

## Effect of EDTA on divalent metal adsorption onto grape stalk and exhausted coffee wastes

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### Abstract

In the present work, two industrial vegetable wastes, grape stalk, coming from a wine producer, and exhausted coffee, coming from a soluble coffee manufacturer, have been investigated for the removal of Cu(II) and Ni(II) from aqueous solutions in presence and in absence of the strongly complexing agent EDTA. Effects of pH and metal–EDTA molar ratio, kinetics as a function of sorbent concentration, and sorption equilibrium for both metals onto both sorbents were evaluated in batch experiments. Metal uptake was dependent of pH, reaching a maximum from pH around 5.5. EDTA was found to dramatically reduce metal adsorption, reaching total uptake inhibition for both metals onto both sorbents at equimolar metal:ligand concentrations.

Kinetic results were successfully modelled by means of the pseudo second order model. Langmuir and Freundlich models were used to describe the sorption equilibrium data.

Grape stalk showed the best performance for Cu(II) and Ni(II) removal in presence and in absence of EDTA, despite exhausted coffee appears as less sensitive to the presence of complexing agent.

The performance of Cu(II) and Ni(II) sorption onto grape stalk in a continuous flow process was evaluated. In solutions containing EDTA, an initial metal concentration in the outlet flow corresponding to the complexed metal fraction was observed from the beginning of the process. A high metal recovery yield (>97%) was achieved by feeding the metal-loaded column with 0.05 M HCl.

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### 1. Introduction

By the harmful effects of heavy metals, it is necessary to almost totally remove them from waste effluents. Among others, Cu and Ni are considered in the European Union regulations as substances which have a deleterious effect on the aquatic environment and should be subject to authorization with specification of emission standards prior to discharge [1]; the emission standards must be calculated in terms of environmental quality standards for water. Spanish environmental quality standards are fixed in 5–120 µg/L range for Cu and in 50–200 µg/L range for Ni [2]. European Union health standard in drinking water is 2 mg/L for Cu and 20 µg/L for Ni [3].

Adsorption has emerged as a cost effective technique for the removal of low concentration of heavy metals from wastewaters, and has been widely studied during recent decades [4]. One of the most widely used adsorbents has been activated carbon because of its effectiveness in the removal of both organic [5–8] and inorganic pollutants [9–14]. Nevertheless, in the past years and due to the high cost of this material, considerable attention has been directed to low cost sorbents. An alternative inexpensive adsorbent could drastically reduce the operation cost of an adsorption system [15]. Therefore, there is a need for the development of low cost, easily available materials, which could adsorb metals from aqueous solutions. Natural materials that are available in large quantities such as wood bark and sawdust [16], peat [17–19], grape stalk [20], spent grain [21], marine algae biomass [22] and sunflower stalk [23] or waste products from industrial operations like red mud and fly ash [24–26] may have potential as inexpensive sorbents.

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Effluents produced in metal finishing, electroplating, painting, dying, printed circuit board manufacturing, photography, or surface treatment industry usually contain different complexing agents, being one of the most frequent the ethylenediaminetetraacetate, an aminocarboxylic derivative commonly known as EDTA. It is well known that, in presence of chelating agents like EDTA, the performance of metal removal can be adversely affected due to the formation of soluble complexes that could not be uptaken by the sorbent. When chelating agents become an important interference in the metal removal process, the destruction of the ligand is needed, and this process normally involves the addition of several chemicals or the use of oxidative techniques that, in last term, contribute to increase the economical cost of the wastewater treatment.

While sorption of different heavy metal ions on its free form on low cost sorbents has been widely studied [27–29], little effort has been focused on studying the effect of organic complexing agents on metal ions removal [4,30–34].

The objective of this study was to investigate the effect of complexing organic ligand EDTA on the adsorption of Cu(II) and Ni(II) onto two locally abundant industrial wastes, grape stalk (GS) and exhausted coffee (EC). Kinetic and equilibrium experiments in batch mode in presence and in absence of complexing agent were performed to obtain information about the contact time needed to reach equilibrium and about the maximum sorption capacity of both materials. The effectiveness of the Cu(II) and Ni(II) sorption process by grape stalk in a continuous bed up-flow column was also evaluated, as well as the possibility of recovering the sorbed metals in a concentrated form by elution with HCl 0.05 M.

## 2. Experimental

### 2.1. Materials, reagents and solutions

Grape stalk and exhausted coffee wastes generated in wine and soluble coffee production were kindly supplied by a wine manufacturer (Cuenca, Spain) and a soluble coffee production industry (Girona, Spain). Grape stalk wastes were washed with distilled water, cut in small pieces, dried and ground. Exhausted coffee wastes were dried and used without any previous treatment. Both materials were sieved for a particle size of 0.25–0.50 mm. The properties of the biosorbents are listed in Table 1.

Metal solutions were prepared by dissolving appropriate amounts of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  or  $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$  in distilled water. EDTA–chelated copper(II) and EDTA–chelated nickel(II) solutions of different concentrations were prepared by mixing the required amounts of metal salts and disodium salt of ethylenediaminetetraacetic acid (EDTA). 0.05 M HCl and NaOH were used for pH adjustment and for metal desorption experiments. Standard solutions of  $1000 \text{ mg L}^{-1}$  of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  or  $\text{Ni}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in  $\text{HNO}_3$  0.5N were used for Flame Atomic Absorption Spectroscopy (FAAS) calibrations. All reagents were analytical grade (Panreac, Barcelona, Spain).

Table 1

Physical and chemical properties of grape stalks and exhausted coffee wastes used in the experiments

	Grape stalks	Exhausted coffee
Elemental analysis <sup>a</sup> (%)		
C	42.38	57.50
H	5.81	7.39
N	0.80	2.06
S	Nd	<0.30
pH <sub>ZPC</sub> <sup>b</sup>	5.1	3.9
Specific surface area <sup>c</sup> ( $\text{m}^2 \text{g}^{-1}$ )	21.6	7.5
Total porosity <sup>c</sup> (%)	45.06	69.75
Bulk density <sup>c</sup> ( $\text{g dm}^{-3}$ )	909.3	426.0
Apparent density <sup>c</sup> ( $\text{g dm}^{-3}$ )	1655.1	1408.5

<sup>a</sup> Elemental Analyzer EA 1110 CE Instruments (Italy).

