Removal of copper and nickel ions from aqueous solutions by grape stalks wastes

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Abstract

In the present work, the usefulness of grape stalks wastes generated in the wine production process has been investigated for the removal of copper and nickel ions from aqueous solutions. The sorption process was relatively fast and equilibrium was reached after about 60 min of contact. The influence of pH, sodium chloride and metal concentration on metal removal has been studied. Uptake showed a pH-dependent profile. Maximum sorption for both metals was found to occur at around pH 5.5–6.0. An increase of sodium chloride concentration caused a decrease in metal removal. Langmuir isotherms, at pH 6.0, for each metal were used to describe sorption equilibrium data. Maximum uptake obtained was 1.59×10^{-4} mol of copper and 1.81×10^{-4} mol of nickel per gram of dry sorbent.

Sorption of copper and nickel on grape stalks released an equivalent amount of alkaline and alkaline earth metals (K^+, Mg^{2+}, Ca^{2+}) and protons, indicating that ionic exchange is predominantly responsible for metal ion uptake. Fourier transform infrared (FTIR) spectrometry analysis indicated that lignin C–O bond might be involved in metal uptake.

Equilibrium batch sorption studies were also performed using a two metal system containing (Cu(II) + Ni(II)). In the evaluation of the two metal sorption system performance, single isotherm curves had to be replaced by three-dimensional sorption isotherm surface. In order to describe the isotherm surface mathematically, the extended-Langmuir model was used. Nickel was found to be much more sensitive to the presence of copper than copper is to the presence of nickel.

1. Introduction

The presence of heavy metals in the environment can be detrimental to a variety of living species including humans. Metals can be distinguished from other toxic pollutants, since they are not biodegradable and can be accumulated in living tissues, causing various diseases and disorders. Environmental pollution by toxic metals occurs globally through military, industrial, and agricultural processes and waste disposal. Conventional methods for removing metals from industrial effluents include chemical precipitation, coagulation, solvent extraction, electrolysis, membrane separation, ion exchange, and adsorption [1]. Activated carbon and different types of ion-exchange resins are very often used in adsorption processes. The high capital and regeneration costs of the materials limits their large-scale use for the removal of metals, and has encouraged researchers to look for low cost sorbing materials [2,3].

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Relatively recently, biological materials (algae, bacteria, fungi, and yeasts) [4,5] or certain waste products from industrial or agricultural operations, have also been recognized as cheap sorbents in the removal of toxic metals. Studies to assess the ability of crab shell [6], peat [7], sunflower stalks [8], pine bark [9] or seafood processing waste sludge [10] for the decontamination of metal-containing effluents, found them to be moderately effective. These sorbents, compared to others, have several advantages. They are cheap raw material or waste products from industries or naturally abundant biomass. In addition, these materials that are considered as waste products can be reused for effluents decontamination. It is also important to note that these sorbents appear to have an application as preconcentration agents since concentration of a specific metal could be achieved during the metal uptake.

The sorption of metals by these kinds of materials might be attributed to their proteins, carbohydrates, and phenolic compounds that have carboxyl, hydroxyl, sulfate, phosphate, and amino groups that can bind metal ions. It is also possible that the metals bind to different kinds of sites. Metal sorption consists of several mechanisms that quantitatively and qualitatively differ according to the metal species in solution and the origin and processing of the sorbent.

Nickel is found in the effluents of electroplating, inorganic and dyes industries. Sorption of nickel with different materials has been reported in literature. The use of marine algae *Sargassum fluitans* was studied by Holan and Volesky [11] and a maximum uptake of $2.32 \, mol \, kg^{-1}$ dry mass, at pH 6.0 was obtained. Other reports [12,13] are also found in the literature using filamentous fungus for nickel removal, with a maximum uptake capacity of $0.32 \, mol \, kg^{-1}$ (pH 4) and $3.6 \, mol \, kg^{-1}$ dry material (initial pH 7.0), respectively. Al-Asheh and Duvnjak [9] who also studied the sorption of this metal by pine bark achieved an uptake of $0.10 \, mol \, kg^{-1}$ dry mass at pH 4.0.

Copper is used extensively by a variety of industries and its uptake by alternative sorbents has been widely studied. Among these materials, are *Rhizopus arrhizus* [14], sunflower stalks [8], pine bark [9] and apple wastes [15]. In these studies carried out at pH 4.0, uptakes of 0.53, 0.46, 0.15 and $0.17 \, mol \, Cu \, kg^{-1}$ dry material, respectively, were reported.

Sorption process modeling is a topic of interest for the prediction of the metal partitioning between the aqueous solution and the solid surface, and its subsequent application to the design of sorption treatment units, as well as for the evaluation of the fate of heavy metals in natural environments. In particular, the non-competitive Langmuir and Freundlich isotherms have been useful tools for the description and comparison of heavy metal sorption by different sorbents [16,17].

In the present work, the usefulness of grape stalk wastes generated in the wine production process has been investigated for the removal of copper and nickel ions from aqueous solutions. For each single metal, batch experiments were designed to study the influence of pH, sodium chloride and metal concentration on the sorption process. Langmuir isotherms were used to describe sorption equilibrium data.

Ion exchange is one of the proposed mechanisms involved in the cation metal biosorption [3]. In order to recognize ion exchange mechanism during metal sorption by grape stalks, the release of Ca^{2+}, Mg^{2+}, K^+ and H^+ while sorbing Cu(II) and Ni(II) ions from single metal systems was determined. Fourier transform infrared (FTIR) spectra were carried out as a preliminary and qualitative analysis to determine the main functional groups present in the sorbent that might be involved in metal uptake.

