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The application of a micro-algal/bacterial biofilter for the detoxification of copper and cadmium metal wastes

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ABSTRACT

In the present study the potential of a biofilter containing a mixture of dried micro-algal/bacterial biomass for removing heavy metals (Cu^{2+} , Cd^{2+}) from dilute electroplating waste was tested. The biomass was produced in an artificial stream using the effluent of a municipal waste water treatment plant as a nutrient source, with the additional benefit of reducing phosphorus and nitrogen loadings. Baseline batch experiments determined that optimum adsorption for both metals (80–100%) were achieved with the deionized- H_2O conditioned biomass at initial pH 4.0. Other biosorption variables (contact time, initial metal concentration) were also tested. Biosorption data were fitted successfully by the Langmuir model and results showed a high affinity of the used biomass for both metals (q_{max} 18–31 mg metal/g.d.w). Flow-through column experiments containing Ca-alginate/biomass beads showed that metal adsorption depends also on flow-rate and volume of treated waste. Desorption of both metals with weak acids was very successful (95–100%) but the regeneration of the columns was not achieved due to the destabilization of beads.

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1. Introduction

Heavy metal contamination exists in aqueous waste streams of many industries, such as metal electroplating facilities, mining operations and tanneries. Heavy metals are not biodegradable and tend to accumulate in living organisms causing various diseases and disorders, as well as deleterious ecological effects. When considering the environmental impact of metals usually mercury, lead and cadmium are in focus (Bailey et al., 1999). The major spread of lead in the environment has been curbed by introduction of unleaded fuels and catalyst technology in modern cars. Although the use of mercury and lead is limited for the time being, cadmium is toxic and ubiquitous in distribution throughout the world. With the use of cadmium on the increase in electroplating, batteries, alloys, pigments, stabilisers for catalysts and in semiconductors and TV tube phosphorus, it represents a recognised great hazard to humans and the environment.

The content of residual toxic metals in wastewater treatment plants influences the choice of the removal method to be used. Several methods have been applied for final (tertiary) treatment, such as adsorption using activated carbon or other appropriate sor-

bents (alumina, zeolites, etc.), post-precipitation, ion-exchange, reverse osmosis, electrochemical treatment and evaporation (Bakkaloglu et al., 1998; Matsumoto et al., 2007). Conventional methods for removing metals are either becoming inadequate to address current stringent regulatory effluent limits or are increasing in cost. As a result, alternative, cost effective technologies are in high demand. The use of biological materials, including living and non-living micro-organisms, to remove and recover toxic or precious metals from industrial waste waters has gained popularity over the years due to good performance, availability and low cost of raw materials (Ahluwalia and Goyal, 2007; Benaissa and Elouchdi, 2007; Bunluesin et al., 2007). Micro-organisms including bacteria (Ansari and Malik, 2007), algae (Mallick, 2003), fungi and yeasts (Dursun, 2003) can efficiently accumulate heavy metals from their external environment (Ghimire et al., 2007; Ziagova et al., 2007; Pan et al., 2007). Additionally, other materials or by-products such as degreased coffee beans (Kaikake et al., 2007), hydroxyapatite surfaces (Corami et al., 2007), even tea waste (Amarasinghe and Williams, 2007), are currently under scrutiny. Adsorption of heavy metals can be high and depends on many factors, including the capacity, affinity and specificity of the biosorbents and the physical or chemical conditions in effluents. So biosorption – a term describing the process when non-living biomass is used – is of industrial interest because the removal of toxic metals from liquid wastes can result in detoxification and safe environmental discharge. Subsequent treatment of loaded biomass

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by elution can enable the recovery of valuable elements or further containment of highly toxic species (Kaikake et al., 2007).

In the present study we used domestic sewage as a nutrient source for producing, in an artificial stream, a mixture of micro-algal/bacterial biomass. The potential of this dried biomass for the removal of heavy metals from dilute single-metal electroplating waste was then examined. Optimum Cd^{2+} and Cu^{2+} biosorption conditions (biomass conditioning, initial pH, contact time, initial metal concentration) were determined in batch experiments. Subsequently, the ability of adsorption/desorption of metals with a continuous flow-through filter was assessed in a small-scale system. This procedure has the combined advantage of radically decreasing nutrient loading of domestic effluents while producing at the same time a low cost absorbent suitable for metal biosorption.

