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# Integrated Process for Biosorption of Copper from Liquid Effluents Using Grape Stalks

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## ABSTRACT

A multistage process was used for biosorption of heavy metals from liquid effluents using grape stalks as the biosorbent. The biosorption was carried out with a free biomass suspension in a two-stage, countercurrent, stirred batch system. The biomass was separated from the treated effluent using flocculation, sedimentation, and filtering. The filter cake was used, as a small packed column loaded with heavy metals where the elution was performed.

The efficiency of the overall system was studied using three synthetic effluents. The first two effluents labeled in this work as F1 and F2 had 10 and 50 ppm of copper, respectively. The third effluent had a complex metal mixture containing 10 ppm of copper, 50 ppm of zinc, 5 ppm of nickel, 100 ppm of calcium, and 100 ppm of sodium. The biosorption system was able to remove 99% of the copper from the F1 effluent (0.08 ppm of copper in the final effluent), using a biomass concentration of 2 g/L. For the F2 effluent, a biomass concentration of 4 g/L was

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required to obtain a final copper concentration 0.18 ppm. Copper was also removed from the F3 effluent with an efficiency of 98% (final metal concentration of 0.15 ppm). However, it required a biomass concentration of 6 g/L in the two biosorption stages and the other target metals under study, Zn and Ni, had modest removals of 46% and 35%, respectively.

The results from the elution experiments demonstrate that the key variables to obtain high metal concentration in the eluate are the metal concentration bounded to the biomass, the superficial velocity of the eluant, and the filter cake depth. Using the F2 effluent to load the biomass up to 12.5 mg/g of copper and performing the elution with a superficial velocity of 0.9 cm/min in a filter cake with depth of 10 cm, a copper concentration in the eluate of 1.8 g/L was achieved, which correspond to a concentration factor of 38-fold.

*Key Words:* Bisorption; Heavy metals; Biomass; Grape stalks.



## INTRODUCTION

Pollution of the environment by toxic metals is a world environmental problem. Traditional methods for the elimination of heavy metals from aqueous effluents are hydroxide or sulfide precipitation.[1] Those technologies only offer modest removals of heavy metals, require expensive consumption of reagents, and produce large amounts of toxic sludge that require landfill disposal. Alternative technologies, like cementation[2,3] and emulsion liquid membranes,[4,5] are still subject to development.

Biosorption, has been explored in the last decade as a potential technology for removing toxic heavy metals from aqueous effluents. There is an extensive list of published research results with potential biosorbents, and the studied materials included bacteria, yeast, and fungi[6–9] by-products of the forest industries,[10] and algae.[11] Biosorption in dead biomass involves metal binding by ionic and covalent complexion to the surface matrix of the biomass.[12]

The present work investigates the possible use of grape stalks in a bench-scale, integrated process of biosorption and elution. The biosorption was carried out as a free suspension of ground grape stalks in a two-stage, counter-current, stirred batch system. The solid separation was carried out by flocculation and settling. The biomass slurry was then transferred to a filter under controlled pressure. The filter unit had a filtration chamber of 10 cm of height that allowed the immobilization of the biomass as a small, packed column. The metals were then removed from the biomass by passing through the small packed column a solution of 1-molar sodium sulfate and 0.25-molar

tri-sodium citrate di-hydrate. The high sodium concentration in the eluant displaced the ionic interaction between copper and the binding center of the biomass. This effect is helped by the tri-sodium citrate, which forms a strong covalent complex with copper. The integrated system was tested using synthetic effluents of 10 ppm (F1) and 50 ppm (F2) of copper and a complex metal mixture containing 10 ppm of copper, 50 ppm of zinc, 5 ppm of nickel, 100 ppm of calcium, and 100 ppm of sodium (F3). Butter et al[13,14] used a similar overall approach for removing heavy metals from liquid effluents. This work involved the use of a novel biosorbent and includes a discussion of the key variables in the integrated process.

