Biosorption of Copper Cu (II) in aqueous solution by chemically modified crushed marine algae (*Bifurcaria bifurcata*): Equilibrium and kinetic studies

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Abstract: The Moroccan coastlines are known to be rich in marine algae species. Among these seaweed species; *Bifurcaria bifurcata* with its important biomass has been employed as a new adsorbent for the removal of copper in aqueous solution. Indeed, adsorption tests showed that the equilibrium is established after 60 minutes. Our experimental results demonstrate that the adsorption of copper on the algae is dependent on the pH of the solution and the initial concentration of copper. The adsorption capacity was determined using the Langmuir and the Freundlich isotherms. The maximum adsorption capacity is 101,9 mg.g^{-1}. The kinetic studies carried out showed that the adsorption of copper by the algae follows pseudo-second order kinetic model with high R^2 values.

Keywords: *Bifurcaria bifurcata*; adsorption; biosorption; Copper, pollution; environment.

Introduction

Copper is an element found naturally in the earth's crust and diffuses into the environment through natural phenomena. This compound, essential for the development of all known forms of life, is widely used in metallurgy for making alloys and especially as a fungicide in viticulture [1,2]. The increase in its production in recent years is the origin of the increasing amounts found in nature.

Copper is one of the most toxic heavy metals. Therefore, when the soil contains high amounts of copper (II) ions, the effects are harmful on humans and other living beings. Acute poisoning due to inhalation following exposure to copper (II) ions is very common and can cause irritation, headaches, stomach upsets, dizziness, vomiting and diarrhea[3]. In contrast, oral poisoning is very rare, usually accidental and is accompanied by renal insufficiency, and in severe cases, loss of consciousness or other disorders leading to death [3].

Decontamination of heavy metals from wastewater has been a challenge for a long time. A number of methods have been developed for removal of copper from industrial effluents in order to protect the environment and to possibly re-use water, especially in arid countries [4,5].

However, these conventional technologies are expensive [6,7]. Hence, an alternative adsorption on biological materials (ie biosorption); available and relatively inexpensive; may give rise to a technically reliable and economically viable clearance process.

In this work, we proposed to study at first the biosorption capacity of copper by a marine biomass *Bifurcaria bifurcata,* from aqueous solutions prepared in the laboratory with different concentrations of copper. Thereafter, to optimize the influence of some key parameters on biosorption, we performed a modeling of isotherms and a kinetic study.

Materials and methods

Chemical pretreatment of biomass

Once collected from the Atlantic coast of the city of El Jadida (Morocco), algae *Bifurcaria bifurcata* were washed with water, dried in an oven at 60 ° C for 24 hours, then ground and sieved to obtain the fraction size of 0,50 mm. The crude material has been activated by successive immersions in solutions of NaOH (0,75 M), HCl (0,75 M) then NaCl (2 M) following a method developed in the laboratory.

Preparation and dosage of Copper solutions

A copper stock solution was prepared by dissolving a given amount of copper sulphate in distilled water to obtain a concentration of 100 mg.L^{-1}, further concentrations are obtained if necessary by successive dilutions. The initial pH was adjusted with dilute solutions of HCl (0,1M) and NaOH (0,1M).

The residual copper concentration in the reaction mixture was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and the copper adsorption capacity was calculated using the following formula [8].

$$q_t = \frac{(C_0 - C_t) * V}{m}$$

Where q_t (mg.g^{-1}) is the amount adsorbed at time t (min), C_0 (mg.L^{-1}) is the initial concentration of copper, C_t (mg.L^{-1}) is the concentration at time t, V is the solution volume (mL) and m (g) is the amount of the adsorbent used.

Batch method

The experiments were conducted in "batch method". Basically, 0.1g of the algae was added to 50 ml of a copper solution of known concentration, in a 250 ml Erlenmeyer. This solution is left under constant stirring at room temperature. After 60 min, the solution is filtered and then stored away from light, at 3°C and a pH <2 in order to avoid any changes on the samples before analysis.

Adsorption kinetics

The kinetic study of copper biosorption was performed to determine the contact time required to reach equilibrium. During the contact time, the solution is kept under constant agitation, at temperature and pH both constant (pH = 5,6 and T = 298 K). Samples were taken every 10 min for 100 min.

Adsorption isotherm

In order to obtain the adsorption isotherms, we mixed 0,1g of the adsorbent with 50 ml of the copper solution at different initial concentrations ranging from 10 mg.L-1 to 1 g.L^{-1}, with constant stirring at room temperature.

