of brown seaweeds is alginic acid. Alginic acid is a polymer constituted by two uronic acids (b-1,4-D-mannuronic and a-1,4-L guluronic), with molar ratio between the acids ranging from 0.25 to 2.5. Alginic acid is present in these seaweeds usually as calcium, magnesium, sodium and potassium salts, mainly in the cell wall. It is a structural polysaccharide with strong ion-exchange properties. Beyond its high metal uptake capacity, this algal genus has been selected for study due to their wide distribution in most tropical countries, being available at high quantities as a waste biomaterial (Costa et al. 2001).

In this work, the use of *Sargassum* sp. as a biosorbent for copper ions from aqueous solution was studied. The influence of different parameters on copper uptake such as sorption time, agitation speed, initial pH, temperature and initial copper concentration was investigated. The kinetic and equilibrium of biosorption process were evaluated and

the maximum biosorption capacity of the biomass, based on dry weight, was determined from the equilibrium data measured under optimized conditions of pH and modeled according to Langmuir model.

MATERIALS AND METHODS

Seaweed

The brown seaweed *Sargassum* sp. (*Chromophyta*) used in this work was harvested from the sea (Northeastern Coast of Brazil), sampled, extensively washed with distilled water to remove particulate material from their surface, and oven-dried at 343 K for 24 hrs. One kg of biomass was sub-sampled for use in the experiments. In order to ensure that homogeneous samples were used, standard sampling techniques were applied. Dried biomass was cut, ground in a mortar with pestle and then sieved. The fraction with 0.3-0.7 mm was selected for use in the sorption tests.

Copper solutions

Stock copper solution (1000 mg/mL) was prepared by dissolving 2.683 g of copper chloride dihydrate (Merck, Darmstadt, Germany) in 100 mL of deionized distilled water (DDW) and diluting quantitatively to 1000 mL using DDW. Copper solutions of different concentrations were prepared by adequate dilution of the stock solution with DDW.

Determination of the copper contents in the solutions

The concentration of copper in the solutions before and after the equilibrium was determined by flame atomic absorption spectrometry (FAAS), using a Perkin-Elmer Analyst 300 atomic absorption spectrometer equipped with deuterium arc background corrector, an air-acetylene burner and controlled by IBM personal computer. The hollow cathode lamp was operated at 15 mA and the analytical wavelength was set at 324.8 nm. Glassware and polypropylene flasks used were overnight immersed in 10% v/v HNO_3 and rinsed several times with DDW.

Batch biosorption studies

All batch biosorption experiments were performed using 100 mg of dried biomass added to 25 mL of copper solution in 500 mL polypropylene flasks. The flasks were placed on a rotating shaker (Tecnal, Brazil) with constant shaking. At the end of the experiment, the flasks were removed from the shaker and the solutions were separated from the biomass by filtration through filter paper (Whatman n° 40, ashless).

Preliminary tests were carried out in order to determine the equilibrium time. They were performed at 298 K using an initial copper concentration of 18.4 mg/mL (initial pH = 5.0), and 150 rpm. The sorption time was varied from 3 to 120 min and the equilibrium on copper uptake was attained

after 20 min. The optimum speed of agitation was determined from experiments carried out at 298 K for 120 min, using an initial copper concentration of 18.4 mg/mL (pH = 5.0). The shaking rate was varied from 0 (without agitation) to 250 rpm. Due to the protonation properties of the carboxyl groups present at the cell walls of the seaweed, pH can affect the biosorption process. So, the effect of initial pH on copper ions uptake was investigated within 2.0 - 5.0. The experiments were performed in similar conditions, using the optimum value of shaking rate. The initial pH was adjusted using 0.10 mol/L HCl solution. No further adjustment on pH was done during the experiment.

The equilibrium isotherms were determined at 298, 313 and 3238 K under optimized conditions, changing the initial copper concentration into the range of 18.4 to 1000 mg/mL and using an equilibrium time equal to 120 min. For the kinetic study, the initial copper concentration was 18.4 mg/mL, the sorption time varied between 3 and 120 min, and the studied temperatures were 298, 313 and 328 K. The remaining parameters were kept under optimized conditions.