## METHODOLOGY

### Biomass Pretreatment

The grape stalks were supplied by the Portuguese winery Adega Cooperativa de Arruda dos Vinhos. The grape stalks were ground with the Pulverisette 14 mill (Fritsh Industriestrasse, Germany). The rotor speed was 18,000 rpm and a ring sieve with 200 mm of aperture was used. The ground material was then washed for 30 minutes in a batch stirred vessel with a solid to liquid ratio of 6 g/L. The flocculent Zetag 64 (Allied Colloids UK) in a concentration of 5 ppm was added and the flocks were allowed to settle for 15 minutes. The supernatant was then siphoned and discarded. The resulting biomass slurry was transferred to the filtering unit, forming a cake of 10 cm of height and 12 cm of diameter. Two L of a solution made of 1-M sodium sulfate and 0.25-M tri-sodium-citrate were passed through the filter cake under an applied pressure of 100 mm Hg. After this, the biomass was washed with 2 L of deionized water.

### Equilibrium Biosorption Curves

Equilibrium biosorption experiments for each aqueous phase were carried out by putting a fixed amount of dry weight of biomass in contact with different volumes of aqueous phase. Using this procedure, the solid to liquid ratio for the F1 effluent ranged between 0.03 g/L and 3.6 g/L, between 0.27 and 6 g/L for the F2 effluent, and 0.6 and 15.9 g/L for the F3 effluent. The contact was performed putting an Erlenmeyer with the biomass suspension in an orbital agitator for 2 hours at 25°C. In this work, all metal solutions were prepared using the sulfate salts and all reagents were of analytical grade.

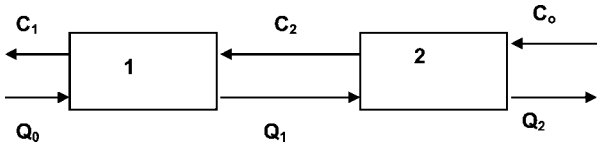


***Figure 1.*** Diagram of a biosorption counter current process in two stages.

## Counter-Current Two-Stage Biosorption Process

Figure 1 presents a diagram of a counter-current process with two stages of biosorption. Figure 2 shows a simplified diagram of the apparatus used. The biosorption cycle starts with the contact between fresh biomass and the intermediate effluent from the second stage of biosorption labeled as C2 in Fig. 1. In the first cycle, this effluent of intermediate metal concentration is not available and requires preparation, which was carried out in the cylindrical reactor 1 shown in Fig. 2. The fresh biomass was then put in contact with the aqueous phase for 15 minutes in the mechanically stirred vessel of reactor 1.

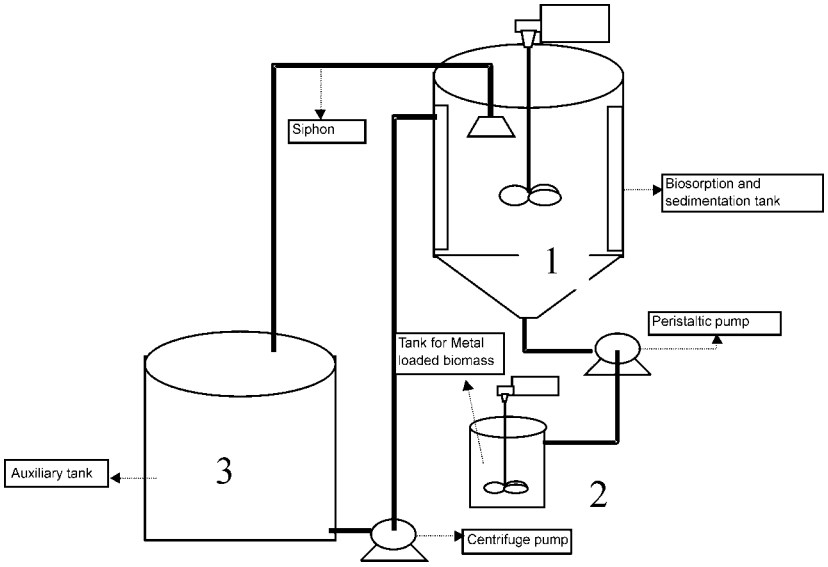


***Figure 2.*** Apparatus used for biosorption in a two-stage, counter-current biosorption process. 1. Biosorption reactor (75 $dm^3$). 2. Auxiliary tank for metal loaded biomass. 3. Auxiliary tank to keep current C2.

