Sorption and desorption of Cd, Cu and Pb using biomass from an eutrophized habitat in monometallic and bimetallic systems

J.M. Lezcano*, F. González, A. Ballester, M.L. Blázquez, J.A. Muñoz, C. García-Balboa

Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica, Facultad de Ciencias Químicas, Universidad Complutense, Madrid, Spain

1. Introduction

The fast development experienced by industry in the last century has had a dramatic effect on the natural environment. Pollutants change the natural quality of the environment in physical, chemical, or biological characteristics (Gupta et al., 2009). Certainly that is the case of pollution of aquatic systems by heavy metals (Capó Martí, 2002).

Separation methods based on physical or chemical properties of solutions have been usually applied in the treatment of industrial effluents contaminated with heavy metals. The main drawbacks of those methods are the generation of large amounts of sludges and the fact that they cannot lower metal concentrations below 100 mg/L, despite that some metals are still extremely toxic at such concentration.

The potential use of biological materials (biomass) for the treatment of contaminated sites has been proposed, since several decades ago, as a substitute to physicochemical decontamination methods. Among biological methods, biosorption has the unique advantage that can be performed in the absence of microbial metabolism which allows the use of dead biomass with the subsequent economic savings.

In recent years, there has been an increasing interest in developing the sorption uptake of many industrial by-products such as: fertilizers, used for the treatment of hexavalent chromium solutions (Gupta et al., 2010); sugar, for the treatment of heavy metals including lead, nickel and copper (Gupta and Ali, 2004; Gupta and Ali, 2000; Gupta et al., 2003); and even different kind of residues such as red mud, an aluminium industry waste, for the sorption of cadmium and zinc (Gupta and Sharma, 2002). In addition, algae have shown good sorbent properties (Gupta and Rastogi, 2008a,b,c; Gupta et al., 2006) and, in general, low cost adsorbents (Ali and Gupta, 2007).

However, the feasibility of biosorption versus traditional methods has been questioned on the base of a series of limitations: the relatively low metal uptake, the high brittleness of the biomass and the inherent poor reproducibility. Those limitations may be overcome, at least in part, whether recovering the metal biosorbed or reusing the biomass in a new process. In this way, the scale up of biosorption technology involves studies to minimize both costs and the environmental impact caused by waste generation (Lister and Line, 2001; Jalai-Rad et al., 2004; Vijayaraghavan et al., 2005a,b).

On the other hand, in an attempt to approach to actual conditions of water pollution by heavy metals, where is very improbable...
to have just one metal species in solution, research studies have been extended to systems concerning two or more metals (Chong and Volesky, 1996; Yu and Kaewsarn, 1999; Gardea-Torresdey et al., 2004; Pagnanelli et al., 2004a,b; Mehta and Gaur, 2005). Those studies have focused on the effect of a given metal on the sorption uptake of another one by a certain biomass and on the relative affinity of the biomass for each metal. Nevertheless, the number of biosorption studies published on multimetallic systems is comparatively less than those related to monometallic systems (Yu and Kaewsarn, 1999; Romera et al., 2006). In this way, the evaluation, interpretation and representation of multimetallic systems is more complex than for monometallic systems because of competition phenomena between metals in solution for the biomass active sites (Lee and Volesky, 1999; Hammaini et al., 2003; Volesky, 2003). These competition phenomena, in turn, depend on factors such as metal speciation, solution pH, nature of bond sites, metal concentration or selectivity of the biomass to metal species.

This work examines the metal sorption uptake of a biomass collected in an eutrophized habitat, both in monometallic and bimetallic systems. The recovery of the adsorbed metals using NaHCO3 and HCl as eluents and the reuse of the biomass in subsequent biosorption cycles. The use of residual biomass provides two important advantages: low cost of the biosorbent material and recycling of a natural residue with an environmental impact. Metal biosorption was evaluated for three different metals (Cd, Cu and Pb) frequently found in industrial effluents and with a high level of toxicity. The study was performed both in monometallic and in bimetallic systems and the biomass sorption uptake was quantified from the isotherms plot and the fit of experimental data to different mathematical models.

2. Materials and methods

2.1. Biomass

The residual biomass tested was collected from an eutrophized ecosystem, an irrigation pond located at the Forestry Research Centre of Madrid, Spain (CIFOR). The composition of the biomass, shown in Table 1, indicates a wide compositional variety of several species of chlorophyte algae (61.41%) and caducipholic plants (37.65%) and, in less extent, photosynthetic bacteria (0.31%) and protistes (0.63%).

