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Biosorption of copper by grape stalks and pine bark biomasses

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ABSTRACT

The removal of copper from aqueous solutions by biosorption onto grape-stalks and pine bark biomass is reported. The adsorption isotherms were determined, along with the effect of different variables, such as the pre-treatment of the biomass, pH, metal concentration and reaction time on the copper removal efficiency. The uptake capacity for copper with grape stalks and with pine bark is 19.9mg/g and 49.8mg/g, respectively. In both cases, the biosorption is favoured by an increase in pH. The pre-treatment of the pine bark with a solution containing 0.005M of calcium chloride increases 20% its uptake capacity. The kinetics of copper biosorption in both biomasses was studied and a pseudo second order model was used to fit the experimental data. Copper biosorption is a fast process and within the first 2 minutes 80% of the metal is removed from the solution. The elution experiments shows that all the copper bound to the grape stalks could be eluted using a solution containing 1 molar of sodium sulphate and 0.1M of tri-sodium citrate, and no more than 84% (maximum) of the copper bound to pine bark could be eluted using an acid solution of H_2SO_4 3.7M. The biomasses did not loose their binding capacity for, at least, four cycles of biosorption/elution.

Keywords: Grape stalks; Pinus-bark; Biosorption; Elution

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1. INTRODUCTION

In recent years there has been a great effort in studying and developing cost-effective processes that allow the recovery of heavy metals from different type of effluents. Heavy metals are particularly toxic in their chemical combined forms. It is known that cadmium, copper, zinc, lead and mercury ions bind to the cell membranes hindering transport processes through the cell wall. The classical abatement of heavy metals from wastewater is chemical precipitation in the form of hydroxides or sulphides (Metcalf and Eddy, 1991). This technology only achieves moderate removal and generates large amounts of sludge containing metals that require stabilisation and must be disposed in a landfill. Moreover, many times the legal discharge limits for heavy metals are lower than the levels obtained after the physico-chemical treatment (Forster and Wase, 1997). It is thus important to have some "polishing" treatment and biosorption with a low cost biomass might be an alternative effluent treatment (Forster and Wase, 1997; Volesky, 2001). Recently, Bailey *et al.* (1999) published an excellent review of low cost sorbents for heavy metals.

The biosorption of metal by biomass has been ascribed to many different mechanisms, which includes ion exchange or complexation, adsorption of simple ionic species and hydrolysis products of metal ions (Forster and Wase, 1997). Hard metal cations such as Na^+, K^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{3+} form predominantly ionic bonds. However, substantial biosorption of soft metals that form mainly covalent metal-ligand bonds (such as Cu^+, Pb^{2+}, Ti^+, Hg^{2+}) is also found in the literature for yeasts and fungi such as *Rhizopus and Penicillium* (Volesky, 1987). Metal cations of intermediate hardness such as Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} exhibit interactions of both types. The ionic binding of metallic ions to biomass can be described by the following equation:

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$$M^{n+} + H_nB \leftrightarrow MB + nH^+ \tag{1}$$

where M represents the metal, *n* its charge and B the biosorptive active centre.

The metal concentration biosorbed by the biomass, *q* (mg/g), can be obtained using the following mass balance:

$$q_e = \frac{(C_0 - C_e)\,V}{M} \tag{2}$$

where C_0 and C_e are, respectively, the initial and the equilibrium metal concentration in solution (mg/dm^3), q_e is the amount of metal adsorbed onto the unit mass of adsorbent at equilibrium (mg/g), V (dm^3) is the total volume of the solution and M (g) is the mass of biomass present in the suspension. A non-linear least square fitting of the empirical Langmuir-type equation to the equilibrium data was used, thus producing the following equation:

$$q_e = \frac{q_{\max}\, C_e}{\dfrac{1}{K} + C_e} \tag{3}$$

where q_{max} (mg/g) is the maximum metal concentration biosorbed by the biomass and K (dm^3 mg^{-1}) is the affinity constant. Within the range of validity of the Langmuir equation and for known values of q_{max} and K, equations 2 and 3 can be used to predict the metal concentration at equilibrium. Therefore, equalizing equation 2 and 3 and solving for C_e, the following expression is obtained:

$$C_e = \frac{-\left([B]\,q_{\max} + \dfrac{1}{K} - C_0\right) + \sqrt{\left([B]\,q_{\max} + \dfrac{1}{K} - C_0\right)^2 + \dfrac{4\,C_0}{K}}}{2} \tag{4}$$

where *[B]* is the biomass concentration (g dm^{-3}).