For stirring, a three-blade marine type impeller of 12-cm diameter was used at 360 rpm. The cationic flocculant [Zetag 64 Allied Colloid (UK)] was then added to the reactor in a concentration of 5 ppm. To disperse the flocculant, the stirring was kept up for 20 seconds and then stopped. The flocs were allowed to settle for 10 minutes and then the supernatant was decanted with the siphon as presented in Fig. 2. The biomass slurry in the bottom of the reactor was then transferred to tank 2 with a peristaltic pump. A synthetic solution with the initial metal composition of the target effluent was then prepared in the reactor. This effluent was then contacted with the partially metal loaded biomass. This step corresponds to the biosorption stage 2 of in Fig. 1. After the biosorption step, flocculation and sedimentation were performed as indicated previously. The supernatant was siphoned to the auxiliary tank 3 shown in Fig. 2. The flocculated biomass in the bottom of the reactor was then transferred to the biomass storage tank 2 for subsequent regeneration in the elution step. The supernatant kept in tank 3 was then transferred with a centrifuge pump to the biosorption reactor and, in conjunction with regenerated biomass, was used in the first stage of the next biosorption/elution cycle. The overall process was repeated until stationary metal concentrations were obtained in the final effluent (C1) and in the intermediate treated effluent. Samples for analyses of metal concentration as well as turbidity and biologic oxygen demand (BOD) were collected. All metal analyses were performed in an atomic absorption spectrometer model 3100 Perkin Elmer, the turbidity analysis in a turbimeter from Hanna Instruments model LP 2000, and the biologic oxygen demand in a manometric BOD sensor Aqualytic from GmbH&Co.



## Biosorption Data Analysis

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

$$q = \frac{(C_0 - C_e)V}{M} \tag{1}$$

where $C_0$ and $C_e$ are, respectively, the initial and the equilibrium metal concentration in solution (ppm), V ($dm^3$) is the total volume of the solution, and M (g) is the mass of biomass present in solution. A nonlinear, least squares fitting of the empirical Langmuir-type equation was used to adjust the

equilibrium data.

$$q = \frac{Q_{max} C_e}{\frac{1}{K} + C_e} \tag{2}$$

where $Q_{max}$ (mg/g) is the maximum metal concentration biosorbed by the biomass and K ($ppm^{-1}$) is the affinity constant.

To calculate the metal concentrations in a generic counter current system (Fig. 3) the following mass balance between the first stage and the *n*th stage was used:

$$q_n = \frac{1}{[B]} * C_{n+1} + \left( q_0 - \frac{C_1}{[B]} \right) \tag{3}$$

where $q_n$ is the metal concentration in the biomass at stage $n$, $C_{n+1}$ is the metal concentrations in the aqueous phase on the $n + 1$ stage (see Fig. 3), and the slope 1/[B] is equal to the inverse of the biomass concentration to be used. This equation is the operating line of the biosorption system. It can be considered to represent the fact that in any biosorption stage, the increase in metal concentration in the solid phase equals the decrease in metal concentration in the aqueous phase multiplied by the phase ratio. $C_{n+1}$ is in equilibrium with the metal concentration in the solid phase ($q_{n+1}$) so the equilibrium relationship Eq. (2) can be used to substitute $C_{n+1}$ in the operating line.

$$q_{n+1} q_n + \left( \frac{1}{K[B]} + \frac{C_1}{[B]} - q_0 \right) q_{n+1} - Q_{max} q_n + \left( q_0 - \frac{C_1}{[B]} \right) Q_{max} = 0 \tag{4}$$

Eq. (4) is a Ricatti finite difference equation[15] that has the following analytical solution:

$$\frac{1}{q_n - \delta} = P \left[ -\frac{A + \delta}{B + \delta} \right]^n - \frac{1}{(A + B + 2\delta)} \tag{5}$$