All biosorption experiments were done in duplicate. Error bars were not reported, because all the replicate values from the experiments are presented in the figures.

Metal uptake

The copper uptake was calculated by the simple concentration difference method (Volesky and Holan, 1995). The initial concentration C_O (mg/mL) and metal concentrations at any time, C_t, (mg/mL) respectively, were determined and the metal uptake q (mg metal adsorbed/g adsorbent) was calculated from the mass balance as follows:

$$q = \frac{(C_0 - C_t)V}{1000w} \quad (1)$$

where V is the volume of the solution in mL and w is the mass of the sorbent in g. Preliminary experiments had shown that copper adsorption losses to the flask walls and to the filter paper were negligible.

RESULTS AND DISCUSSION

The influence of several operational parameters such as shaking rate, initial pH, temperature and copper concentration on biosorption of copper ions by *Sargassum* sp. was investigated. The results were expressed as the amount of copper ions adsorbed on dried algae at any time (q, mg/g) or at equilibrium (q_e) and the concentration of copper ions that remain in solution at the equilibrium (C_e, mg/mL). The fraction of copper ions adsorbed (X_a, %) was also reported.

$$X_a, \% = \left(1\frac{C_e}{C_0}\right)x100 \quad (2)$$

Influence of shaking rate

The uptake of copper ions by *Sargassum sp*. was evaluated varying the agitation rate from 0 (without agitation) to 250 rpm, aiming at determining the optimal shaking rate. Figure 1 shows that copper uptake increases with the increase in shaking rate ($q = 2.7$ mg/g in absence of agitation and 3.8 mg/g at 50 rpm), and that the adsorption capacity of algae remained constant at 4.3 mg/g for agitation rates greater than 100 rpm. The results show significant difference using t test (P = 0.05), presenting standard deviation equal to 0.1.These results can be associated to the fact that the increase of the agitation speed, improves the diffusion of copper ions towards the surface of the seaweed. This also indicates that a shaking rate in the range 100-250 rpm is sufficient to assure that all the cell wall binding sites are made readily available for copper uptake. Then, the effect of external film diffusion on biosorption rate can be assumed not significant, being ignored in any engineering analysis. For the sake of convenience 150 rpm was chosen for further experiments.

Influence of initial pH

It is well known that the pH of the medium affects the solubility of metal ions and the concentration of the counter ions on the functional groups of the biomass cell walls, so pH is an important parameter on biosorption of metal ions from aqueous solutions.

Sargassum sp. presents a high content of ionizable groups (carboxyl groups from mannuronic and guluronic acids) on the cell wall polysaccharides, which makes it, at least in theory, very liable to the influence of the pH. As shown in Figure 2, the uptake of free ionic copper depends on pH, increasing with the increase in pH from 2.0 to 3.0 and then reaching a plateau in the range 4.0 – 5.0. Similar results were reported on literature for different Cu(II)-biomass systems (Sag et al. 1998; Zhou et al. 1998; Matheickal and Yu, 1999). At pH values lower than 3.0, copper (II) removal was inhibited, possibly as a result of the competition between hydrogen and copper ions on the sorption sites, with an apparent preponderance of hydrogen ions, which restricts the approach of metal cations as in consequence of the repulsive force. As the pH increased, the ligands such as carboxylate groups in *Sargassum* sp. would be exposed, increasing the negative charge density on the biomass surface, increasing the attraction of metallic ions with positive charge and allowing the biosorption onto the cell surface.

The experiments were carried out with initial pH values lower than 6.0 since insoluble copper hydroxide starts precipitating from the solutions at higher pH values, making true sorption studies impossible.

Effect of temperature on copper biosorption equilibrium

Table 1 compares the equilibrium uptakes and the fraction of copper adsorbed obtained at different temperatures and initial copper concentrations. For initial copper concentrations in the range 18-500 mg/mL, the influence of temperature on Cu(II) uptake was not important (*t* test; P = 0.05). Whereas for initial copper concentrations greater than 500 mg/mL, the capacity of copper adsorption at equilibrium slightly increases with the increasing temperature in the range 298-328 K. (*t* test; P = 0.05).

