Removal efficiency of Cu^{2+}, Cd^{2+} and Pb^{2+} by waste brewery biomass: pH and cation association effects

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Abstract

In this work two distinct (flocculent and non-flocculent) yeast wastes from Portuguese breweries were used for the selective removal of Cu^{2+}, Cd^{2+} and Pb^{2+} from aqueous solutions. One of the goals was to establish both the pH profiles for the removal of each metal ion (1.0 mM) and the effect on the biomass biosorption capacity of pH adjustment during the process. The effect of the presence of multiple metal ions, in the 0.1–1.0 mM range, on metal removal efficiency was also studied. The results showed that, in the absence of pH adjustment, the optimum initial pH for the removal of three cations was in the 4.5–5.5 range for both types of biomass. However, a gradual pH increase was observed during the removal process, up to a final equilibrium value of 7.0–8.0. Regarding the biomass efficiency for metal removal in multi-cation systems, it was verified that only Cu^{2+} was significantly affected by the presence of the other metals in solution and only when the non-flocculent yeast biomass was used as biosorbent. Cd^{2+} was only slightly affected by the presence of both Cu^{2+} and Pb^{2+}, and Pb^{2+} removal was not affected by the presence of any or both of the interferent metals for the two biosorbents used in this work. The highest and lowest metal removal yields were obtained for Pb^{2+} and Cu^{2+}, respectively.

Keywords: Biosorption; Multiple-cation systems; Cadmium; Copper; Lead; Non-viable yeast biomass; pH

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1. Introduction

Recent industrialization in many regions has increased the discharge of industrial wastes, especially those containing heavy metals, into natural aquatic receptors or into the soils. These contaminants have been found to be among the most toxic pollutants [1]. As legislation governing the maximum admissible values for the concentration of pollutants species in aqueous media is becoming increasingly strict, it is necessary to find simple and cheap processes for the treatment of industrial wastewaters [2].

The concentration limits of copper, cadmium and lead in wastewaters for discharge in aquatic media in Portuguese legislation are 1.0, 0.2 and $1.0\,mgl^{-1}$, respectively [3]. The use of biological materials for heavy metal removal and recovery technologies has gained important credibility during recent years because of the good performance and the low cost of this type of sorbent [4]. The natural affinity of biological compounds for metal ions can be used to economically purify even heavily metal-loaded wastewaters.

The mechanism of metal bioaccumulation may involve intracellular uptake and storage by active cation transport systems, surface binding or other still undefined mechanisms. Among the several resources in biological wastes, the biomass of non-viable microorganisms exhibits particularly interesting metal-binding capacities as biosorbent. Non-viable cells have also the advantage of not depending on a supply of nutrients for cell growth, not needing to be resistant to aggressive environments and representing a reduced health hazard [5–7].

Many of the studies on the effectiveness of biosorbents have been carried out with single-metal solutions. However, in practice, industrial wastewaters usually contain more than one metal ion. Moreover, other parameters such as changes in the solution pH and the metal concentration may influence the biomass metal uptake capacity [5,8]. When more than one metal ion is present, competition for the adsorption sites can occur [9]. In multiple cation systems, the assessment of the sorption performance becomes more complicated.

For successful practical application of biosorption, it will be necessary to understand and take into account the influence of the solution composition and the physical-chemical characteristics of the ion species and of the biosorbent on metal biosorption [8]. The aim of this work was to study the pH effect on Cu^{2+}, Cd^{2+} and Pb^{2+} removal and the removal efficiency of one, two or three metal systems by two types of non-viable waste brewery biomass in a perspective of effective re-use of waste biomass for heavy metal recovery from contaminated water.

2. Materials and methods

2.1. Microorganisms

Two industrial strains, one flocculent and one non-flocculent, were collected from wastes of two Portuguese brewing industries (Unicer, Leça do Balio, Portugal, and Centralcer, Vialonga, Portugal, respectively). These microbial wastes, containing a concentration of 50–60 g cell dry weight.cm^{-3}, were stored at 4°C. The pH of the concentrates was around 5.0 and remained unchanged for several months. For the biosorption tests, the biomass from Unicer and Centralcer was directly diluted into the test flasks containing the metal solutions to a final concentration of 0.95 and 1.2 g cell dry weight.l^{-1} ($gcdwl^{-1}$), respectively.

