

Removal of lead(II) and cadmium(II) from aqueous solutions using grape stalk waste

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Received 15 June 2005; received in revised form 28 September 2005; accepted 5 October 2005

Available online 28 November 2005

Abstract

The sorption of lead and cadmium from aqueous solutions by grape stalk waste (a by-product of wine production) was investigated. The effects of the contact time, pH of the solution, ionic medium, initial metal concentration, other metal ions present and ligands were studied in batch experiments at 20 °C. Maximum sorption for both metals was found to occur at an initial pH of around 5.5. The equilibrium process was described well by the Langmuir isotherm model, with maximum grape stalk sorption capacities of 0.241 and 0.248 mmol g⁻¹ for Pb(II) and Cd(II), respectively, at pH around 5.5. Kinetic studies showed good correlation coefficients for a pseudo-second-order kinetic model. The presence of NaCl and NaClO₄ in the solution caused a reduction in Pb and Cd sorption, the latter being more strongly suppressed. The presence of other metals in the uptake process did not affect the removal of Pb, while the Cd uptake was much reduced. HCl or EDTA solutions were able to desorb lead from the grape stalks completely, while an approximately 65% desorption yield was obtained for cadmium. From the results obtained it seems that other mechanisms, such as surface complexation and electrostatic interactions, must be involved in the metal sorption in addition to ion exchange. © 2005 Elsevier B.V. All rights reserved.

Keywords: Metal sorption; Heavy metals; Biomaterials; Biosorption; Low-cost sorbents

1. Introduction

Different methods can be used for removing metals, including filtration, chemical precipitation, coagulation, solvent extraction, electrolysis, ion exchange, membrane process and adsorption [1]. Ion exchange and adsorption are the most common and effective processes for this purpose. Activated carbon and different types of ion-exchange resins are very often used in adsorption processes. However, their high price and regeneration costs have encouraged researchers to look for low-cost sorbing materials for the removal of heavy metals. A low-cost sorbent is here defined as one which is abundant in nature, or is a by-product or waste material from another industry. Such materials could be an alternative for the conventional sorbents [2,3]. Various waste materials produced as a result of different industrial processes,

such as pine bark [4], cork and yohimbe bark [5], spent grain [6], peanut hull pellets [7], and rice milling by-products [8] have been studied for the decontamination of metal-containing effluents. The sorption of metals by this kind of material might be due to the presence of carboxyl, hydroxyl, sulphate, phosphate, and amino groups that can bind metal ions.

In this context, we are investigating the potential of some vegetable wastes from industrial processes as alternative low-cost metal sorbents. One of these is grape stalk waste generated in the wine production process, which has been satisfactorily applied in copper and nickel removal [9]. In the present work, this sorbent is investigated for cadmium and lead removal from aqueous solutions. Both metals are released into the environment from different anthropogenic sources e.g. metal processing industries, battery and paint manufacturing, fossil fuel combustion, etc. There, they tend to accumulate and become concentrated throughout the food chain. This aspect, coupled with their persistence, results in a serious health hazard threatening water supplies and populations depending on them [10].

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Batch experiments were designed to study the influence of contact time, pH, ionic medium, metal concentration and the presence of other metal ions and ligands on the metal sorption process. Langmuir and Freundlich sorption isotherms were used to describe sorption equilibrium data.

Disposal of the exhausted sorbent loaded with heavy metal ions creates another environmental problem. This problem may be overcome to some extent by elution of the sorbed metals. This operation would allow both the recovery of metal solutions at higher concentrations for inertization and the recycling of the sorbent for subsequent uses. Desorption experiments were therefore carried out using HCl and EDTA solutions to investigate the possible elution of metal ions from the grape stalk waste.

2. Materials and methods

2.1. Materials, characterization of grape stalk waste, reagents and instrumentation

Grape stalk waste generated in wine production (supplied by a wine manufacturer from the Empordà-Costa Brava region, Girona, Spain) was rinsed three times with distilled water, dried in an oven at 110 °C until reaching constant weight, cut, and sieved for a particle size of 1.0–1.5 mm. The total ionic content had been determined previously [9] and the results were 0.61 mequiv. g⁻¹ of dry waste (0.36 mmol g⁻¹). The specific surface area of grape stalk waste (0.3760 m² g⁻¹) was determined by applying the BET (Brunauer, Emmet, Teller) method [11] using a gas mixture of 30% N₂/Ar on a Flowsorb II 2300, Micromeritics. In this method the external surface area can be determined from the quantity of gas adsorbed to form a monolayer over the surface of the solid. Elemental analysis of grape stalk waste performed with an elemental analyser (EA1110 CE Instruments, Italy) showed the material composition to be: 42.38% C, 0.8% N and 5.81% H.

Metal solutions were prepared by dissolving appropriate amounts of Pb(NO₃)₂(s) and Cd(NO₃)₂·4H₂O(s) in distilled water. Metal standard solutions of 1000 mg l⁻¹ were used for flame atomic absorption spectroscopy (FAAS) (VARIAN Absorption Spectrometer (Model 1275)) and inductively coupled plasma atomic emission spectroscopy (ICP-AES) (SPECTROFLAME, Spectro Analytical Instruments) calibration. All metal reagents were purchased from Merck (Darmstadt, Germany).

Measurement of pH was performed using a Crison Model Digilab 517 pH meter.

2.2. Metal uptake procedure

Batch experiments were carried out at 20 °C in stoppered glass tubes of 20 ml capacity by shaking a fixed mass of 0.1 g of dry grape stalks, with 15 ml of metal solution at 30 rpm (rotary mixer SBS-ABT4) until equilibrium was reached.

The solid was then removed by filtration through 0.45 μm cellulose filter paper (Millipore Corporation).

The final metal concentrations in the filtrates as well as in the initial solution were determined by FAAS.