Since industrial effluents can contain several metals, it is necessary to study the simultaneous sorption of two or more metals and also to quantify the interference of one metal with the sorption of the other [13,18]. So, the simultaneous sorption of copper (II) and nickel (II) ions was also studied. In the evaluation of the binary metal mixture system performance, equilibrium data where fitted to the extended Langmuir isotherm model [9].

2. Experimental

2.1. Materials

Grape stalks wastes generated in the wine production process (supplied by a wine manufacturer of the Empordà-Costa Brava region, Girona, Spain), were rinsed three times with distilled water, dried in an oven at 110°C until constant weight, cut and sieved for a particle size of 1.0–1.5 mm. Metal solutions were prepared by dissolving appropriate amounts of $CuCl_2 \cdot 2H_2O(s)$ and $NiCl_2 \cdot 2H_2O(s)$ in distilled water. NaOH and HCl solutions were used for pH adjustment. All reagents were analytical grade and were purchased from Panreac (Barcelona, Spain). Metal standard solutions of $1000 \, mg \, L^{-1}$ purchased from Carlo Erba (Milano, Italy) were used for Flame Atomic Absorption and Inductively Coupled Plasma Atomic Emission Spectroscopy calibration.

2.2. Major cation content of grape stalks

In order to measure approximately the ion exchange capacity of the material, the release of alkaline and alkaline earth metals Na^+, K^+, Mg^{2+} and Ca^{2+} from acid-washed grape stalks wastes was determined. The protonation of the solid was performed to show that the exchangeable cations that were present on the raw

material could be released into the solution after the proton uptake.

Grape stalks of 1 g was treated with 50 mL of 0.1 M HCl. The suspension was stirred for 1 h at room temperature in a rotary mixer, then filtered through a 0.45 μm cellulose filter paper (Millipore Corporation). The grape stalks were resuspended in the same HCl solution, and the previous treatment was repeated three times. As control, the same procedure was carried out contacting 1 g of grape stalks with 50 mL of deionized water. The filtrates so obtained were analyzed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) (SPECTROFLAME, Spectro Analytical Instruments) to determine Na^+, K^+, Mg^{2+} and Ca^{2+} released from grape stalks.

2.3. Fourier transform infrared analysis (FTIR)

To give a qualitative and preliminary analysis of the main functional groups that might be involved in metal uptake, a FTIR analysis in solid phase was performed using a Fourier Transform Infrared Spectrometer (Galaxy Series FTIR 5000, Mattson). Spectra of the sorbent before and after copper and nickel sorption process were carried out. For the sorption process, samples of grape stalks were loaded with a 500 mg L^{-1} of metal solutions at pH 6.0 following the batch procedure described below. For FTIR analysis, 300 mg KBr disks containing 3 mg of finely ground sample of grape stalks were prepared.

2.4. Metal uptake procedure

Batch experiments were carried out at 25°C in stoppered glass tubes by shaking a fixed mass of 0.1 g of dry grape stalks, with 10 mL of metal solution at 25 rpm (rotary mixer Cenco Instrument) until equilibrium was reached.

In order to ascertain the contact time that was necessary to achieve the equilibrium state (characterized by unchanging sorbate concentration in the solution), simple preliminary sorption-kinetic experiments were performed stirring in different tubes 0.1 g of dry solid with 10 mL of 10 mg L^{-1} of metal solution at initial pH around 6. Samples were drawn at intervals of 15 min for 2 h.

After agitation the solid was removed by filtration through a 0.45 μm cellulose filter paper (Millipore Corporation). The final metal concentration in the filtrates as well as in the initial solution was determined by Flame Atomic Absorption Spectrometry using a Varian Absorption Spectrometer (Model 1275). The metal determination was performed at wavelengths of 324.8 nm for Cu and 232.0 nm for Ni.

The adsorbed metal concentrations were obtained from the difference between initial and final metal concentration in solution. The percent removed was calculated as $\%R = ((C_i - C_{eq})/C_i) \times 100$, where C_i and C_{eq} are the initial and final equilibrium metal concentration in solution, respectively.

When the initial pH of metal solutions was adjusted to the desired value no efforts were made to maintain the solution pH while copper or nickel was being sorbed. The initial and final pH of the metal solutions was monitored using a combined electrode connected to a Crison Model Digilab 517. Each experiment was carried out in duplicate and the average results are presented in this study.

2.5. Effect of pH

The pH of metal solutions has been identified as the most important variable governing sorption on hydrous solids [3]. This is partly due to the fact that hydrogen ions themselves are strong competing sorbates and partly that the solution pH influences the chemical speciation of metal ions.

The effect of pH on the sorption was studied by adjusting the initial solution pH within the range 1.0–6.5. The experiments were carried out at pH values below the pH where metal hydroxide chemical precipitation occurs, which has been estimated as pH > 6.3 for $Cu(OH)_2(s)$ and pH > 8.3 for $Ni(OH)_2(s)$ [19]. In these experiments initial metal concentration was 10 mg L^{-1} (1.57×10^{-4} mol L^{-1} for Cu and 1.70×10^{-4} mol L^{-1} for Ni).

2.6. Effect of sodium chloride concentration

In order to study the influence of the presence in solution of other ions on metal uptake, sodium chloride was chosen as ionic medium. The concentration of this salt was varied within the range 0.1–2.0 mol L^{-1}. In these experiments initial metal concentration was 10 mg L^{-1} and the pH was around 6.0.