2. Methods

2.1. Batch biosorption experiments (1st phase)

2.1.1. Biomass conditioning

For the batch biosorption experiments micro-algal/bacterial biomass from the secondary treatment stage of the Lavrio wastewater treatment plant (Prefecture of Attica, Greece) was used. The biomass was dried at 65 °C until constant weight, following initial sun-drying and autoclave sterilisation after thorough washing with deionized water. Conditioning involved stirring for 15 min in 200 mL solution of 0.2 M H_2SO_4 , 1 M NaOH, 1 M Na_2CO_3 , or dH_2O . After precipitation and washing with deionized water, the biomass was dried at 65°C until constant weight (Table 1).

2.1.2. Determination of optimum initial pH, and biomass conditioning

For all phase-one experiments artificial cadmium and copper solutions of 10 mg/L were prepared from stock solutions of 1000 mg/L. The biomass was pulverized and 0.1 g were stirred in 250 mL conical flasks ($\times 4$ replicates) for all treatments. These included all combinations of the two metals, three initial pH values (2.0, 4.0, 5.5) and four biomass conditioning procedures (0.2 M H_2SO_4 , 1 M NaOH, 1 M Na_2CO_3 and dH_2O).

2.1.3. Determination of the effect of contact time and initial metal solution concentration

Biosorption efficiency (using optimum initial pH and biomass conditioning) was assessed by allowing biomass to contact 10 and 1000 mg/L solutions of each metal (Cd^{2+} and Cu^{2+}) for 1, 5, 15, 30, 60 & 120 min. Separate experiments with dH_2O treated biomass were also performed, at pH 4.0 for 15 min continuous stir-

ring, to test the effect of different initial metal concentrations (10, 50, 100, 200, 300, 400, 500 and 1000 mg/L) (Table 1). The data obtained by these tests were fitted to adsorption isotherms for Cu^{2+} and Cd^{2+} (q versus residual metal concentration, C_e) using the Langmuir isotherm and isotherm constants.

In all batch experiments the biomass was removed prior to analysis by centrifugation from all samples, and 5 mL of the supernatant were collected and stored in small plastic containers at 4 °C with the addition of 0.1 mL 65% HNO_3 solution.

2.2. Biomass production (2nd phase)

A mixed culture of algae/bacteria was grown in an artificial stream constructed in the Korinthos–Loutraki Wastewater Treatment Plant (Prefecture of Korinthos, Greece). Effluent from the WWTP, before the chlorination stage, was introduced into a 900 L tank and recirculated (turnover time approx. 10 min) over the “algal” mat growing in the 5 m long, 1.5 cm deep “closed” artificial “stream”. The streambed was covered with a plastic mesh of very small pore diameter to facilitate anchoring of the micro-algae and better absorption of nutrients (Table 1). The produced biomass was a mixture of bacteria, Cyanobacteria (i.e. *Chroococcus* sp., *Pseudoanabaena* sp., *Leptolyngbya* sp), Chlorophyceae (i.e. *Scenedesmus* sp., *Tetraedon* sp., *Chlorella* sp., and *Chlorococcus* sp.), and Diatoms (i.e. *Navicula* sp., *Nitzschia* sp., *Cyclotella* sp.). This procedure reduced the phosphorus and nitrogen load of the wastewater by 70–80% within four days and produced approximately 12 g d.w. of biomass for every 2,000 m³ of effluent.

The biomass used in batch experiments (phase 1) and the biomass produced in phase 2, for the construction of the flow-through biofilters, were identical in terms of species composition and were similarly prepared as described above (phase 1). The final product used in the experiments was dry pulverized biomass particles, less than 250 mesh size, with a specific density of 0.8809 ± 0.0098 (APHA, 1998). The specific surface area for Cu^{+2} and Cd^{+2} solutions was 2.75 and 4.26 m²/gr respectively, and was estimated from the maximum biosorption capacity, q_{max} (Ho et al., 2002; Keskinan et al., 2007).