2.2. Biosorption experiments

Batch biosorption experiments were carried out in 250 ml shake flasks containing 100 ml of solutions of $CuSO_4$, and/or $CdCl_2 1/2H_2O$ and/or

Pb $(NO_3)_2$ in distilled water, in concentrations of 0.1, 0.25, 0.5 and 1.0 mM of each metal. Analytical grade reagents were used in all cases. The resulting pH of these solutions was in the 4.5–5.5 range. Flasks were agitated in a New Brunswick Scientific (USA) G25 orbital shaker, at 150 rpm and 30°C.

The effect of the initial solution pH was tested by adjusting the pH of the aqueous metal solutions to values between 4.5 and 8.0. Initial metal concentrations were measured after pH adjustment and before biomass addition. The biosorbent was then added and dissolved metal concentrations were followed during 96 h without further pH adjustment. Parallel sets of flasks were followed, without added biomass. Stock solutions, in distilled water, of NaOH (0.1 M) and one of the three following acids, H_2SO_4, HCl or HNO_3 (0.1 M), were used for pH adjustment and control, depending on the metal salt used — $CuSO_4$, $CdCl_2.1/2H_2O$ or Pb $(NO_3)_2$, respectively. The pH adjustments introduced changes in the final assay volumes always under 1%.

The effect of metal cross-interference on biosorption, in two- and three-metal systems was assessed by two different procedures. Using equimolar concentrations of each cation in the 0.1–1.0 mM range, or maintaining constant the concentration of one metal, Cu^{2+}, Cd^{2+} or Pb^{2+} (1.0 mM) in the presence of varying initial concentrations of another, between 0.25 and 1 mM. Sorption experiments using single- and multiple-solute systems were conducted in the same conditions referred to above, without initial pH adjustment.

Samples of 1.5 ml were taken at different times from the mixed adsorption flasks, clarified by centrifugation and the supernatants were analyzed for metal ion content. Cu^{2+}, Cd^{2+} and Pb^{2+} concentrations were determined by flame atomic absorption spectrophotometry using a Perkin Elmer (USA) 1100B spectrophotometer.

3. Results and discussion

3.1. pH effects on metal removal

Taking into account the reported importance of medium pH on metal ion biosorption [5,10], tests were undertaken with different initial pH values of unbuffered Cu^{2+}, Cd^{2+} and Pb^{2+} solutions in water. In these tests, initial pH values of 1 mM aqueous metal solutions were adjusted in the range 4.5–8.0 before addition of the biosorbent.

Fig. 1 shows the effect of initial solution pH on Cu^{2+}, Cd^{2+} and Pb^{2+} uptakes after 96 h of incubation (equilibrium attained). Results correspond to an average of at least six independent experiments, with the standard deviation always lower than 10%. The pH profile was also registered along the process. It was observed that in all tests an increase of pH occurred to a final value in the 7.0–8.5 range, which could have caused a metal precipitation effect associated to metal biosorption. It should be noted that in the biomass-free runs metal precipitation, causing up to 50% metal removal from solution, was observed for pH values above 6.0. Since the values of metal load given in Fig. 1 were calculated on the bases of residual metal concentration after pH adjustment, the pre-precipitation effect could account for the lower apparent biosorption capacity at higher pH values. However, some biosorption capacity was exhibited by the biomass, even at pH 7.0–8.0. The behaviour of both biosorbents types was similar for Pb^{2+} and Cu^{2+}, but strikingly different for Cd^{2+}, suggesting different binding mechanisms. The cell surface characteristics leading to biomass flocculation (Fig. 1b) could thus also be involved in favouring Cd^{2+} sorption. As can be seen from Fig. 1, the initial pH that led to higher metal removal for all three cations and both biosorbents was in the 4.5–5.5 range. For that, this initial pH range, corresponding to no initial pH adjustment, was used for the further
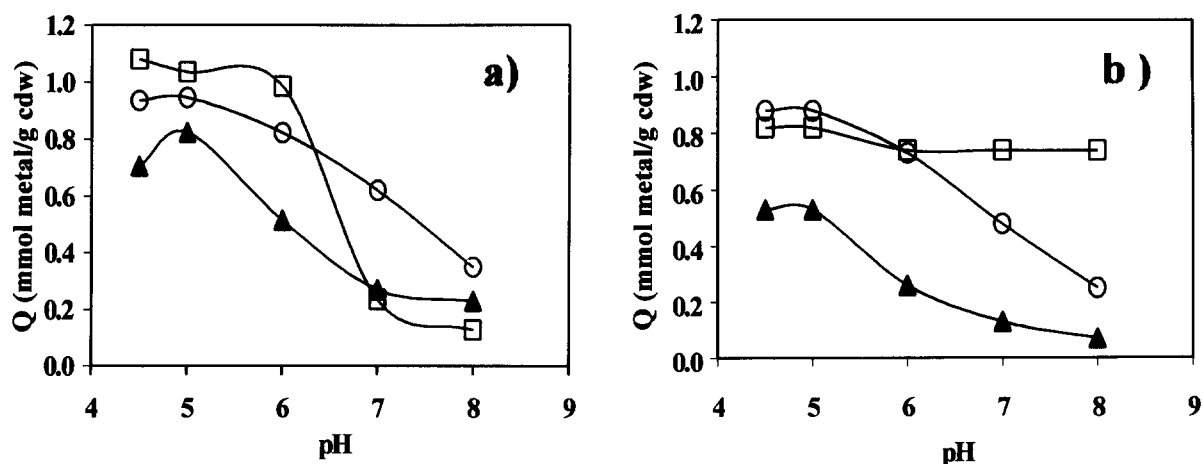
Fig. 1. Effect of initial solution pH on the equilibrium metal loads (Q), attained after 96 h of incubation on waste biomass from Centralcer (a) and Unicer (b) for biosorption runs with Cu^{2+} (▲), Cd^{2+} (□) and Pb^{2+} (○) unbuffered solutions.