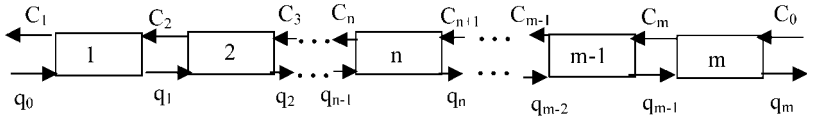


***Figure 3.*** Diagram of a multistage biosorption process.

where:

$$A = \left(\frac{1}{K[B]} - q_0 + \frac{C_1}{[B]}\right) \tag{6a}$$

$$B = -Q_{max} \tag{6b}$$

$$C = \left(q_0 - \frac{C_1}{[B]}\right) Q_{max} \tag{6c}$$

and δ gives the roots of the following second-order equation:

$$\delta^2 + (A+B)\delta + C = 0 \tag{7}$$

The values of δ have a simple geometric interpretation. They correspond to the $q_n$ values of the points of intersection of the operating line and the equilibrium curve.[15] P is the arbitrary constant of the general solution of Eq. (5) and can be evaluated using the following initial condition: $n = 0$, $q = q_0$

$$P = \frac{1}{q_0 - \delta} + \frac{1}{(A+B+2\delta)} \tag{8}$$



## Filtration

After biosorption, the metal-loaded biomass was transferred to a filter under controlled pressure (Fig. 4) using a peristaltic pump. The filtering medium used had two superimposed membranes of nylon of 30-μm pore size and 113 $cm^2$ of area. The pressure within the filtration chamber was measured with a mercury pressure gage and the pressure was kept constant by a line of compressed air. The pressure control was carried out with the help of a pressure valve reducer. The filtration chamber allowed the formation of filter cakes up to 10 cm of depth. The tank of the biomass suspension was mechanically stirred to keep constant and homogeneous the solid to liquid ratio of the biomass suspension. During the filtration process, the volume and times of filtration were recorded. The biomass suspension had a concentration of 75 g/L.

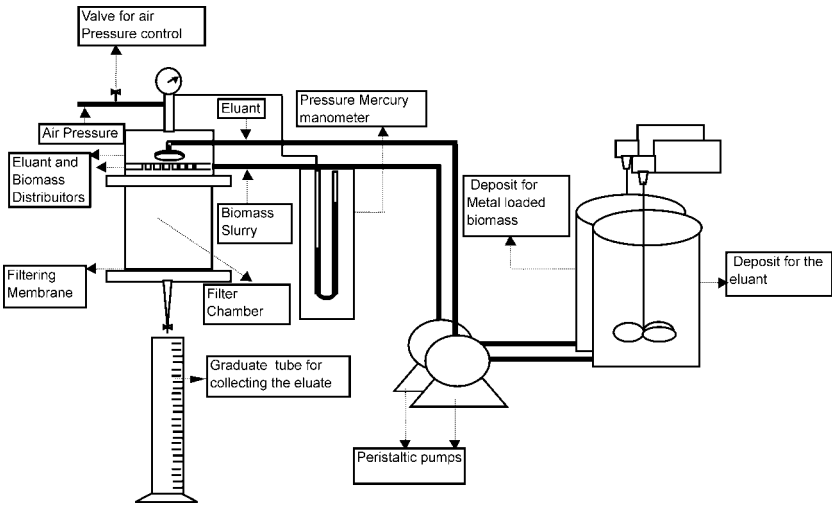


***Figure 4.*** Apparatus used for filtration and elution of the biomass.

## Elution

The filter unit had a filtration chamber of 10 cm of height and allowed the immobilization of the biomass as a small packed column. The metals were removed from the biomass by passing as eluant a solution of 1 molar in sodium sulfate and 0.25 molar in tri-sodium citrate di hydrate throughout the filter cake.

A layer of at least 0.5 cm of the eluant was kept above the top surface of the cake. Times and volumes of eluant flowing from the bottom of the cake were determined and samples were drawn. The mean concentration $Cu_{av}$ of metal in the eluate was calculated using the following expression:

$$Cu_{av} = \frac{\int_{V_0}^{V_f} [Cu]dv}{V_f - V_0} \tag{9}$$

where [Cu] is the instantaneous concentration of copper in a volume V of eluate. The limits of the integral, $V_0$ and $V_f$ are given by the volumes of the eluates at the start and at the end of the elution respectively. To perform the numerical integration of the experimental data, the software Matlab (MatLab Student Edition Vers.4 Math Work, Inc., Massachusetts) was used.