If C_e is known, the expected percentage of copper biosorbed, $\%Cu_{bio}$, can be calculated as:

$$\%Cu_{bio} = \frac{(C_0 - C_e)}{C_0}\,100 \tag{5}$$

The kinetics of the biosorption of metal ions can be modelled using the Lagergren approach (Singh *et al.*, 1997), that assumes a first order mechanism described by equation 6:

$$\frac{dy}{dt} = K'_c\,(1-y) \tag{6}$$

where y, defined as $q(t)/q_e$, is the dimensionless ratio between the metal concentration bound to the biomass at a time t, $q(t)$, and the metal concentration bound to the biomass at equilibrium, while K'_c is the kinetic constant.

In this work it was assumed a second order mechanism correspondent to following equation:

$$\frac{dy}{dt} = K_c(1-y)^2 \tag{7}$$

where K_c is the kinetic constant.

Integrating equation 6 one obtains the Lagergren equation (Singh *et al.*, 1997) described by:

$$\log(q_e - q) = \log q_e - \left(\frac{K'c}{2.303}\right)t \tag{8}$$

while solving the ordinary differential equation described by equation 7 and using the condition that for $t=0$, $y=0$:

$$y = \frac{K_c\,t}{1 + K_c\,t} \tag{9}$$

or substituting y by its definition:

$$q = \frac{q_e\ t}{\frac{1}{K_c} + t} \tag{10}$$

Equation 10 can be linearized into the following form:

$$\frac{t}{q} = \frac{1}{K_c\, q_e} + \frac{1}{q_e}\, t \tag{11}$$

that allows the calculation of q_e and K_c, respectively, from the slope and intercept of the previous straight line. The initial rate of the biosorption reaction can thus be obtained by the derivative of equation 10 for t=0:

$$\frac{dq}{dt_{t=o}} = K_c\ q_e \tag{12}$$

Ho *et al.* (2000) obtained a similar equation assuming that the rate limiting step of the reaction may be chemical sorption or chemisorption involving valence forces through sharing or exchange of electrons between the sorbent and the sorbate. In latter, the intercept of the straight line is $1/(K_c.q_e^2)$ instead of $1/(K_c.q_e)$ of equation 11.

The objective of this paper is to study the removal of copper by biosorption in grape stalks and pine bark and to compare the results with the ones obtained with other sorbents.

2. MATERIALS AND METHODS

All the chemicals were analytical grade and were supplied by Merck. Copper was added in the sulphate form and the analyses were carried out by atomic absorption spectroscopy (Perkin-Elmer 3100). pH measurements were made using a Metrohm pH meter. NaOH and H_2SO_4 were used for pH adjustment.

The biomasses used in this work were grape stalks, a by-product of the winery industry, and Pinus (Pinus Pinaster) bark. Grape stalks biomass was supplied by the Portuguese winery “Adega cooperativa da Arruda dos Vinhos”, while pine bark was obtained from the National Park of “Peneda-Gerês”. Both biomasses abound in Portugal and have a negligible commercial value. Different groups such as lignin, polysaccharides, alkanes and long chain alcohols have been identified in the chemical analysis of this type of biomass.

2.1. Biomass pre-treatment

For the biosorption studies, samples of the biomasses were ground, sieved, homogenised and stored. Only the size fraction smaller than 0.1mm was used in these experiments.

For the isotherm experiments, the biomasses were washed with deionised water or pre-treated according to the procedure described below.