Regarding the influence of the initial concentration of copper ions, the equilibrium sorption capacity of the biomass increased with the increase in the initial copper ions concentration up to 1000 mg/mL while the fraction of copper adsorbed presented the opposite trend. The difference between bulk and surface metal ions concentration is one of the driving-forces to overcome the resistances to adsorption process. In the absence of mass-transfer resistances (as observed in our experiments), surface and bulk concentrations are identical, so the increase in initial concentration of copper ions will enhance the adsorption process, as noticed in Table 1. As can be seen in Figure 3, negligible increase in the values of q_e are observed for equilibrium concentrations greater than 400 mg/mL, suggesting that above this level of solute, solid-liquid equilibrium is probably limited by the diffusion of the copper ions towards the negative charged metal-sequestering sites on the surface of the seaweed; in fact, the algae surface does not display free sites for metal uptake, being saturated.

Equilibrium modeling

Modeling the equilibrium data is fundamental for the industrial application of biosorption since it gives information for comparison among different biomaterials under different operational conditions, designing and optimizing operating procedures (Benguella and Benaissa, 2002). To examine the relationship between sorbed (q_e) and aqueous concentrations (C_e) at equilibrium, sorption isotherm models are widely employed for fitting the data, of which the Langmuir and Freundlich equations are the most widely used. To get the equilibrium data, initial copper concentrations were varied while the biomass weight in each sample was kept constant. Two hours of equilibrium periods for sorption experiments were used to ensure equilibrium conditions. This time was chosen considering the results of kinetics of copper removal by *Sargassum* sp., which will be further presented.

The Langmuir model assumes the form:

$$q_e = \frac{Q_0.K_L.C_e}{1 + K_L.C_e} \ (3)$$

where Q_0 (mg/g) is the maximum amount of metal ion per unit mass of algae to form a complete monolayer on the surface and K_L is the equilibrium adsorption constant which

is related to the affinity of the binding sites. Q_0 represents a practical limiting adsorption capacity when the surface is fully covered with metal ions and allows the comparison of adsorption performance, particularly in the cases where the sorbent did not reach its full saturation in experiments (Aksu, 2001). The Langmuir parameters can be determined from a linearized form of equation (4), represented by:

$$\frac{C_e}{q_e} = \frac{1}{Q_0.K_L} + \frac{1}{Q_0}C_e \ (4)$$

Therefore, a plot of (C_e/q_e) versus C_e, gives a straight line of slope $1/Q_0$ and intercept $1/(Q_0K_L)$.

On the other hand, Freundlich equation is given by:

$$q_e = K_F C_e^{1/n} \ (5)$$

where K_F and n are the Freundlich constants characteristics of the system, indicating the adsorption capacity and the adsorption intensity, respectively. To simplify the derivation of K_F and $1/n$, equation (5) can be linearized in logarithmic form (6).

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \ (6)$$

The corresponding constants and the coefficients of correlation (R) associated at each linearized model of Langmuir (4) and Freundlich (6) adsorption isotherms, obtained at 298, 313 and 328 K, are presented in Table 2. The results indicate that Langmuir isotherm best fits the experimental data over the experimental range studied, since it presents the greater coefficients of correlation in all temperatures. Experimental data and the predicted profiles are in agreement with all range of C_e and temperature evaluated (Figure 3).

The maximum value for the limiting capacity of *Sargassum* sp. for copper(II) ($Q_0 = 94$mg/g) was obtained at 328 K, and it slightly decreases with the decrease in biosorption temperature. On the other hand, K_L values are not statistically different (*t* test; P = 0.05) for the studied temperatures, confirming that in the range 298 – 328 K an increase in temperature does not affect significantly biosorption of copper on *Sargassum* sp.

A comparison with Cu(II) uptake capacities (Q_0) of *Sargassum* sp. and those other biosorbents reported in the literature is given in Table 3. Although a direct comparison with *Sargassum* sp. and other reported biosorbents presents different values due to the varying experimental conditions employed, in general, the Cu(II) uptake capacity of *Sargassum* sp. is higher than the majority of the biosorbents related in the literature.