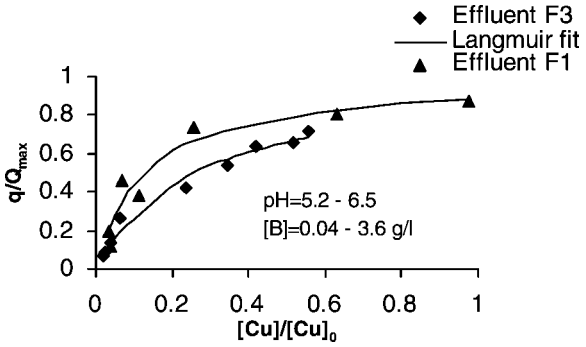


***Figure 5.*** Equilibrium curves obtained for the F1 and F3 effluents: $[Cu]_i = 10$ ppm.



## RESULTS AND DISCUSSION

### Biosorption and Equilibrium Curves

The equilibrium curves obtained by changing the solid phase/aqueous phase ratio are presented in Figs. 5 and 6. The parameters resulting from the fitting of Eq. (2) to the experimental equilibrium data for each effluent are presented in Table 1.

In the equilibrium curve, the pH of the F2 effluent was in the range of 4.2 and 5.4 and the F1 effluent ranged from 5.23 and 6.5. This is due to the hydrolysis reaction of $Cu^{2+}$ that decreases the pH of the aqueous phase. This effect is more pronounced at higher $Cu^{2+}$ concentrations.

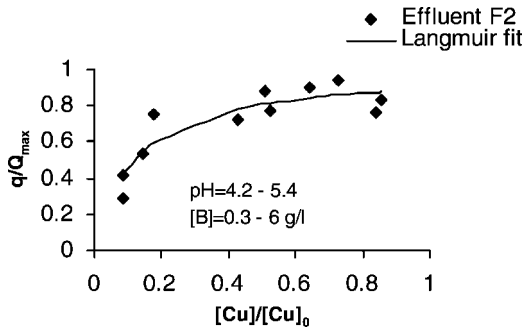


***Figure 6.*** Equilibrium curve obtained for the F2 effluent: $[Cu]_i = 50$ ppm.

***Table 1.*** Parameters resulting from the fitting of the experimental equilibrium data to the Langmuir equation.

| Parameter | Effluent (F1) | Effluent (F2) | Effluent (F3) |
|---|---|---|---|
| $Q_{max}$ (mg/g) | 23.4 | 27.3 | 8.66 |
| K ($ppm^{-1}$) | 0.74 | 0.16 | 0.38 |

Comparing the parameters obtained for the equilibrium curves for effluents F1 and F2, the major difference is in the affinity constant that changes, respectively, from $0.74\,ppm^{-1}$ to $0.16\,ppm^{-1}$. This result can be easily interpreted if biosorption is described with a more realistic multicomponent equation that involves the aqueous concentration of $Cu^{2+}$ and $H^+$ in equilibrium with the solid biomass phase[16,17]:

$$q = \frac{Q_{max}K_1[Cu^{2+}]}{1 + K_2[H^+] + K_1[Cu^{2+}]} = \frac{Q_{max}[Cu^{2+}]}{\frac{1+K_2[H^+]}{K_1} + [Cu^{2+}]} \tag{10}$$

Eq. (10) is equivalent to the Langmuir equation if the affinity constant is substituted by:

$$\frac{K_1}{1 + K_2[H]} \tag{11}$$

where $K_1$ and $K_2$ are, the affinities constant of $Cu^{2+}$ and $H^+$ to the active binding centers of the biomass. The previous expression clearly shows that a decrease in the pH of adsorption decreases the observable Langmuir affinity constant. Comparing the parameters for the F1 and F3 effluents, a sharp decrease in $Q_{max}$ is observed, suggesting a strong competitive effect for the active binding center between copper and the other metal cations present in solution.

