Biosorption of Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II) using different residual biomass

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The sorption behaviour of a biomass sample collected in an irrigation pond has been investigated. The biomass sample was selected from several ones collected in different eutrophised habitats of the Community of Madrid (Spain). The selection was made based on its effectiveness in the recovery of heavy metals from aqueous solution. The biomass sample selected was mainly composed of several Chlorophyta algae species and deciduous plants, and was tested to evaluate its behaviour in the biosorption of Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II), metals commonly found in industrial effluents. Preliminary studies were started in monometallic systems to determine the optimum values of pH, biomass concentration and sorption kinetics. The quantification of the sorption process was accomplished with sorption isotherms by fitting the experimental data to two mathematical models. The Langmuir model gave the best fit. Copper and lead were adsorbed in higher proportions, followed by nickel and zinc and, finally, cadmium. The metals more easily adsorbed in monometallic systems were also preferentially adsorbed in bimetallic systems. FTIR and acid-base titration were the analytical techniques used to establish sorption mechanisms, and carboxylic groups were identified as the main functional groups involved in the process.

Keywords: biosorption; heavy metals; Langmuir; Freundlich; residual biomass

1.   Introduction

Contamination by heavy metals is a form of pollution which usually results from industrial and mining drainage. Its importance is supported by the fact that such types of metals tend to accumulate and concentrate into different living organisms. Thus it can become a dangerous issue, considering that human beings are top of the food chain. Such kinds of pollution are especially relevant in aquatic media, since heavy metals are usually rare elements in such ecosystems [1,2]. Cadmium, copper, nickel, lead and zinc are the polluting metals most frequently found in industrial effluents.

Traditionally, the remediation of this type of pollution has been overcome by the use of separation methods based on physical or chemical properties of the components present in the solution to be treated, such as: chemical precipitation, filtration, cementation or electrodialysis, and so on.

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Nevertheless, the main drawback of those methods is that they produce large amounts of solid wastes like sludge residues, and additionally they are inefficient or economically non-viable at metal concentrations lower than 100 mg/L. Furthermore, some metals are extremely toxic for the environment at that concentration.

Biosorption with different types of biomass has been proposed as an alternative clean-up technique for aqueous effluents for decades. There are many works dealing with this process using different pure species of biomass: bacteria [3–5], yeasts [6–8] and algae [9–11]. Nevertheless, the inherent difficulty of using this kind of biomass has promoted another more economic and eco-friendly option, based on the use of biomass that is widespread and easily available [12]. In this way, recent studies have tested agricultural wastes [13], sawdust [14], rice polish [15], orange wastes [16], lawny grass [17], hemp fibres [18] and breweries' waste biomass [19], among other biosorbent materials. All these types of biomass contain cellulose, hemicelluloses, lignin and pectins that combine with functional groups (carboxylic, hydroxyl or phenolic) which have shown a good bond performance with metal cations through complexation and ion exchange as the main mechanisms involved.

However, biosorption studies using biomass from eutrophised habitats, with similar characteristics to the previous residual adsorbents and, therefore, also with a high sorption uptake, are not mentioned in the literature.

In an attempt to widen the spectrum of biomass with potential use as a biosorbent, the aim of the present work was to investigate the sorption behaviour of four heterogeneous types of biomass collected from different sources of the Community of Madrid in Spain. Residual types of biomass have the double advantage that they are biosorbent materials of low (or nil) economic cost and also that there is a contribution to recycling, decreasing the environmental impact in nature caused by this kind of residue. One of the types of biomass was selected to evaluate its sorption uptake of five metal ions: Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II). Previously, the optimum test conditions were determined with respect to pH, biomass concentration and contact time between the biomass and the metal solution. Later, the equilibrium parameters were determined from the plot of the sorption isotherms of Langmuir and Freundlich. The sorption uptake study with the residual biomass was extended to the treatment of bimetallic solutions. Finally, information on the molecular binding mechanism between the metal and the biomass was gathered from two different analytical techniques (FTIR spectroscopy and acid-base titration).

2. Materials and methods

2.1. *Biomass*

The residual biomass used was collected within the Community of Madrid (Spain) and can be divided into two groups: biomass obtained in eutrophised ecosystems and the leaves of deciduous trees. For the former group, three different potential locations were sampled: the Manzanares river near El Pardo, the Meaques stream near Siete Hermanas in Casa de Campo and an irrigation pond located in the Centro de Investigaciones Forestales (CIFOR). The composition of all biomasses are shown in Table 1 and are expressed as grams of each species per 100 g of biomass. The leaves of deciduous trees were collected at the campus of the Universidad Complutense de Madrid (UCM) and belonged to the arboreal species *Platanus hispanica* and *Populus alba*, in practically identical proportions.

Before biosorption experiments, all biomasses were dried in an oven at 60 °C until they reached constant weight, then ground in a ball mill and screened to a particle size <0.1 mm.

2.2. *Metal solutions*

The solutions tested were prepared from stock solutions of 1000 mg/L of Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II), using the following chemical reagents of analytical grade: $CdSO_4.8/3H_2O$, $CuSO_4.5H_2O$, $NiSO_4.7H_2O$, $Pb(NO_3)_2$ and $ZnSO_4.4H_2O$, respectively. pH was adjusted with dilute H_2SO_4 (0.1% v/v) for the metal solutions prepared from sulphate salts and with dilute HNO_3 (0.3% v/v) for those prepared from nitrates. In all cases, NaOH at a concentration of 1 g/L was used as the alkaline reagent.

2.3. *Biosorption tests*

The biosorption tests were carried out at a constant temperature in 100 mL of Erlenmeyer flasks containing the biomass and the metal solution in adequate proportions. The flasks were stirred magnetically for the whole biosorption process. During the control of tests, liquid aliquots, removed at different times, were centrifuged at 3,000 rpm for 3 minutes to allow the settlement of the biomass. Finally, the pH was measured and the metal concentration of the supernatant analysed by atomic absorption spectrophotometry in a Perkin Elmer 1100B spectrophotometer.