A flocculation-sedimentation pre-treatment was used in order to eliminate the fines. First, the biomass particles (d<0.1mm) were washed with deionised water in a conical flask. Flocculation was carried out by adding to the suspension of biomass a cationic polyelectrolyte Zetag 64 (Allied Colloids Ltd) up to a concentration of 5mg/dm^3. The stirring speed was 150rpm in the first 20 seconds, followed by 2 minutes at 10rpm. The solid was allowed to flocculate and settle and the supernatant, including biomass fines, was decanted and discarded. The solids were then filtered.

Two different types of pre-treatments were used for the pine-bark
i) Acid pre-treatments: after the flocculation/sedimentation, the cake was removed from the filter, suspended in distilled water and shacked for 15 minutes. The pulp was again filtered and suspended in an acid solution (H_2SO_4 3.7M or HCl 5.6M) for 30 minutes. After the solid-liquid separation, the solid was thoroughly washed with distilled water to remove the excess of acid, filtered, dried at 40°C for 12 hours and stored.
ii) Metal chlorides pre-treatment: these procedures were performed by bringing into contact the pine bark particles (<0.1mm) with solutions of $CaCl_2$ 0.005M, $CaCl_2$ 0.05M and NaCl 0.05M, using a solid-liquid ratio of 117g/dm^3. After shaking for 24h, the mixture was filtered and washed with distilled water. Subsequently, the slurry was filtered and dried at 40°C during 12h.

The pre-treatment used for grape stalks biomass was converting it into the sodium form with a solution 1M sodium sulphate and 0.1M tri-sodium citrate de-hydrate following the methodology described below for the elution operation.

2.2. Biosorption experiments

The biosorption experiments were carried out by suspending a specified dry weight of biomass material in the desired volume of the metal-ion solution. The slurry was placed in a temperature controlled orbital shaker for 2h at 20°C. The pH of the pulp was measured at the beginning and at the end of each experiment. For the $CaCl_2$ pre-treated biomass, the sorption studies were also carried out with pH adjustment (pH 5.5) with HCl or $Ca(OH)_2$ solutions. The suspensions were placed in conical flasks and shacked. The reaction mixture was then allowed to settle and the supernatant was analysed for the metal. The final metal concentration was determined by AAS.

2.3. Adsorption kinetics

The kinetic studies were carried out in a baffled stirred tank reactor (1000cm^3) immersed in a temperature controlled water bath. For stirring, a three bladed propeller (diameter=6cm) at 320min^{-1} was used. The initial metal solution (350cm^3) was added to the reactor and the pH was adjusted with H_2SO_4 or NaOH. When the desired temperature was reached (22°C), 0.8g of biomass, of known dry weight, was then suspended in 50cm^3 of deionised water and then rapidly injected into the initial metal solution using a 60cm^3 plastic syringe. Timing was started when approximately half of the biomass had been added to the stirred vessel. At pre-determined time intervals, samples were then withdrawn using 20cm^3 syringes equipped with a glass filter membrane that allowed an extremely fast solid liquid separation.

2.4. Elution and biosorption/elution studies

After biosorption, the solids were separated from the aqueous phase by sedimentation and filtration. Subsequently, the biomass is eluted with an electrolyte solution in batch tests or with the biomass immobilised as a filter cake. In the latter, after the biosorption stage, 5mg/dm^3 of Zetag was added and the biomass was allowed to flocculate and settle. The supernatant was separated and analysed for copper. The remaining solids were poured onto a Watman GFA 47 mm diameter filter and the excess of aqueous phase was drained off by applying a gentle vacuum. 20cm^3 of eluant solution were then drawn through the cake under 2-6mm Hg vacuum. A sample of the eluate was then taken, the collecting vessel replaced, and another 20cm^3 of deionised water were drawn through the filter cake. A sample of the washing water was also taken for metal content analysis.

For grape stalks the eluant composition was a 1M sodium sulphate solution and 0.1M tri-sodium citrate de-hydrate. The same solution was also used for pine-bark, although for this biomass other eluants were tested, such as H_2SO_4 3.7M, 0.5M < [HCl]< 1M and NaCl-0.05M.

In the biosorption/elution cycles the procedure was similar. After elution, the biomass was removed from the filter and suspended in a fresh metal solution for another adsorption cycle.