## Biosorption Results in the Two-Stage, Counter-Current System

Figures 7–9 show the biosorption results obtained with the two-stage, counter-current system. Copper is successfully removed from the three effluents under study. For the F1 effluent and using a biomass concentration of 2 g/L, removal of 96.5% (0.35 ppm) of copper is readily achieved in the first biosorption stage and 99% of removal in the second stage (final metal concentration of 0.08 ppm). For the F2 effluent, two biosorption stages and a biomass concentration of 4 g/L are required to obtain 99% removal of copper

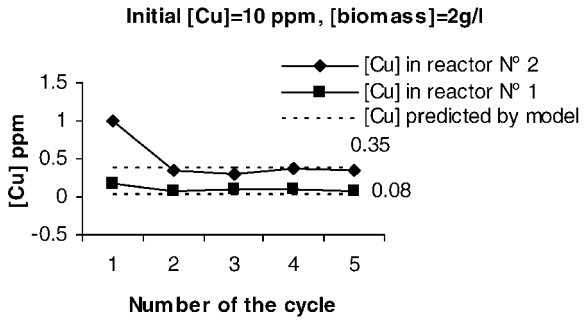


***Figure 7.*** Biosorption results obtained in the two-stage, counter-current system for the F1 effluent.



(final copper concentration 0.18 ppm). In the complex F3 effluent, copper is also removed up to 98% (final metal concentration of 0.15 ppm). However, a biomass concentration of 6 g/L was required in the biosorption stages. The other target metals under study, Zn and Ni, had modest removals of 46% and 35%, respectively. In all the three effluents, most of the biosorption occurs in the first stage of biosorption (reactor 2, see Fig. 1); while the second stage acts as a polishing step that pushes down the final concentration of copper to acceptable values for water discharge. The dashed lines of Figs. 7–9 indicate the predicted copper concentration in the biosorption reactors using Eq. (5). There is a good agreement between the model and experimental values. The only exception is the predicted value for copper concentration in the reactor number 2 in Fig. 8, which is 5.6 ppm and the experimental steady state

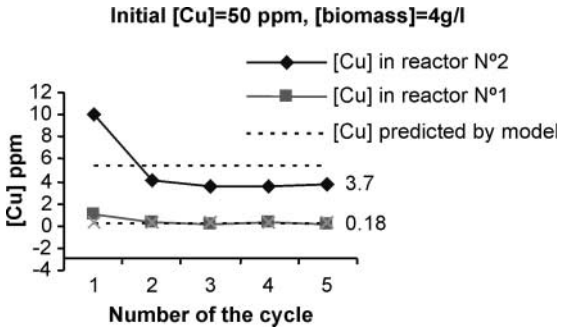


***Figure 8.*** Biosorption results obtained in the two-stage, counter-current system for the F2 effluent.

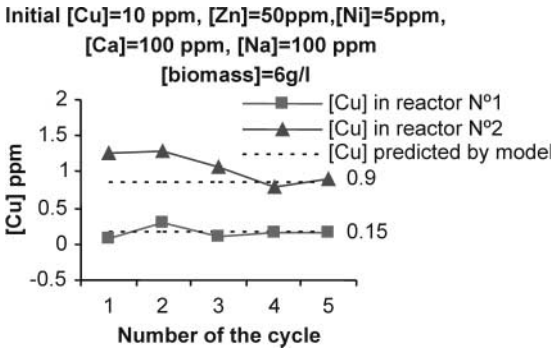


***Figure 9.*** Biosorption results obtained in the two-stage, counter-current system for the F3 effluent.



value is 3.6 ppm. The values predicted by the model are dependent on the equilibrium parameters presented in Table 1 obtained from the correspondent equilibrium curves. The equilibrium data corresponding to the F2 effluent is scattered and, therefore, considerable error is expected in the calculated equilibrium parameters. In fact, using the value of $0.25\,ppm^{-1}$ for the affinity constant in the model instead of 0.16, the predicted value for the copper concentration in reactor number 2 is 3.6 ppm. It should be stressed that the value of $0.25\,ppm^{-1}$ continues to be significantly lower than the values of $0.38\,ppm^{-1}$ obtained for the affinity constant of the F1 effluent and, therefore, the conclusions regarding the effect of pH in the Langmuir affinity constant continue to be valid.