Previous to biosorption experiments, the as-received biomass was dried to a constant weight in a stove at 60 °C then ground in a Fritsch Pulverisette grinding mill model 6 and screened to a particle size of <0.1 mm.

2.2. Metal solutions

Metal solutions were prepared from stock solutions of 1000 mg/L of Cd2+, Cu2+ and Pb2+, using the following chemical reagents of analytical grade (Panreac): CdSO4·8H2O, CuSO4·5H2O and Pb(NO3)2, respectively. In bimetallic systems with lead, all metal solutions were prepared from the corresponding nitrate salts, also of analytical grade, in order to avoid metal precipitation.

The initial pH in monometallic systems was set at 4 for Cd and Cu and at 5 for Pb (Lezcano et al., 2010). All tests were done in duplicate. In bimetallic systems, the pH values selected were: 4 for Cu–Cd and 4.5 for Cu–Pb and Pb–Cd. pH was adjusted with dilute H2SO4 (0.1% v/v) for metal solutions prepared from sulphate salts and with dilute HNO3 (0.3% v/v) for those prepared from nitrate salts. In all cases, NaOH at a concentration of (0.001% w/w) was used as alkaline reagent.

The experiments were controlled measuring metal concentration over time by atomic absorption spectrometry in a Perkin Elmer 1100B spectrophotometer (detection limits (micrograms/liter): Cd: 0.8, Cu: 1.5 and Pb: 15).

2.3. Kinetic study: biosorption tests

The biosorption tests were performed at constant temperature and magnetic stirring in 100 mL flasks containing 0.5 g/L of dry biomass and 40 mL of the corresponding metal solution. After 120 min, pH and metal concentration were measured.

The sorption kinetics was evaluated in several biosorption tests at different metal concentrations: from 10 mg/L (0.16, 0.09 and 0.05 mmol/L for copper, cadmium and lead, respectively) up to 150 mg/L (2.36, 1.33 and 0.72 mmol/L for copper, cadmium and lead, respectively) in monometallic systems. Identical concentrations of both metals were used in bimetallic systems. During the biosorption tests, 5 mL of liquid sample were removed at different times and, after sample centrifugation (at 3000 rpm for 5 min), pH and metal concentration were measured.

2.4. Sorption isotherms

Metal sorption in monometallic systems was quantified from the isotherms plot by fitting the experimental data to two mathematical models. The sorption isotherms were plotted from several biosorption tests at different metal concentrations ranged between 10 and 150 mg/L.

The linear Langmuir equation (that provides two parameters: qmax, the maximum metal uptake by the biomass, and K constant, which is inversely proportional to the affinity between metal and biomass) and the linear expression of the Freundlich model (that also provides two parameters: Kf, a constant which is related to the biomass sorption uptake, and (1/n) which is an indicative of the sorption degree and gives the exponential relationship between the sorption uptake by the biomass and the equilibrium metal concentration) have been used (Volesky, 2003).

In addition, the sorption uptake, qe, was determined in biosorption tests as follows:

\[
q_e = \frac{V(C_0 - C_e)}{B}
\]  

(1)

Table 1

Composition of the biomass collected at CIFOR.

<table>
<thead>
<tr>
<th>Species</th>
<th>Amount (g) in 100 g of biomass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oedogonium sp. a</td>
<td>26.93</td>
</tr>
<tr>
<td>Eichhornia crassipes b</td>
<td>25.00</td>
</tr>
<tr>
<td>Cladophora sp. a</td>
<td>20.18</td>
</tr>
<tr>
<td>Spirogyra sp. b</td>
<td>13.52</td>
</tr>
<tr>
<td>Aesculus hippocastanum b</td>
<td>6.94</td>
</tr>
<tr>
<td>Platanus orientalis b</td>
<td>3.80</td>
</tr>
<tr>
<td>Acer negundo b</td>
<td>1.27</td>
</tr>
<tr>
<td>Diatomeae c</td>
<td>0.47</td>
</tr>
<tr>
<td>Scenedesmus sp. a</td>
<td>0.47</td>
</tr>
<tr>
<td>Cyanobacteria d</td>
<td>0.31</td>
</tr>
<tr>
<td>Microcystis sp. a</td>
<td>0.31</td>
</tr>
<tr>
<td>Hedera elix b</td>
<td>0.20</td>
</tr>
<tr>
<td>Eulogena sp. a</td>
<td>0.18</td>
</tr>
<tr>
<td>Ulmus sp. b</td>
<td>0.12</td>
</tr>
<tr>
<td>Ligustrum sp. b</td>
<td>0.11</td>
</tr>
<tr>
<td>Vinca sp. b</td>
<td>0.10</td>
</tr>
<tr>
<td>Bambusa sp. b</td>
<td>0.08</td>
</tr>
<tr>
<td>Ilex sp. b</td>
<td>0.03</td>
</tr>
</tbody>
</table>