Linear regression analysis

In this study, all the model parameters were evaluated by linear regression to determine the best fitting of the equation to the experimental data. The sole correlation coefficient (R^2) is not sufficient; to this purpose we have also used the residual root mean square error (RMSE) and the Chi-square test χ^2 to measure the goodness-of-fit. RMSE can be represented as follows [9]:

$$RMSE = \sqrt{\frac{1}{m-2} \sum_{i=1}^{m} (Y_i - y_i)^2}$$

Where:

   Y_i: the experimental value;
   y_i: the value obtained by calculating from the model;
   m: the number of observations .

Smaller RMSE values indicate better curve fitting.

The Chi-square test is basically the sum of the squares of the differences between the experimental values and the values obtained by calculating from the model, with each squared difference divided by the corresponding values calculated from the model [9]. It can be defined as follows:
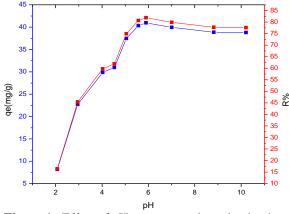
$$\chi^2 = \sum_{i=1}^{m} \frac{(Y_i - y_i)^2}{y_i}$$

If data from the model are similar to the experimental data, the χ^2 test is a small number.

Results and Discussion

Effect of pH

Copper biosorption by *Bifurcaria bifurcata* depends on the pH influencing the nature of the biosorbent surface, the degree of ionization and the nature of the adsorbate ionic species. In fact various adsorption studies at different pH values ranging from 1 to 10, show that copper adsorption is pH dependent as we can notice in Figure 1.

Figure 1. Effect of pH on copper adsorption by the algae. Adsorbent mass = 0.1 g; solution volume = 50 mL; concentration = 10 mg.L^{-1}; time = 60 min; temperature = 298 K.

Figure 1 clearly shows the influence of the pH on the adsorption rate. Based on the curve, we see that at low pH values, the adsorption rate is low, it reaches 15% at pH = 2.

When the pH value is between 2 and 6, the copper retention rate increases rapidly to a maximum of 82% at pH 5,6. Thereafter, the adsorption rate decreases to 75% between pH 6 and 10. These results allowed us to determine the pH corresponding to the best adsorption efficiency. Accordingly, all the copper adsorption studies were carried out at pH 5,6.

The main functional groups responsible for the absorption of metals, including copper on the algae are the carboxylic, hydroxylic and sulfonates groups [11] of the polysaccharide present within the surface of the biosorbent, the carboxylic groups being the most active.

Thus, at low pH, the adsorption of copper is low. The active groups are poorly ionized and the concentration of $[H_3O^+]$ is higher in solution favoring the protonation of the functional active sites on the surface of the algae [12,13].
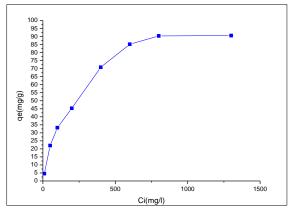
Beyond pH = 2, the concentration of $[H3O^+]$ decreases compared to that of Cu^{2+} ions, which explains the increase in the rate of adsorption.

At high pH, the active sites are deprotonated enabling an interaction with the metallic ions instead of $H3O^+$ ions.

The reduction in the adsorption rate observed at pH=10 is probably due to the formation of soluble hydroxyl complexes displaying more affinity with the functional sites of algae at the expense of copper.

Effect of the initial concentration

To study the effect of the initial concentration of the pollutant on the adsorption process, we varied the concentration of copper from 10 to 1500 mg $.L^{-1}$. The results obtained are shown in Figure 2 below:
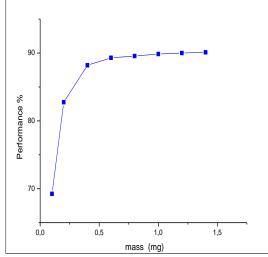

Figure 2. Effect of initial concentration on copper adsorption by the algae. Adsorbent mass = 0,1 g; solution volume = 50 ml; pH = 5,6; time = 60 min; temperature = 298 K
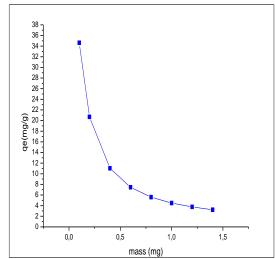
The curve indicates a rapid increase in storage capacity at low concentrations (10 to 200 mg.L^{-1}). Binding capacity continues to increase with the rise of the initial concentration, indicating the existence of attractions forces between the exchange surface and the metal cation. Then, an equilibrium plateau appears as the concentration reaches the value of 500 mg.L^{-1}. This plateau may reflect the saturation of active sites involved in the adsorption process.