The solid–liquid separation by flocculation and sedimentation was also very efficient. In the first and second cycles, turbidity measurements performed after the second stage of biosorption with the F2 effluent lead to values of 15 and 8 NTU. These values improved in the subsequent cycles to an average value of 2.5 NTU. Measurements of the biologic oxygen demand in the same effluent (after the second stage of biosorption) led to values of 23 mg/g in the first cycle and 15 mg/L in the second cycle. On the subsequent cycles, the value stabilized to an average of 6.5 mg/g.

## Elution in the Filter Cake

The elution results are presented in Table 2 all of them correspond to a minimum elution efficiency of 94%. Experiments 1, 2, and 3

***Table 2.*** Elution results obtained in the filtration unit using grape stalks previously loaded with heavy metals from the biosorption experiments.

| | Variables | | | Results | | |
|---|---|---|---|---|---|---|
| Elution number | Copper concentration bounded to the biomass (mg/g) | Superficial velocity (cm/min) | Filter cake depth (cm) | Copper in the eluate $Cu_{av} = \frac{\int_{V_0}^{V_f}[Cu]dv}{V_f - V_0}$ (ppm) | Concentration factor $Fc = \frac{Cu_{av}}{[Cu]_{ini}}$ | Label of the effluent used to load copper into the biomass |
| 1 | 12.5 | 0.8 | 8.6 | 1300 | 26 | F2 |
| 2 | 5 | 0.9 | 7.9 | 543 | 54 | F1 |
| 3 | 1.7 | 1.2 | 8.6 | 323 | 32 | F3 |
| 4 | 1.7 | 1.8 | 8.8 | 261 | 26 | F3 |
| 5 | 1.7 | 2.3 | 5 | 208 | 21 | F3 |
| 6 | 1.7 | 2.1 | 3 | 150 | 15 | F3 |
| 7 | 1.7 | 3 | 9 | 130 | 11 | F3 |
| 8 | 1.7 | 1.7 | 8.5 | 293 | 29 | F3 |
| 9 | 12.5 | 0.86 | 10 | 1809 | 38 | F2 |
| 10 | 5 | 2.54 | 7.6 | 336 | 34 | F2 |

The effluents F1, F2, and F3 and using as eluant a 1-M sodium sulfate and 0.25-M tri-sodium citrate di hydrate solution.

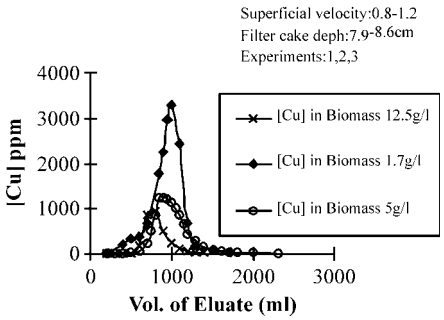


***Figure 10.*** Effect of the metal concentration bounded to the biomass in the elution curve.

(see Table 2, Fig. 10) clearly demonstrate that the concentration of copper bounded to the biomass is a key factor to obtain a high concentration of copper in the eluate. In fact, for this set of experiments, where the filter cakes have depths of 8 cm and the superficial velocity of the eluant was 1 cm/min, the values obtained for the mean concentration of copper in the eluate values ranged from 323 ppm to 1300 ppm. This large variation is due to the fact that the copper concentration loaded in the biomass ranged from 1.7 mg/g to 12.5 mg/g. High metal concentration in the biomass can be achieved when working with a low biomass concentration in the biosorption step, which correspond to high slopes for the operating line. However, under those experimental conditions, more biosorption stages are required to obtain low metal concentration in the final treated effluent.