a Chlorophyta algae.
b Deciduous plants.
c Protistes.
d Photosynthetic bacteria.
where $V$ is the liquid volume (L), $C_0$ the initial metal concentration (mg or mmol/L), $C_e$ the metal concentration at equilibrium (mg or mmol/L) and $B$ the biomass concentration (g/L).

For bimetallic systems, the sorption isotherms plot was obtained by contacting the biomass with metallic solutions of different concentration (0, 10, 25, 50, 100 and 150 mg/L). In these tests, the concentration of the first metal was set while the concentration of the second metal varied within such range.

The competition between metals for the sorption sites of the biomass was quantified by fitting the experimental data to the binary-type Langmuir model. This model assumes the equilibrium between two metals in solution ($M_1$ and $M_2$) with the species resulting from their sorption ($BM_1$ and $BM_2$) by the biomass ($B$) (Sánchez et al., 1999; Hammami et al., 2003; Volesky, 2003):

$$B + M_1 \rightleftharpoons BM_1; K_1 = \frac{k_{-1}}{k_1} = \frac{[B][M_1]}{[BM_1]}, b_1 = \frac{1}{K_1} \quad (2)$$

$$B + M_2 \rightleftharpoons BM_2; K_2 = \frac{k_{-2}}{k_2} = \frac{[B][M_2]}{[BM_2]}, b_2 = \frac{1}{K_2} \quad (3)$$

The binary Langmuir model as a function of parameter $K$, or the inverse of the equilibrium constant, is given by the following expressions:

$$q_e(M_1) = \frac{q_{max} C_e(M_1)}{1 + \frac{K_1}{K_2} C_e(M_1) + \frac{1}{K_2} C_e(M_2)} \quad (4)$$

$$q_e(M_2) = \frac{q_{max} C_e(M_2)}{1 + \frac{K_2}{K_1} C_e(M_1) + \frac{1}{K_1} C_e(M_2)} \quad (5)$$

Thus, parameter $K$ is inversely proportional to the affinity of the biomass for one of the two metals in solution. Then, a high value of $K$ for metal $M_2$ ($K_2$) versus $M_1$ ($K_1$) means that the biosorbent presents a higher affinity for the latter than for the former metal since a high value of $K$ is associated to a high metal desorbed/metal adsorbed ratio. Those constants together with the maximum biomass sorption uptake were determined with the MATLAB® 5.1 software (MATLAB, 1997).

2.5. Recovery of the metal adsorbed

The reuse of the biomass was considered in consecutive sorption–desorption cycles. After sorption, the biomass was recovered by filtration and dried in a stove at 60 °C for 12 h. In that way, desorption tests were performed using the same biomass concentration as in sorption tests. Then, the biomass loaded with metal was treated with an eluent (HCl at pH 3 or 0.1 N NaHCO₃) and samples of 5 mL were removed at different times to evaluate desorption kinetics. After 120 min, tests were centrifuged and pH and metal concentration determined in the supernatant solution. This process was repeated two times.

3. Results and discussion

3.1. Sorption kinetics

There is a double interest in sorption kinetics: 1) to gather information on the biosorption process at different pH and metal concentrations and 2) to estimate the time required to complete the process.

Furthermore, the sorption rate of the process will determine the type of reactor to be used and contribute final costs. In general, the sorption rate depends on several factors (Veglio et al., 2002; Jalai-Rad et al., 2004; Rangsayatorn et al., 2004; Diniz and Volesky, 2005): 1) the biosorbent or type of biomass (chemical composition and number of active sites) and its physiological state (active or inactive, free or immobilized) and structural properties (surface area, morphology); 2) the metal, its diffusion in the biosorbent, concentration, and competition with other metal ions by active sites; and 3) experimental conditions, especially stirring.