The metal concentrations sorbed on the solid were calculated from the difference between the initial, C_i , and final, C_{eq} , metal concentration in solution. The following equations were used to compute the sorption percentage, %S, and the specific uptake by the sorbent, q_{eq} (mmol g⁻¹ of dry solid), respectively:

$$\%S = \frac{C_i - C_{eq}}{C_i} \times 100 \quad (1)$$

$$q_{eq} = (C_i - C_{eq}) \frac{V}{w} \quad (2)$$

where V (in l) is the solution volume and w (in g) the amount of dry sorbent used.

While the initial pH of the metal solution was adjusted to the desired value, no efforts were made to maintain the solution pH while metal was being sorbed. The pH was measured at the beginning and end of the experiments.

Each experiment was carried out in duplicate and the average results are presented.

2.3. Sorption kinetics and isotherm experiments

Initial experiments were performed to determine the contact time necessary to reach equilibrium. Different tubes were treated following the general procedure described above and samples were taken at predetermined time intervals ranging from 2 to 120 min. The initial metal concentration was 0.05 and 0.07 mmol l⁻¹ for Pb and Cd, respectively, and pH of 5.5.

For sorption isotherm experiments, the concentration ranges used were 0.15–1.9 mmol l⁻¹ for lead and from 0.039 to 4.5 mmol l⁻¹ for cadmium. The solution pH was 5.5 and the tubes were agitated for 2 h.

2.4. Effect of pH and ionic medium

The pH of metal solutions has been identified as the most important variable governing metal sorption [2]. 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 as well as the ionization of functional groups onto sorbent surfaces.

In order to evaluate the influence of this parameter on sorption, experiments were carried out at different initial pH values. The pH ranges chosen were 1–6.5 for lead and 1–8.0 for cadmium in order to avoid precipitation of metal hydroxides, which has been estimated to occur at pH > 6.5 for Pb(OH)₂(s) and pH > 8 for Cd(OH)₂(s) [12]. For these experiments, the initial metal concentrations were 0.96 and 1.2 mmol l⁻¹ for Pb and Cd, respectively, and the contact time was 2 h.

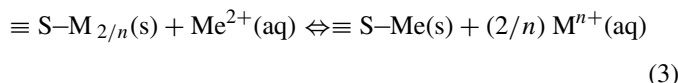
To study the influence of the presence in the solution of other ions on metal uptake, NaCl and NaClO₄ were chosen as ionic media. In media containing chloride, the metals studied form chloro-complexes while complexation does not take place in perchlorate media [13]. Therefore, the use of these media allowed us to observe the influence of chloride and sodium ions on metal uptake. For these experiments, different concentrations of the following sodium salts were used: 0.1, 0.5, 1.0, 1.5 and 2.0 mol l⁻¹.

The initial metal concentrations were 0.96 mmol l^{-1} . For all the experiments the initial pH was 5.5 and the contact time 2 h.

2.5. Ionic exchange mechanism

Villaescusa et al. [9], who determined the concentrations of K^+ , Mg^{2+} and Ca^{2+} released during copper and nickel sorption on grape stalks, reported that ionic exchange was the main mechanism involved in the sorption of these two metals. Therefore, in order to identify ion-exchange mechanisms during Cd(II) and Pb(II) ions sorption on grape stalks, we also measured the release of these cations in the filtrates obtained in single metal sorption experiments.

The ionic exchange reaction could be represented as



where M^{n+} represents K^+ , Mg^{2+} or Ca^{2+} and Me^{2+} , Pb^{2+} or Cd^{2+} .

For these experiments, 0.1 g of grape stalk waste was placed in contact with 15 ml of metal solution (2.4 and 4.5 mmol l^{-1} for Pb and Cd, respectively) with an initial pH of 5.5, for 2 h. After washing the material with deionized water, the release of the cations mentioned above was also measured and considered as a control. The filtrates thus obtained were analysed by ICP-AES to determine the cations released from the grape stalks.

2.6. Desorption experiments

For these experiments, grape stalk waste was pre-loaded with 1.9 and 4.33 mmol l^{-1} Pb and Cd solutions, respectively, following the general metal uptake procedure described above. The amount of both metals loaded on the grape stalks was around 0.25 mmol g^{-1} . After gently washing with distilled water, aliquots of these metal-loaded grape stalks (0.1 g) were then placed in contact with 15 ml of different solutions of either HCl (0.01 – 1.0 mol l^{-1}) or EDTA (0.001 – 0.1 mol l^{-1}) for 24 h. After the first experiment was completed, the suspensions were filtered, washed with distilled water and once again placed into contact with a fresh eluting solution (HCl or EDTA) of the same concentration. This operation was repeated three times.

2.7. Effect of the other metal ion on sorption

In order to study the influence of the presence of another metal in the solution, sorption of lead and cadmium was investigated in binary mixtures containing lead or cadmium and another metal at different concentrations and pH 5.5 and the tubes were agitated for 2 h.

For a constant Pb concentration of 1 mmol l^{-1} three different concentrations of cadmium, nickel and copper were studied: 0.5 , 1 and 2 mmol l^{-1} and for a constant Cd concentration of 1.78 mmol l^{-1} , the Pb, Ni and Cu concentrations tested were: 0.89 , 1.78 and 3.56 mmol l^{-1} . These concentrations represent half, equal and double concentration ratios of the additional metal with respect to the metal ions studied (Pb or Cd, respectively).

2.8. FTIR, SEM and EDX analysis

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 with a Bomem Michelson MB 100 Fourier Transform Infrared (FTIR) Spectrophotometer with a resolution of 4 cm^{-1} in the transmittance mode. An attenuated-total-reflection (ATR) accessory with a diamond crystal ATR (Golden Gate heated single-reflection diamond ATR, Specac-Teknokorma) was used to determine the spectra of the grape stalks before and after lead and cadmium sorption process. The surface structure of the grape stalks before and after lead and cadmium sorption process was also analysed by scanning electronic microscopy (SEM, Jeol JSM-6400) coupled with energy dispersive X-ray analysis (EDX).