The filtrate was analysed for metals by AAS. After eluting the biomass with H_2SO_4 or HCl solutions, the cake was washed with water until a constant pH was obtained in the filtrate.

3. RESULTS AND DISCUSSION

3.1. Biosorption Equilibrium

3.1.1. Effect of the pre-treatment

The pre-treatment tested for grapes stalks biomass was converting it into the sodium form with a solution of 1M sodium sulphate and 0.1M tri-sodium citrate de-hydrate. Since this solution is a very good eluant for the copper bound to grape stalks (Table 5 of the elution section), it was thought worth to investigate its use as a pre-treatment solution. It is obviously advantageous to perform the pre-treatment and the elution of the biomass in same stage. For the pine bark biomass, the elution of copper with the sodium sulphate/tri-sodium citrate solution was not so effective and so this pre-treatment was not investigated. Actually, for pine bark it was decided to study only the salt and the acid pre-treatments.

The pre-treatment of the biomasses with sodium or calcium salts aims to convert the active binding centres from the H^+ to the calcium or sodium forms, thus avoiding the decrease of pH during biosorption due to H^+ exchange, which has a negative effect on biosorption. In what concerns the acid pre-treatment, it was found interesting to test the effect of acids in the capacity of the biomass, since it is well known that acids are good eluants for metals. Additionally, it has also been reported (Vasconcelos *et al.*, 1997) that this treatment increases the number of groups in the biomass responsible for the removal of heavy metals. The introduction of sulphonic groups in the biomass by sulphonation of some aromatic positions, or of carboxylic groups by oxidation of aliphatic ones after the treatment with sulphuric acid, are cited examples of the effect of acids treatments.

The equilibrium isotherms of grape stalks show that the equilibrium capacity for copper was 20mg Cu/g biomass after the washing with water and 23.3mg/g after the treatment with a solution 1M in sodium sulphate and 0.1M in sodium citrate. These results show that, in fact, the pre-treatment with salts increased although slightly, the biomass capacity.

The results obtained for pine bark are shown in Figure 1 and the correspondent values for the Langmuir parameters are listed in Table 1.

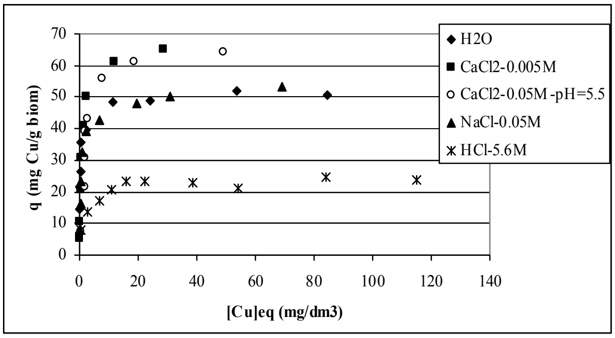

Figure 1. Influence of the pre-treatments on copper removal by pine bark. Experimental conditions: biomass concentration - 1g/dm^3; T=22ºC; t=1h

The experimental results show that the biosorption capacity of pine-bark is twofold the grape stalks capacity. It was also found that the pre-treatment with calcium chloride allows an increase of 20% of pine-bark capacity for copper. On the contrary, the use of acids leads to a marked decrease of this property, due to the negative effect that the observed decrease in the pH has on copper removal (see below). Furthermore, the above-mentioned increase in the number of active binding sites for copper after acid pre-treatment was not confirmed by our experimental results.

Table 1
Influence of the pre-treatments on copper removal by pine bark (biomass concentration - 1g/dm^3; T=22°C; t=1h)

Pre-treatment	q_{max} (mg/g)	K (dm^3/mg)
H_2O	51.1±0.3	3±1
$CaCl_2$ 0.005M	66.6±0.4	1.3±0.1
$CaCl_2$ 0.05M	67±1	0.48±0.08
NaCl 0.05M	53.5±0.6	0.9±0.2
HCl 5.6M	24.0±0.5	0.6±0.4
H_2SO_4 3.7M	12.7±0.5	0.16±0.06

3.1.2. Biosorption studies

The equilibrium curves for copper biosorption on pine bark and grape stalks are shown in Figure 2. Data were obtained using biomasses washed with deionised water. The Langmuir model was fitted to the experimental data, thus producing the parameters listed in Table 2.