Biosorption kinetics of copper ions

As can be seen in [Figure 4], for an initial concentration of copper ions equal to 18.4 mg/mL, regardless the temperature studied, the rate of removal of copper ions is extremely rapid in the first 10min, but, next, it decreases significantly and approaches zero (equilibrium). The fast biosorption kinetics observed is typical for biosorption of metals involving no energy-mediated reactions, where metal removal from solution is due to purely physico-chemical interactions between biomass and metal solution (Aksu, 2001).

The shape of q versus *time* curves are similar to those reported by different authors concerning other Cu(II)-biomass systems (Chang et al. 1997; Zhou et al. 1998; Kapoor et al. 1999; Mehta and Gaur, 2001; Nuhoglu et al. 2002; Sag and Aktay, 2002). It can also be observed for this initial concentration (18.4 mg/mL), that the temperature does not affect the equilibrium uptake although it slightly influences the adsorption rate.

Kinetic modeling

Two different kinetic models were used to adjust the experimental data of Cu(II) biosorption on *Sargassum* sp. The pseudo first-order Lagergren model is generally expressed as:

$$\frac{dq}{dt} = k_{1,ads}(q_e - q) \quad (7)$$

where q_e(mg/g) and q are the amounts of adsorbed metal ions on the biosorbent at the equilibrium and at any time t, respectively; and $k_{1,ads}$ is the Lagergren rate constant of the first-order biosorption. Integrating (7) between the limits, t =0 to t =t and $q = 0$ to $q = q_e$, it becomes:

$$\log(q_e - q) = \log q_e - \frac{k_{1,eds}}{2.303}t \quad (8)$$

Linear plots of $\log(q_e\text{-}q)$ *versus* t indicate the applicability of this kinetic model. However, to adjust equation (8) to the experimental data, the value of q_e (equilibrium sorption capacity) must be pre-estimated by extrapolating the experimental data to t = ¥.

The pseudo-second order model is based on the assumption that biosorption follows a second order mechanism. So, the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites:

$$\frac{dq}{dt} = k_{2,ads}(q_e - q)^2 \quad (9)$$

where $k_{2,ads}$ is the rate constant of second order biosorption (g/mg.min). Integrating (9) for the boundary conditions t = 0 to t = t and $q = 0$ to $q = q_e$, and then linearizing it determines an equation (10) such as:

$$\frac{t}{q} = \frac{1}{k_{2,ads}.q_e^2} + \frac{1}{q_e}t \quad (10)$$

q_e and $k_{2,ads}$ can be calculated from the slope and the intercept of the plot t/q versus t. It is important to notice that it is not necessary to estimate the experimental value of q_e for the application of such a model.

The Lagergren first-order rate constant ($k_{1,ads}$) and q_e determined from the model indicated that this model failed to estimate q_e since the experimental values of q_e differed from those estimated ([Table 4]). By plotting t/q against t, a straight line could be obtained for all the studied temperatures, allowing the determination of the second-order rate constant ($k_{2,ads}$) and q_e values. The coefficients of correlation for the second order kinetic model were equal to 1 for all temperatures and the estimated values of q_e also agreed with the experimental ones. Both facts suggest that the sorption of copper(II) ions follows the second-order kinetic model, which relies on the assumption that biosorption may be the rate-limiting step.

The second-order rate constant is expressed as a function of temperature by an Arrhenius-type correlation:

$$k_{2,ads} = k_0 \exp\left(\frac{-E}{R_g.T}\right) \quad (11)$$

where k_0 is the temperature independent factor (g/mg.min), E is the activation energy of sorption (kcal/mol), R_g is the gas constant (1.987 cal/mol.K) and T is the sorption temperature (K). The corresponding linear plot of ln$k_{2,ads}$ as a function of $10^3/T$, allows to calculate the activation energy from the slope of this plot. In the present work, the activation energy for the biosorption of copper ions on *Sargassum* sp. was found as 5.2 kcal/mol.

CONCLUDING REMARKS

The obtained results also showed that initial pH, temperature, shaking rate and initial metal ion concentration affected the uptake capacity of the biosorbent.

The Langmuir adsorption model described well the biosorption equilibrium of copper (II) ions on *Sargassum* sp. in the studied conditions. The temperature did not influence this equilibrium since K_L is practically constant in the range of the temperature studied. Additionally, the monolayer capacity slightly decreases from 328 to 298 K. Biosorption of copper(II) ions onto biomass followed a second-order adsorption kinetics and the activation energy of biosorption was evaluated as 5.2 kcal/mol.