In the study of the influence of pH on the biosorption uptake, tests were run with 50 mg/L of metal solution and 0.5 g/L of biomass. The four values of pH selected were within the solubility range of metal species: 2, 4, 6 and 8 for Cd(II); 1.5, 3, 4 and 5 for Cu(II); 1.5, 3, 5 and 7 for Ni(II); 2, 4, 5 and 6 for Pb(II); and 1.5, 3, 5 and 7 for Zn(II).

Parallel to this, different biosorption tests were performed with four biomass concentrations (0.5, 1, 2 and 3 g/L) for each of the five metals and, in all cases, at a metal concentration of 10 mg/L. The initial pH was adjusted as in the previous study.

The biosorption study also included the plot of the corresponding isotherms, which were determined under the experimental conditions established in the preliminary studies and by varying the metal concentration between 10 and 150 mg/L. Therefore, the sorption process was quantified

Table 1. Composition of the different samples of biomass used (amount (g) in 100 g of biomass).

Species	Manzanares river (El Pardo)	Casa de Campo	CIFOR (First collection)	CIFOR (Second collection)
Acer negundo (1)	–	–	1.27	5.40
Aesculus hippocastanum (1)	–	–	6.94	24.70
Bambusia sp. (1)	–	–	0.08	0.01
Cladophora sp. (2)	–	66.70	20.18	–
Cyanobacteria (3)	0.70	0.20	0.31	1.01
Diatomea (4)	0.70	0.10	0.47	1.51
Eichhornia crassipes (1)	–	–	25.00	53.50
Euglena sp. (4)	–	–	0.16	0.50
Hedera helix (1)	–	–	0.20	–
Ilex sp. (1)	–	–	0.03	0.07
Ligustrum sp. (1)	–	–	0.11	0.27
Micrasterias sp. (2)	–	–	0.31	–
Oedogonium sp. (2)	–	–	26.93	–
Platanus orientalis (1)	–	5.00	3.80	11.21
Scenedesmus sp. (2)	0.70	–	0.47	1.51
Spirogyra sp. (2)	97.90	8.00	13.52	–
Ulmus sp. (1)	–	–	0.12	0.31
Ulothrix sp. (2)	–	20.00	–	–
Vinca sp. (1)	–	–	0.10	–

Notes: (1) Deciduous plants, (2) Chlorophyta algae, (3) Photosynthetic bacteria, (4) Protistes.

using the corresponding equilibrium parameters derived from the two mathematical models of Langmuir and Freundlich.

The equation of Langmuir was used in its linear form (1):

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{K}{q_{max}},$$

(1)

where q_{max} is the maximum metal uptake by the biomass and K the constant of Langmuir, which is inversely proportional to the affinity between metal and biomass. C_e and q_e are the metal concentration and the biomass sorption uptake at equilibrium, respectively.

In addition, the sorption uptake, q_e, was calculated as follows:

$$q_e = \frac{V(C_0 - C_e)}{B},$$

(2)

where V is the volume of the solution, C_0 the initial metal concentration and B the biomass concentration.

In the linear expression of the Freundlich model used (3), K_e represents the constant of Freundlich, which is related to the biomass sorption uptake, and $(1/n)$ is an indication of the sorption strength.

$$\log q = \log K_e + \frac{1}{n}\log C_e.$$

(3)

Finally, tests with two metals in solution were performed for two systems (Cu(II)–Cd(II) and Cu(II)–Pb(II)) by setting the concentration of each metal at 10, 25, 50 and 100 mg/L and varying the concentration of the other metal within the same range.

All experiments were performed in duplicate and the final values shown are the average of both tests.

2.4. *IR spectroscopy*

Fourier transform infrared spectroscopy (FTIR) allows a deeper understanding of the binding mechanism between the metal and the biomass through the identification of the functional groups involved in the process. For comparison purposes, the biomass was analysed in the presence of adsorbed metal (obtained in biosorption tests with Cd(II), Cu(II), Ni(II), Pb(II) or Zn(II)) as it was in its absence. The characterisation of the biomass by this technique required the preparation of compressed disks made of 100 mg of KBr and 2 mg of biomass. The transmittance spectra were obtained in a MIDAC Prospect-IR spectrophotometer in a wavelength range between 500 and 4,000 cm^{-1} and with a resolution of 4 cm^{-1}. The correction of the base line and the identification of bands were achieved using Nicolet OMNIC ESP software.

2.5. *Acid-base titration*

The acidity constant of the biomass (K_a), which controls its behaviour as a function of pH, was determined by titration. The determination of such constant is a way of establishing the main functional groups and the active sites of the biomass involved in the biosorption process. Titration was performed by adding 0.1 g of biomass into 100 mL of deionised water and keeping the mixture under magnetic stirring. The initial pH was adjusted to 3 with 0.1% HCl (v/v) to assure that all functional groups in the biomass were completely protonated. The titration started from that initial pH value by adding consecutive aliquots of 0.1 mL of 0.1 M NaOH and measuring the pH after each addition.

3. Results and discussion

3.1. *The sorption uptake of four types of residual biomass: comparative study*

The aim of this preliminary study was to select the biomass with the best metal sorption uptake from the four types of biomass collected, for future tests.

Table 2 shows the metal sorption uptake values obtained for the different biomasses at two different initial metal concentrations. The higher amount of metal per mass unit was recovered by the biomass collected in the irrigation pond of Centro de Investigación Forestal (CIFOR), followed by the biomass from the Merques stream (Casa de Campo), then from the leaves of deciduous trees collected at Universidad Complutense de Madrid (UCM) and, finally, from the Manzanares river (El Pardo).