<sup>b</sup> Potentiometric mass titration [36].

<sup>c</sup> Mercury Porosimeter Pascal 240 Thermo Electron Corporation (USA).

### 2.2. Effect of pH experiments

Batch experiments at different pHs within the range 1–7 were carried out at  $20 \pm 1$  °C in  $100 \text{ cm}^3$  glass flasks covered with cap. 0.1 g of dry sorbent with 20 mL of metal or EDTA–chelated metal solutions were shaken using a New Brunswick Scientific Model G25KC orbital shaker for 24 h. The concentration of Cu(II) and Ni(II) was fixed at 0.4 mM and the EDTA concentration was varied in order to get the metal–EDTA molar ratios of 1:0, 1:0.5 and 1:1. In these experiments, pH was periodically readjusted by addition of negligible volumes of either HCl or NaOH.

After agitation the solid was removed by filtration through a Millipore filter with filter holders (25 mm diameter, 1.2  $\mu\text{m}$  pore size). The initial metal concentration and the final metal concentration in the filtrates after sorption, previously acidified, were determined by Flame Atomic Absorption Spectrometry (FAAS) (Unicam Model 939).

The metal concentration in the solid phase,  $q_e$  ( $\text{mg g}^{-1}$ ) was calculated from the difference between the initial,  $C_i$  and equilibrium,  $C_e$  metal concentration in solution ( $\text{mg L}^{-1}$ ). The following equation was used to compute the specific uptake of the sorbent:

$$q_e = (C_i - C_e) \frac{V}{w} \quad (1)$$

where  $V$  (expressed in L) is the solution volume and  $w$  (in g) is the amount of dry sorbent.

### 2.3. Sorption kinetics

Batch kinetic experiments were carried out at  $20 \pm 1$  °C in  $1000 \text{ cm}^3$  flasks by mixing, at 200 rpm,  $750 \text{ cm}^3$  of Cu(II), Ni(II), Cu(II)–EDTA and Ni(II)–EDTA solutions with three different GS or EC masses (1.87, 3.75 or 7.50 g). Metals concentration was fixed at 0.4 mM. For metal–EDTA solutions, 0.2 mM EDTA concentration was used. Initial pH was adjusted to 5.2.

Five millilitres samples were withdrawn at suitable time intervals within the range 0–250 min. Samples were filtered; pH was measured and metal concentration was determined by FAAS.

The percentage of metal removal for each contact time was calculated following the equation:

$$\text{Removal\%} = \frac{C_i - C_e}{C_i} \times 100 \quad (2)$$

#### 2.4. Sorption isotherms

Equilibrium isotherms were obtained by contacting, as described in Section 2.2, 0.1 g of GS or EC with 20 mL of different Cu(II) and Ni(II) solutions within the initial concentration range 5–300 mg L<sup>-1</sup> in absence of EDTA and in presence of EDTA at doses of 1:0.5 and 1:1 metal:EDTA molar ratios. Initial pH was adjusted to 5.2 and readjusted if necessary after each 24 h in order to reach sorption equilibrium at this pH. pH adjustment was performed by addition of negligible volumes of concentrated solutions of either HCl or NaOH. After equilibration, for at least 24 h from the last pH adjustment, the samples were filtered, metal concentration in solution was determined by FAAS, and metal sorbed amount per mass unit was calculated according to Eq. (1).

#### 2.5. Column adsorption experiments

Fixed bed sorption experiments were carried out in glass columns of 35 cm length and 1.0 cm inner diameter. To pack the column, glass beads were introduced at the bottom up to around 25 cm length. Then, 0.7 g of grape stalk of 0.25–0.5 mm particle size were packed to a bed height of around 8.5 cm. Finally, some glass beads were added at the top in order to fill up the column. The operation was carried out in the up-flow mode to avoid possible short-circuiting by clogging and channelling.

The feeding single metal and metal–EDTA solutions contained 0.2 mM (12.50 mg L<sup>-1</sup> of Cu(II), or 11.75 mg L<sup>-1</sup> of Ni(II)). In the case of metal–EDTA solutions, the ligand con-

centrations used were: 6.25 and 12.50 mg L<sup>-1</sup> for the copper experiments; 5.87 and 11.74 mg L<sup>-1</sup> for the nickel assays. Initial pH was adjusted to 5.20.

The solutions were pumped at room temperature (20 ± 1 °C) upwards the grape stalk packed column by a peristaltic pump (Watson–Marlow model 101 U/R) at a flow rate of 30 mL h<sup>-1</sup>. By using an automatic fraction collector, samples of 7 mL were collected each 2 h, the pH was measured and metal concentration in solution was determined by FAAS.

#### 2.6. Column desorption experiments

Continuous wastewater treatment requires a reversible sorption–desorption process in order to reuse the adsorbent and to recover the metals in a concentrated form. Desorption experiments were carried out by feeding the column containing the metal loaded sorbent, with 0.05 M HCl at a flow rate of 30 mL h<sup>-1</sup>, as in the sorption experiments. Samples were collected by following the same procedure described above, pH was measured and metal concentration was determined by FAAS. Metal desorption ratio was calculated by mass balance.

### 3. Results and discussion

#### 3.1. Effect of pH

pH of the solution can affect the extent of the adsorption because it strongly influences the metal speciation, precipitation and the protonation degree both of the ligand (EDTA) and of the sorbent surface. Concentration of EDTA influences on the degree of metal complexation and subsequently the concentration of free metal in solution.