For the sorption process, samples of grape stalks were loaded with a 1000 mg l^{-1} of metal solutions at pH 5.5 following the batch procedure described in metal uptake procedure section. Before analysis, suspensions were filtered, washed with 15 ml distilled water and this operation was repeated three times.

3. Results and discussion

3.1. Equilibrium contact time

The results are presented in Fig. 1. Those revealed that cadmium sorption was very fast compared to that of lead. After 5 min, sorption of cadmium was practically complete while after the same contact time only 50% of lead sorption took place. Taking into account these results, a contact time of 2 h was chosen for further experiments. It must be remarked that when both systems reached equilibrium, final pH also remained constant.

The rate at which sorption takes place is of most importance when designing batch sorption experiments. Consequently, it is important to establish the time dependence of such systems under various process conditions. Various sorption kinetic models have been used to describe the uptake of metals and the pseudo-second-order rate equation proposed by Ho and McKay has been widely used to describe metal ion and organic compound sorption on different biosorbents [14]. The

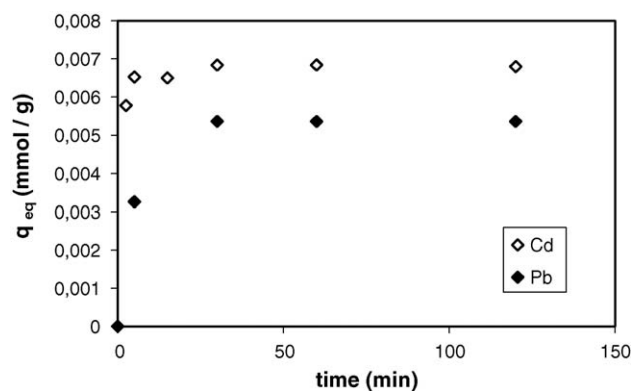


Fig. 1. Lead and cadmium sorption using grape stalks as a function of time at initial metal concentration of 0.05 and 0.07 mmol l^{-1} for Pb and Cd, respectively, and pH 5.5 and 25°C .

pseudo-second-order kinetic rate equation is

$$\frac{t}{q_t} = \frac{1}{kq_{eq}^2} + \frac{1}{q_{eq}}t \quad (4)$$

where q_{eq} is the amount of metal sorbed at equilibrium (mmol g^{-1}), k the rate constant of sorption ($\text{g mmol}^{-1} \text{min}^{-1}$) and q_t is the amount of metal sorbed on the surface of the sorbent at any contact time, t (mmol g^{-1}).

When the experimental data corresponding to Cd(II) and Pb(II) sorption on grape stalks at an initial concentration of 0.06 mol l^{-1} were introduced into Eq. (4), straight lines were obtained by plotting t/q_t against t , indicating that the process follows the pseudo-second-order rate equation (Fig. 2). Similar equilibrium metal sorption, q_{eq} , for Pb and Cd were obtained (0.0068 and $0.0069 \text{ mmol g}^{-1}$, respectively). The value of metal sorption rate (k) for cadmium sorption was almost 10 times higher than that for lead (81.0 and $8.4 \text{ g mmol}^{-1} \text{min}^{-1}$ for Cd and Pb, respectively). The obtained correlation coefficient values ($R^2 > 0.999$) indicate that both Cd and Pb sorption on grape stalks proceeds followed the pseudo-second-order equation. The fit of the experimental data to this equation suggests that the process controlling the rate may be a chemical sorption involving valence forces through sharing or exchange of electrons between sorbent and sorbate [15,16].

3.2. Effect of pH

Fig. 3 shows the percentage of Pb(II) and Cd(II) sorbed from solution versus equilibrium solution pH. As can be seen, metal removal increased with increasing solution pH and a maximum value was reached at an equilibrium pH of around 4.5 and around 6.5 for Pb and Cd, respectively. The same trend has also been reported in the removal of these ions by other vegetable materials such as spent grain [6], *Pinus sylvestris* [15] and crop milling wastes [17].

The absence of sorption at low pH values can be explained by the fact that at low pH values the H^+ concentration is high and therefore protons can compete with the lead and cadmium cations for surface sites, since at low pH values both metals are present in solution as Pb^{2+} and Cd^{2+} free cations. In addition, when pH increases, there is a decrease in positive surface

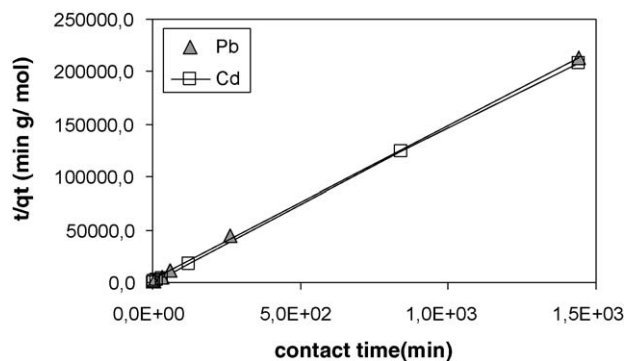


Fig. 2. Plots of Pb(II) and Cd(II) for the pseudo-second-order kinetic model using grape stalks at initial metal concentration of 0.05 and 0.07 mmol l^{-1} , respectively, at pH 5.5 and 25°C .

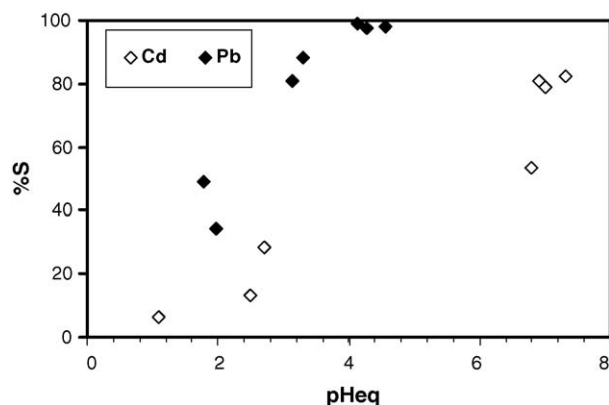


Fig. 3. Lead and cadmium sorption using grape stalks as a function of equilibrium pH. Initial metal solution concentration 0.96 and 1.2 mmol l^{-1} for Pb and Cd, respectively.

charge (since the deprotonation of the sorbent functional groups could occur), which results in a lower electrostatic repulsion between the positively charged metal ion and the surface of the grape stalks, favouring sorption.