The comparison of the composition of the different types of biomass used (Table 1) could justify the different sorption uptake values recorded. For instance, the biomass from UCM constituted 100% of deciduous plants, whereas the biomass from Casa de Campo and El Pardo contained more than 90% Chlorophyta algae. Finally, the biomass originally from CIFOR had the most variable composition: 61.4% Chlorophyta algae and 37.7% deciduous plants. Moreover, in the latter case there was a higher eutrophisation since it was a stagnant aquatic system with growth of photosynthetic and aerobic organisms. Since these organisms are consumers of the oxygen dissolved in water, they can generate an anaerobic medium incompatible with the metabolism of obligate aerobic microorganisms. As a consequence of this, the collection zone environment could have favoured a high diversity of biomass and, thus, a greater number of functional groups available for metal uptake.

Based on this preliminary study, the biomass from CIFOR was selected for subsequent studies.

3.2. *pH and biomass concentration: optimum test conditions*

The value of pH affects the distribution of metallic ion species in solution and the protonation or deprotonation of the biomass according to its pK_a [20]. This would explain the experimental results obtained for the five metals and the different pH values tested (Figure 1). In all cases, the metal sorption uptake increased with increasing values of pH. The most plausible explanation is that an increase of pH would favour the deprotonation of the biomass and the subsequent equilibrium shift to the right (4), provoking a greater attraction between metal cations and negatively charged ligands [21–24]. After reaching a predetermined sorption pH value (4 for Cu(II) and Cd(II) and 5 for Zn(II), Pb(II) and Ni(II)), the value of q slightly disminished possibly because hydrolysis transformed metal cations into alkaline cations, which are more difficult for the biomass to adsorb [20].

Table 2. Metal sorption uptake, q (mmol metal/g biomass), of several biomass samples from different locations at an initial metal concentration of 10 and 150 mg/L.

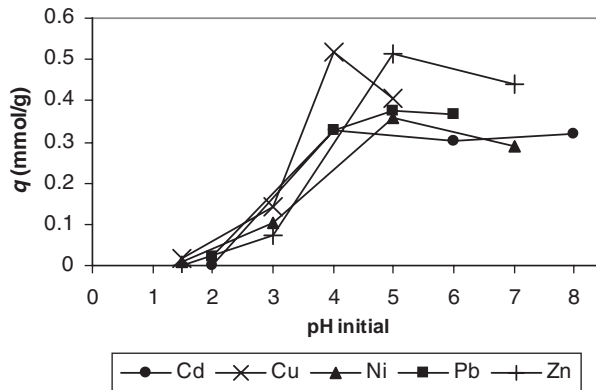|	CIFOR		Casa de Campo		UCM		El Pardo	
	10 mg/L	150 mg/L	10 mg/L	150 mg/L	10 mg/L	150 mg/L	10 mg/L	150 mg/L
Cd(II)	0.071	0.267	0.068	0.222	0.048	0.150	0.012	0.067
Cu(II)	0.142	0.504	0.134	0.393	0.079	0.157	0.044	0.110
Ni(II)	0.126	0.341	0.158	0.290	0.044	0.073	0.044	0.153
Pb(II)	0.043	0.405	0.043	0.347	0.043	0.267	0.039	0.159
Zn(II)	0.147	0.306	0.135	0.229	0.067	0.102	0.061	0.229

Figure 1. Influence of pH on metal sorption uptake.

Those pH values were used in the rest of biosorption experiments.

$$HB \leftrightarrows H^+ + B^- \qquad K_a = \frac{[H^+][B^-]}{[HB]} \qquad (4)$$
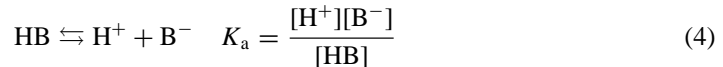
Figure 2 depicts the evolution of pH versus time for zinc. Similar results were obtained for the rest of metals. In all cases, changes in pH were negligible over time for initial pH values lower than 2, either because of the large amount of protons in the solution or due to the damage of the biomass by the high acidity. At initial pH values in the range between 3 and 5, there was an increase of pH over time and the biomass behaved as an acceptor of protons. Conversely, at initial pH values higher than 6, the solution was acidified and the biomass behaved as a donor of protons. Those changes of pH would justify the shift of equilibrium in reaction (4).

For the selection of the biomass concentration, tests were performed in the range between 0.5 and 3 g/L (Figure 3) and showed that metal sorption uptake decreased with increasing this parameter; this is in agreement with other results published by different authors [25,26]. The most effective biomass concentration (0.5 g/L) was selected for the subsequent tests. In spite of the fact that these experiments should be considered only as a pre-evaluation of the effect of the biomass concentration on the sorption level, different authors [27,28] have pointed out that such
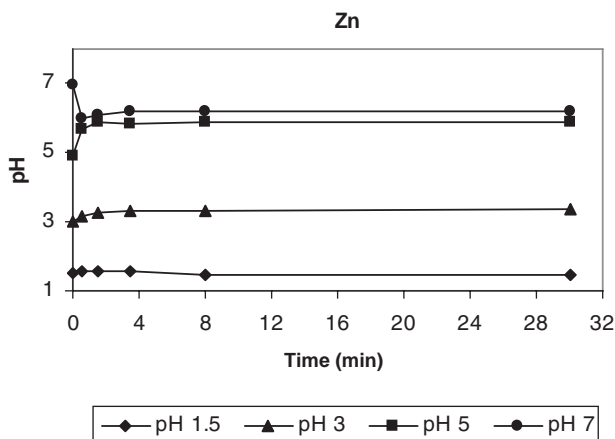

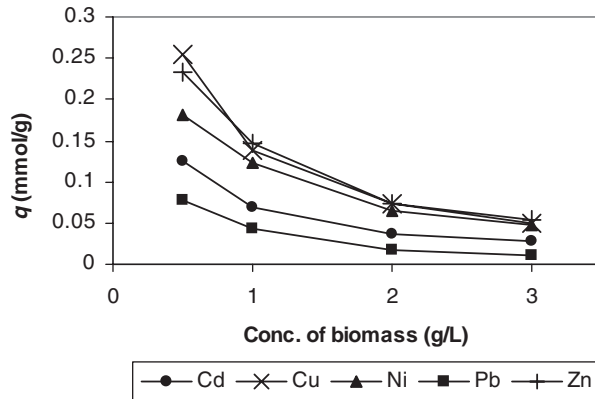Figure 2. Evolution of pH versus time.