Fig. 1 shows the amount of metal removed on GS and EC for both metals in absence of EDTA and in presence of EDTA at two

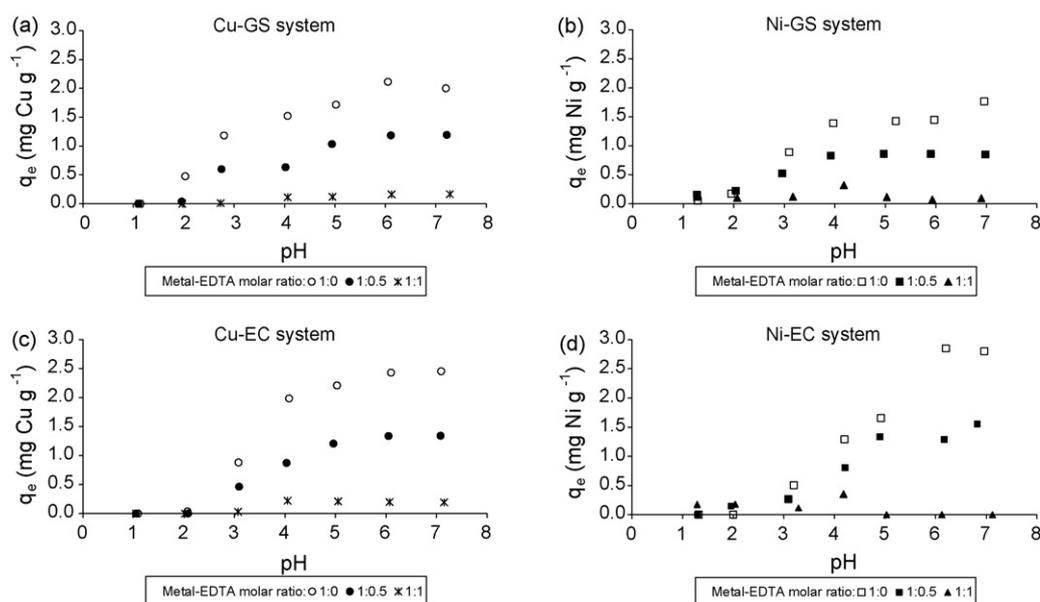


Fig. 1. Effect of pH on the adsorption of Cu(II) and Ni(II) on (a and b) grape stalks (GS) and (c and d) exhausted coffee (EC) in presence and in absence of EDTA. Initial metal concentration: 0.4 mM.

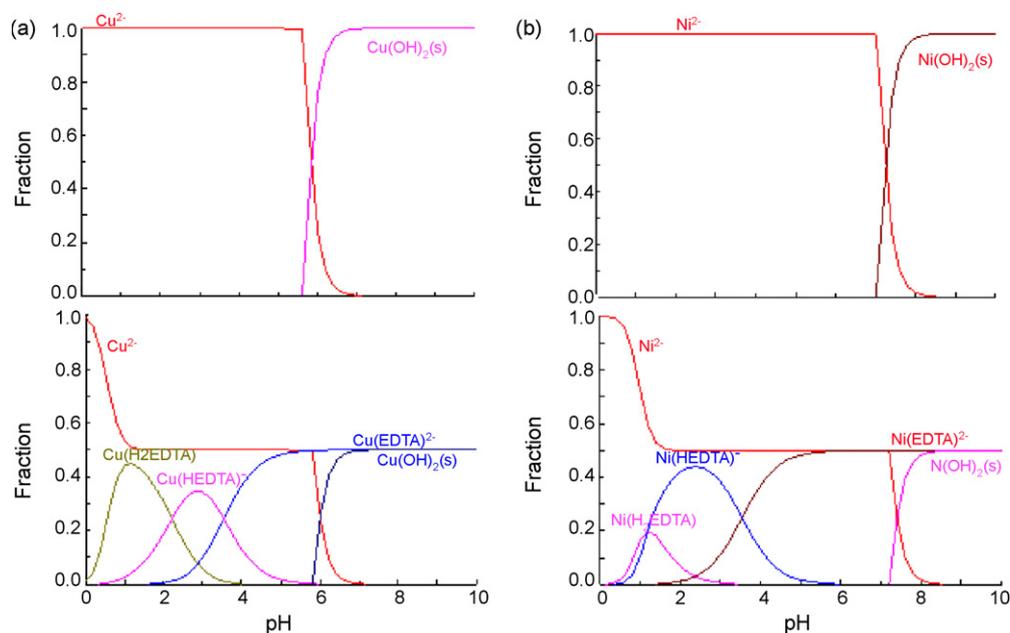


Fig. 2. Speciation diagrams for (a) Cu(II) and (b) Ni(II) as a function of pH for the free metal cation and for the 1:0.5 metal:EDTA molar ratio. Initial metal concentration: 0.4 mM.

different metal–EDTA molar ratios, as a function of pH. As can be seen, in all the cases the amount of metal removed increased when increasing the pH of the solution. In particular, there was an abrupt increase of metal uptake when the pH varied from 3 to 5 and maximum removal value was achieved from a pH around 5.5. Further increase in the pH did not improve significantly the metals uptake. From the results, it seems that the optimum pH for the removal of both metals was not affected by the presence of the complexing agent. Similar results have been reported for Cu(II) sorption onto activated carbon in presence of EDTA [4] and onto chitosan in presence of citrate ions [33].

Fig. 2 shows the species distribution diagram as a function of pH, calculated by MEDUSA computer program [35], for copper and nickel solutions of 0.4 mM in presence and in absence of EDTA. As it can be observed, in absence of ligand, both metals are 100% as divalent free metal cation until reaching precipitation pH around 6.0 in the case of Cu(II) and around 7.0 in the case of Ni(II). When EDTA is present in solution at 1:0.5 metal:ligand molar ratio, free metal cation concentration dramatically decreases due to the formation of neutral or anionic metal:EDTA species. Nevertheless, free  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  cations are still the predominant species at  $\text{pH} < 5.5$  and  $\text{pH} < 7.0$ , respectively. Therefore, the adsorption observed in the pH range 1–6 may be basically attributed to the interaction of free metal cations, and the sorbent surface. The low adsorption observed at low pH values can be explained by the fact that at high  $\text{H}^+$  concentration in solution protons compete with the cationic metal species for the coordination sites of basic nature of the sorbent. Conversely, as the pH of the solution increases, the decrease in  $\text{H}^+$  concentration in solution favours the binding of the heavy metal to the sorbent surface.