Metal species fraction diagrams at a fixed pH 6.0 as a function of different chloride concentration, were performed using equilibrium constants in aqueous solutions given in the literature [20] and a specially made computer program [21].

2.7. Sorption isotherm experiments

Sorption isotherms are plots of the sorbate uptake and the final equilibrium concentration of the residual sorbate remaining in the solution. The classical model of Langmuir was used to compare the single metal sorption performance and to determine the capacity of grape stalks for copper and nickel. However in the binary metal systems the extended Langmuir model was used.

For single metal systems, initial metal concentration was varied from 2.4×10^{-4} to 2.4×10^{-3} mol L^{-1}. In

binary metal mixtures systems, for each initial concentration of Cu(II) solutions: 2.40×10^{-4}, 4.80×10^{-4}, 9.60×10^{-4}, 1.20×10^{-3}, 1.96×10^{-3}, 2.4×10^{-3} mol L^{-1}, Ni(II) concentration was varied: 2.40×10^{-4}, 4.80×10^{-4}, 9.60×10^{-4}, 1.20×10^{-3}, 1.96×10^{-3}, 2.4×10^{-3} mol L^{-1}. In all the cases, the initial pH of the solution was around 6.0. This pH was selected based on batch test conducted to determine the effect of pH on sorbent capacities. In order to avoid addition of strange ions, the initial pH of metal solutions was 6.0 without further adjustments during the sorption process.

3. Results and discussion

3.1. Major cation content of grape stalks

The amount of cations released when grape stalks were treated with acidic solutions (HCl 0.1 M) and with deionized water (control) is presented in Table 1. The total amount of cations released indicates a total ionic content in grape stalks of 0.61 meq g^{-1} dry waste (0.36 mmol g^{-1}), consisting of 0.0010, 0.1071, 0.1258 and 0.3820 meq g^{-1} of Na$^+$, K$^+$, Mg^{2+} and Ca^{2+}, respectively. This total ionic content can be considered as an approximate measure of the cation exchange capacity (CEC) of the grape stalks wastes [5].

3.2. Fourier transform infrared analysis FTIR

In Fig. 1 the FTIR spectra of grape stalks and grape stalks loaded with copper and nickel are presented. As shown in the figure, the spectra display a number of absorption peaks, indicating the complex nature of the material examined. The broad absorption peaks around 3350 cm^{-1} are indicative of the existence of bonded hydroxyl groups (3340–3380 cm^{-1}). The peaks observed at 2921 cm^{-1} can be assigned to the C–H group. The peaks around 1620 cm^{-1} correspond to the C=C stretching that may be attributed to the lignin aromatic C–C bond. The strong C–O band at 1058 cm^{-1} also confirms the lignin structure of the grape stalks [22]. This C–O band absorption peak is observed to shift to 1032–1034 cm^{-1} when grape stalks are loaded with copper and nickel, respectively. Thus, it seems that this type of functional group is likely to participate in metal binding.

3.3. Equilibrium contact time

In Fig. 2 the percentage of Cu(II) and Ni(II) removed by grape stalks wastes versus contact time is shown together with variation of final pH. It can be seen that within 30 min both metals major sorption process was completed and the curve became flattened. It can also be observed that after this time no significant changes in final pH were observed. However, a shaking time of 1 h was used in all further sorption experiments to ensure equilibrium. Other authors using agriculture by-products and biomass wastes found similar sorption kinetics [8,15,17]. The rapid metal removal has significant practical importance, as this will facilitate the use of small sorbent volumes to ensure efficiency and economy.

3.4. Effect of pH

Although, the pH of initial metal solutions was varied within the range 1.0–6.5, it was observed that, initial

Table 1
Major cation content of the grape stalk wastes

No of washing	Ca^{2+}	Mg^{2+}	K$^+$	Na$^+$
(a) *Amount of cation released with 0.1 M HCl* (mg L^{-1})				
1	118.03	25.69	200	11.84
2	33.58	5.52	47.27	0.86
3	17.89	<0.16	8.24	<0.16
4	16.28	<0.16	1.70	<0.16
(b) *Amount of cation released with deionized water* (mg L^{-1})				
1	18.52	0.48	132.08	11.37
2	6.39	<0.16	41.41	4.29
3	5.24	<0.16	17.71	3.54
4	2.78	<0.16	14.02	2.45
(c) *Net amount of cation released* (meq g^{-1})[a]				
Total	0.382	0.1258	0.1071	0.0010