Figure 3. Influence of biomass concentration on metal sorption uptake.

behaviour could be mainly due to the fact that high biomass concentrations favour the electrostatic interaction between cells and the formation of agglomerates that result in a decrease of the number of available active sites for metal sorption caused by a shell effect.

3.3. *Sorption isotherms*

The sorption isotherms allow the determination of both the influence of metal concentration on sorption uptake and the equilibrium parameters to quantify the process by fitting the experimental data to mathematical models such as Langmuir's (1) or Freundlich's (3). Both models have been commonly used in the interpretation of biosorption processes [29–31].

This study was also performed using the biomass of a second collection from the irrigation pond (CIFOR) (Table 1). This biomass collection was made one year later but at the same seasonal time, with the idea of avoiding the effect of climatic factors. This also allowed a check on whether the results obtained were reproducible or not.

Figure 4 shows the sorption isotherms obtained with the five metals studied and the biomass corresponding to the first (a) and to the second (b) collection. In both cases, there is an increase of the equilibrium metal concentration in solution (C_e) and also an increase of the sorption uptake (q) until reaching a limit value corresponding to the saturation of all metal binding sites on the biomass (q_{max}). That limit value is the maximum metal amount that can be recovered by the biomass. Figures 5 and 6 depict the linear regressions of the data of the isotherms of Langmuir and Freundlich, respectively. The values of constants from both models, and the linear correlation coefficient (R^2), which is a measurement of the fitting adjustment of experimental data to the given model, are displayed in Table 3. The correlation coefficients shown in those tables were always higher for the Langmuir model. That means that the experimental results corresponding to the biomass from both collections adjusted better to that model than to the Freundlich model. Therefore, these results would be an indication that: (1) the biosorption process takes place in monolayers; (2) the process is uniform for all the active sites; (3) there is no effect of the adsorbed ions on the sorption of other ions on neighbouring active sites; and (4) the saturation of the biomass by metal is possible [24,30].

Thus, from the values of q_{max} in the Langmuir model, except for a few minor differences, copper and lead were the metals preferentially adsorbed while cadmium had the lowest retention by the biomass. Zinc and nickel presented an intermediate behaviour. The same order was deduced from the comparison of the sorption uptake given by the K_e parameter from the Freundlich model: Pb(II) $\sim$ Cu(II) > Zn(II) $\sim$ Ni(II) > Cd(II). The metal sorption uptake sequence given above
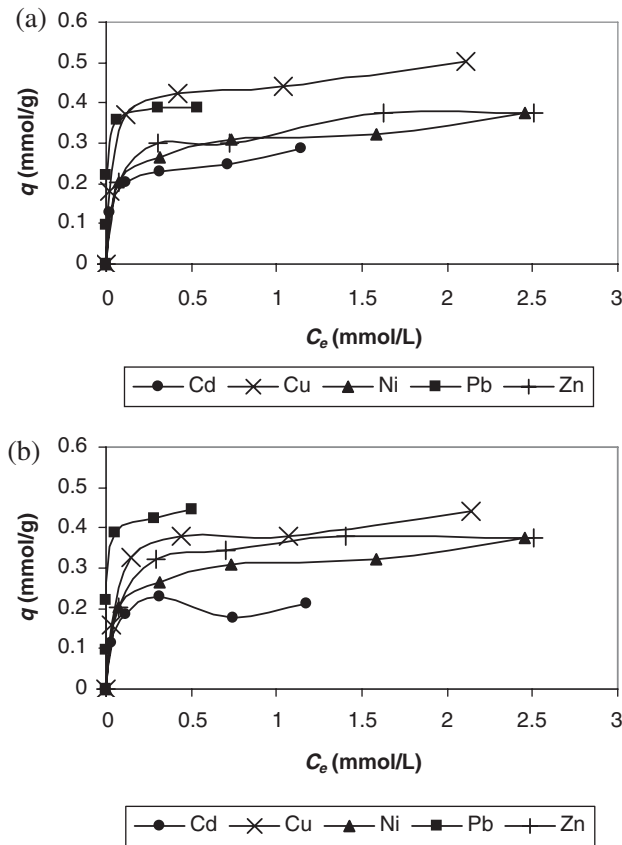
Figure 4.   Sorption isotherms of the biomass collected in the irrigation pond (CIFOR): (a) first and (b) second collection.

could be justified considering the electronegativity values of different metal cations [32]. In fact, the higher the ion electronegativity the higher the attraction for its electrons, and stronger becomes the attraction to the negative charge of the biomass ligands. Of the five metals tested, lead and copper present the higher electronegativity (2.33 and 1.91, respectively), and they were mainly adsorbed. The other three metals (cadmium, nickel and zinc), with lower electronegativity values (1.69, 1.7 and 1.65, respectively), were adsorbed in smaller amounts, especially cadmium, because of its large ionic radius.