3.3. Effect of ionic medium

Table 1 shows the effect of NaCl and NaClO_4 concentration on metal removal by grape stalk waste. From the results, it can be observed that NaCl exerts a greater influence than NaClO_4 on both metal sorption and that the effect of the salt is more accentuated for Cd than for Pb; 0.1 mol l^{-1} NaCl provokes a dramatic decrease in cadmium uptake (only 20% sorption) while 60% of Cd was removed when the same concentration of NaClO_4 was added to the metal solution. The results also show that in general, an increase in the medium ionic strength resulted in a decrease of uptake of both metals, NaClO_4 being more strongly suppressed as from a concentration 0.5 mol l^{-1} of both salts null cadmium uptake was observed.

The formation of chloro-complexes with both metal cations can explain the difference in metal sorption when NaCl was used instead of NaClO_4 . An increase in chloride concentration results in a decrease in the free Pb^{2+} and Cd^{2+} species and an increase in the corresponding chloro-complexes [13]. The decrease in metal removal in the presence of NaCl was also observed when cork

Table 1
Influence of NaCl and NaClO_4 concentration on metal uptake by grape stalk wastes

Concentration of ionic medium (mol l^{-1})	Removed (%)			
	NaCl		NaClO_4	
	Pb	Cd	Pb	Cd
–	100	100	100	100
0.1	84.9	19.6	89.0	59.1
0.5	45.9	0	69.0	0
1.0	27.3	0	54.9	0
1.5	17.9	0	52.2	0
2.0	11.9	0	43.3	0

Initial metal concentration 0.96 mmol l^{-1} at pH 5.5.

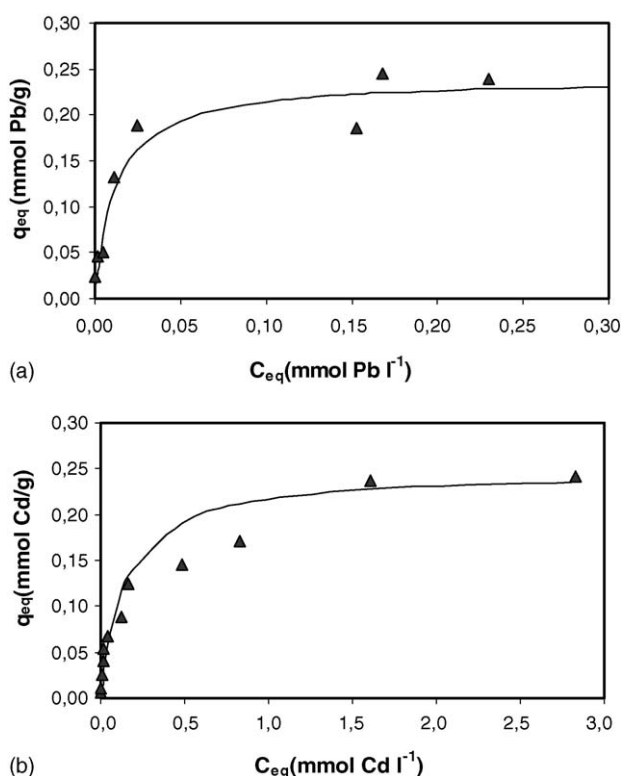


Fig. 4. Sorption isotherms of Pb(II) (a) and Cd(II) (b) using grape stalks. Symbols are the experimental data and the solid lines represent predicted data by the Langmuir model. Initial pH 5.5.

and grape stalk waste were used to remove copper and nickel from aqueous solutions [5,9] and spent grain for the removal of lead and cadmium [6].

The observed decrease in sorption in both media could be explained by considering the competitive effect of Na^+ cations on metal binding [18] and this effect is more accentuated for cadmium.

Other authors report that there is a decrease in sorption when increasing the ionic strength if the sorption process involves electrostatic attraction between the sorbent and the sorbate [19,20]. In this case, the increased amount of electrolyte can swamp the sorbent surface, decreasing metal ion access to the surface for sorption, and therefore the metal sorbed may be significantly decreased. Thus, in the case of cadmium and lead sorption by grape stalks, both phenomena could be considered to provoke the decrease in metal uptake, though electrostatic attraction is more important in the case of cadmium.

3.4. Sorption isotherms

The experiments were performed at the pH that resulted from solving the metal in water (around 5.5) without further adjustment, which correspond to maximum sorption obtained for both metals. Sorption experimental data for both metals are presented in Fig. 4.

To model the experimental equilibrium data, the Langmuir and the Freundlich isotherm models were used. The theoretical Langmuir sorption isotherm is the best known of all isotherms,

and describes the sorption of a solute from a liquid solution as follows:

$$q_{\text{eq}} = \frac{q_{\text{max}} b C_{\text{eq}}}{1 + b C_{\text{eq}}} \quad (5)$$

where q_{eq} is the amount of sorbate sorbed at equilibrium (mmol g^{-1}), q_{max} the q_{eq} value for a complete monolayer (mmol g^{-1}), C_{eq} the equilibrium concentration of sorbate in solution (mmol l^{-1}) and b is the Langmuir constant (l mmol^{-1}) related to the energy of sorption, which reflects quantitatively the affinity between the sorbent and the sorbate.

The Freundlich isotherm is an empirical equation based on sorption on a heterogeneous surface. This equation is commonly presented as

$$q_{\text{eq}} = K C_{\text{eq}}^{1/n} \quad (6)$$

where K and n are empirical constants indicative of sorption capacity and sorption intensity, respectively.