The results confirmed that *Sargassum* sp. is a potential biomaterial to remove copper ions with a high biosorption capacity: 1.48 mmol/g. This value can be compared with

those observed for other marine micro algae and it is considerably higher than the values obtained with the majority of the biosorbents.

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APPENDIX

Tables

Table 1. Equilibrium uptakes (q_e) and fraction of copper removed (X_a, %) by *Sargassum* sp. at different temperatures and initial concentrations.

C_0 (µg/mL)	298K		313K		328K	
	q_e (mg/g)	X_a (%)	q_e (mg/g)	X_a (%)	q_e (mg/g)	X_a (%)
18.4	4.3 (0.1)[a]	89.1 (1.6)	4.3 (0.1)	89.3 (1.5)	4.1 (0.1)	87.6 (1.5)
36.9	8.3 (0.2)	90.1 (1.8)	8.3 (0.2)	90.2 (1.7)	8.3 (0.2)	86.8 (1.9)
92.2	21.3 (0.5)	92.4 (1.7)	21.3 (0.6)	92.3 (1.9)	21.4 (0.4)	91.6 (1.8)
184	40.0 (0.8)	87.0 (1.9)	38.0 (0.9)	82.6 (1.7)	42.5 (1.0)	92.4 (1.8)
277	53.3 (1.3)	77.0 (1.5)	53.1 (1.2)	76.6 (1.8)	57.0 (1.3)	82.2 (1.9)
369	57.9 (1.7)	62.8 (1.6)	57.6 (1.5)	62.4 (1.4)	60.8 (1.6)	65.9 (1.5)
585	70.1 (1.9)	47.9 (1.7)	75.6 (2.0)	51.7 (1.9)	80.1 (1.9)	54.8 (1.8)
780	76.2 (2.0)	39.1 (1.4)	86.0 (1.8)	44.1 (1.6)	86.6 (1.9)	44.4 (1.8)
878	77.4 (2.1)	35.3 (1.7)	86.2 (2.0)	36.6 (2.0)	87.1 (2.0)	39.7 (1.9)

a: Figures in parenthesis are standard deviations obtained for triplicate measurements of the parameter for two identical samples (n = 6).

Table 2. Freundlich and Langmuir adsorption constants associated to adsorption isotherms of copper(II) ions on *Sargassum* sp. at different temperatures.

T (K)	Freundlich constants			Langmuir constants		
	K_F	n		Q_0 (mg/g)	K_L (L/gmol)	
298	5.7 (1.0)[a]	2.3 (0.2)	0.908	82.6 (1.2)	1654 (217)	0.998
313	5.2 (0.8)	2.1 (0.2)	0.953	88.0 (1.7)	1522 (200)	0.997
328	5.4 (1.2)	2.0 (0.2)	0.917	93.9 (2.1)	1611 (233)	0.996

a: Figures in parenthesis are standard deviations (n = 20).

Table 3. Copper(II) adsorption capacities of reported sorbents.

Adsorbent	q_{max} (mmol/g)	References
Granulated activated carbon, F-400	0.03	Muraleedharan et al. 1995
Rhizopus arrhizus	0.25	Volesky, 1990
Pseudomonas aeruginosa	0.29	Chang et al. 1997
Phanerochaete chrysosporium	0.42	Say et al. 2001
Rhizopus arrhizus	0.53	Sağ et al. 1998
Pre-treated *Ecklonia radiata*	1.11	Matheickal and Yu, 1999
Pre-treated *Durvillaea potatorum*	1.30	Matheickal and Yu, 1999
Chlorella vulgaris	1.40	Mehta and Gaur, 2001
Ulothrix zonata	2.77	Nuhoglu et al. 2002
Sargassum sp.	1.48	This study

Table 4. Comparison between adsorption rate constants, q_e estimated and coefficients of correlation associated to the Lagergren pseudo first-order and to the pseudo second-order kinetic models (C_0 = 18.4 μg/mL, w = 0.100g, V = 25mL, pH 5.0, agitation rate 150 rpm).