On the other hand, the surface charge of the sorbents is characterised by a point of zero charge or  $\text{pH}_{\text{zpc}}$ . The surface of

the sorbent is positively charged at  $\text{pH} < \text{pH}_{\text{zpc}}$ , and negatively charged at  $\text{pH} > \text{pH}_{\text{zpc}}$ . The  $\text{pH}_{\text{zpc}}$  of GS and EC determined by potentiometric mass titration [36], is 5.1 and 3.9, for GS and EC, respectively. Therefore, the increase of pH towards higher pH than the sorbents  $\text{pH}_{\text{zpc}}$  can be related to a decrease of the positive surface charge, which results in a lower electrostatic repulsion between the surface and the positively charged metal ion.

In Fig. 1, it can also be observed an important decrease of metal sorption in the experiments performed with 1:0.5 Cu(II)–EDTA and Ni(II)–EDTA molar ratio at pH values within 3.0 and 7.0 in comparison with the results obtained in absence of EDTA. The species distribution diagrams in Fig. 2 show that at  $\text{pH} > 2$  copper and nickel are 50% complexed with the subsequent decrease to half of free cations predominance and the appearance in solution of the neutral  $\text{CuH}_2\text{EDTA}$  and the negative  $\text{CuHEDTA}^-$  and  $\text{CuEDTA}^{2-}$  species. These anionic species are not likely to be electrostatically bound at  $\text{pH} > \text{pH}_{\text{zpc}}$  when the sorbent is partially or totally negatively charged. Therefore, it seems that only free  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  cations would be adsorbed.

The species distribution diagram corresponding to solutions of 1:1 Cu(II)–EDTA and Ni(II)–EDTA molar ratio (figure not shown), indicates that 100% of metals are complexed as neutral or anionic metal–EDTA species. Therefore, the almost total absence of free metal cations in equimolar metal–EDTA solutions would explain the low metal adsorption observed. An adverse effect of complexing agents like citrate [31,33], acetate and EDTA [31] on metal sorption on different sorbents has been previously reported.

Taking into account the obtained results further experiments were carried out at pH around 5.2 in order to avoid metal hydroxides precipitation.

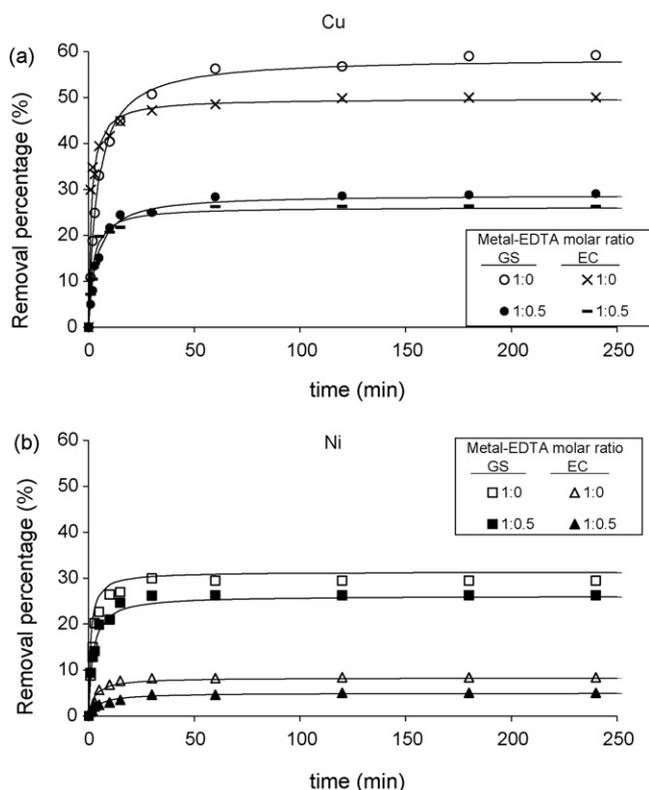


Fig. 3. Effect of contact time on the removal of (a) Cu(II) and (b) Ni(II) onto GS and EC in presence and in absence of EDTA. pH<sub>0</sub> 5.2; sorbent dose, 5 g/L; initial metal concentration: 0.4 mM. Symbols show the experimental results and solid line represents the prediction of the Pseudo-second order model.

### 3.2. Sorption kinetics

The percentage of metal removal as a function of time for metal sorption from single metal solutions and from 1:0.5 metal–EDTA molar ratio solutions are depicted for a sorbent dose of 5 g L<sup>-1</sup>, as an example, in Fig. 3 for copper (a) and nickel (b).

As can be seen, metal removal seemed to occur in two steps. The first step involves rapid metal uptake within the first 20 min of contact followed by the subsequent removal of metal until equilibrium was reached, at around 60 min. The rapid step was probably due to the abundant availability of active sites on the material, and with the gradual occupancy of these sites, the sorption became less efficient in the slower step. From the results it seems that the presence of the ligand EDTA did not influence on metal sorption equilibrium achievement.

It can also be observed that for the two studied sorbents, GS is the one that showed the best performance for both metals sorption in presence and in absence of the complexing agent EDTA. It must be remarked that the sorption capacity of EC seemed not to be as much affected by the presence of EDTA as GS capacity at the EDTA concentration evaluated. Finally, when comparing the percentage of removal of copper and nickel onto both sorbents, copper was always the most efficiently sorbed.