Amount of cation released by grape stalks after treatment with (a) 0.1 M HCl and (b) deionized water.
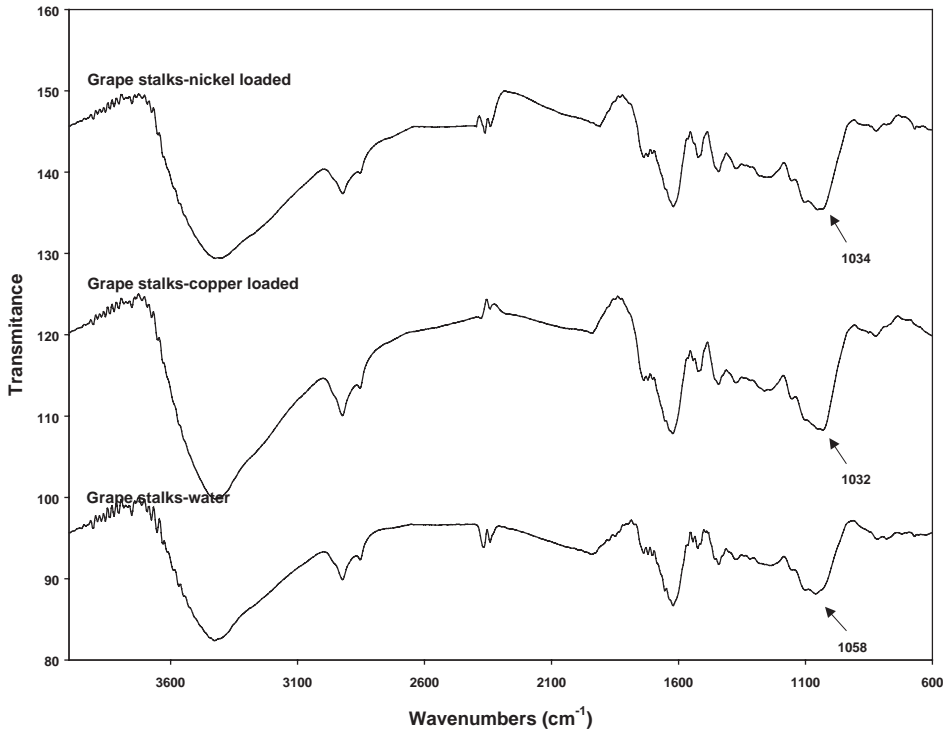[a] Difference between cations released with 0.1 M HCl and that by deionized water.

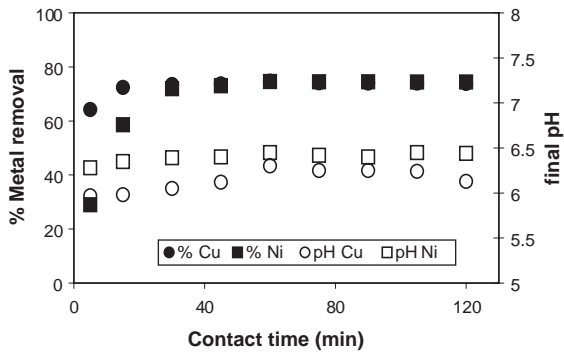Fig. 1. FTIR spectra of the grape stalks wastes in BrK disk.

Fig. 2. Copper and nickel removal using grape stalks and solution pH as a function of contact time. Total metal concentration $10 \, mg \, L^{-1}$; initial pH 6.0.
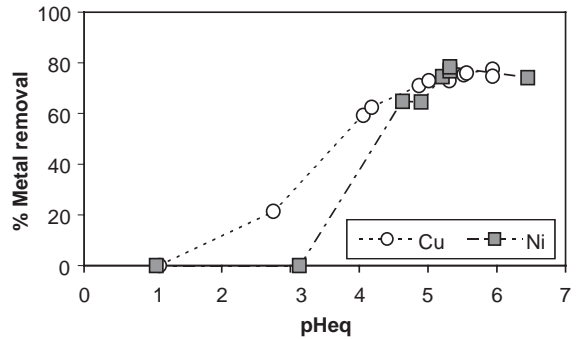

Fig. 3. Copper and nickel removal using grape stalks as a function of equilibrium pH. Initial metal concentration $10 \, mg \, L^{-1}$.

pH values greater than approximately 3.0 increased to pH values of around 5.5–6.0 after metal sorption. In Fig. 3 the percentage of Cu(II) and Ni(II) removed from solution versus equilibrium solution pH has been plotted. As shown metal removal increased with increasing pH solution and a plateau was reached at around pH 5.5–6.0. The same trend has also been reported in the removal of these ions by some other materials [23,24]. Other authors found similar optimum equilibrium pH values for the same metal sorption [15,17,25].

It is shown that for an initial metal concentration of $10 \, mg \, L^{-1}$, the uptake increased from practically zero at equilibrium pH 1.0 to 78% at pH 5.5 for both metals. The absence of sorption at low pH values, can be explained by the fact that at these pH values the H^+ concentration is high, which can compete with copper and nickel cations (at acidic pH both metals are present in solution as Cu^{2+} and Ni^{2+}) for surface sites. This fact is corroborated by the results obtained when the sorbent was washed with a 0.1 M HCl solution (Table 1). In this table, it is shown the amount of the alkaline and alkaline

earth metals (Na^+, K^+, Mg^{2+}, Ca^{2+}) displaced by protons into the solution.

3.5. Effect of sodium chloride concentration

The effect of sodium chloride concentration on metal uptake is shown in Fig. 4 where copper and nickel removal percentages at different sodium chloride concentrations (pH 6.0) are shown. In order to relate the metal removal with the different chloro-complexes, the species fraction diagrams of copper (II) and nickel (II) species in function of chloride concentration are also superimposed in the same figure. In both cases the percentage of metal removed decreased dramatically with increasing NaCl concentration, however, the reduction of the uptake was greater for nickel than for copper. For example increasing up to 0.1 mol L^{-1} NaCl results in about a 40% and 70% decrease of copper and nickel removal, respectively (see Fig. 4). The same effect was observed when cork wastes were used to remove copper and nickel from aqueous solutions [25], and when different sorbents were used to remove copper ions [15,23].