The global analysis of the parameters of the Langmuir model for both biomass collections show that they behaved similarly. However, important differences arise when analysing their composition (Table 1). Unlike the first collection of biomass that contained 61.4% Chlorophyta algae and 37.7% deciduous plants, in the second collection, 90% of the dry weight biomass consisted of deciduous plants. Nevertheless, considering the basic constituents of the cell walls, both the samples would have contained similar polymeric compounds. The cell wall of green algae is rich in cellulosic carbohydrates and proteins that, in turn, are bonded to polysaccharides, forming glycoproteins. Those compounds contain several functional groups potentially involved in biosorption processes (amino, carboxyl, phosphate, hydroxyl, etc.). In the case of the vegetal cell wall of deciduous plants, their principal components are also carbohydrates (mainly cellulose) and structural proteins. In fact, green algae have more similarities with Embryophyta (terrestrial plants) since they derive from the same phylogenetic branch as Bryophyta and vascular plants [33]. The contribution to the biosorption process of the rest of species (photosynthetic bacteria and protists) was probably insignificant due to their very low content in the biomass.
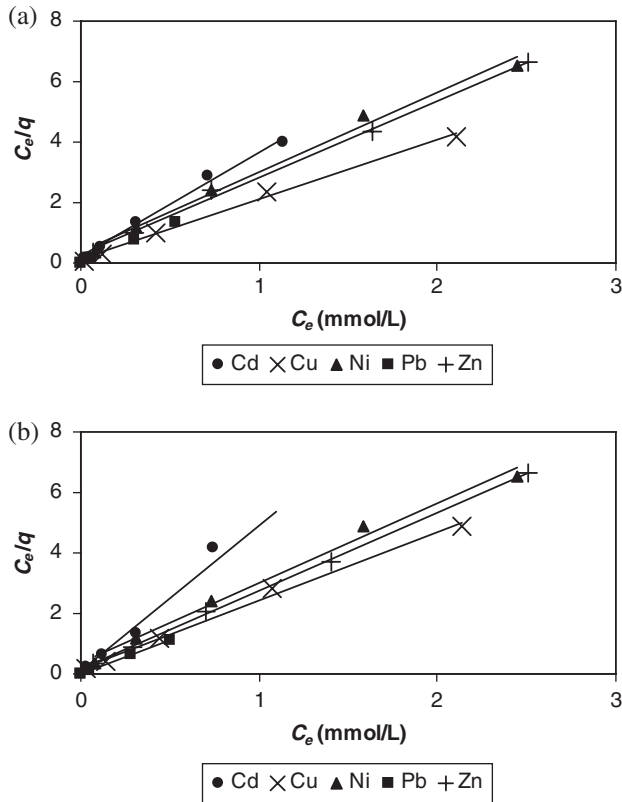
Figure 5. Langmuir sorption isotherms of the biomass collected in the irrigation pond (CIFOR): (a) first and (b) second collection.

In addition, since both samples of biomass collected in the irrigation pond (CIFOR) showed similar sorption uptakes, those results could be extrapolated to further collections without having important errors. Thus, the later characterisation of the biomass was only focused on the first collected biomass.

3.4. *Bimetallic tests*

In an attempt to investigate more complex systems, the behaviour of the biomass was analysed in solutions containing two metals. Two bimetallic systems were tested: the Cu(II)–Pb(II) system, since these two metals presented the best sorption uptake in monometallic systems, and the Cu(II)–Cd(II) system, as these metals represent the best and the worse sorption uptake. The idea was to analyse the competition between different metal cations for the same active sites of the biomass.

The pH value was set at 4.5, the average value between those found as the most adequate for such metals, and the concentration of the second metal was varied for each concentration of the first metal. The sorption uptake of each other metal for each system is shown in Figures 7 and 8. For the Cd(II)–Cu(II) system, the most relevant finding was that copper provoked a very marked decrease in the sorption level of cadmium (Figure 7(a)) than in the opposite case (Figure 7(b)). Cadmium sorption was practically nil at higher concentrations of copper, in agreement with the better sorption uptake shown by the biomass towards copper in monometallic systems. Nevertheless, copper sorption gradually decreased when cadmium concentration increased from 10 mg/L (0.09 mmol) to 100 mg/L (0.89 mmol). Conversely, for the Cu(II)–Pb(II) system, both metals had
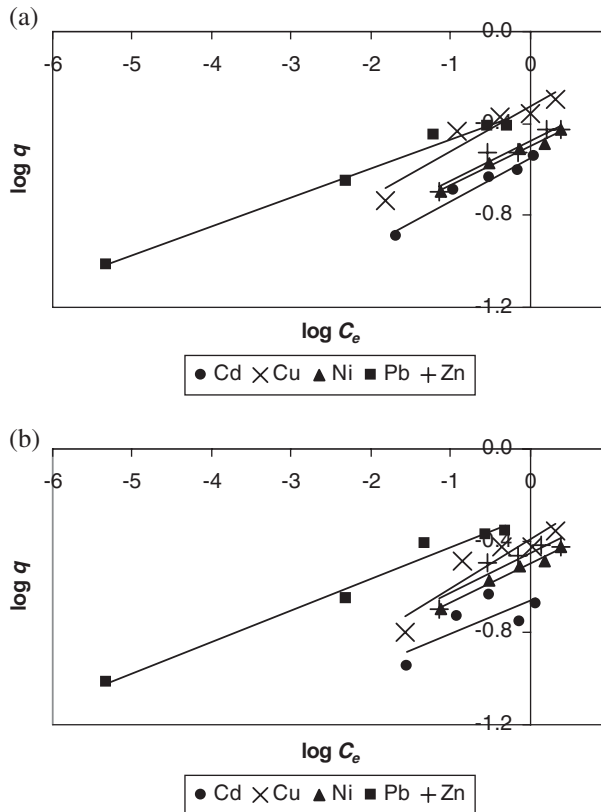
Figure 6.   Freundlich sorption isotherms of the biomass collected in the irrigation pond (CIFOR): (a) first and (b) second collection.

Table 3.   Langmuir and Freundlich constants.