Fig. 1 depicts the evolution of metal concentration versus time in monometallic systems for an initial concentration of 10 mg/L. The biosorption process was very fast and around 80% of metal was recovered in the first 8 min while equilibrium was reached at 30 min. Similar results were obtained for the rest of initial metal concentrations tested in agreement with other studies that have established biosorption times shorter than 15 min after bio- mass–metal solution contact (Reddad et al., 2002; Deng and Bai, 2004; Martins et al., 2004; Chojnacka et al., 2005; Goksungur et al., 2005; Seki et al., 2005). Fig. 2 shows the variation of pH versus time for tests at different initial Pb concentrations. pH values increased with decreasing the concentration of this metal in solution. This was expected since the binding mechanism of protons to active centres of the biomass is similar to that of metal cations in solution (Matheickal et al., 1999; Yu and Kaewsarn, 1999; Yu et al., 2001; Gulnaz et al., 2005; Han et al., 2005; Lin and Lin, 2005; Saeed et al., 2005). For biomass with free active sites,
the simultaneous uptake of metal cations and protons increased the solution pH.

The fast biosorption rate would be related to two facts: the process takes place mainly on the biosorbert surface (Herrero et al., 2005; Kamala et al., 2005) and metal binding is accomplished by fast reversible reactions independent of metabolism (Cruz et al., 2004; Pagnanelli et al., 2004a,b).

In general, biosorption in bimetallic systems was slightly slower than for monometallic systems, and this is in agreement with other experimental studies (Ozdemir et al., 2005). Those differences could be due to the absence of competition phenomena in monometallic systems.

3.2. Sorption isotherms in monometallic systems

The sorption process was quantified from the equilibrium parameters obtained by fitting the experimental data to the two mathematical models usually employed in literature: Langmuir and Freundlich (Chojnacka, 2005; Goksungur et al., 2005; Gulnaz et al., 2005; Han et al., 2005; Herrero et al., 2005; Kamala et al., 2005; Lodeiro et al., 2005; Mehta and Gaur, 2005; Saeed et al., 2005).

Table 2 collects the values of the relative constants for both models and the linear regression coefficient ($R^2$). The latter values indicate a better fitting of experimental data to the Langmuir than to the Freundlich model. According to the former model, the biosorption process: 1) takes place in a monolayer; 2) there is homogeneity with respect to the type and affinity of metal by the active sites; 3) the adsorbed ions do not affect the sorption of other ions by neighbour active centres; and 4) metal can saturate the biomass (Puranik and Paknikar, 1997; Satiroglu et al., 2002; Goksungur et al., 2005; Saeed et al., 2005).

A similar conclusion can be reached from the analysis of constants for each metal derived from both models: values of $q_{\text{max}}$ for the Langmuir model and $K_f$ for the Freundlich model gave the following sorption order: Pb ~ Cu > Cd. This sequence is in agreement with the electronegativity values of the different metal cations tested (Sheng et al., 2007): the higher the electronegativity of the ion the stronger is the attraction for the negatively charged ligands on the biomass. Of the three metals tested, Pb and Cu, with the highest electronegativity (2.33 and 1.91, respectively), were adsorbed in a greater extent. Cadmium, with a lower electronegativity (1.69) and a larger volume, presented the lowest metal uptake.

The metal ion affinity order of the biomass, deduced from the values of $K$ from the Langmuir model, was: Pb > Cd ~ Cu. In spite that the affinity for cadmium was high, the metal uptake was low as indicated by the value of $q_{\text{max}}$. This behaviour could be related to the presence of few active sites, but with low activation energy, on the cell wall to bind this metal. In such case, Cd would be easily bioadsorbed at low concentrations but saturation is rapidly reached (Hashim and Chu, 2004).

3.3. Sorption isotherms in bimetallic systems

The analysis of bimetallic systems is based on competition between metal species in solution and can be treated in three different ways (Chong and Volesky, 1995; Loaec et al., 1997; Lee and Volesky, 1999; Hammaini et al., 2002; Volesky, 2003; Mehta and Gaur, 2005):

(i) Fitting experimental data to bidimensional isotherms, as for monometallic systems. Thus, each isotherm represents the different sorption uptakes of the first metal, as a function of its equilibrium concentration, for each given concentration of the second metal. This method allows a qualitative but not quantitative analysis of the sorption influence of one metal over the other one.