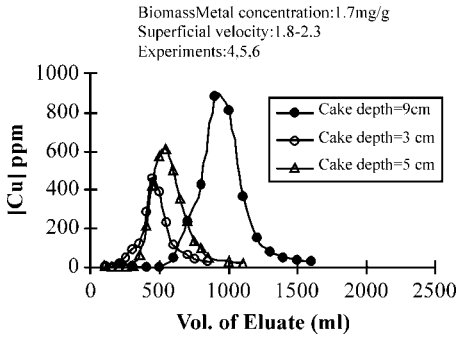


***Figure 11.*** Effect of the filter cake depth to the elution curve.

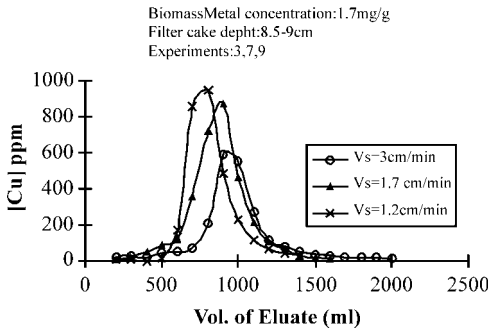


***Figure 12.*** Effect of the superficial velocity of the eluant in the elution curve.



Elution experiments 4, 5, and 6 (see Table 2, Fig. 11) demonstrate the importance of the filter cake depth. In this set of experiments, it is possible to see that the concentration factor changed from 15-fold to 32-fold, when the filter cake increased from 3 cm to 9 cm. This set of experiments was conducted using a superficial velocity of the eluant of 2.1 cm/min and a copper concentration in the biomass of 1.7 mg/g. The same effect can partly explain the difference observed in the concentration factor between the experiments number 1 and 9 that were performed with similar copper concentration in the biomass (12.5 mg/g) and superficial velocities of the eluant (0.8 cm/min) (see Table 2). However, a close inspection of the elution curve corresponding to experiment number 1 in Fig. 11 shows in the left part of the curve (the region between 300 mL and 750 mL of eluate) a smooth increase in copper concentration. This indicates that some eluant channeling throughout the filter has occurred and contributed to the decrease of the concentration factor. Experiments 3, 7, and 8 (Table 2, Fig. 12) show the importance of the superficial velocity in the concentration factor. As expected, increasing the superficial velocity from 1.2 cm/min to 3 cm/min reduces the concentration factor from 32-fold to 11-fold for filter cakes depths of 8.5 to 9 cm and metal concentration in the biomass of 1.7 mg/g. The same effect is also demonstrated with experiments 2 and 10.

## CONCLUSION

The results show that grape stalks can be successfully used in a two-stage, counter-current and steady-state biosorption process. For the F1 effluent and using a biomass concentration of 2 g/L, removal of 99% of copper was

achieved (final concentration of 0.08 ppm). For the F2 effluent, two biosorption stages and a biomass concentration of 4 g/L were required to obtain 99% of copper removal (final concentration of 0.18 ppm). In the complex F3 effluent, copper was also removed up to 98% (final metal concentration of 0.15 ppm) but a biomass concentration of 6 g/L was required in the biosorption stages. The other target metals under study (Zn, Ni) had modest removals of 46% and 35%, respectively. For all the three effluents most of the metal biosorption occurred in the first stage of biosorption; the second stage acted as a polishing step that pushed down the final concentration of copper to acceptable values for water discharge.

Solid–liquid separation by flocculation and sedimentation was also very efficient. Turbidity values of 2.5 NTU and a biologic oxygen demand of 6.5 mg/g were obtained in the treated effluent after the second stage of biosorption.

Finally, it is possible to conclude that copper can be efficiently removed from the biomass by passing a 1-M sodium sulfate and 0.25-M tri-sodium citrate di-hydrate solution throughout a small packed column of grape stalks.

The results demonstrate that a high concentration of metal bounded to the biomass, low superficial velocity of the eluant, as well as high filter cake depths are key factors to obtain high metal concentration in the eluate.

A metal concentration of 1.8 g/L and a concentration factor of 38-fold were achieved using the F2 effluent (complex metal mixture containing 10 ppm of copper, 50 ppm of zinc, 5 ppm of nickel, 100 ppm of calcium, and 100 ppm of sodium) to load the biomass with 12.5 mg/g of copper and performing the elution at a superficial velocity of 0.9 cm/min in a filter cake depth of 10 cm.

A metal concentration of 543 ppm and a concentration factor of 54-fold were achieved using the effluent with 10 ppm of copper to load the biomass with 5 mg/g of copper and performing the elution at a superficial velocity of 0.9 cm/min in a filter cake depth of 8 cm.



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