2.3. Continuous flow-through biosorption experiments (3rd phase)

In the third and final phase of the study, the biomass produced in the artificial stream was used as a biosorbent in continuous flow-through column experiments. The columns were made of polyethylene tubes, 15 cm tall and 1.5 cm in diameter. Flow-rate was controlled by the speed of a peristaltic pump. Artificial cadmium and copper metal solutions of 100 mg/L at pH 4.0 were pre-

Table 1
Summarized flowchart of the three phases to develop a bio-filter for removing heavy metals from dilute electroplating waste and recovering the metal via desorption cycles.

1st Phase: Batch biosorption experiments with dried microalgal/bacterial (micro algal) biomass	
Initial batch experiments (conditioning, pH, contact time, initial metal concentration) with microalgal biomass harvested from the secondary treatment stage of the Lavrio wastewater treatment plant (Greece). Number of samples 416.	
2nd Phase: Production of microalgal/bacterial biomass	
A mixed culture of algae was grown in artificial stream in the area of Korinthos–Loutraki Wastewater Treatment Plant (WWTP) (Prefecture of Korinthos, Greece). Effluent from the WWTP, before the chlorination stage, was circulated over an algal mat growing in a 1.5 cm deep “closed” artificial “stream”, over a 5 m long (turnover time approx. 10 minutes).	Use of the microalgal/bacterial biomass as a biological biosorbent for the removal of Cu^{2+} and Cd^{2+} from low concentration (10 mg/L) artificial solutions during batch biosorption experiments. Number of samples 4788
3rd Phase: Continuous flow-through biosorption experiments using the dried biomass produced during the 2nd Phase. The dried biomass was mixed with Na-alginate to produce algal-beads to overcome flow issues.	
Determination of optimum pH (3.0, 4.0, 5.5) and flow-rate during continuous flow-through biosorption experiments of Cu^{2+} and Cd^{2+} . The effect on biosorption efficiency was examined with two flow-rates, 136 mL/h and 44 mL/h during biosorption of other metals i.e. Cu^{2+} . The maximum flow-rate of 136 mL/h was used for practical reasons in the biosorption experiments with Cd^{2+} . Number of samples 1680	Desorption of Cu^{2+} and Cd^{2+} : Initial Cd^{2+} biosorption on the biomass followed by desorption with 0.2 M HCl. Number of samples 960

pared from stock solutions of 1000 mg/L. When the dried and pulverized biomass was directly used to fill up the columns, the biofilters (all 4 replicates) were blocked and the free flow of metal solution was impaired. For this reason a method described in Prakasham et al. (1999) was adopted for the formation of spherical beads 2 mm in diameter containing Ca-alginate and biomass. The amount of immobilized biomass (known as beads) used in the biofilters had a volume of 10 mL (approximately 5.41 g of wet weight or 0.24 g of dry weight). During the preliminary experiments, two different flow-rates (44 mL/h and 136 mL/h) were tested, while all final experiments were performed at the high flow-rate. Samples were collected at the outlet of the biofilters at increments of 55 ml every 24 min (high flow-rate), and after a 12 h run period a total of 30 collections (total volume 1650 ml) were made per replicate column (Table 1).

2.4. Metal desorption

Different concentrations of sulfuric and hydrochloric acids (0.2 N H₂SO₄, 0.1 N and 0.2 N HCl) were used as elution solutions in the desorption experiments (Wilhelmi and Duncan, 1996). Experimental trials with 1 M Na₂CO₃ solution were also conducted for the regeneration of the immobilized microalgal biomass (Blanco et al., 1998). For the desorption experiments the biosorption cycle was interrupted at approximately 6 h of operation in order to initiate desorption. During the biosorption stage 20 collections were made, and a similar number was also collected during desorption.

All batch and flow-through experiments were conducted at an ambient temperature of 25 °C. Multi factor and single factor analysis of variance was used to test the significance of observed differences. A Buck Scientific Model 210 VGP atomic absorption spectrophotometer was used for the determination of metal concentrations.