(ii) Fitting experimental data to 3-D surfaces, using three axes: $X$ and $Y$ axes represent the equilibrium concentrations of both metals and $Z$ axis the sorption uptake of one of the two metals or the sum of both. This method is a better plot than the former but, as main drawback, sometimes shows irregular surfaces that are far from being the real behaviour of the bimetallic system. In addition, it only provides qualitative information.

(iii) Fitting experimental data to a mathematical model. This method, unlike the others, provides quantitative information of the biosorption process in bimetallic systems. Among the mathematical models described in the literature for bimetallic systems, the binary-type Langmuir model has been the most applied since, besides being the most simple, it allows the determination of the equilibrium constant of the biomass–metal interaction given whether by the value of $b$ or by its inverse ($K$). This method was adopted in the present work.

The values of the Langmuir constants corresponding to the three systems studied and obtained using the MATLAB 5.1 software are given in Table 3. The maximum sorption uptake of the biomass, $q_{\text{max}}$, remained practically constant for all systems around 0.5 mmol of cation adsorbed/g of biomass. That would be an indication that the number of active sites in the biomass available for metal binding is fixed and independent of the working solution (Romera et al., 2008).

Considering the values of the affinity parameters, $K_1$ and $K_2$, for the Cu–Cd and Pb–Cd bimetallic systems, the affinity of the biomass was five times higher for Cu or Pb than for Cd. In contrast, the biomass presented a high and similar affinity for both metals for the Pb–Cd system.

Similar results were obtained by Sheng et al. (2007), in binary systems and using the marine alga Sargassum sp. Moreover, our results agree with those recorded in monometallic systems, especially for Pb, the metal with the lowest value of $K$ (Table 2). However, unlike monometallic systems, the biomass presented a different affinity for Cu and Cd in bimetallic systems. A similar biosorption behaviour was observed using Fucus spiralis as biosorbent (Romera et al., 2008). In this case, the different electronegativity of both ions (higher for Cu) and the different ion radius (bigger for Cd) could be responsible for such results.

### Table 2

<table>
<thead>
<tr>
<th>Metal</th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_{\text{max}}$ (mmol/g biomass)</td>
<td>$K$ (mmol/L)</td>
</tr>
<tr>
<td>Cd</td>
<td>0.290</td>
<td>0.055</td>
</tr>
<tr>
<td>Cu</td>
<td>0.508</td>
<td>0.067</td>
</tr>
<tr>
<td>Pb</td>
<td>0.388</td>
<td>0.003</td>
</tr>
</tbody>
</table>

### Table 3

<table>
<thead>
<tr>
<th>System</th>
<th>$K_1$ (mmol/L)</th>
<th>$K_2$ (mmol/L)</th>
<th>$q_{\text{max}}$ (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu–Cd</td>
<td>Cu: 0.066</td>
<td>Cd: 0.340</td>
<td>0.474</td>
</tr>
<tr>
<td>Pb–Cu</td>
<td>Pb: 0.001</td>
<td>Cu: 0.004</td>
<td>0.452</td>
</tr>
<tr>
<td>Cd–Pb</td>
<td>Cd: 0.340</td>
<td>Pb: 0.086</td>
<td>0.474</td>
</tr>
</tbody>
</table>
Let us consider each bimetallic system separately:

3.3.1. Cd–Cu system

The competition between Cd and Cu for the active sites of the biomass is depicted in Fig. 3. The surface isotherms show a decrease of cadmium uptake in the presence of increasing amounts of Cu (Fig. 3b). In contrast, Cu uptake was kept high even at high Cd concentrations (Fig. 3a). The higher affinity of the biomass for Cu agrees with the previous values of $K$. The sorption for the simultaneous uptake of both metals reached a constant value independently of each metal concentration, as expected from the values of $q_{\text{max}}$ obtained (Fig. 3c).

3.3.2. Cu–Pb system

The isotherm for this system (Fig. 4) shows that the influence of Pb on the Cu sorption uptake was similar to its reciprocal, in agreement with the low values of $K$ obtained for both metals. In this bimetallic system, the biomass reached saturation faster than in the previous system which is a clear indication of the high affinity of the biomass for both metals (Fig. 4c).