experiments. To distinguish from sorption and precipitation, the effect of stepwise and continuous pH adjustment to the 4.5–5.0 range on metal removal was compared with the situation of no pH adjustment for the Centralcer (non-flocculent) biomass. The results obtained showed that pH adjustment altered the pattern of metal removal. With continuous pH control, Cd^{2+} was not biosorbed and Cu^{2+} removal was roughly reduced by 50%. However, Pb^{2+} was always extensively removed and only slightly (less than 10%) affected by pH control [11].

3.2. Cation association effects on metal removal efficiency

Metal removal efficiency by yeast biomass in one-, two- and three-metal sorption systems was evaluated using the two different industrial waste yeasts. The effect of metal interference was studied by maintaining constant the concentration of interfering metal (1.0 mM) and measuring the removal of another for initial concentration between 0.25 and 1 mM or by using equimolar concentrations of each cation in the same

solution. The results observed were compared with these obtained for one-solute systems.

As can be observed in the Fig. 2, Cu^{2+} was the cation less removed from the contaminated solution in the absence and in the presence of interfering metals (Fig. 2a and b), suggesting a lower affinity of this cation for both biosorbents used in this work. However, with the flocculent biomass from Unicer, the removal efficiency of Cu^{2+} was maintained in the presence of Pb^{2+} and Cd^{2+} (Fig. 2b), while with the Centralcer yeast decreases in the Cu^{2+} removal of around 43% and 62% were observed when Pb^{2+} or Cd^{2+} (1.0 mM), respectively, were present (Fig. 2a). This behaviour suggests that the Unicer cells have a higher number of ligand groups for Cu^{2+} on the cell surface than the Centralcer biomass. Data presented by Kapoor and Viraraghavan [12] concerning the same cations studied here showed that, in the fungal biomass of *Aspergillus niger*, amine and carboxyl groups were important functional groups involved in lead, cadmium and copper biosorption. However, the biosorption of copper by binding to the amino groups was much more significant than by binding to the
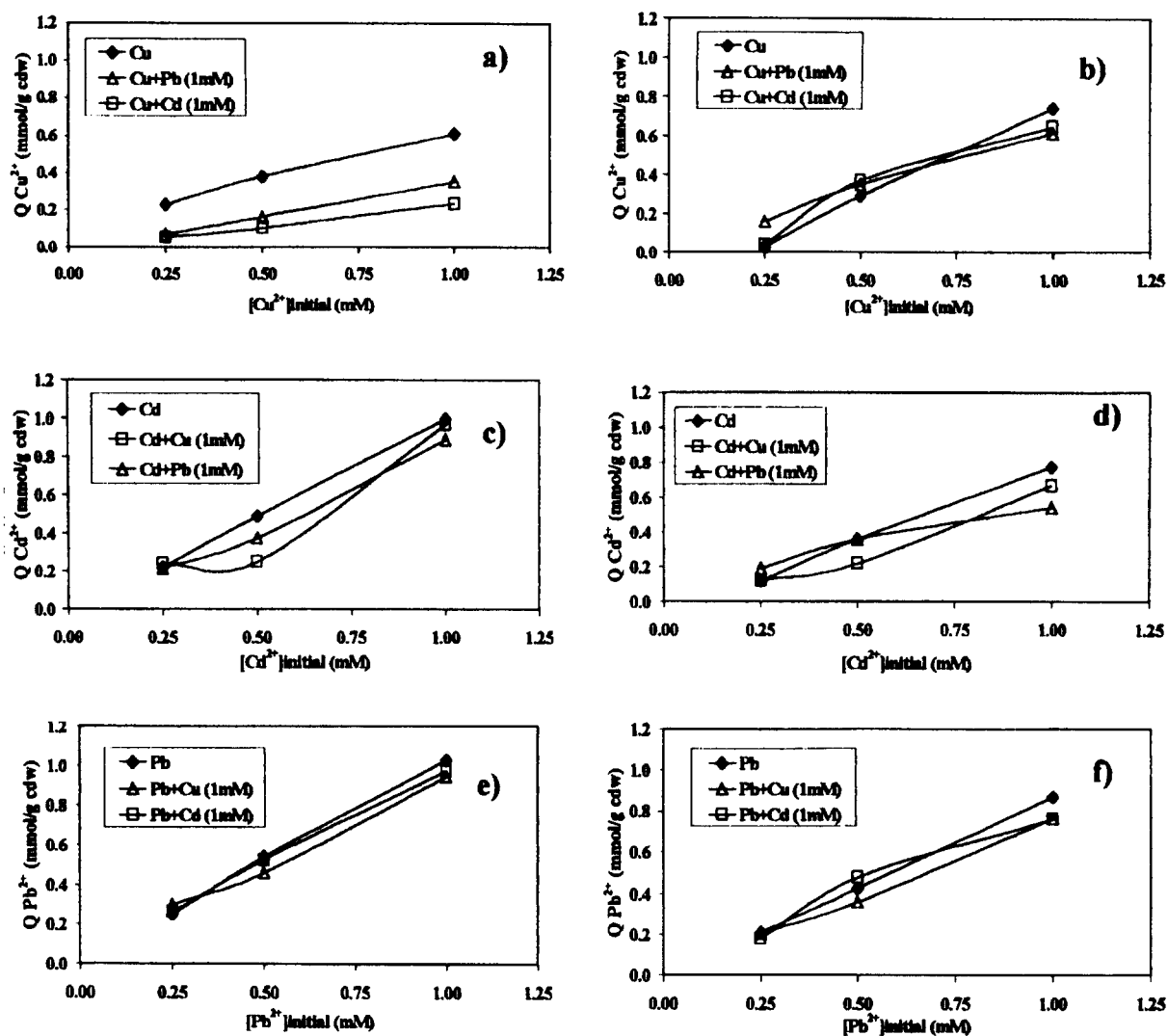
Fig. 2. Effect of the presence of a second metal cation on the removal efficiency (equilibrium metal loads, Q), of Cu^{2+} (a,b), Cd^{2+} (c,d) and Pb^{2+} (e,f) after 96 h of incubation, by waste biomass from Centralcer (a, c and e) and Unicer (b, d and f). The initial concentration of the interfering metal was always 1.0 mM for initial test concentrations of Cu^{2+}, Cd^{2+} and Pb^{2+}, 0.25 and 1.0 mM.

carboxyls. In the present case, different fractions of these groups could have been available in the two yeast types tested.

Cd^{2+} cation removal was only slightly affected for initial concentrations higher than 0.25 mM by the presence of interfering metals for both biosorbents, though Centralcer cells seemed to be a better biosorbent for cadmium cation. It should

be noted that equilibrium pH values of 6.5–7.0 were obtained from the runs using cells from Unicer as biosorbent, while the final pH using the cells from Centralcer was in the 7.5–8.0 range. This behaviour could have promoted a higher metal precipitation or co-precipitation effect, leading to apparently higher removal yields [11].