Effect of biosorbent dosage

To examine the effect of the biosorbent dosage, we varied the amount of biosorbent from 0,1 to 1,4 g using a fixed solution volume.

Figure 3a. Effect of the biosorbent dosage on copper adsorption efficiency by the algae. pH = 5,6; solution volume = 50 ml; time = 60 min; concentration = 100 mg.L^{-1}; temperature = 298K

Figure 3b. Effect of biosorbent dosage on the amount of copper absorbed by the algae. pH = 5,6; solution volume = 50 ml; time = 60 min; concentration = 100 mg.L^{-1}; temperature = 29

Figure 3a shows that the copper removal efficiency increases strongly with the increasing amount of the adsorbent till 0,5 mg. In contrast, Figure 3b shows that the amount of copper absorbed (q_e) in mg decreases rapidly. Starting from 0,5 mg of algae, a plateau appears on both studies (efficiency and q_e) [14, 15.16].

The decrease in biosorption efficacy with increasing doses of biomass can be explained as follows:
•   As the amount of adsorbent added to the copper solution is low, Copper ions can easily access the adsorption sites. The addition of adsorbent can increase the number of adsorption sites but copper ions have greater difficulty in approaching these sites because of congestion.
•   A large amount of adsorbent creates aggregates of particles, resulting in a reduction of the total surface area for adsorption, and therefore, a decrease in the amount of adsorbate per unit mass of adsorbent [17, 18].

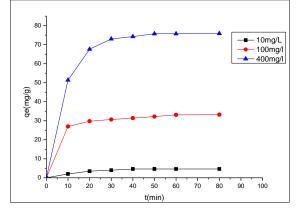According to both Figures 3a and 3b, we can deduce the following results:
For an amount of 1,4g of adsorbent, we have a copper removal efficiency of 90% and a q_e of 5 mg.g^{-1}. However, for an amount of 0,1 g of adsorbent, we have a 70% of efficiency and a q_e of 35 mg.g^{-1}. It is clear that the use of 0,1g of seaweed (14 times less) leads to the best results (35 mg of copper adsorbed per g of algae instead of 5 mg.g^{-1} for 1,4 g of algae). All these data, obtained with simple experiments may be of great interest to optimize the purification of industrial effluents. Therefore, in the following studies, we used the amount of 0,1g adsorbent with 50 ml of solution.

Adsorption kinetics

One of the most used parameters to estimate the purification performance of an adsorbent is the adsorption kinetics. Not only it estimates the amount of adsorbed pollutants over time but also it gives the contact time between the biosorbent and pollutants to reach equilibrium. Moreover, kinetics provides information on the adsorption mechanism and the mode of transfer of solutes from liquid to solid phase [19].

Contact time

Initially, we were interested in the effect of contact time on copper adsorption by the algae. We have studied the evolution of three solutions with concentrations of 10,100 and 400 mg.L^{-1}. The results obtained are summarized in Figure 4.

Figure 4. Effect of contact time on copper adsorption by the algae. Adsorbent mass = 0,1 g; solution volume = 50 ml; pH = 5,6; temperature = 298 K; time = 0-80 min

Figure 4 shows the effect of the initial concentration of copper on the retention rate at different contact times. For the three concentrations used, the retention rate increases with the increase in reaction time following two different slopes. The first is rapid, in the first 20 minutes, while the second is slow and may express the balance between retained and desorbed Copper fractions. The adsorption capacity increases with increasing concentration of the solution to reach the values of 76, 33 and 4,6 mg.g^{-1} respectively to the concentrations of 400, 100 and 10 mg.L^{-1}.

Kinetic study

Like the adsorption equilibrium, the kinetics of adsorption of a material can be modeled. In this regard, the literature reports a number of models, such as the model of Lagergren (first-order model), the kinetic model of second order and intra-particle diffusion model. The majority of works consulted evaluate the kinetic potential of biosorbents by second order kinetic model [20,21].

Then, to examine the mechanism of the adsorption processes (mass transfer or chemical reaction), we have used kinetic models to analyze our experimental results. Different models such as the external diffusion model on homogeneous area, the intra-particle diffusion model and the surface reaction model are applied in a batch system in order to describe the phenomenon of transport of the adsorbate through the pores of the adsorbent [22].