![Fig. 3. Sorption isotherms for the Cu–Cd system.](image)

![Fig. 4. Sorption isotherms for the Cu–Pb system.](image)
3.3.3. \( \text{Pb} - \text{Cd} \) system

Fig. 5 shows that \( \text{Pb} \) had a negative effect on the uptake of \( \text{Cd} \), especially at high concentrations of the former metal. Conversely, the effect of \( \text{Cd} \) on the \( \text{Pb} \) sorption uptake was practically negligible (Fig. 5a). This behaviour is in agreement with the previous quantitative analysis according to which the affinity of biomass is preferentially towards \( \text{Pb} \) than \( \text{Cd} \). Also, the simultaneous sorption uptake of both metals reached a constant value independently of metal concentration (Fig. 5c).

Let us consider all bimetallic systems globally:

In all cases, an increase of concentration of a given metal led to a lower sorption uptake of the other metal present in solution since both metals compete for the same active centres of the biosorbent (Chong and Volesky, 1995; Loaec et al., 1997).

The affinity order of the biomass agrees with that obtained for monometallic systems: \( \text{Pb} \approx \text{Cu} > \text{Cd} \). A higher affinity of a given metal with respect to the other one can be due whether to lower activation energy, to a stronger binding strength towards the active centre, or to a different binding mechanism. Some authors have pointed out that the affinity can be related to specific properties of each metal, such as (Chong and Volesky, 1996): ionic radius (the smaller the radius the higher the affinity) or cation charge density (the higher the charge density the higher the affinity because a higher electrostatic attraction).

In the three cases studied, the total amount of metal adsorbed, obtained from the sorption uptakes of both metals in solution, tends to a maximum and constant value around 0.5 mmol/g. This would be in agreement with Langmuir’s hypothesis that the number of active centres available on the biomass is fixed and remains constant over the whole surface and that each metal ion could bind any of them (Chong and Volesky, 1995; Loaec et al., 1997).

3.4. Recovery of the metal adsorbed

The desorption process for the recovery of metals is based on several mechanisms. Basically, there are three desorption mechanisms (Huang et al., 1998; Kapoor et al., 1999; Gardea-Torresdey et al., 2004):

(i) Precipitation of the metal adsorbed by formation of insoluble compounds with the desorbent agent, e.g. \( \text{H}_2\text{S} \).

(ii) Complexation of the metal adsorbed by reaction with compounds which have pairs of electrons available to share with the metal cation. Desorbent agents such as \( \text{NaHCO}_3 \), \( \text{Na}_2\text{CO}_3 \) and EDTA follow this mechanism.

(iii) Ion exchange. This mechanism gives good yields by exchanging a cation from the desorbent agent for the metal adsorbed. The most common desorbent agents in this category are: \( \text{HCl}, \text{H}_2\text{SO}_4 \) and \( \text{NaOH} \).

There is a large number of desorbent agents that can be used but acids, inorganic or organic, have the highest metal desorption capacity (Huang et al., 1998; Davis et al., 2000). The desorbent agent should fulfill four basic requirements: 1) a high elution efficiency; 2) low damage of the biomass in order to be reused in subsequent cycles; 3) low degree of contamination; and 4) low cost (Davis et al., 2000; Gardea-Torresdey et al., 2004; Chojnacka et al., 2005; Mehta and Gaur, 2005).

In the present study, two different eluent agents were selected: one acidic (HCl) and another complexing (NaHCO\(_3\)), both with a relatively low cost.

3.4.1. HCl as desorbent

Fig. 6 shows the elution kinetics with HCl quantified as a function of the amount of metal release. Like biosorption, the desorption process took place rapidly and more than 80% of metal retained on the biomass was released within the first 5 min. In addition, the increase of pH during desorption (Fig. 6) would indicate an exchange between metal cations adsorbed and protons supplied by the desorbent agent, in agreement with other authors (Huang et al., 1998; Gardea-Torresdey et al., 2004; Mehta and Gaur, 2005).

Fig. 7 shows the amount of metal retained by the biomass after each biosorption or desorption step. HCl was markedly efficient as desorbent agent (Desorption I) with metal recoveries of 85.7% for \( \text{Cd} \), 66.7% for \( \text{Cu} \) and 63.2% for \( \text{Pb} \). Thus, the desorption sequence was inverse to the sorption order recorded. These results agree with...
those obtained by several authors (Mattuschka et al., 1993; Puranik and Paknikar, 1997; Davis et al., 2000; Lin and Lin, 2005; Saeed et al., 2005).