		Langmuir			Freundlich		
Element		q_{max}(mmol/g biomass)	K (mmol/L)	R^2	K_e (mmol/g biomass)	$1/n$	R^2
Cd(II)	1st rec.	0.290	0.055	0.993	0.576	0.188	0.955
	2nd rec.	0.207	0.019	0.982	0.517	0.143	0.602
Cu(II)	1st rec.	0.508	0.067	0.996	0.719	0.196	0.897
	2nd rec.	0.446	0.079	0.994	0.675	0.213	0.859
Ni(II)	1st rec.	0.388	0.141	0.991	0.606	0.169	0.979
	2nd rec.	0.381	0.141	0.991	0.606	0.169	0.979
Pb(II)	1st rec.	0.388	0.003	1.000	0.707	0.125	0.986
	2nd rec.	0.445	0.005	0.999	0.746	0,137	0.981
Zn(II)	1st rec.	0.393	0.116	0.996	0.621	0.174	0.929
	2nd rec.	0.388	0.067	1.000	0.634	0.175	0.868

a similar effect on the sorption uptake of the other metal, decreasing this value while increasing the concentration of the second metal. However, this effect was more pronounced on copper (Figure 8(a)) than on lead sorption (Figure 8(b)), which would confirm the better sorption uptake of the biomass for lead than for copper. These results seems to indicate that, in a first approach,
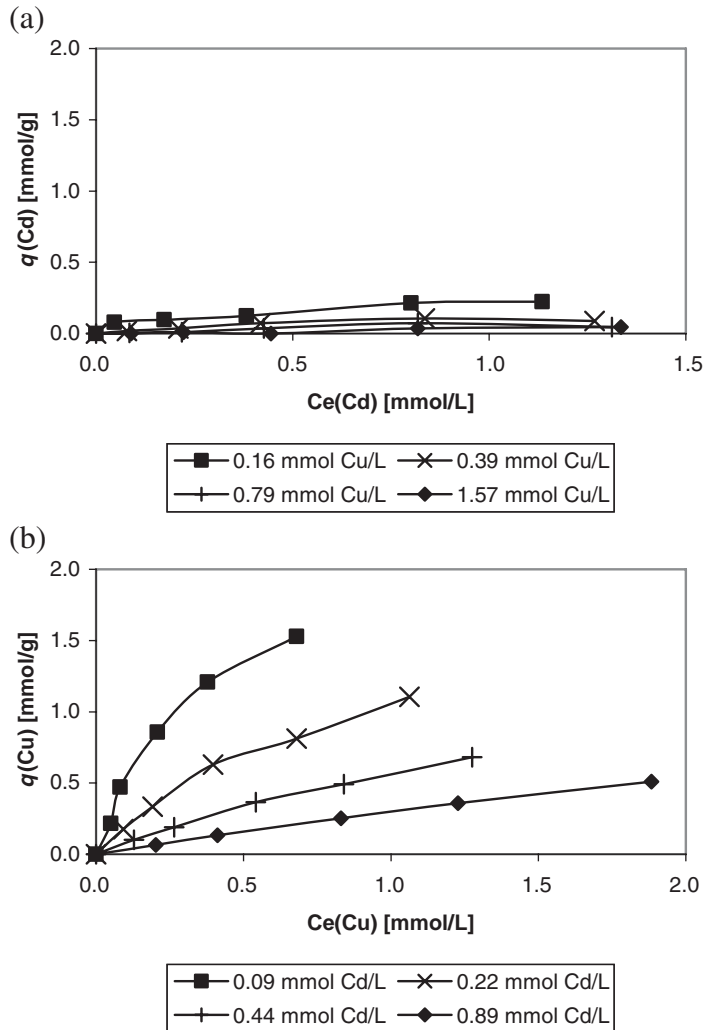
Figure 7. Variation of cadmium sorption uptake at different concentrations of copper (a) and of copper at different concentrations of cadmium (b).

the metals more easily adsorbed in monometallic systems are also preferentially adsorbed in bimetallic systems, and this could probably be extrapolated to more complex systems [34–36].

3.5. *Analysis by Fourier transform infrared spectroscopy (FTIR)*

FTIR is a useful technique to gain information about sorption processes on the biomass structure by determining the functional groups responsible for metal binding based on their ability to adsorb electromagnetic energy in the infrared spectral region.

The infrared spectrum of the original biomass (Figure 9(a)) shows several vibrational bands as described below. The stretching band at $3400\,cm^{-1}$ corresponds to the hydroxyl group ($-OH$) of celluloses, proteins and pectic compounds [37–39]; nevertheless it could also correspond to carboxylic groups as they show an intense band between 3550 and $2500\,cm^{-1}$ [40]. The stretching band at $2900-2800\,cm^{-1}$ is related to the alkene $-C-H$ bond, which frequently shows more than
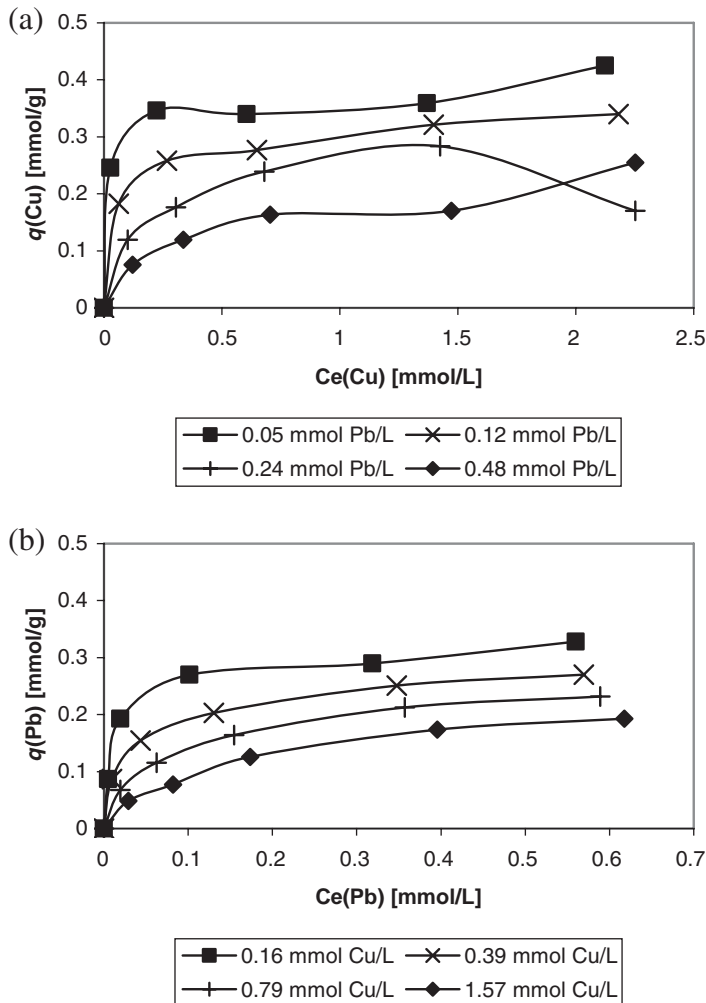
Figure 8. Copper sorption uptake at different concentrations of lead (a) and lead sorption uptake at different concentrations of copper (b).