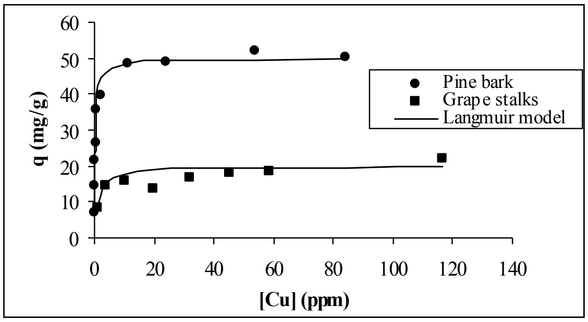

Figure 2. Adsorption isotherm for copper using pine bark and grapes stalks after washing with deionised water. Experimental conditions: biomass concentration - 2g/dm^3; T=22°C; initial pH=5

Table 2
Langmuir parameters for the biosorption of copper with grape stalks and pine bark washed with deionised water

Biomass	q_{max} (mg/g)	K (dm^3/mg)
Grape stalks	22±1	0.2±0.1
Pine bark	51.1±0.3	3±1

For comparison purposes, the adsorption capacities as well as the affinity constants of some typical adsorbents reported in the literature are given in Table 3.

Table 3
Maximum uptake capacity and affinity constant for copper biosorption by some typical adsorbents

Biomass	q_{max} (mg/g)	K (dm^3/mg)	Biomass conc. (g/dm^3)	pH	References
Chlorella vulgaris (1)	48.2	0.12	1	5	Çetinkaya *et al.*, 1999
Chlorella Miniata	23.26	0.42	3.75		Lau *et al.*, 1999
Chlorella vulgaris (2)	18.72	0.11	3.75		Lau *et al.*, 1999
Scenedus obliquus	33.3	0.02	1	5	Çetinkaya *et al.*, 1999
Synechocystis sp.	38.1	0.02	1	5	Çetinkaya *et al.*, 1999
Chitosan	175.5	0.006	1	5-6	Juang *et al.*, 1999
Ascophyllum nodosum	75.6	0.096	2		Yu *et al.*, 1999

By comparing values in Table 2 and 3, it is possible to conclude that pine bark presents the larger values for the Langmuir parameters. In fact, only the biomasses Chitosan and *Ascophyllum nodosum* present higher values for q_{max}, although those biomasses have a K

value lower than the pine bark one. Grape stalks biomass has a q_{max} of the same order of magnitude of the values presented in Table 3, while only the biomass *Chlorella Miniata* presents an higher value for K than grapes stalks.

In order to compare the performance of grape stalks and pine-bark with other biomasses, the yield of copper removed in a simulated batch experiment was calculated by using Equations 4 and 5. The simulation was carried out for a biomass concentration of 2g/dm^3 and three different initial copper concentrations: 10, 50 and 100mg/dm^3. The results are reported in Figure 3.

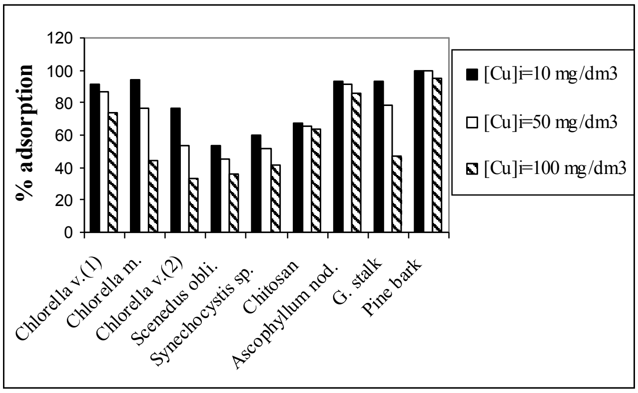

Figure 3. Comparative results of copper biosorption by some typical biosorbents (the correspondent references are listed in Table 3)