3. Results and discussion

3.1. Batch biosorption experiments (1st phase)

3.1.1. Influence of biomass conditioning and initial pH on copper and cadmium biosorption

The dependence of metal biosorption on pH is well documented and is related to the functional groups on the surface of the biomass cell wall, as well as the ionic status and solubility of the metal in question (Rangsayatorn et al., 2002; Bayramoğlu et al., 2006; Saeed and Iqbal, 2006; Kaikake et al., 2007; Keskinan et al., 2007; Amarasinghe and Williams, 2007). These functional carboxylate, phosphate, and amino groups of the biomass cell wall are negatively charged, thus acting as scavengers of heavy metals (Bunluesin et al., 2007). Biosorption of heavy metals was recently reviewed by Ahluwalia and Goyal (2007) who give a full account of the mechanisms involved.

In the present study significant differences were detected in metal removal ($p < 0.05$) depending on metal species, biomass conditioning and initial pH (Fig. 1). The percentage of Cu²⁺ removal was significantly higher (60–80%) for the H₂SO₄ and dH₂O-conditioned biomass at pH 4.0 and pH 5.5 (Fig. 1a), whereas for the untreated biomass it was lower (approx. 50%). Actually, the untreated biomass has shown a steady performance in% copper removal for all three pH values tested. Conditioning of biomass with Na₂CO₃ or NaOH resulted in significantly lower% copper removal at pH 4.0 and pH 5.5 (Fig. 1a). Copper removal was also significantly lower than 50% at pH 2.0 for all types of biomass conditioning, especially with H₂SO₄ and NaOH. There was no significant difference in% cadmium removal between pH 4.0 and pH 5.5 ($p < 0.05$) using the untreated and the dH₂O-conditioned biomass reaching values

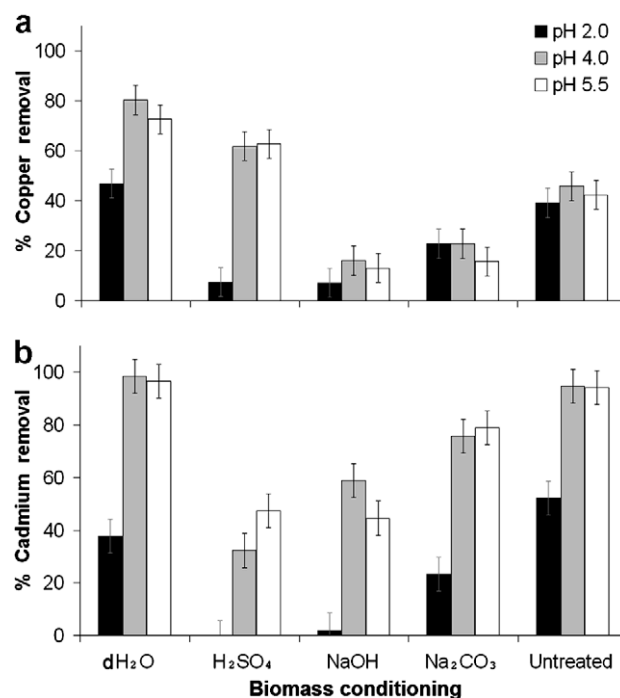


Fig. 1. Batch biosorption experiments -% removal of (a) Cu²⁺ and (b) Cd²⁺ at pH 2.0, 4.0 and 5.5 using conditioned (dH₂O, H₂SO₄, Na₂CO₃, NaOH) and untreated microalgal/bacterial biomass. There are significant differences ($p < 0.05$) between treatments (error bars: 95% LSD intervals).

of approximately 100% (Fig. 1b). Biomass conditioned with Na₂CO₃ gave good results (≈80%, Fig. 1b) but it was significantly less efficient in cadmium removal than the untreated and dH₂O-conditioned biomass for the same pH range. Although cadmium removal at pH 2.0 was significantly lower when conditioning of biomass was with H₂SO₄, Na₂CO₃ and NaOH, the untreated and dH₂O-conditioned biomass showed a mediocre performance between 38 and 50%. Therefore, our biomass mixture shows improved performance in metal removal as the pH increases from acidic to more neutral conditions (optimum pH range 4.0–5.5). This supports previous findings for other biomass materials such as tea waste (Amarasinghe and Williams, 2007), degreased coffee beans (Kaikake et al., 2007) and micro-algae or marine green algae (Kaewsarn and Yu, 2001; Bayramoğlu et al., 2006; Kumar et al., 2006a,b).