The external diffusion step:

The following kinetic expression is often cited and used to model the external diffusion of any solute transfer from liquid to any another phase, including solid one [23].

$$-\frac{dC_t}{dt} = k\left(\frac{a}{v}\right).(C_t - C_e)$$

C_e: concentration of solute in the solution at equilibrium;
a: area of the solid interface / liquid;
V: volume of solution.

The integrated form is the following:

$$\ln\left[\frac{(C_0 - C_e)}{(C_t - C_e)}\right] = k\left(\frac{a}{v}\right).t = Kt$$

A simple plot of ln [C_0- C_e) / (C_t - C_e)] in function of the reaction time should allow us to evaluate whether the external diffusion step is determining for the entire reaction [24].

Intra-particle diffusion step:
The model of the intra-particle diffusion is represented by the following equation [25, 26].

$$q_t = k_D t^{1/2} + C_D$$

K_D: rate constant of intra- particle diffusion $(mg.g^{-1}.min^{1/2})$;
C_D: constant connected to the trendline.

Surface reaction step:
Expression of pseudo first order
The expression of pseudo-first order, often cited, is the following [11, 27].

$$+\frac{dq_t}{dt} = k_1.(q_e - q_t)$$

The linear form is the following:

$$\ln(q_e - q_t) = \ln(q_e) - k_1.t$$

K_1: the first-order rate constant (min^{-1});
t: time (min).

Expression of pseudo- second order
The expression of pseudo- second order is often used [22, 28].

$$+\frac{dq_t}{dt} = k_2(q_e - q_t)^2$$

The linear form is the following:

$$\frac{t}{q_t} = \frac{1}{K_2.q_e^2} + \frac{1}{q_e}t$$

K_2: pseudo-second-order rate constant $(g.mg^{-1}. min)$.

The set of kinetic parameters of biosorption is determined from the linearity straights according to the equations of the models described above.

In order to examine the reliability of the proposed kinetic models, we calculated the equations correlation coefficients, as well as the kinetic constants of each model which are summarized in Tables 1a and 1b.

Table 1a. Parameters of the external diffusion model and the intra-particle diffusion model of the kinetics of copper biosorption by the algae

C_0 (mg.l^{-1})	The external diffusion model				the intra-particle diffusion model				
	k	R^2	RMSE	χ^2	kd (mg.g^{-1}·min$^{-0,5}$)	C	R^2	RMSE	χ^2
10	0,0443	0,9784	0,1059	0,0095	0,6796	2,3456	0,9031	0,3380	0,1064
100	0,0717	0,9784	0,0992	0,0118	1,2713	23,460	0,9387	0,4958	0,0253
400	0,1218	0,9182	0,5684	0,2393	6,0025	36,577	0,8000	1,1245	0,9166

Table 1b. Parameters of the reaction surface model of kinetics of copper biosorption by the algae

C_0 (mg.l^{-1})	surface reaction models									
	Pseudo-first order					Pseudo-second order				
	k_1 (min^{-1})	q_e (mg .g^{-1})	R^2	RMSE	χ^2	k_2 (g.mg^{-1}.min^{-1})	q_e (mg.g^{-1})	R^2	RMSE	χ^2
10	0,0027	27,66	0,9084	0,0331	0,0016	0,456	4,757	0,9994	0,0164	0,0014
100	0,0020	28,31	0,8604	0,0393	0,0274	9,2.10^{-3}	34,55	0,9996	0,0159	0,0013
400	0,0087	52,17	0,8573	0,0953	0,0407	4,59.10^{-3}	75	0,9976	0,0090	0,0008

From these results, it appears that the adsorbed amount at equilibrium q_e increases with the increase of the initial concentration. Furthermore, the R^2 values obtained with the model of pseudo- second order are very high and greater than 0,99, the values of RMSE and χ^2 instead, are poor .They far exceed those obtained with the model of pseudo-first order, the intra- particle diffusion and the external

diffusion. The amounts absorbed at equilibrium qe reach 4,757; 34.55 and 75 mg.g-1 corresponding respectively to the concentrations of 10; 100 and 400 mg.L^{-1} which are very close to the experimental values of 4.625, 33 and 76 mg.g-1. This finding leads us to confirm that the adsorption process follows the pseudo-second-order model.