The same trend was observed for both metals sorption by using the other two sorbent concentrations (2.5 and 10 g L<sup>-1</sup>)

investigated, that is, sorption kinetics in two steps, higher adsorption of copper, better performance of GS, and less influence of EDTA complexation on both metals sorption onto EC than onto GS.

In order to investigate the sorption rate law of metal sorption the obtained kinetic data were analysed using the pseudo-second order equation proposed by Ho et al. [29]:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \quad (3)$$

where  $q_e$  and  $q_t$  are the sorption capacity at equilibrium and at time  $t$ , respectively (mg g<sup>-1</sup>) and  $k$  is the rate constant of pseudo-second order sorption (g mg<sup>-1</sup> min<sup>-1</sup>). For the initial condition  $t=0$  and  $q_t=0$ , the integrated form of Eq. (3) becomes:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + kt \quad (4)$$

which is the integrated rate law for a pseudo-second order reaction. Eq. (4) can be rearranged to obtain the linear form:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \quad (5)$$

When the experimental data were introduced into the Eq. (5), straight lines for all cases were obtained by plotting  $t/q_t$  versus  $t$ , indicating that the processes follow the pseudo-second order rate equation. As an example, Fig. 4 shows the pseudo-second order plot for the sorption of Cu(II) and Ni(II) onto GS and

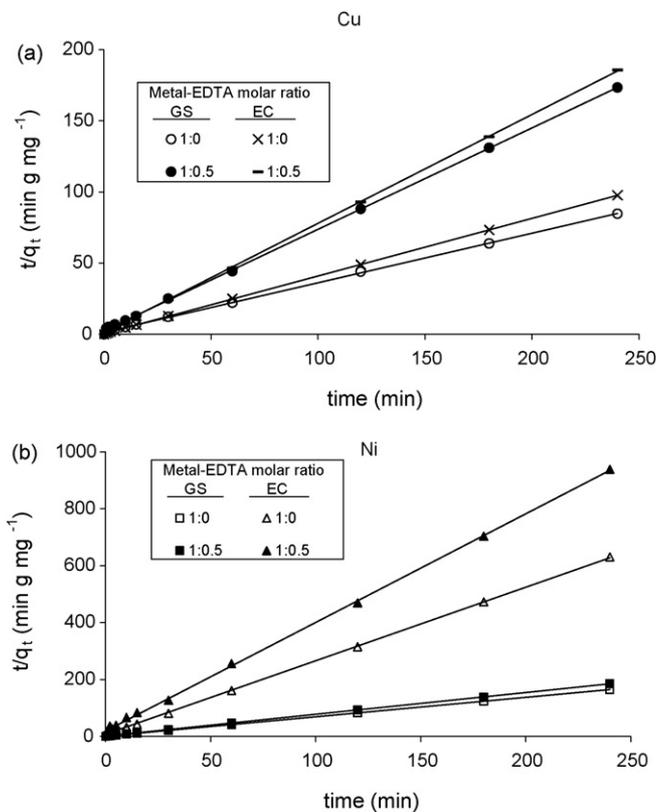


Fig. 4. Pseudo-second order plot for the adsorption of (a) Cu(II) and (b) Ni(II) onto GS and EC. pH<sub>0</sub> 5.2; sorbent dose, 5 g/L; initial metal concentration: 0.4 mM.

Table 2  
Pseudo-second order kinetic parameters for Cu(II) adsorption on GS and EC in presence and in absence of EDTA

Sorbent	Sorbent dose (g L <sup>-1</sup> )	EDTA concentration (mM)	Pseudo-second order model		
			<i>K</i> (g mg <sup>-1</sup> min <sup>-1</sup> )	<i>q<sub>e</sub></i> (mg g <sup>-1</sup> )	<i>R</i> <sup>2</sup>
GS	2.5	–	0.022	4.09	0.9906
		0.2	0.039	2.82	0.9996
	5	–	0.086	2.87	0.9999
		0.2	0.198	1.40	0.9952
	10	–	0.651	1.73	0.9999
		0.2	1.766	0.89	0.9998
EC	2.5	–	0.058	3.60	0.9985
		0.2	0.051	1.77	0.9919
	5	–	0.313	2.47	0.9999
		0.2	0.373	1.30	0.9999
	10	0.0	3.612	1.79	1.0000
		0.2	2.100	0.92	0.9999

EC for a sorbent concentration of 5 g L<sup>-1</sup>. The pseudo-second order rate constant *k* and the equilibrium metal sorption capacity, *q<sub>e</sub>*, were calculated from the linear regressions, and are presented in Tables 2 and 3 for copper and nickel, respectively, along with the correlation coefficient, *R*<sup>2</sup>. In all cases, *R*<sup>2</sup> values were higher than 0.99, indicating the good compliance of the experimental data with the pseudo-second order model. The *k* values for copper sorption show that the pseudo-second order constant rate increase in the presence of complexing agent in the case of grape stalk while complexation seemed to have a fairly influence on *k* when EC was the sorbent. Complexation seems also not to have a clear influence on nickel sorption constant rate onto both GS and EC sorbents. When comparing the obtained values for the sorption rate constant, *k*, it can be seen that independently of the presence/absence of complexing agent, *k* increases on increasing the sorbent dose. When sorption of both metals onto both materials was compared, it was observed

that, in general, nickel sorption was faster than for copper, as it corresponds from the higher values of the pseudo-second order constant *k*.

For all the systems studied, the amount of metal sorbed at equilibrium (*q<sub>e</sub>*) decreased on increasing the sorbent concentration. In the case of copper, the presence of EDTA in a 1:0.5 molar concentration ratio provoked around a 50% decrease in the amount of metal sorbed on both GS and EC. In the same conditions the sorption of nickel was only fairly decreased. The results clearly show that copper sorption was more affected by the presence of complexing agent than nickel one.

As an example of the prediction of the pseudo-second order model, calculated curves corresponding to metal uptake by both biomaterials for a sorbent concentration of 5 g L<sup>-1</sup> have been plotted together with the experimental data in Fig. 3 for both metals. Good agreement between the different sets of experimental data to the model was obtained.