The Langmuir and Freundlich parameters presented in Table 2 were obtained by fitting the experimental data to the linearized equations (plot of C_{eq}/q against C_{eq} and of $\log q_{\text{eq}}$ against $\log C_{\text{eq}}$). By comparing the correlation coefficients obtained from both sorption models, one can see that the non-competitive Langmuir model provides the best correlation for the sorption of the two metal ions on grape stalks. The applicability of the Langmuir model to the experimental data indicates monolayer coverage on the grape stalks' surface by each of the metals. When considering the metals separately, it can be observed that the maximum uptake, q_{max} , is the same for both metals (0.24 mmol g^{-1}), while the affinity of the sorbent for lead is higher than it is for cadmium, as is indicated by the higher b value.

Similar maximum uptakes were found for copper and nickel: 0.182 and $0.159 \text{ mmol g}^{-1}$, respectively [9], when using the same material as sorbent. Nevertheless the maximum sorption values for Pb and Cd obtained in this work are greater than those found by Pagnanelli et al. [21] using olive pomace (0.076 and $0.062 \text{ mmol g}^{-1}$ for Pb and Cd, respectively), or by Taty-Costades et al. [15] using sawdust of *Pinus sylvestris* (0.106 and $0.169 \text{ mmol g}^{-1}$ Pb and Cd, respectively). Although, sorption capacities were similar to the values found for the removal of lead(II) and cadmium(II) by crop milling waste (0.242 and $0.356 \text{ mmol g}^{-1}$, respectively). In addition, these authors when studying the simultaneous uptake of lead and cadmium with the sorbents above mentioned also found that the material showed a higher affinity for Pb than for Cd.

The order of the affinity constants yields important information about the mechanisms operating in metal removal considering Pearson's Hard Soft Acid Base theory (HSAB) about complex formation [22]. This theory classifies different species as acids and bases arranged in a specific order of hardness assuming that hard bases react preferentially with hard acids and soft bases with soft acids. The supposed active sites on the sorbent contain oxygen atoms which are a hard base that will react preferentially with hard acids (the metals in solution). The order of hardness for acids of the metal ions gives Pb as harder than Cd, which is in agreement with the affinity constants, b , observed in

Table 2
Langmuir and Freundlich parameters for lead(II) and cadmium(II) sorption on grape stalks at initial pH 5.5

Metal ion	Langmuir			Freundlich		
	q_{\max} (mmol g ⁻¹)	b (l mmol ⁻¹)	R^2	K	$1/n$	R^2
Lead	0.241	82.84	0.959	0.296	0.161	0.729
Cadmium	0.248	7.00	0.983	0.212	0.457	0.910

the experimental data. In addition, several authors have related the metal ions' electronegativity to the preference shown by the sorbent for the metal ions. The electronegativity values for Cd and Pb are 1.69 and 2.33, respectively [23]. Again, this fact would explain the higher affinity of the sorbent for lead compared to cadmium [8].

From the Langmuir model parameter values, theoretical curves were calculated and plotted, and are also shown in Fig. 4. It can be seen that the experimental data correlate well with the Langmuir model.

3.5. Ionic exchange mechanism

The net release of Ca²⁺, Mg²⁺ and K⁺ due to the sorption process was calculated by subtracting the amount of these cations released when washing with deionized water (used as a control) from the amount of cations measured in the supernatant after metal sorption. The results in Table 3 show a significant release of Ca²⁺ followed by Mg²⁺ and K⁺ from grape stalks

due to the uptake of Pb(II) and Cd(II). This might indicate the displacement of these cations by the heavy metals. When the equivalent ratio of the heavy metals bound to the metal cations released is equal to unity, this means that heavy metals are taken up from solution predominately in exchange for cations present in the sorbent [24]. The coefficients $R_{b/r}$, calculated as the ratio of mequiv. g⁻¹ for each heavy metal (Pb and Cd) bounded on the grape stalks surface to the sum of cations released (also in mequiv. g⁻¹) are shown in Table 3. In this study it noticed that values of $R_{b/r}$ are around 2 for both metals, as opposed to the value obtained for Cu and Ni sorption with the same sorbent, which was close to unity [9]. Thus, from the results obtained, other mechanisms (i.e. surface complexation and electrostatic interactions) in addition to ion exchange must be involved in the case of the sorption of these two metals on grape stalks.

3.6. Desorption experiments

The desorption experiments demonstrate that three contacts with HCl 0.01 mol l⁻¹ or EDTA 0.001 mol l⁻¹ solutions was sufficient to desorb Pb from the grape stalks completely. However, for the Cd system, only 70% and 60% desorption was obtained when HCl 1.0 mol l⁻¹ or EDTA 0.1 mol l⁻¹ were used, respectively. In both systems it was observed that the first contact yielded practically the maximum desorption.

The results indicate that in the case of Pb, the grape stalks may be recovered for consecutive uses and, this metal may be recovered at higher concentrations.

The difference in behaviour observed between the two metals could be due to the different mechanisms of metal sorption. This is corroborated by the results obtained from IR spectra and the influence of ionic strength.