Some authors explain the reduction of metal removal percentage due to the increase of NaCl by the presence of competing Na^+ ions for metal binding [15], nevertheless this reduction can also be explained on the basis of the different ionic species present at different chloride concentrations. Looking at the species fraction diagrams of copper and nickel as a function of chloride concentration, it can be seen that an increase of chloride concentration results in a decrease of the free Cu^{2+} and Ni^{2+} species (solid lines in Fig. 4) and an increase in the formation of chloro-complexes (dashed lines in Fig. 4). Thus, the observed decrease in sorption might indicate that the sorbent has low affinity for copper and nickel chloro-complexes. It is likely, therefore, that high
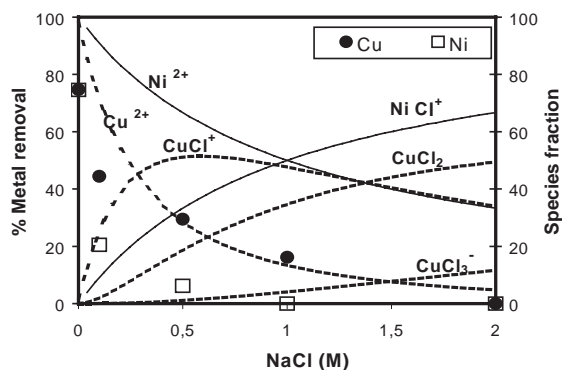

Fig. 4. Copper and nickel removal using grape stalks as a function of sodium chloride concentration. The fraction diagram of copper(II) and nickel(II) species is superimposed (dashed and solid lines). Initial metal concentration 10 mg L^{-1}; Initial pH 6.0.

sodium chloride concentration would cause a reduction of Cu^{2+} and Ni^{2+} on the surface of the solid. Thus, the observed decrease in metal sorption when NaCl concentration increases could be due either to the presence of sodium cation that would compete with metal cations and the chloride anion that provokes the decrease of free metal species (Cu^{2+} and Ni^{2+}) in solution.

3.6. Sorption isotherms

3.6.1. Single metal isotherms
Experimental equilibrium data points were fitted to the Langmuir-type adsorption isotherm model:

$$q = \frac{q_{max} \, b C_{eq}}{1 + b C_{eq}}, \tag{1}$$

where q is the amount of sorbate adsorbed per unit mass of sorbent, q_{max} is the maximum metal uptake per unit mass of sorbent (i.e. saturation), C_{eq} is the equilibrium concentration of sorbate in solution and b is the Langmuir constant related to energy of sorption which reflects quantitatively the affinity between the sorbent and the sorbate. The specific uptake q (mol g^{-1} dry solid) was calculated using the following equation:

$$q = (C_i - C_{eq})\frac{V}{w}, \tag{2}$$

where V(L) is the volume, C_i and C_{eq} (mol L^{-1}) are the initial and final solution concentration of the metal ion, respectively, and w(g) is the dry mass of the solid.

From the batch equilibrium data, a non-linear fit was done by means of the program SPSS 10.1 for Windows in order to obtain the model parameters q_{max} and b. This program minimizes the sum square of residuals (SSR):

$$SSR = \sum_{i=1}^{N} \left(q_i - \frac{q_{max} \, b C_i}{1 + b C_i} \right)^2. \tag{3}$$

The obtained results for q_{max} and b for copper and nickel are presented in Table 2, as well as the correlation coefficient and the SSR values. The applicability of the Langmuir model to the experimental data indicates monolayer coverage on the grape stalks surface by each of these metals. When considering both metals separately, it can be observed that the maximum uptake is slightly larger for nickel than for copper while the affinity of the sorbent toward copper is higher than for nickel as is indicated by the higher b value. The Langmuir parameters, q_{max} and b values obtained in this work are compared with other results reported in literature in Table 3. In general, values found in this work are similar to those obtained using yohimbe and pine bark wastes and slightly higher than the reported ones by the other referred wastes.

From the values obtained for these parameters the theoretical Langmuir curves were calculated. In Fig. 5,

Table 2
Langmuir parameters for copper(II) and nickel(II) sorption at pH 6.0 by grape stalks

Metal ion	q_{max} (mol g^{-1})	b (L mol^{-1})	R^2	SSR (mol^2 g^{-2})
Copper	1.593×10^{-4}	1.461×10^3	0.93	4.5×10^{-10}
Nickel	1.818×10^{-4}	1.365×10^3	0.99	1.1×10^{-10}

Table 3
Comparison of Langmuir parameters values obtained for copper(II) and nickel(II) sorption using grape stalks with values reported in literature using other similar materials at the same experimental conditions

Metal ion	Material	q_{max} (mol g^{-1})	b (L mol^{-1})	Source
Copper	Pine bark	1.49×10^{-4}	5.50×10^3	[9]
	Yohimbe bark	1.50×10^{-4}	1.60×10^4	[25]
	Cork bark	4.70×10^{-5}	1.10×10^4	[25]
	Grape stalks	1.59×10^{-4}	1.46×10^3	This work
Nickel	Pine bark	1.07×10^{-4}	1.27×10^3	[9]
	Yohimbe bark	1.50×10^{-4}	6.16×10^4	[25]
	Cork bark	7.00×10^{-5}	3.20×10^4	[25]
	Grape stalks	1.82×10^{-4}	1.37×10^3	This work