Figure 3 shows that for solutions containing 10 and 50mg/dm^3 of copper, pine bark can remove 99% of the metal, while for a 100mg/dm^3 solution 95% of copper removal is achieved. From among the biomasses listed in Table 3, only *Ascophyllum* can give comparable although lower results. Using grape stalks, and an initial copper concentration of 10mg/dm^3, 88% of the copper is removed. Similar results are only achieved with the *Ascophyllum nodosum, Chlorella v(1) and Miniata* and *Pinus-bark* biomasses. However, for initial copper concentrations of 50 and 100mg/dm^3, the percentage of copper biosorbed by grape stalks decreased to 68% and 40% respectively. These values are comparable with the majority of the biomasses, but are largely exceeded by the *Ascophyllum*, *Chlorella* and *Pinus-bark* biomasses.

Figure 3 clearly demonstrates that to evaluate the efficiency of a biomass it is necessary to consider both the maximum uptake capacity and the affinity. In fact, a high value for q_{max} but a low affinity constant indicates that the biomass only reaches metal saturation at very high copper concentration in equilibrium in the aqueous phase. However, for low metal concentrations in solution the majority of active sites remain unoccupied and a low percentage of removal is achieved.

3.1.3. Effect of pH

Figure 4 presents the influence of pH on copper biosorption by grape stalks and pine bark biomasses. In order to check if precipitation of copper had occurred in the pH range studied, tests with biomass free blanks were carried out. The results show that, for the experimental conditions studied, no chemical precipitation occurred.

From Figure 4 it may be concluded that copper biosorption is almost negligible for a pH value below 2, although it increases significantly in the pH range from 2 to 5. Grape stalks reached the maximum biosorption at pH 5 while pine bark reached its maximum uptake at pH 7.

The dependence of copper uptake by the biomasses on pH is related to the association-dissociation of the functional groups like the carboxylic groups, and also to the competition between the H^+ and Cu^{2+} ions for the active biosorption sites (Evans *et al.*, 2002; Yalçinkaya *et al.*, 2002). In fact, it is known that at low pH most of the carboxylic groups are not dissociated and cannot bind the metal in solution (although they can probably still take part in complexation reactions). On the other hand, as predicted by equation 1, at low pH values the concentration of H^+ exceeds that of Cu^{2+} and so protons will also compete with copper to be bound to the biomass.

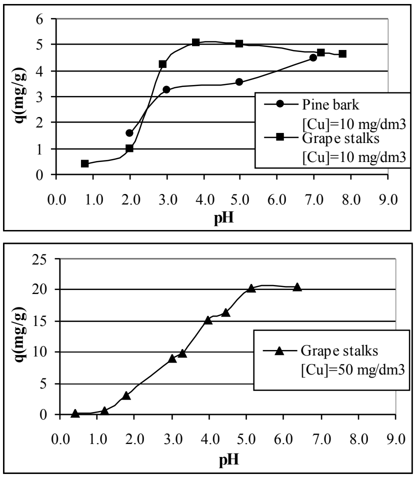

Figure 4. Influence of the initial pH on copper biosoption by grape stalks and pine bark. Conditions: Biomass concentration - $2g/dm^3$; T=22°C

3.2. Biosorption Kinetics

The kinetic data for copper biosorption by grape stalks and pine bark are shown in Figure 5. Each curve corresponds to a different initial copper concentration ranging from $10mg/dm^3$ to $157mg/dm^3$. The temperature was kept constant at 25°C. The grape stalks biomass particles had an average Sauter mean radius of 33μm measured with a particle analyser Masterzise X from Malvern Instruments. The pine bark samples used in the kinetic tests were obtained by sieving (d<0.1mm).