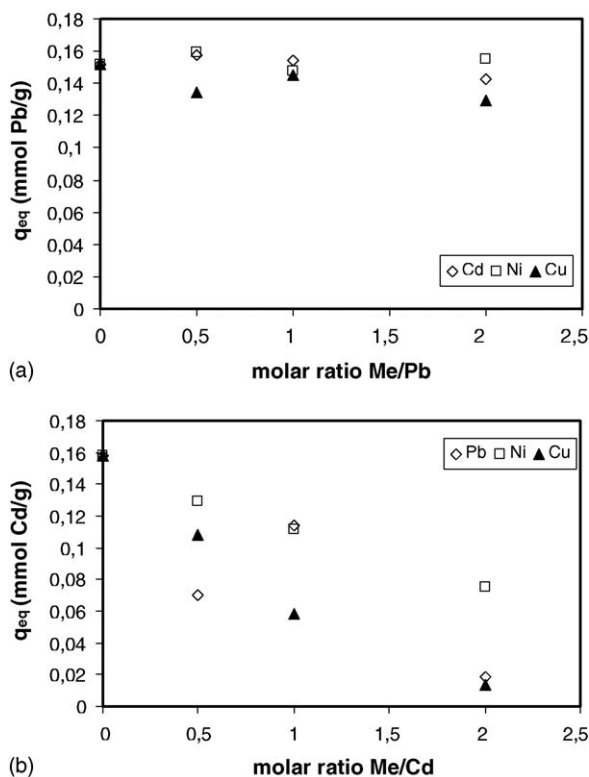


Fig. 5. The effect of Cd, Ni and Cu on the sorption of Pb for a initial lead concentration of 1.00 mmol l⁻¹ (a) and the effect of Pb, Ni and Cu on the sorption of Cd for an initial cadmium concentration of 1.78 mmol l⁻¹ (b) using grape stalks at initial pH 5.5.

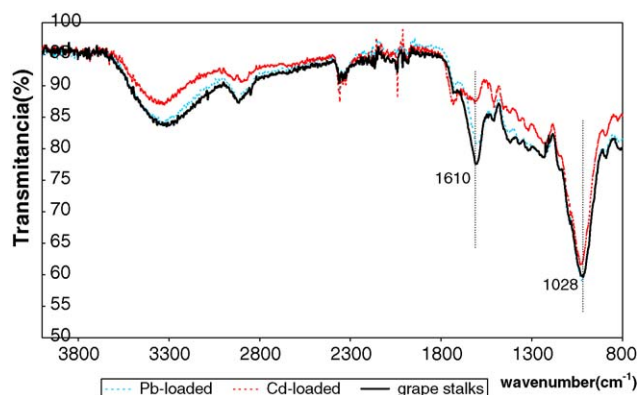


Fig. 6. FTIR spectra of the intact grape stalks and after loading with 1000 mg l⁻¹ of Pb and Cd solutions at pH 5.5.

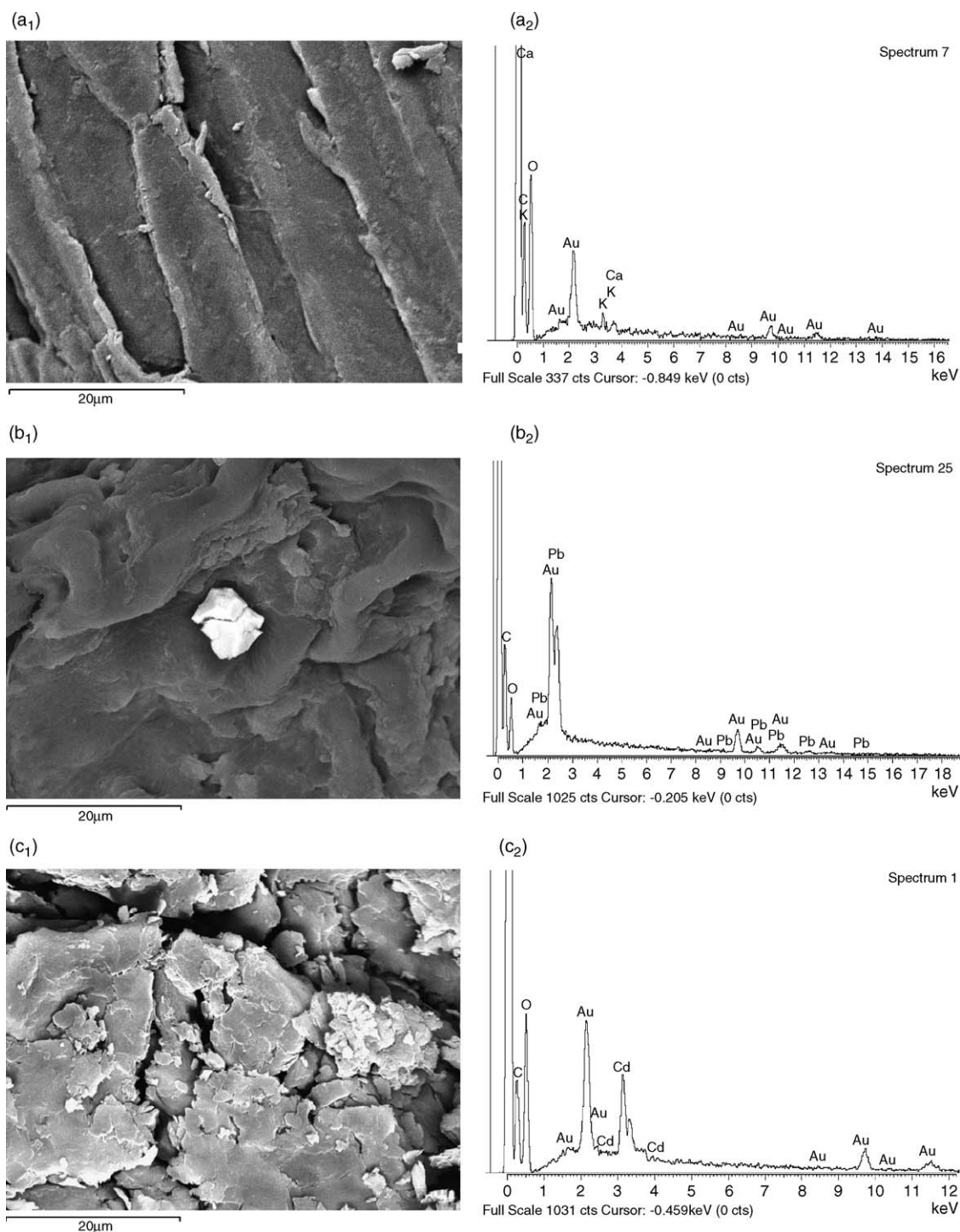


Fig. 7. (a₁) Bar 20 μm SEM micrograph and (a₂) EDX spectra of intact grape stalks. (b₁) Bar 20 μm SEM micrograph and (b₂) EDX spectra of grape stalks after loading with lead nitrate solution (1000 mg l⁻¹). (c₁) Bar 20 μm SEM micrograph and (c₂) EDX spectra of grape stalks after loading with cadmium nitrate solution (1000 mg l⁻¹).