T (K)	First-order kinetic model			Second-order kinetic model			$q_{e,exp}$(mg/g)
	$k_{1,ads}$(min^{-1})	q_e (mg/g)		$k_{2,ads}$(g/mg.min)	q_e (mg/g)		
298	0.150 (0.011)[a]	1.21 (0.35)	0.967	0.349 (0.043)	4.30 (0.03)	1.000	4.26
313	0.180 (0.012)	1.51 (0.46)	0.950	0.307 (0.035)	4.30 (0.03)	1.000	4.26
328	0.232 (0.020)	1.25 (0.29)	0.989	0.791 (0.118)	4.09 (0.03)	1.000	4.10

a: Figures in parenthesis are standard deviations (n = 10 first-order kinetic model; n = 20 second-order kinetic model).
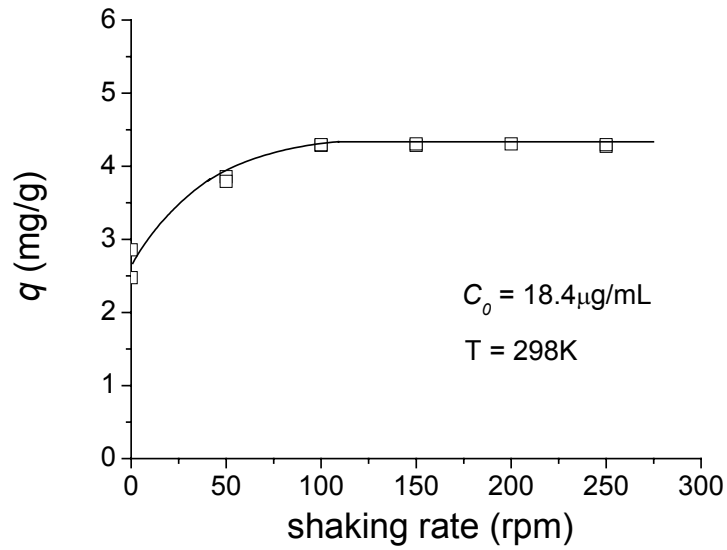
Figures

C_0 = 18.4µg/mL

T = 298K

Figure 1. Influence of shaking rate on equilibrium copper ions uptake by *Sargassum* sp.
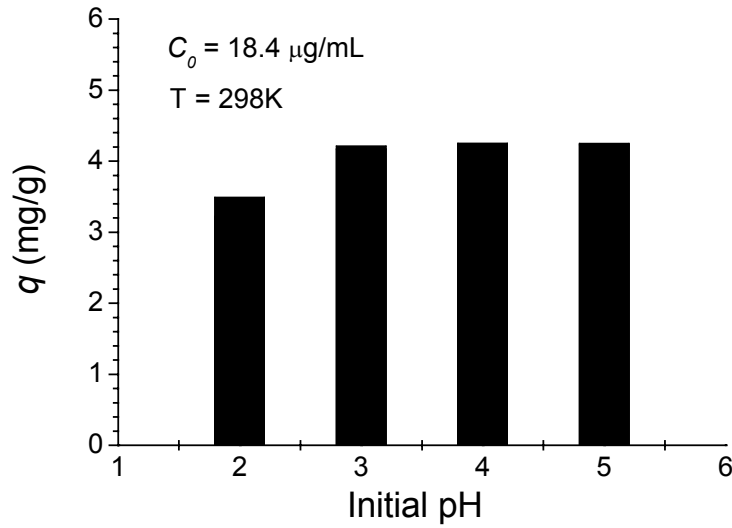