Adsorption isotherm

The adsorption isotherms provide evaluation of copper adsorption capacity on the seaweed. These curves link the amount of copper adsorbed per unit mass of the algae (qe) to the concentration of copper remaining in solution (C_e).

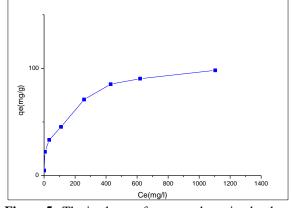Figure 5 shows the isotherm of copper adsorption by the algae.

Figure 5. The isotherm of copper adsorption by the algae. Adsorbent mass = 0,1 g; solution volume = 50 ml; time = 60 min ; pH = 5,6 ; temperature = 298K

To determine the amount of copper adsorbed per unit mass of the algae (q_e), several authors have proposed theoretical or empirical models to describe the relationship between the amount adsorbed and the residual concentration both at equilibrium. The main models described in literature are [11,29].

- **Langmuir model:**

$$q_e = \frac{q_{m,L} * K_L * C_e}{1 + K_L * C_e}$$

$$\frac{C_e}{q_e} = \frac{1}{q_{m,L} * K_L} + \frac{1}{q_{m,L}} C_e$$

Where q_e: adsorption capacity at equilibrium (mg.g^{-1});

q_m: adsorption capacity of saturation (mg.g^{-1});

K_L: Langmuir constant.

The plot of C_e/q_e in function of C_e, allows to determine q_m and K_L.

Another parameter; R_L can explain the adsorption according to Langmuir as following:

$$R_L = \frac{1}{1 + K_L * C_0}$$

Based on the R_L value, we can say that the adsorption is favorable when R_L tends to zero ($R_L \rightarrow 0$) or unfavorable when R_L tends to one ($R_L \rightarrow 1$) [29].

- **Freundlich model:**

The simple and empirical model of Freundlich is the most commonly used[29].

$$\mathbf{q_e = K_F * C_e^n}$$

The linear form is the following:

$$\mathbf{Ln q_e = Ln K_F + n Ln C_e}$$

K_F: constant relative to the adsorption capacity (mg mg $^{(1-n)}$.L^n.g^{-1});

n: constant (dimensionless) giving an indication of the adsorption intensity.

It is generally accepted that low values of n (0,1 <n < 0,5) are characteristics of a good adsorption, whereas higher values indicate a moderate adsorption (0,5 <n<1) or low (n> 1). The constant « n » is often replaced by « 1/n » or heterogeneity factor [29].

The adsorption isotherm is an L type [30], suggesting a progressive saturation of the solid. When the equilibrium concentration (C_e) tends to zero, the slope of the isotherm is constant.

In order to explain the obtained equilibrium isotherms, experimental data were treated according to the isotherms models described above (Freundlich model and Langmuir model).

Table 2. Parameters of isotherms models of copper adsorption by the algae

Langmuir model						Freundlich model				
q_m (mg.g$^-$)	K_L (l.mg^{-1})	R_L	R^2	RMSE	χ^2	K_F mg$^{(1-n)}$.l^n.g^{-1}	n	R^2	RMSE	χ^2
101,9	70,466	0,124	0,9927	0,0276	0,0454	7,333	0,3974	0,9461	0,3660	0,1129

From the values of the correlation coefficients R^2, the residual root mean square error (RMSE) and the Chi-square test (Table.2) we can conclude that the Langmuir model is the closest to the experimental results. We also note that the R_L coefficient of this model tends to 0 which explains that the adsorption of copper on the algae is favorable.

Conclusion

In the present work, we studied copper biosorption capacity by a marine biomass*; Bifurcaria bifurcata*; very available along the Moroccan Atlantic coast. Experimental results show that the adsorption process depends on the solution pH, the initial concentration of copper and the amount of biomass. The kinetic study of copper adsorption on the algae showed that the adsorption process follows the pseudo-second-order model. The modeling of isotherms reveals that the Langmuir model best expresses this type of adsorption. The copper ions are adsorbed as monolayers, without interaction with adjacent ions, increasing the order of their distribution on the bioadsorbent surface. It is interesting to note however, that based on the Langmuir isotherm, the exceptional value of the maximum adsorption capacity reaches 101,9 mg.g^{-1}.

Taking together the results of this study, we suggest that *Bifurcaria bifurcata* algae may be considered a promising biological material to be used as an effective adsorbent for the removal of copper present in liquid effluents.

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