one peak due to the symmetric or asymmetric stretching bond [32]. Carboxylic groups ($-COOH$) or derivates, such as carboxylates ($-COONa$, $-COOCa$) or metoxils ($-COOCH_3$), also appear at $1800–1600\,cm^{-1}$; specifically the $-C=O$ bond presents an intense band at the end of the lower wavenumber of such a range. Another band associated to carboxylic groups, though less important, appears around $1400\,cm^{-1}$ and is related to the OC–OH bond (together with $-ONa$, $-OCa$ and $-OCH_3$). The carboxyl:carboxilate ratio is higher the smaller the size of the latter peak. Those groups are mainly found in pectic compounds of the matrix [37–41]. At $1100\,cm^{-1}$, the stretching band of the C–O bond appears, usually the ether group ($-C-O-C-$) or C–OH. Those functional groups are frequently found in bonds between units along cellulose chains or pectic compounds [37]. The weak stretching band assigned also to carboxyl groups is shown at $876\,cm^{-1}$ [40] and alkene groups (C=C−H) or Ar-H at $700–500\,cm^{-1}$; the latter especially is abundant in cellulose chains [41].

After FTIR characterisation of the functional groups in the original biomass, the technique was used to determine the groups involved in the metal–biomass binding of the biomass with
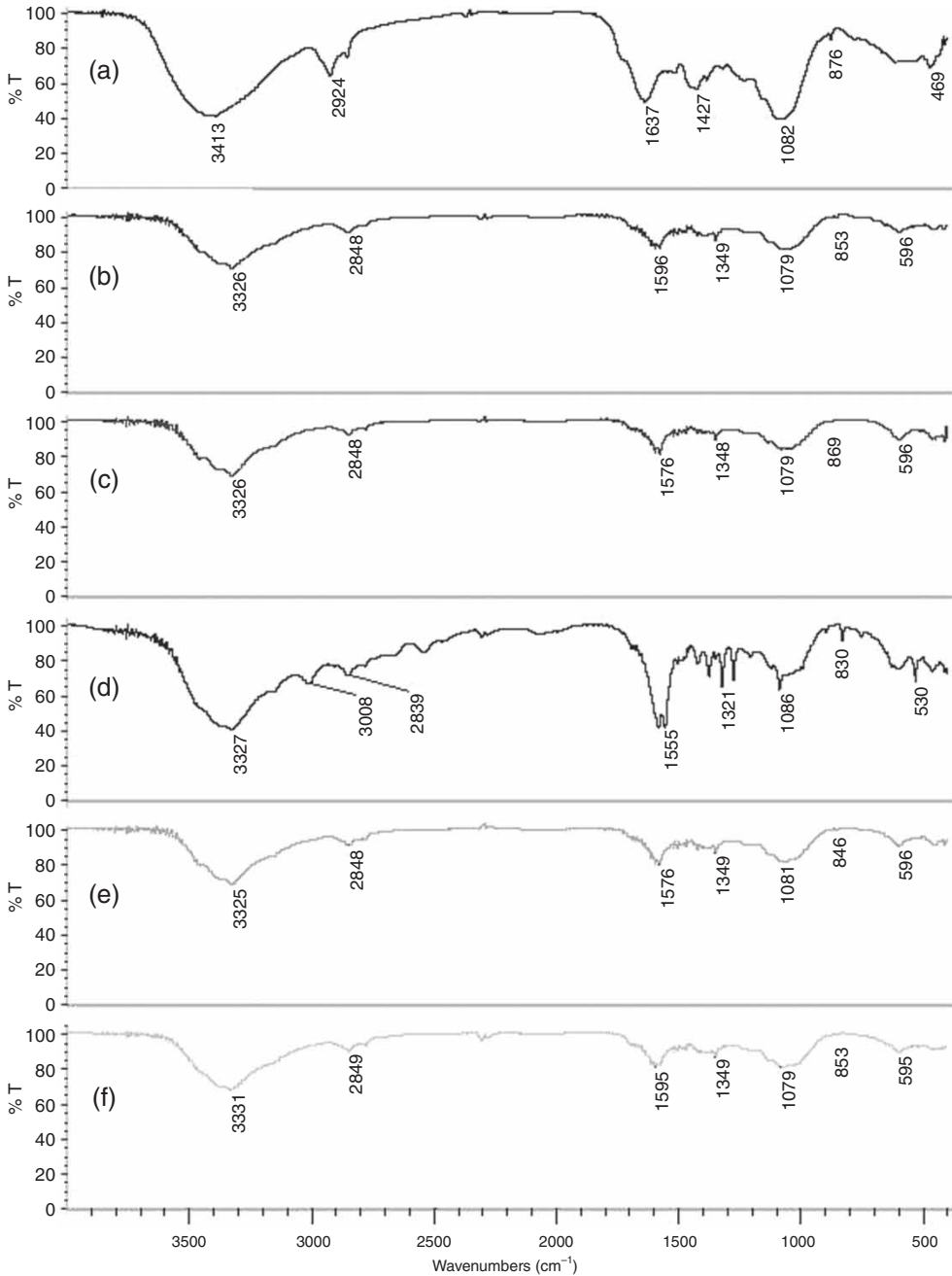
Figure 9. Infrared spectra of the biomass collected in the irrigation pond: without metal (a) and with metal adsorbed: cadmium (b), copper (c), nickel (d), lead (e) and zinc (f).