It has been reported that biomass conditioning with acids prior to biosorption greatly improves metal removal (Zeroul et al., 2003; Zafar et al., 2007). This was not fully supported by our results since only Cu²⁺ showed some evidence of slightly increased biosorption with H₂SO₄ conditioning (pH 4.0–5.5) in comparison to the untreated biomass. On the other hand, conditioning with NaOH and Na₂CO₃ did not improve metal sorption under any condition. For both Cu²⁺ and Cd²⁺, biomass conditioning with dH₂O yielded the best results, although in the case of Cd²⁺ the untreated biomass was equally effective.

Finally, in our study, cadmium% removal was significantly higher ($p < 0.05$) than copper when initial pH was 4.0 and 5.5 under any biomass conditioning, with the exception of H₂SO₄ where this result was reversed.

3.1.2. Influence of contact time on copper and cadmium biosorption

In accordance to the results of the previous experiments an initial pH 4.0 and the dH₂O biomass conditioning were selected as optimum conditions for investigating the influence of contact time and initial metal concentration on cadmium and copper biosorption.

The maximum rate of copper and cadmium removal (74% and 60%, respectively) was achieved within one minute of biomass contact with the 10 mg/L metal solution, and after five minutes Cu^{2+} was reduced by 81% and Cd^{2+} by 94%. Thereafter, as contact time increased the removal rate of copper and cadmium decreased gradually until steady state was reached after 20 min. At the completion of this 20-min cycle, about 85% of copper and 97% of cadmium were removed and the final pH of the solution for both metals ranged between 6.0–7.0. Using the same as above quantity of dH_2O treated biomass and an initial metal concentration of 1000 mg/L, the maximum Cu^{2+} and Cd^{2+} removal rate (circa 30%) was achieved within 1 minute of contact. After the completion of a 60-min cycle copper was reduced by about 40%, and cadmium by approximately 50%. The final pH of the solution after biosorption was in the range 4.0–5.0. This two staged biosorption of metals, with a first rapid phase and a second slower one, is typical for biomass where metal uptake initially occurs at surface strongly active sites, followed by adsorption at weaker sites laying at surface or deeper in the cell membranes (Amarasinghe and Williams, 2007; Kumar et al., 2006a,b; Zafar et al., 2007). Nevertheless, biosorption in a single phase was previously reported for dry cyanobacteria biomass (Blanco et al., 1998).

3.1.3. Influence of initial metal concentrations on copper and cadmium biosorption

The average percentage removal of Cu^{2+} (initial pH 4.0, dH_2O conditioning, contact time 20 min) from metal solutions of increasing initial concentration up to 100 mg/L was rising significantly ($p < 0.05$) reaching values of circa 90%. Higher initial metal concentration resulted in gradually lower% removal, since the biomass weight and contact time were kept constant (Fig. 2). Cadmium, on the other hand, showed a constant high value of 97–99% removal when initial concentrations up to 100 mg/L were used (Fig. 2), which thereafter decreased significantly. The adsorption capacity q (mg of adsorbed metal/g microalgal biomass) for both Cu^{2+} and Cd^{2+} is increasing exponentially with increasing initial metal concentration in the range 10–1000 mg metal/L. Copper reached a q maximum of approximately 24 mg Cu^{2+} /g biomass while cadmium was considerably higher, circa 36 mg Cd^{2+} /g biomass. This increase of biomass adsorption capacity with the increasing initial metal concentration has been previously reported for both single and mixed metal solutions and is attributed to the higher mass transfer and kinetic energy, thus the increased probability for collision between metal ions and the biosorbents. (Atkinson et al., 1998; Dönmez et al., 1999; Lesage et al., 2007).