Fig. 6. The effect of nickel concentration on the sorption of copper using grape stalks, for (a) initial Cu(II) concentration of 0.24×10^{-3} mol L^{-1} and (b) initial Cu(II) concentration of 2.4×10^{-3} mol L^{-1}; Initial pH 6.0.
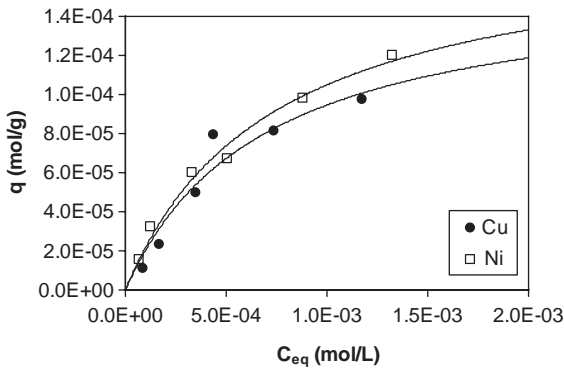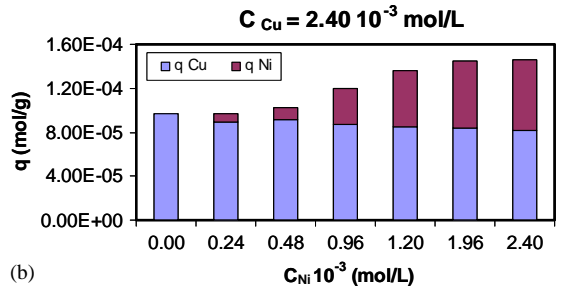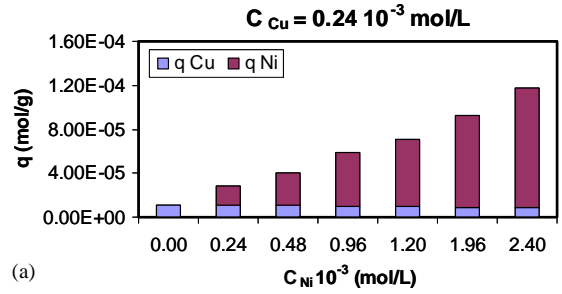

Fig. 5. Sorption isotherms of Cu(II) (●) and Ni(II) (□) using grape stalks. Solid lines represent predicted data by the Langmuir model, and the symbols are the experimental data. Grape stalks concentration: 10 mg mL^{-1}; Initial pH 6.0.

the experimental data of copper and nickel sorption and the respective Langmuir isotherms are plotted.

3.6.2. Binary-metal isotherms

Simultaneous removal of copper and nickel was investigated at pH around 6.0. The effect of the presence of nickel ions on the sorption of copper can be observed in Fig. 6 where the uptake of copper and nickel from the two-metal solution has been plotted versus the initial concentration of nickel, while the initial concentration of copper is held as a constant

parameter, $C_{Cu} = 0.24 \times 10^{-3}$ mol L^{-1} (Fig. 6a), $C_{Cu} = 2.40 \times 10^{-3}$ mol L^{-1} (Fig. 6b). The results indicate that removal of copper is moderately affected by the presence of nickel under the present experimental conditions. It can be pointed out that at the highest initial concentrations of nickel, a decrease of around 20% could be noted in the copper uptake. Seco et al. [24] found similar results when studying copper uptake in presence of nickel, cadmium and zinc. The effect of the presence of copper ions on the sorption of nickel can be observed in Fig. 7 that correspond to the initial nickel concentrations, $C_{Ni} = 0.24 \times 10^{-3}$ mol L^{-1} (Fig. 7a) and $C_{Ni} = 2.40 \times 10^{-3}$ mol L^{-1} (Fig. 7b). As shown the influence of the presence of copper on nickel sorption uptake is important, for both nickel initial concentrations, a decrease of around 50% in the nickel uptake can be noted for the highest copper concentrations.

The collected equilibrium data from the binary systems, were fitted to the extended-Langmuir model which can be written as [9]

$$q_1 = \frac{q_{max\,1}\,b_1\,C_{eq\,1}}{1 + b_1 C_{eq\,1} + b_2 C_{eq\,2}}, \tag{4}$$

$$q_2 = \frac{q_{max2}\,b_2\,C_{eq2}}{1 + b_1 C_{eq1} + b_2 C_{eq2}}, \tag{5}$$

where q_1 and q_2 are the amount of sorbate adsorbed per unit mass of sorbent for the first and the second component, respectively; $C_{eq\,1}$ and $C_{eq\,2}$ are the

equilibrium concentrations, $q_{max\,1}$ and $q_{max\,2}$ represent the maximum sorbate uptake and b_1 and b_2 are the Langmuir constants for the first and second components in a mixture of metal ions, respectively. The parameters of the model were found using the program SSPS 10.1 for Windows by minimizing [26]:

$$\text{SSR} = \sum_{i=1}^{N} \left[(q_{1\,i} + q_{2\,i}) - \left(\frac{q_{max\,1}\,b_1 C_{eq\,1\,i}}{1 + b_1 C_{eq\,1\,i} + b_2 C_{eq\,2\,i}} + \frac{q_{max\,2} b_2 C_{eq\,2\,i}}{1 + b_1 C_{eq\,1\,i} + b_2 C_{eq\,2\,i}} \right) \right]^2 .$$

The obtained results are shown in Table 4. As can be deduced from b values grape stalks affinity for copper is higher than for nickel; noted that this could also be concluded from single metal systems results. Based on the extended Langmuir model (Table 4), the q_{max} values of copper in the binary Cu–Ni system is similar to that for the single system while the q_{max} of nickel is slightly lower that of the single Langmuir isotherm (Table 2).
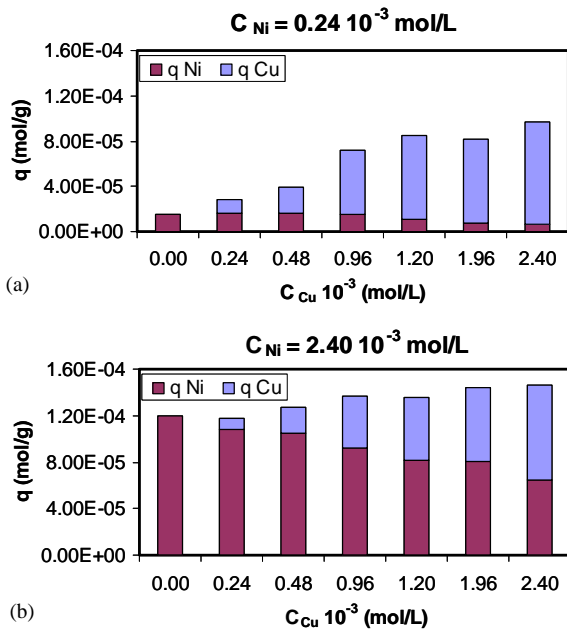