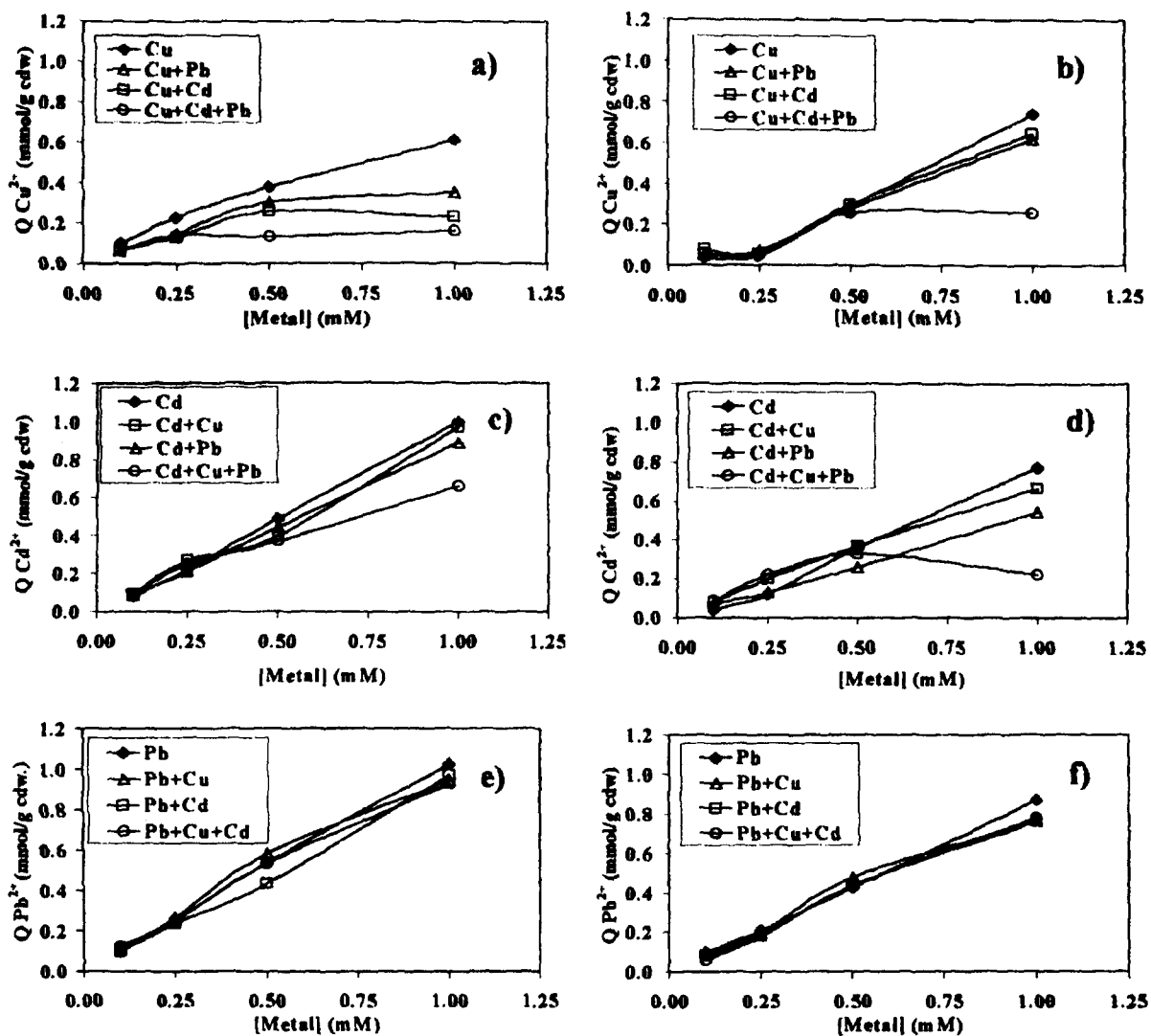For the Pb^{2+} cation it was observed that the

Fig. 3. Effect of the presence of one or two additional metal cations on the removal efficiency (equilibrium metal loads, Q) of Cu^{2+} (a,b), Cd^{2+} (c,d) and Pb^{2+} (e,f) after 96 h of incubation by waste biomass from Centralcer (a, c and e) and Unicer (b, d and f). Equimolar initial concentrations of each metal between 0.1 and 1.0 mM were used in two- or three-metal solutions.

removal of increasing concentrations of Pb^{2+} was not affected by the presence of 1.0 mM of Cu^{2+} or Cd^{2+} for both biosorbents (Fig. 2e and 2f). Slightly higher removal yields were obtained with the non-flocculent cells from Centralcer (Fig. 2e). In fact, in all experiments undertaken,

Pb^{2+} removal yields obtained were between 95–100%, indicating that both waste biomass have a high capacity for Pb^{2+} even in the presence of other metals.