adsorbed metal. Samples of biomass loaded with each metal tested were separated from solution by filtration and then dried at 60°C for 24 hours.

Figure 9(b)–(f) shows the infrared spectra of the biomass loaded with Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II), respectively. For the biomass in contact with metal, there is a certain shift to the right of the peaks corresponding to the stretching band of carboxyl groups ($-C=O$ and

−C=OH). Since the bond between a metal and a given functional group can be weaker than that between such functional groups and hydrogen, the energy necessary to excite to the former would be lower than for the second. Therefore, there is a shift of the infrared spectrum peak to the right at shorter/lower wavenumbers [39,40,42]. These results would be a demonstration of the preferential participation of carboxyl groups in the bond with metals. In fact, several authors have reported the main role of these functional groups in the metal uptake by different types of biomass [43].

For the band corresponding to −OH groups, there is also a certain shift which is probably related to the participation of that functional group in metal microprecipitation phenomena [43]. The slight differences observed in the C−H bonds of the spectrum would not be attributable to the biosorption process since it is a major bond in the biomass, but to multiple vibrational states of the alkane group which are meaningless for this study. Finally, the peaks of ester groups (−C−O−C−) do not show significant shifts corresponding to groups without a direct participation in the metal sorption process.

3.6. *Acid-base titration of the biomass*

The determination of the acid-base behaviour of the biomass may be very useful to obtain information on the mechanism of metal uptake by evaluating the possibility of exchange between metals and proton release by the biomass. This is related to the progressive acid dissociation of their functional groups and, in turn, with their ionisation constants expressed by reaction (4).

The ionisation constant (K_a) is also related to pH by the Henderson-Hasselbach Equation (5):

$$\mathrm{pH} = pK_a + \log \frac{[B^-]}{[HB]} \tag{5}$$

When concentrations of deprotonated, [B⁻], and protonated biomass, [HB], are equal, which is known as the semi-equivalence point, the value of pK_a coincides with the pH of the medium. The equivalence point is the inflection point on the titration graph.
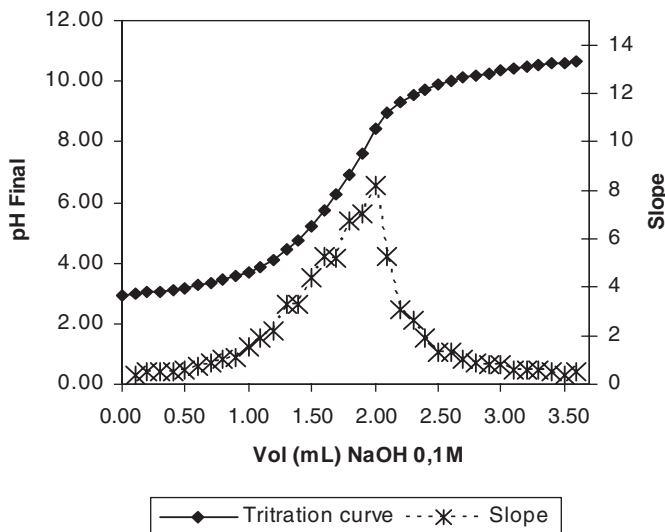

Figure 10.   Acid-base titration curve of the biomass.

The acid-base titration curve of the biomass and its slope value are shown in Figure 10. The inflection point of the slope, which is the equivalence point of the biomass, corresponds to the steepest value in the curve (in this case, for a titrant volume spent of 2 mL), around pH 8.45. The semi-equivalence point is reached at the half titrant volume spent, 1 mL in this case. The pH at the semi-equivalence point is approximately equal to 3.75, and also the value of pK_a.

According to several authors, the pK_a of carboxylic groups is around 3.7 [44,45]. That value is coincident with the pK_a determined experimentally in this work. Therefore, the biomass tested probably principally contains these functional groups. This is in agreement with other works related to the composition of vegetable biomass [46,47]. The presence of carboxyl groups in pectic substances has been commonly reported in different research studies performed with vegetable extracts, such as sugar beet pulp [44,45,48].

4. Conclusions

The biomass sample with the highest metal uptake was that collected in an irrigation pond (CIFOR).

The higher metal sorption uptake was achieved at pH values of 4 (Cu(II) and Cd(II)) and 5 (Ni(II), Pb(II) and Zn(II)) and at a biomass concentration of 0.5 g/L.

At an initial pH between 3 and 5, the biomass retains protons, while at pH values higher than 6, the biomass behaves as a proton donor.

The order of sorption in monometallic systems was as follows: Cu(II) $\sim$ Pb(II) > Ni(II) $\sim$ Zn(II) > Cd(II). The metals more easily adsorbed in monometallic systems were also preferentially adsorbed in bimetallic systems: for the Cd(II)−Cu(II) system, the most relevant finding was that copper provoked a very marked decrease in the sorption level of cadmium; for the Cu(II)−Pb(II) system, both metals have a similar effect on the sorption uptake of the other metal.

According to FTIR, metals bind preferentially to carboxylic groups and, according to acid-base titration, these are the functional groups most abundant in the biomass.

Acknowledgements

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