(a)

(b)

Fig. 7. The effect of copper concentration on the sorption of nickel using grape stalks, for (a) initial Ni(II) concentration: $0.24 \times 10^{-3}\,\text{mol}\,\text{L}^{-1}$ and (b) initial Ni(II) concentration: $2.4 \times 10^{-3}\,\text{mol}\,\text{L}^{-1}$; Initial pH 6.0.

Thus, it seems an apparent case of sorption competition. Some authors state that the unequal q_{max} values for single metal sorption and the estimated ones for the binary systems indicate that the solutes occupy different amounts of surface area [9]. Comparison of the b values obtained from the binary system with those of the single metal systems indicates that the presence of one metal increase the grape stalks affinity for the other metal. Al-Asheh and Duvnjak [9] obtained similar results by observing the effect of the presence of competing ions (Ni(II) and Cd(II)) on Cu(II) removal.

The most appropriate and correct way of representing the sorption equilibrium of two metal systems is to draw a three-dimensional sorption isotherm plot whereby one single metal uptake is plotted as a function of the final equilibrium concentration of the two metals.

A three-dimensional sorption isotherm plot has been constructed to represent the sorption equilibrium of copper and nickel for the binary system. In 3D plots (Figs. 8a–c) the copper uptake (q_{Cu}), nickel uptake (q_{Ni}) and total metal uptake (q_{Cu+Ni}), respectively, have been plotted as a function of the equilibrium concentration of the two metals (C_{Cu}, C_{Ni}). As shown in the three cases the experimental data points fit adequately the correspondent sorption isotherm surface.

In order to confirm that these surfaces describe the equilibrium with accuracy, we plotted the calculated (q_{cal}) versus the experimental (q_{exp}) amount of metal sorbed (see Fig. 9). The corresponding regression equations turned out to be $q_{cal} = 0.92\,q_{exp} + 0.47 \times 10^{-5}$ ($R^2 = 0.95$) and $q_{cal} = 0.95\,q_{exp} + 0.26 \times 10^{-5}$ ($R^2 = 0.95$) for copper and nickel, respectively. The near zero intercept and the slope close to unity confirm that the proposed model fits adequately the experimental data.

3.7. Ion-exchange mechanism

The existence of ion-exchange mechanism during the metal sorption by grape stalks wastes was investigated in this work by following the release of Ca^{2+}, Mg^{2+}, K^+ and H^+ from this sorbent after the sorption of copper and nickel. For these experiments 0.1 g of grape stalks were put into contact with 10 mL of metal solution ($500\,\text{mg}\,\text{L}^{-1}$) at pH 6. The release of cations after washing successively with deionized water was also

Table 4
Estimated parameters for copper(II) and nickel(II) sorption from the binary mixture copper(II)–nickel(II) using the extended Langmuir isotherm model

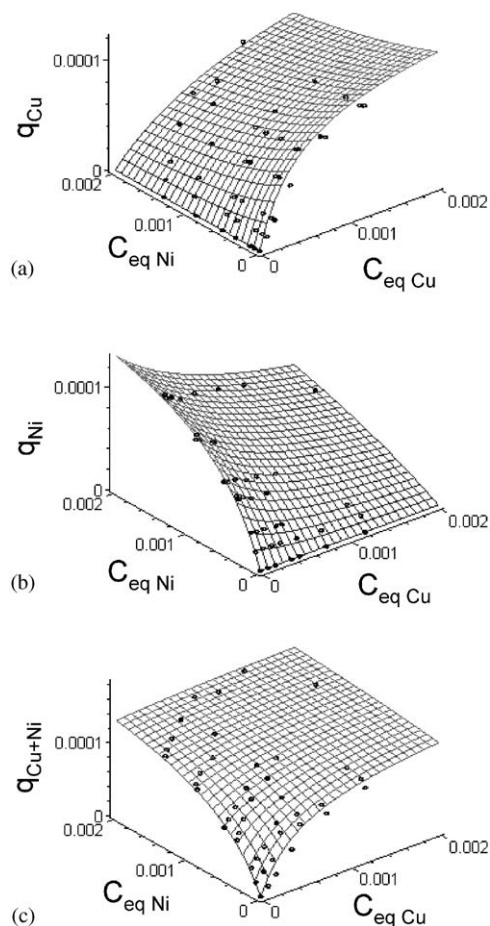| Metal ion	q_{max} (mol g^{-1})	b_1 (L mol^{-1})	b_2 (L mol^{-1})	SSR (mol^2 g^{-2})
Copper	1.509×10^{-4}	2.106×10^{3}		6.8×10^{-9}
Nickel	1.308×10^{-4}		1.848×10^{3}	6.2×10^{-9}

Fig. 8. Binary sorption isotherms Cu(II)–Ni(II). The surfaces are predicted by the extended Langmuir model and the symbols are experimental data. (a) Cu(II) uptake (b) Ni(II) uptake and (c) Cu(II) + Ni(II) uptake. Grape stalks concentration: 10 mg mL^{-1}; initial pH 6.0.