The metal association effects on the removal of Cu^{2+}, Cd^{2+} and Pb^{2+} (0.25–1.0 mM), using equi-

molar concentrations of the interfering metals, were also studied. It was observed that, using the non-flocculent biomass from Centralcer as biosorbent, the removal yield of Cu^{2+} suffered a significant decrease in the presence of Cd^{2+} and/or Pb^{2+} in both two and three-metal systems (Fig. 3a). In the two-metal systems, copper was more affected by Cd^{2+} than by Pb^{2+}. With the cells from Unicer the Cu^{2+} removal yield was only significantly affected in the more concentrated three-metal system (Fig. 3b). This supports the supposition that more binding groups for copper are available on the flocculent biomass.

Cd^{2+} removal (Fig. 3c and 3d) was affected by the presence of one or two interfering metals in equimolar concentrations, though less by Cu^{2+}, and more extensively when the cells from Unicer were used as biosorbent (Fig. 3d). Again, it must be noted that in the presence of Unicer cells the pH shift, which occurred during the biosorption process, was lower than with the cells from Centralcer, which probably affected the apparent Cd^{2+} removal yields. Furthermore, it was observed that using either of one biosorbents, the final process pH was in the three-metal systems in the 6.5–7.0 range, possibly leading also to the lower Cd^{2+} removal capacities.

As in the experiments in Fig. 2, Pb^{2+} removal was not affected by any or both of the two interference metals in equimolar concentrations (Fig. 3e and 3f). For both biosorbents, Pb^{2+} removal yields were in the 95–100% range and the Centralcer cells confirmed their capacity for Pb^{2+}.

5. Conclusions

Waste brewery biomasses of non-flocculent and flocculent types were found to be promising biosorbents for the removal of Cu^{2+}, Cd^{2+} and Pb^{2+} in concentrations up to 1.0 mM from unbuffered aqueous solutions. The experimental conditions which led to higher metal removal yields were initial pH in the 4.5–5.5 range and no adjustment or control of the pH during the biosorption process. Metal removal, however, was shown to be strongly affected by changes in the solution pH, further investigation into this effect being required. On the whole, removal capacities for one metal, with both waste biomass types, did not suffer significant interference from the presence of one or two of the other metals, which favours the use of this biosorption system with multiple-solute effluents. The copper removal capacity of the non-flocculent strain was, however, negatively affected by the presence of the other metals, an effect that was much less significant with the flocculent biomass. The inverse, though only for the more concentrated three-metal systems, was observed for Cd^{2+}. These results suggest that different metal binding sites are available in the two waste biomass types, possibly also related to their flocculent /non-flocculent character.

Although Unicer cells showed to be more efficient to removed Cu^{2+} than the Centralcer ones, in general, the higher metal removal yields were obtained using the biomass from Centralcer as biosorbent.

References

[1]   E. Torres, A. Cid, C. Herrero and J. Abalde, Bioresourse Technol., 63 (1998) 213.
[2]   L. T. Vasconcelos and C.G.G. Beça, Europ. Wat. Pollu. Cont., 7(3) (1997) 7.

[3] Diário da República, 1st Series, Dec. lei No. 236/98, 1998.

[4] A.I. Zouboulis, E.G. Rousou, K.A. Matis and I.C. Hancock, J. Chem. Technol. Biotechnol., 74 (1999) 429.

[5] E. Fourest, C. Canal and J.-C Roux, FEMS Microbiol. Rev., 14 (1994) 325.

[6] A.I. Zouboulis, E.G. Rousou, K.A. Matis and I.C. Hancock, J. Chem. Technol. Biotechnol., 74 (1999) 429.

[7] D. Kratochvil and B. Volesky, Tibtech., 16 (1998) 291.

[8] M. Tsezos, E. Remoudaki and V. Angelatou, Internat. Biodeterioration Biodegradation, 38(1) (1996) 19.

[9] Y.S. Ho, D.A.J. Wase and C.F. Forster, Environ. Technol., 17 (1996) 71.

[10] D. Brady and J.R. Ducan, Enzyme Microb. Technol., 16 (1994) 633.

[11] P.A.S.S. Marques, M.F. Rosa and H.M Pinheiro, Bioproc. Eng., submitted.

[12] A. Kapoor and T. Viraraghavan, Bioresource Technol., 61 (1997) 221.