Table 3  
Pseudo-second order kinetic parameters for Ni(II) adsorption on GS and EC in presence and in absence of EDTA

Sorbent	Sorbent dose (g L <sup>-1</sup> )	EDTA concentration (mM)	Pseudo-second order model		
			<i>K</i> (g mg <sup>-1</sup> min <sup>-1</sup> )	<i>q<sub>e</sub></i> (mg g <sup>-1</sup> )	<i>R</i> <sup>2</sup>
GS	2.5	–	0.410	2.08	1.0000
		0.2	0.399	1.97	1.0000
	5	–	0.609	1.46	1.0000
		0.2	0.546	1.31	0.9999
	10	–	1.956	0.82	1.0000
		0.2	1.778	0.70	1.0000
EC	2.5	–	0.177	0.52	0.9962
		0.2	0.749	0.34	0.9998
	5	–	0.829	0.39	0.9998
		0.2	0.777	0.26	0.9998
	10	0.0	2.788	0.29	0.9994
		0.2	3.185	0.10	0.9990

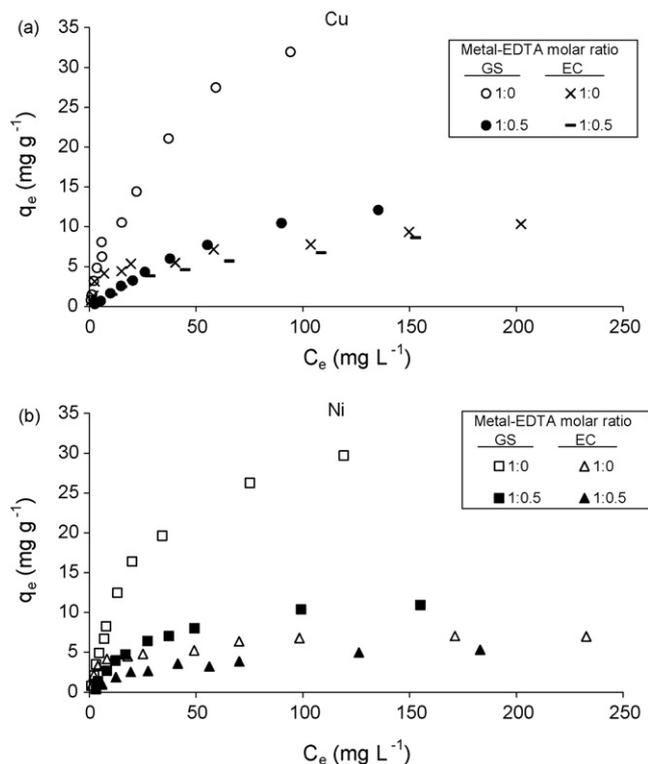


Fig. 5. Sorption isotherms of (a) Cu(II) and (b) Ni(II) onto GS and EC in presence and in absence of EDTA.

### 3.3. Sorption isotherms

Fig. 5 shows the equilibrium experimental data for copper and nickel sorption onto GS and EC in absence of complexing agent and for a 1:0.5 metal:EDTA molar ratio. Results obtained for higher metal:ligand ratios are not shown due to the low adsorption observed. During the experiments, metal hydroxides precipitation was avoided by keeping the pH around 5.2. Experimental results were mathematically treated according to Langmuir and Freundlich models.

The Langmuir model assumes that sorption process takes place onto a homogeneous surface and, at saturation, a monolayer of adsorbate is formed. Langmuir model is represented by

the expression:

$$q = \frac{bq_{\max}C_{\text{eq}}}{1 + bC_{\text{eq}}} \quad (6)$$

where  $q_{\max}$  is the maximum uptake ( $\text{mg g}^{-1}$ ) and  $b$  ( $\text{L mg}^{-1}$ ) is a constant related to energy of adsorption which quantitatively reflects the affinity between the sorbent and the sorbate.

The Freundlich isotherm is an empirical equation based on sorption on a heterogeneous surface and assumes that different sites with different adsorption energies are involved. This equation is commonly presented as:

$$q_e = KC_e^{1/n} \quad (7)$$

where  $K$  and  $n$  are empirical constants that indicate the relative sorption capacity and sorption intensity, respectively.

Langmuir and Freundlich parameters presented in Table 4 were obtained by fitting the experimental data to the linearized equations of Langmuir (plot of  $C_{\text{eq}}/q$  against  $C_{\text{eq}}$ ) and Freundlich ( $\log q_e$  as a function of  $\log C_e$ ) models. As can be seen in the table, both models provided reasonably good correlation coefficients for all the systems studied. As expected,  $q_{\max}$  predicted from the Langmuir model for the systems Cu(II):EDTA and Ni(II):EDTA was lower than the one corresponding to the single metal systems. When the sorbent used was GS, the value of  $q_{\max}$  is decreased in around 50% which was predictable from the fact that in the 1:0.5 metal:EDTA molar ratio, 50% of the metal is complexed, indicating that the free metal cation seems to be the most sorbed species on GS. In the experiments performed with EC, which presented lower sorption capacities, the effect of the presence of EDTA was less noticeable (10–20% of reduction of the maximum sorbent capacity).