Fig. 9. Calculated vs. experimental q_{eq} (a) Cu(II) and (b) Ni(II).

measured. The net release of cations (meq g^{-1}) due to copper and nickel sorption presented in Table 5, have been calculated by subtracting the amount of metal cations released when washing with deionized water (control) to the amount of metal cations measured in the supernatant after copper and nickel sorption process. The results in Table 5 show a significant release of Ca^{2+}, Mg^{2+}, K^{+} and H^{+} from grape stalks due to the uptake of Cu(II) and Ni(II). This might indicate the displacement of these cations by the heavy metals. It appears that there was more Ca^{2+} released than the other cations. In the case that relative quantities of the heavy metals taken up by the sorbent and the alkaline and alkaline earth metals and protons released into the aqueous solution are shown to be approximately equal, this would mean that heavy metals are taken up from water predominately in exchange for cations present in the sorbent [27]. In the case of copper and nickel
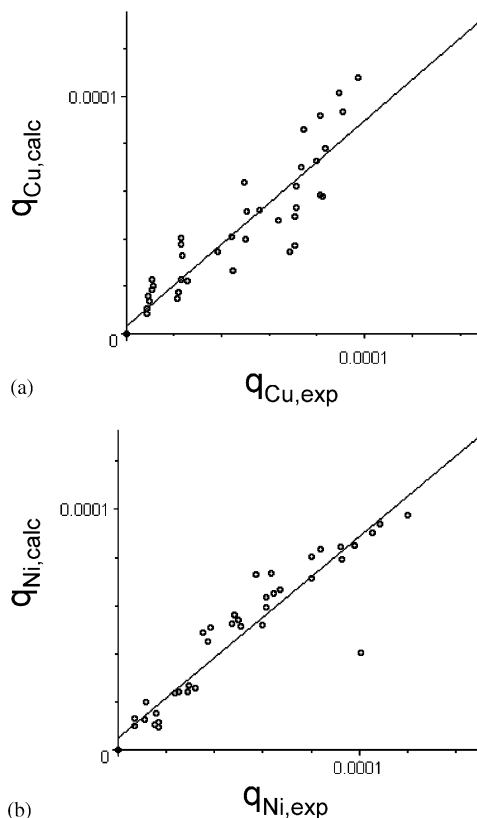
sorption on grape stalks, taking into consideration the stoichiometric ratio of cations, the release of one Ca^{2+} or Mg^{2+} ion would be equivalent to a release of two ions of H^{+} or K^{+}. Thus, the sum of cations released can be calculated as (Ca^{2+} + Mg^{2+} + K^{+}/2 + H^{+}/2). The coefficients $R_{b/r}$ were calculated as the ratio of metal bounded on grape stalks to the sum of cations released. In Table 5 it can be observed that the values of $R_{b/r}$ are close to 1. Thus, it seems that ion exchange might be an important mechanism involved in copper and nickel uptake by grape stalks.

4. Conclusions

Based on the results obtained, the rapid metal uptake facilitates the use of grape stalk wastes as sorbing material for Cu(II) and Ni(II) removal from aqueous solutions

Metal sorption is pH-dependent and maximum sorption for both metals was found to occur at pH 5.5–6.0. The presence of chloride concentration significantly reduced metal removal.

For single metal systems and metal binary systems, the Langmuir isotherm and the extended Langmuir

Table 5
Release of Ca^{2+}, Mg^{2+}, K^+ and H^+ due to sorption of Cu(II) and Ni(II) on grape stalks

System	Total metal bound (mM)		Amount of cation released (mM)				$R_{b/r}$[a]
	Cu^{2+}	Ni^{2+}	Ca^{2+}	Mg^{2+}	K^+	H^+	
Control[b]	—	—	0.483	0.057	1.266	0.006	
Cu^{2+}	1.168	—	1.140	0.214	1.905	0.224	0.95
Ni^{2+}	—	0.928	1.080	0.206	1.757	0.081	0.90
	Total metal bound (meq g^{-1})		Net amount of cation released (meq g^{-1})[c]				
Cu^{2+}	0.234		0.131	0.031	0.063	0.022	
Ni^{2+}		0.186	0.119	0.030	0.049	0.008	

Metal initial concentration: 500 mg L^{-1}. Grape stalks concentration: 10 mg mL^{-1}, pH 6.0.

[a] $R_{b/r}$: Ratio of metal bound to cation released.

[b] Grape stalks contacted with deionized water (control).

[c] Difference between metal released after metal sorption and that by the control.

models, respectively, fit adequately the experimental data.

In the Cu–Ni binary mixtures system a slight reduction was observed in the copper maximum uptake in the presence of nickel whereas the uptake of nickel is very much reduced by the addition of copper. The affinity of the sorbent for copper was always greater than for nickel, from both individual and mixed solutions.

The significant release of Ca^{2+}, Mg^{2+}, K^+ and H^+ from grape stalks due to the uptake of Cu(II) and Ni(II) indicates that ion exchange is the most important mechanism that takes place in the sorption process. However, further work should include performing experiments for making analysis by Scanning Electron Microscopy (SEM), Energy Dispersive X-ray (EDX), and Nuclear Magnetic Resonance (^{13}C NMR) in order to better understand metal binding mechanism.

Finally, we can conclude that grape stalks wastes may be reused for the decontamination of metal-containing effluents.

Acknowledgements

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