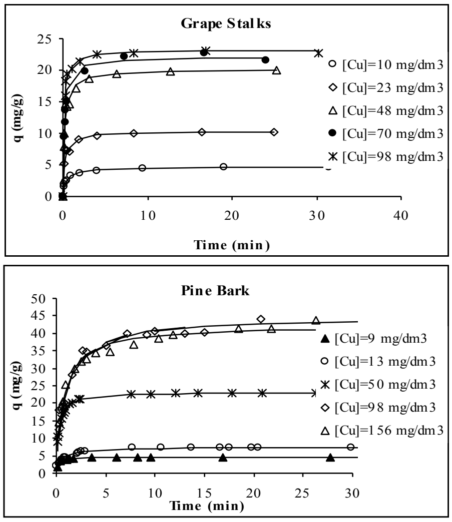

Figure 5. Plot of the adsorption of copper on grape stalks and pine bark *vs* time. Conditions: $10mg/dm^3$ < [Cu]initial< $160mg/dm^3$, T=25°C.

As it follows from Figure 5, for both biomasses the kinetics of copper biosorption is extremely fast, since in the first 2 minutes of reaction, about 80% of the copper present in solution was removed. The very fast kinetics observed in this initial reaction stage suggests that most of the copper biosorption occurs at the surface of the biomass. However, more than 40 minutes are necessary to remove the remaining 20% of the initial copper present in solution. This second stage, which corresponds to a much lower rate of biosorption, indicates that the metal diffusion inside the particles is the rate-limiting step.

The fitting obtained with equation 8 (Lagergren equation) and equation 11 (linear form of the pseudo second order model) to the experimental data is presented, respectively, in Figure 6 and 7. Table 4 presents the kinetic parameters obtained fitting equation 11 to the experimental results.

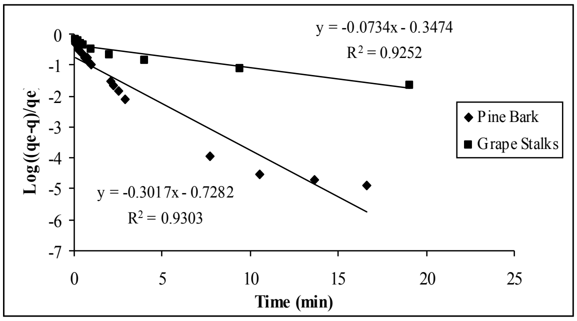

Figure 6. Fitting of the first order model to the experimental results. Experimental conditions: pine bark-$[Cu]_{initial}$=13mg/dm^3 ; grape stalks- $[Cu]_{initial}$=10mg/dm^3

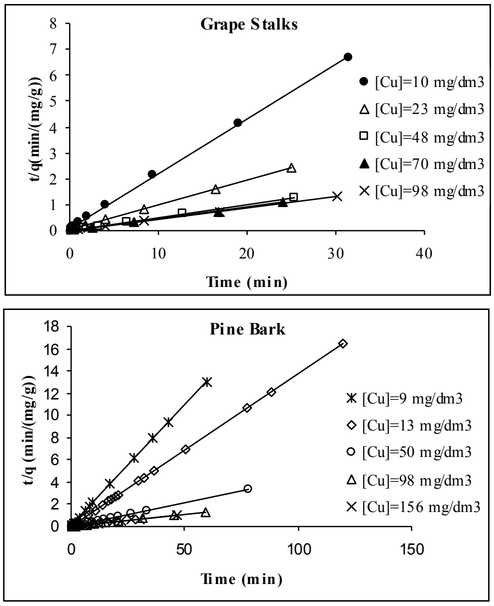

Figure 7. Fitting of the pseudo second order model to the experimental results. Conditions: 10mg/dm^3 < $[Cu]_{initial}$< 160mg/dm^3, *T*=25ºC.

From Figure 6 it can be concluded that the first order is unable to describe the experimental data namely in the region of the curve approaching equilibrium. On the contrary, Figure 7 shows that the second order model was successful in describing the kinetics of copper biosorption for both biomasses, as can be confirmed by the values of the correlation coefficients (R^2) presented in Table 4. Ho *et al.* (2000) and Hamedi *et al.* (2001) also found that for the sorption of divalent metals on moss peat and for the removal of Cr (VI) by adsorbents derived from used tyres and sawdust, respectively, the results were better described by a pseudo second order model.

As it can be seen in Table 4, for grape stalks the initial rates of biosorption increase directly with the initial metal concentration, being this trend very clear.