3.7. Effect of the other metal ion on sorption

Fig. 5a and b shows the uptake of Pb and Cd, respectively, from binary mixtures against the molar ratio between the metals. The results indicate that the removal of Pb is not affected by the presence of other metal ions in solution (Fig. 5a) while the Cd uptake is greatly reduced by the addition of the tree

metal ions tested. This corroborates the greater affinity of grape stalks for Pb than for Cd found from the sorption isotherms experiments.

Fig. 5b shows that the decrease in the removal of cadmium is more marked when the concentration of the additional metal ion increases. Comparing the effect for the three metals, Cu and Pb give a similar fall which is higher than that yielded by Ni.

Table 3
Release of Ca^{2+} , Mg^{2+} , K^{+} due to sorption of Pb(II) and Cd(II) on grape stalks

System	Total metal sorbed (mequiv. g^{-1})		Net amount of cation released (mequiv. g^{-1}) ^a			
	Cd^{2+}	Pb^{2+}	Mg^{2+}	K^{+}	Ca^{2+}	$R_{b/r}$ ^b
Cd	0.520		0.0891	0.0256	0.182	1.8
Pb		0.855	0.105	0	0.260	2.3

Initial metal concentration: 2.4 and 4.5 mmol l^{-1} for Pb and Cd, respectively, at initial pH 5.5.

^a Difference between metal released after metal sorption and that by the control (deionized water).

^b $R_{b/r}$: ratio of metal bounded to cation released.

Thus, for Cd it would seem to be a case of sorption competition, and therefore the sorbent binding sites are not specific for each metal ion. However, in Pb systems, this is a dominant ion.

Other binary mixture studies have shown that Pb is also a stronger competitive ion than Ni for copper removal using apple wastes [18] and the efficiency in the removal of Cd is decreased by the presence of Cu [4].

3.8. Fourier transform infrared analysis FTIR

Fig. 6 shows the FTIR spectra of grape stalks and grape stalks loaded with lead and cadmium. The broad band at 3340 cm^{-1} indicates O–H stretching and the lower intensity band about 2940 cm^{-1} represents stretching of the O–H groups bound to methyl and methylene radicals; these groups are present on the lignin structure [25].

The region between 1610 and 1500 cm^{-1} is associated with C=C stretching in aromatic rings. The peak that was verified at 1610 cm^{-1} may be attributed to this vibration in the case of the grape stalks. This band exhibited a shift to lower frequencies, 1601 and 1603 cm^{-1} , when the grape stalks were loaded with Pb and Cd, respectively. A considerable decrease in the intensity of this band was observed after contact with Cd solutions. Thus, when the grape stalks were loaded with cadmium ions, the intensity of this band was strongly influenced by structures bordering on the aromatic nuclei. When the waste was loaded with Pb, this phenomenon was not observed. This difference can be attributed to the different sorption mechanism; cadmium could be bound to the lignin structure whereas lead is not. The intensities of the typical guaiacyl and syringyl bands observed at 1240 and 1325 cm^{-1} , respectively, also decreased in the case of grape stalks loaded with Cd. The deformations related to the C–H and C–O bonds observed at 1028 cm^{-1} also confirm the lignin structure of the grape stalks [26]. Thus, spectral analysis before and after metal binding suggested changes in the lignin structure present in the sorbent, which were more accentuated for cadmium sorption.

3.9. Analysis of grape stalks by SEM-EDX

Scanning electron microscopy, SEM, of grape stalks before and after sorption is shown in Fig. 7. These micrographs reveal clearly the apparition of pellets on the grape stalks surface (Fig. 7b₁ and c₁) whereas these pellets were absent on the sorbent before loading it with metallic ions solution (Fig. 7a₁). Some

modifications on the grape stalks particles after metal sorption can be observed, a strong density of pellets on grape stalks in the case of Cd sorption whereas one type of crystal distributed on the grape stalks surface in the case of Pb.

The pellets observed in SEM was also characterized by energy dispersive X-ray spectrometry (EDX). The EDX analysis shown in Fig. 7b₂ and c₂ reveal Pb(II) and Cd(II) signals, respectively, on the surface of the grape stalks after metal sorption. The presence of gold peaks in all spectra is due to the gold purposely settled to become the samples electric conductive.

4. Conclusions

The present experimental work establishes that grape stalk waste is an efficient sorbent in the removal of Pb(II) and Cd(II) ions from aqueous solutions at a near-neutral pH. The results obtained show that the kinetics of sorption of both metal ions on grape stalks follows a pseudo-second-order pattern. Moreover, sorption capacity is strongly dependent on the initial metal concentration and initial pH of solution.

The experimental data were well fitted to the Langmuir model and similar maximum uptake was found (0.24 mmol g^{-1}) for Pb and Cd at an initial pH of 5.5, and $20\text{ }^{\circ}\text{C}$.

The presence of NaCl and NaClO_4 in the medium caused a reduction in Pb and Cd sorption, with the latter being more strongly suppressed. Moreover, HCl or EDTA solutions were able to desorb lead from the grape stalks completely while around 65% desorption was obtained for cadmium. Then, in the case of lead, grape stalks may be recovered for consecutive uses and recovery of this metal at higher concentrations may be achieved.

The removal of Pb is not affected by the presence of other metals during the uptake process, while the Cd uptake is greatly reduced. Thus, for Cd it would seem to be a case of sorption competition, and therefore the sorbent binding sites are not specific for each metal ion while in Pb systems, this is a domination.