C_0 = 18.4 µg/mL

T = 298K

Figure 2. Effect of the initial pH on equilibrium copper ions uptake by *Sargassum* sp.
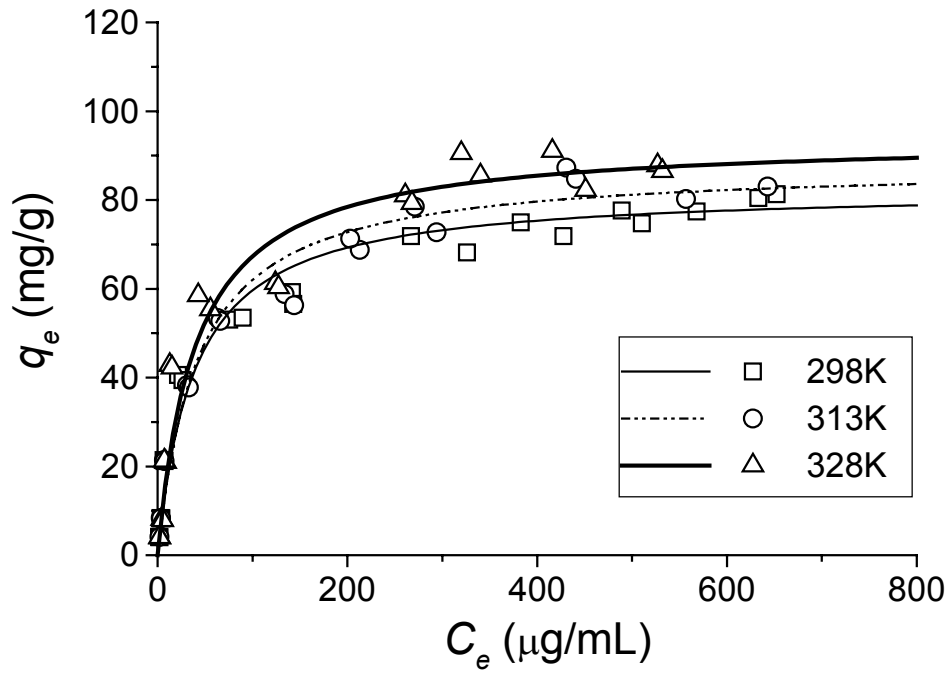
Figure 3. Adsorption isotherms of copper ions by *Sargassum* sp. at different temperatures. (discrete points – experimental data; full and dotted lines – Langmuir isotherm model).
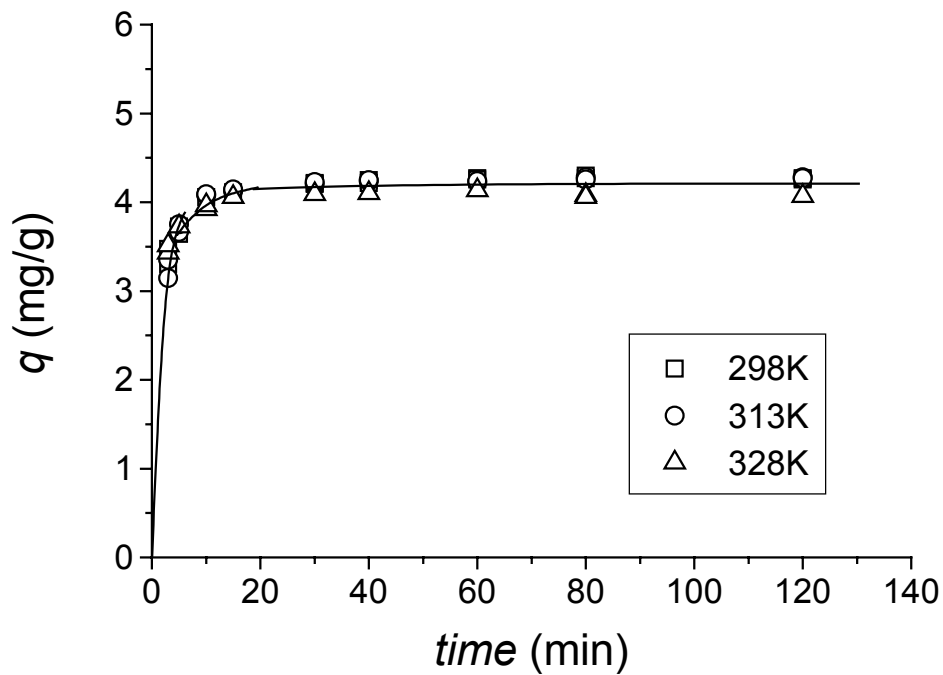

Figure 4. Influence of sorption time on copper ions uptake by *Sargassum* sp. at different temperatures (C_0 = 18.4 μg/mL).