The values of the parameters  $b$  and  $1/n$  of the Langmuir and Freundlich models, respectively, are related to the affinity of sorbent–sorbate. While in the case of  $b$ , higher numerical values indicate a more favourable adsorption, in the case of  $1/n$ , lower values are related to a stronger adsorbate–surface bond. From the fitting of the experimental data, the introduction of the complexing agent resulted in a decrease in the  $b$  values and an increase in  $1/n$  ones. It was also observed that, for both metals in presence and in absence of complexing agent, the parameters  $b$  and  $1/n$  indicate that the sorption onto EC is more favourable

Table 4  
Langmuir and Freundlich parameters for the adsorption of Cu(II) and Ni(II) in presence and in absence of EDTA on GS and EC

Sorbent	Metal	EDTA concentration (mM)	Langmuir model			Freundlich model		
			$q_{\max}$ ( $\text{mg g}^{-1}$ )	$b$ ( $\text{L mg}^{-1}$ )	$R^2$	$K$	$1/n$	$R^2$
GS	Cu	–	42.92	0.0283	0.9477	1.48	0.73	0.9570
		0.2	23.86	0.0082	0.9665	0.16	0.95	0.9699
	Ni	–	38.31	0.0302	0.9793	1.38	0.73	0.9319
		0.2	15.48	0.0189	0.7461	0.42	0.74	0.8277
EC	Cu	–	11.60	0.0541	0.9739	1.31	0.41	0.8782
		0.2	10.52	0.0160	0.9574	0.28	0.72	0.9617
	Ni	–	7.25	0.1227	0.9973	1.55	0.32	0.8041
		0.2	6.30	0.0275	0.9830	0.35	0.57	0.9195

Table 5  
Maximum uptake ( $q_{\max}$ ) of Cu(II) and Ni(II) for selected biosorbent materials

Adsorbent	Adsorbent capacity ( $\text{mg g}^{-1}$ )		References
	Cu	Ni	
Papaya wood	19.85		[37]
Sugar beet pulp (native)	21.16	11.85	[38]
Seeds of <i>Capsicum annuum</i>	16.71		[39]
Crop milling waste (black gram husk)	27.97	20.15	[40]
Activated carbon from almond husk		30.8–37.2	[41]
Brown alga <i>Fucus vesiculosus</i>	61.6	46.9	[42]
Olive stone waste	2.02	2.13	[43]
Green alga <i>Spirogyra</i>	133.3		[44]
GS	42.92	38.31	This work
EC	11.6	7.25	This work

than onto GS. This fact could explain the lower sensitivity to the presence of EDTA on EC compared to GS in the adsorption of both metals. Whatever case, in presence and in absence of EDTA grape stalk showed a higher capacity than exhausted coffee for copper and nickel uptake.

In Table 5 the results of this work are compared to other results obtained by others authors studying copper and nickel sorption at pH 5–5.5 using different biosorbents. As seen in the table, the maximum sorption values obtained for Cu and Ni when using GS are greater than those reported in literature for other sorbents [37–41] except for the algae *Fucus vesiculosus* [42] and *Spirogyra* [44]. The uptake capacity of EC for both metals is greater than those found by Fiol et al. [43] but lower compared to the capacities of the sorbents listed in Table 5.

The reduction of metal ions uptake when EDTA is present in solution has already been reported. Gyliene et al. [30] found around 45% decrease on copper sorption onto chitosan at pH 3 and 1:0.5 metal–EDTA molar ratio; Chu and Hashim [32] reported that copper removal efficiency at pH 6 decreases from 80% to 30% and to 40% when using as sorbent coal-based and coconut shell-based activated carbons, respectively, at 1:1 metal–EDTA molar ratio.

### 3.4. Column adsorption experiments

Adsorption experiments in packed bed-up flow columns using GS as adsorbent were carried out to evaluate the performance of this biomaterial in a continuous process. GS was chosen because from the two materials studied, this one showed a higher removal capacity for copper and nickel from free and EDTA-complexed metal solutions. The breakthrough curves for copper and nickel sorption on GS from free metal and EDTA chelated metal solutions are presented in Fig. 6. It can be observed that when feeding the column with single copper or nickel solutions, no metal was detected in the outlet effluent during the first 22 h in the case of Cu(II), and 18 h in the case of Ni(II). By applying the mass balances to the breakthrough curves, capacity values of 22.52 and 19.05  $\text{mg g}^{-1}$  were obtained for copper and nickel, respectively. These results are almost two folds higher than the sorption values obtained at equilibrium in batch experiments (11.94 and 10.03  $\text{mg g}^{-1}$ ). A

higher adsorption in continuous flow processes than in batch has been previously reported for *Pinus radiata* bark [16], peat [19], activated carbon [45], and Sasafras soils [46]. At the high sorbent-to-solution ratios of column environments, specific interactions between solutes and sorbent result in higher removal capacities than those obtained in batch tests.

When metals were in presence of complexing agent EDTA, a constant metal concentration in the effluent was detected during approximately the first 18 and 10 h for copper and nickel, respectively. As can be seen, the initial effluent concentration increased on increasing the EDTA concentration. This fact sug-

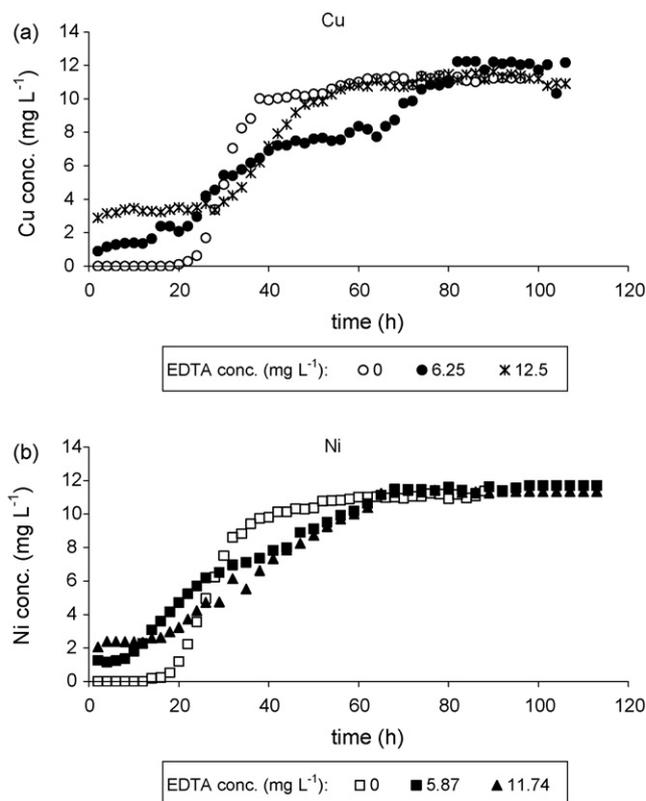


Fig. 6. Breakthrough curves for the adsorption of (a) Cu(II) and (b) Ni(II) onto GS in a packed bed up-flow column in absence and in presence of EDTA. Feeding Cu(II) solution concentration: 12.50 mg/L. Feeding Ni(II) solution concentration: 11.74 mg/L.