However, once the biomass was reused in a new biosorption test (Biosorption II) its efficiency significantly decreased with respect to the first sorption cycle (Biosorption I). This could be due to several factors, such as: structural damages of the active centres provoked by the desorbent agent, or blockage of those sites due to the inefficiency of the eluant leaving less active sites available for the new sorption cycle (Puranik and Paknikar, 1997; Davis et al., 2000; Rangsayatorn et al., 2004; Sekhar et al., 2004; Lin and Lin, 2005; Vijayaraghavan et al., 2005a,b).

3.4.2. NaHCO₃ as desorbent

The desorption kinetics with NaHCO₃ (Fig. 8) showed that despite being a process relatively fast, recoveries higher than 80% can be reached in the first 30 min, had a worse performance than HCl. The desorption mechanism can be explained by the existence of bicarbonate anions with pairs of electrons available that can remove by complexation the metal cations uptaked by the biomass (Puranik and Paknikar, 1997; Gardea-Torresdey et al., 2004).

As in the previous case, an increase of solution pH took place simultaneously to metal desorption (Fig. 8). In this case, however, it should not be due to ion exchange since it is a weak acid salt and its dissociation in the aqueous medium provides alkalinity due to the following equilibria:

\[
\text{NaHCO}_3 \rightleftharpoons \text{Na}^+ + \text{HCO}_3^- \quad (6)
\]

\[
\text{HCO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 + \text{OH}^- \quad (7)
\]

Thus, this would explain the slight increase of pH shown in Fig. 8.

Fig. 9 depicts the amount of metal at the end of each sorption or desorption step. The efficiency of NaHCO₃ as desorbent agent was relatively low, except for Cu, with a recovery of 76.7%, the recovery for the rest of metals was: 11.4% for Pb and 1.4% for Cd.

In spite that in the first desorption process (Desorption I) metal recovery was low, the reuse of the remaining biomass (Biosorption II) in a second biosorption cycle improved significantly both its sorption uptake and metal recovery that was even higher than in the first cycle (Biosorption I). This would be related to chemical changes in the biomass produced by NaHCO₃. Yan and Viraraghavan (2000) have reported similar effects of NaHCO₃, after a second cycle under identical conditions, on Mucor rouxii and the increase of the sorption uptake observed was attributed to several facts: removal of impurities on the biomass surface, breakdown of the cell wall or generation of new sorption active centres.

After a second desorption (Desorption II) in identical conditions to the first one, the desorption yield was even lower than that recorded in the first cycle (Fig. 9). The percentages of metal desorbed, with respect to the total amount of biomass, after the second biosorption cycle, were: 53.8% for Cu, 3.0% for Pb and 0.3% for Cd.
Clearly, metal desorption after the first cycle was higher using HCl than NaHCO3. A plausible explanation is the different performance mechanism of each eluant: ion exchange for HCl and complexation for NaHCO3 (Gardea-Torresdey et al., 2004). Nevertheless, HCl, a strong acid, could provoke a serious damage on the biomass affecting its sorption capacity. On the contrary, NaHCO3 significantly improved the sorption uptake of the biomass.

Therefore, the significant increase of sorption of the biomass treated with NaHCO3 is an indication that this reagent is able to improve its metal sorption uptake.

4. Conclusions

- The eutrophized biomass can be used effectively for decontaminating effluents contaminated with heavy metals.
- The sorption kinetics in monometallic systems was very fast and equilibrium was reached after 30 min. The pH values increased with decreasing metal concentration because of competence phenomena between protons and metal cations for the same active sites of the biomass.
- The sorption kinetics in bimetallic systems was slower than in monometallic systems and the equilibrium was reached after 120 min. That was related to the strong competence between metal cations for the same active sites of the biomass.
- The sorption order in monometallic systems was: Cu > Pb > Cd and the biomass-metal affinity: Pb > Cd > Cu.
- The affinity order in bimetallic systems was: Pb > Cu > Cd. In addition, the maximum total amount of metal adsorbed for the three systems studied was around 0.5 mmol/g.
- The desorption process was fast and released more than 80% of the metal adsorbed within the first 5 min with HCl and in the first 30 min with NaHCO3.
- The percentages of metal recovery obtained with HCl in the first cycle ranged between 63 and 100%. The lower sorption metal uptake with reused biomass was related to damage or blockage of its active centres.
- The percentages of metal recovery obtained with NaHCO3 in the first cycle ranged between 1 and 77%. The sorption metal uptake increased for the reused biomass but the yield of the second desorption cycle was lower than for the first one.

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References