Table 4
Kinetic parameters from the fit of the experimental data to the second order model

Biomass	$[Cu]_0$ (mg/dm^3)	q_e (mg/g)	K (min^{-1})	R^2	$\frac{dq}{dt_{t=o}} = k\, q_e$ (mg/(gmin))
Grape Stalks	10	4.7	2.1	0.9996	10.0
	23	10.4	4.0	0.9999	41.9
	48	20.1	4.8	0.9999	96.2
	70	22.0	6.3	0.9988	137.9
	98	23.2	7.9	0.9999	182.8
Pine Bark	9.2	4.6	4.4	0.9999	20.0
	13.4	7.3	2.8	0.9999	20.7
	50.0	23.2	4.1	0.9999	96.4
	97.5	45.4	0.9	0.9999	41.7
	156.5	42.7	1.1	0.9999	48.7

Pine bark presents a quite different behaviour regarding the relation of the kinetic parameter with copper concentration. In fact, unlike grape stalks, the value of the kinetic constant does not present a consistent trend with the initial metal concentration. This result is probably due to heterogeneities in the diameter of the particles obtained by sieving the pine bark samples.

3.3. Elution studies

Table 5 shows the results obtained in four cycles of biosorption/elution of copper with grape-stalks. The experimental results show that the solution of sodium sulphate and citrate is, not only a good pre-treatment solution, but also a good eluant for copper. Table 5 also shows that grape-stalks can be reused in, at least, four cycles without any loss of activity.

Table 5
Influence of the number of cycles on copper removal from grape stalks
Biosorption- S/L= 2g/dm^3; t=1h; T=22ºC; d<0.1mm. Elution- S/L= 20g/dm^3

Eluant	Cycle nº	q (mg/g)	Cu removed (%)	Cu eluted (%)
Na_2SO_4 Citrate	1	4.7	96.9	78.2
	2	4.7	98.3	100
	3	4.3	89.4	100
	4	4.3	89.3	100

Note: The percentage of elution takes into account the metal obtained in the washing waters.

The elution results for pine bark are presented in Table 6.

Table 6
Influence of the number of cycles on copper removal from pine-bark
Biosorption- S/L= 2g/dm^3; t=1h; T=22ºC; d<0.1mm. Elution- S/L= 20g/dm^3

Eluant	Cycle nº	q (mg/g)	Cu removed (%)	Cu eluted (%)
Na_2SO_4 1M Citrate 0.1M	1	3.4	62	31.3
	2	4.0	77.8	46
	3	4.1	78.9	42.3
	4	4.0	78.1	44.9
H_2SO_4 3.7M	1	4.4	79.5	83.8
	2	4.8	86.7	74.9
	3	5.3	97.1	68.9
	4	2.7	48.6	49.8
HCl 5.6M	1	4.7	92	73.2
	2	5.0	97.8	43
	3	4.8	97.6	55.2
NaCl 0.05M	1	4.7	99.2	0.1
	2	5.0	99.0	0.3

The results presented in Table 6 allow to conclude that the behaviour of pine bark during biosorption is not affected by the number of cycles. However, even with very concentrated acid solutions, it was not possible to elute more than 84% of the copper bound to the biomass. Furthermore, it proved to be much more difficult to remove the copper bound to pine bark than to grape-stalks.

4. CONCLUSIONS

The results obtained in this study lead to the conclusion that grape stalks and pine bark can be used for the removal of copper from an aqueous solution. Pine bark presented the higher capacity (50mg Cu/g for pine bark and 20mg/g for grapes stalks) and the greater affinity constant (3dm^3/mg for pine bark and 0.2dm^3/mg for grapes stalks). Compared to other biomasses, grape stalks can be considered a very good biosorbent for low metal concentrations. The performance of pine bark was very good over the entire range of metal concentrations tested. Increasing pH, increases the yield of copper removal from both biomasses. Finally, it was possible to elute all the copper bound to grape stalks with a solution of sodium sulphate and sodium citrate, while the elution of copper from pine bark is more difficult. However, the biomasses did not loose their binding capacity for, at least, four cycles of biosorption/elution.

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