Table 6

Theoretical fraction and constant effluent concentrations in the initial zone of the breakthrough curves for Cu(II) and Ni(II) adsorption on GS in a packed bed-up flow column in presence of EDTA

Metal	[EDTA] (mg L <sup>-1</sup> )	Theoretical complexed metal concentration (mg L <sup>-1</sup> )	Effluent concentration in the first hours of operation (mg L <sup>-1</sup> )
Cu	6.25	1.37	1.38
	12.50	2.87	3.15
Ni	5.87	1.12	1.16
	11.74	2.46	2.40

Feeding Cu(II) solution concentration: 12.50 mg L<sup>-1</sup>; feeding Ni(II) solution concentration: 11.74 mg L<sup>-1</sup>.

gests that this metal concentration could correspond to the complexed metal fraction that should not be sorbed on the GS. The experimental values along with the theoretical concentration of the complexed metal calculated by using the MEDUSA computer program are summarized in Table 6. The good agreement between experimental and theoretical concentration values suggests that species derived from metal complexation were not adsorbed on the GS. These results, confirm that only free metal cation of Cu(II) and Ni(II) were adsorbed onto GS.

### 3.5. Column desorption experiments

In order to apply the sorption process to real wastewater, regeneration of the sorbent is important for economic reasons. The overall metal recovery also depends on the metal

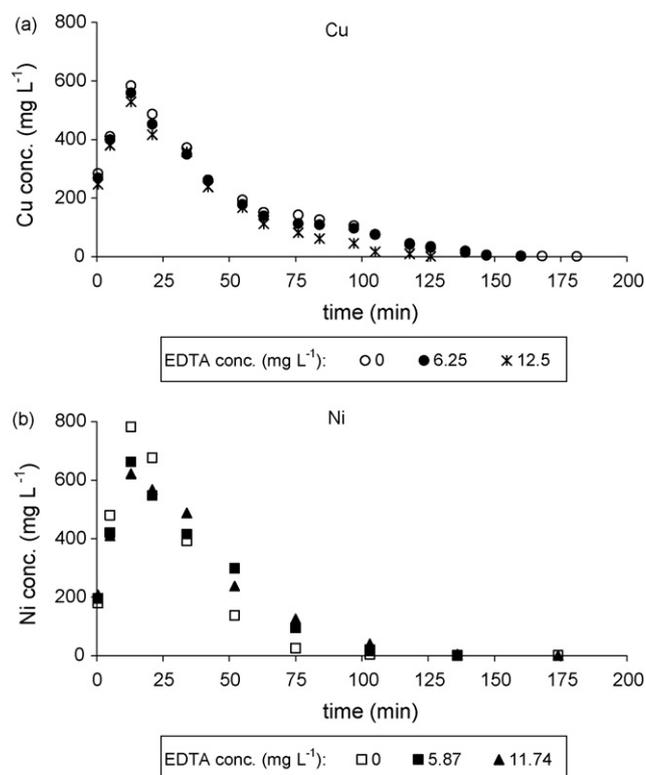


Fig. 7. Desorption profile of (a) Cu(II) and (b) Ni(II) from a GS packed bed-up-flow column by feeding 0.05 M HCl.

elution efficiency of the adsorbed metals. As can be seen in Fig. 7, metal desorption profiles exhibited a sharp increase in metal concentration, reaching a maximum in all the cases after around 13 min. The maximum concentration values ranged from 584.6 to 528.6 mg L<sup>-1</sup> for Cu(II) and from 781.8 to 621.8 mg L<sup>-1</sup> for Ni(II); the lowest values corresponding to desorption from the sorbent loaded with the highest EDTA concentration.

The total amount of copper and nickel eluted during desorption was calculated and compared to the values of adsorption obtained in the sorption process. For all the experiments, the efficiency of the desorption was higher than 97%. It must be noted that desorption of nickel was faster than for copper, which is in accordance with the obtained sorption kinetic rate values; 100 min and a volume of 50 mL was needed to complete nickel desorption, while 140 min and a volume of 70 mL was required for copper.

## 4. Conclusions

Copper and nickel sorption is pH dependent and maximum uptake was obtained from pHs greater than 5.5 onto the both bio-materials investigated: grape stalk and exhausted coffee wastes. The complexing agent EDTA negatively affects the capacity of both sorbents for copper and nickel sorption.

The pseudo-second order has been successfully used to model kinetic data. Equilibrium sorption models Langmuir and Freundlich described adequately the equilibrium data. Grape stalk showed higher capacity for copper and nickel uptake than exhausted coffee in the absence and presence of EDTA, but exhausted coffee capacity resulted to be less affected by the presence of the complexing agent. By other side, parameters related to the metal–sorbent affinity obtained from the isotherm models indicated that exhausted coffee shows higher affinity than grape stalk for Cu(II) and Ni(II) ions in presence and in absence of EDTA.

From the columns experiments, it can be concluded that grape stalk is an efficient sorbent for the free Cu<sup>2+</sup> and Ni<sup>2+</sup> species. The sorbent capacity in column experiments resulted to be 1.9 folds higher than in batch mode for both copper and nickel. In presence of EDTA, the column effluent presented metal leakage from the beginning of the operation which can be related to the complexed metal. This result indicates that only free metal ion was adsorbed onto grape stalk. Finally, sorbed metal was recovered in a concentrated form, by treating the biomaterial in mild acidic conditions.

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