Finally from the IR spectra, it seems that aromatic nuclei were strongly modified for Cd systems compared to lead systems. This can suggest that surface complexation mechanism takes place in the case of Cd sorption.

These findings will be used in further works for the optimization of the sorption experimental conditions using grape stalk waste in continuous processes since this sorbent may be an alternative to more costly materials as activated carbon for the treatment of liquid wastes containing metals. In addition, the

proposed use of grape stalk waste as sorbent material implies the recycling of this waste that is first stored in big piles and is finally burned at the end of the wine production process.

Acknowledgements

We wish to thank Sergio Castillo for the cadmium experimental work, Xavier Ramis and Carlos Escudero for the IR spectra and Montse Marsal for the SEM analysis. This work was supported by the Spanish Ministry of Science and Technology through project grants PPQ2002-04131-C02-01 and PPQ2002-04131-C02-02.

References

- [1] J.W. Patterson, Industrial Waste Water Treatment Technology, Science Publishers, New York, 1997.
- [2] D. Kratochvil, B. Volesky, Advances in the biosorption of heavy metals, Trends Biotechnol. 16 (1998) 291–300.
- [3] S.E. Bailey, T.J. Olin, R.M. Bricka, D.D. Adrian, A review of potentially low-cost sorbents for heavy metals, Water Res. 33 (1999) 2469–2479.
- [4] S. Al-Asheh, Z. Duvnjak, Binary metal sorption by pine bark: study of equilibria and mechanisms, Sep. Sci. Technol. 33 (1998) 1303–1329.
- [5] I. Villaescusa, M. Martínez, N. Miralles, Heavy metal uptake from aqueous solution by cork and yohimbe bark wastes, J. Chem. Technol. Biotechnol. 75 (2000) 1–5.
- [6] K.S. Low, C.K. Lee, S.C. Liew, Sorption of cadmium and lead from aqueous solutions by spent grain, Process. Biochem. 36 (2000) 59–64.
- [7] P.D. Johnson, M.A. Watson, J. Brown, I.A. Jefcoat, Peanut hull pellets as a single use sorbent for the capture of Cu(II) from wastewater, Waste Manage. 22 (2002) 471–480.
- [8] C.R. Teixeira Tarley, M.A. Zezzi Arruda, Biosorption of heavy metals using rice milling by-products. Characterisation and application for removal of metals from aqueous effluents, Chemosphere 54 (2004) 987–995.
- [9] I. Villaescusa, N. Fiol, M. Martínez, N. Miralles, J. Poch, J. Serarols, Removal of copper and nickel ions from aqueous solutions by grape stalks wastes, Water Res. 38 (2004) 992–1002.
- [10] Environmental Protection Agency (EPA), Agency for Toxic Substances and Disease Registry (ATSDR), Toxicology Profiles, U.S. Department of Health and Human Services, Public Health Service, Atlanta, 1999.
- [11] S. Brunauer, P.H. Emmet, E. Teller, Adsorption of gases in multimolecular layer, J. Am. Chem. Soc. 60 (1938) 309–319.
- [12] C.F. Baes, R.E. Mesmer, The Hydrolysis of Cations, Wiley, New York, 1976.
- [13] I. Puigdomènech, 2001. <http://technetium.physchem.kth.se/Medusa>.
- [14] Y.S. Ho, G. McKay, Pseudo second-order model for sorption processes, Process. Biochem. 34 (1999) 451–465.
- [15] V.C. Taty-Costades, H. Fauduest, C. Porte, A. Delacroix, Removal of Cd(II) and Pb(II) ions, from aqueous solutions, by adsorption onto sawdust of *Pinus sylvestris*, J. Hazard. Mater. B 105 (2003) 121–142.
- [16] Y.S. Ho, W.T. Chiu, C.S. Hsu, C.T. Huang, Sorption of lead ions from aqueous solution using tree fern as a sorbent, Hydrometallurgy 73 (2004) 55–61.
- [17] A. Saeed, M. Iqbal, M.W. Akhtar, Removal and recovery of lead (II) from single and multimetal (Cd, Cu, Ni, Zn) solutions by crop milling waste (black gram musk), J. Hazard. Mater. B 117 (2005) 65–73.
- [18] S. Lee, J.W. Yang, Removal of copper in aqueous solution by apple wastes, Sep. Sci. Technol. 32 (1997) 1371–1387.
- [19] W. Stumm, J.J. Morgan, Aquatic Chemistry, Wiley, New York, 1996.
- [20] H. Niu, B. Volesky, Characteristics of anionic metal species biosorption with waste crab shells, Hydrometallurgy 71 (2003) 209–215.
- [21] F. Pagnanelli, S. Mainelli, F. Vegliò, L. Toro, Heavy metal removal by olive pomace: biosorbent characterisation and equilibrium modeling, Chem. Eng. Sci. 58 (2003) 4709–4717.
- [22] R.G. Pearson, Hard and soft acids and bases, J. Am. Chem. Soc. 85 (1963) 3533–3539.
- [23] J. Emsley, The Elements, 2nd ed., Oxford University Press, New York, 1991.
- [24] R.H. Crist, J.R. Martin, P.W. Guptill, J.M. Eslinger, Interaction of metals and protons with algae. 2. Ion exchange in adsorption and metal displacement by protons, Environ. Sci. Technol. 24 (1990) 337–342.
- [25] C.E. López Pasquali, H. Herrera, Pyrolysis of lignin and IR analysis of residues, Thermochim. Acta 293 (1997) 39–46.
- [26] C. Pascoal Neto, J. Rocha, A. Gil, N. Cordeiro, A.P. Esculcas, S. Rocha, I. Delgadillo, J.D. Pedrosa de Jesus, A.J. Ferrer Correia, ¹³C solid-state nuclear magnetic resonance and Fourier transform infrared studies of the thermal decomposition of cork, Solid State NMR 4 (1995) 143–151.