3.1.4. Adsorption isotherms for copper and cadmium

The biosorption process for both metals by the mixed biomass used in the present study was very well described by the Langmuir model, and the optimization by linear regression (Lineweaver–Burk method) of the experimental data gave an excellent fit ($R^2 > 0.99$, see Table 2). An unusual two stage adsorption pattern was observed for both metals (Fig. 3), showing an intermediate plateau approximately at 150 mg/L residual metal concentration. Thereafter, the q values increase further, showing evidence of slow saturation in the higher residual concentration range (around 600 mg/L). A number of explanations were offered for this phenomenon (Schiewer and Patil, 2008), such as the heterogeneity of the mixed biomass at different equilibrium points causing scattering of data, or the formation of cationic metal complexes which may compete with metal ions. Another possibility is the presence of two types of binding sites with different affinities for metal ions, the stronger ones causing the first saturation plateau, and then the weaker sites that are gradually occupied until full saturation of the biomass surface is achieved.

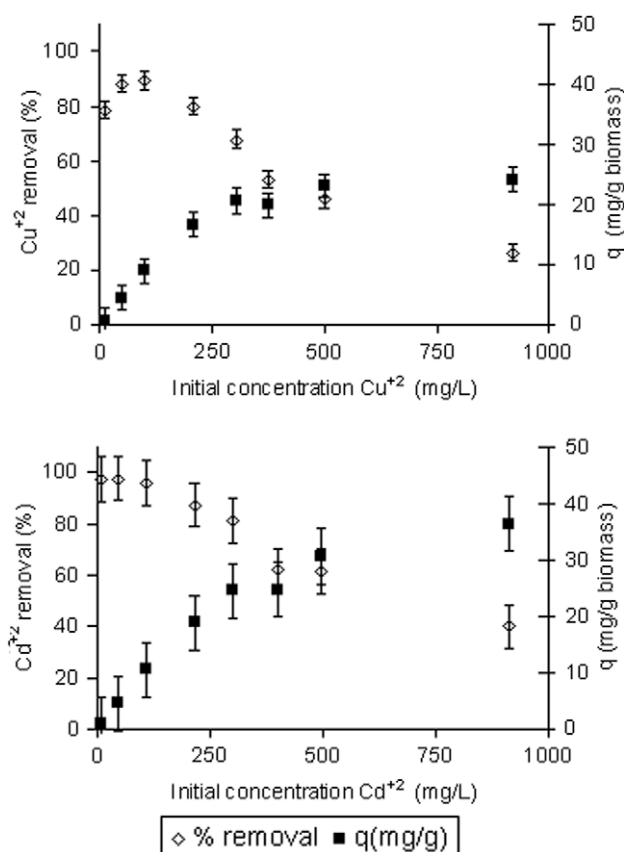


Fig. 2. Batch biosorption experiments with dH_2O -conditioned biomass demonstrating the effect of initial metal concentration on the % removal and adsorption capacity q for (a) Cu^{2+} and (b) Cd^{2+} . Statistical differences are shown by the 95% LSD intervals.

Table 2

The isotherm constants and regression coefficients for copper and cadmium.

Langmuir constants					
Metal	q_{max} (mg metal / g d.wt. biomass)	b	Intercept $1/q_{\text{max}}$	Slope $1/b q_{\text{max}}$	R^2
Cu	18,35709	0,089005	0,054475	0,612043	0,9941
Cd	31,32861	0,123837	0,03192	0,257755	0,9988

Under the experimental conditions of the present study the q_{max} and the adsorption coefficient b values for cadmium were higher than for copper (Table 2), indicating a higher adsorption capacity of our mixed biomass for this metal. Comparing our results to Langmuir biosorption parameters reported in literature for Cu^{2+} and Cd^{2+} biosorption by other low cost adsorbents (Amarasinghe and Williams, 2007; Ansari and Malik, 2007; Bunluesin et al., 2007; Corami et al., 2007; Kaikake et al., 2007; Lesage et al., 2007; Ziagova et al., 2007) our inexpensively produced biomass apart of acting as a tertiary system for treating domestic sewage, has a very good biosorbent potential.

3.2. Continuous flow-through biosorption experiments

The use of “free-floating” biomass in the flow-through column experiments was rejected because, due to its very fine powder like texture, the columns were blocked and the free flow of the metal solution was seized. This technical obstacle was resolved by immobilizing the microalgal/bacterial biomass in alginate beads according to Prakasham et al. (1999).

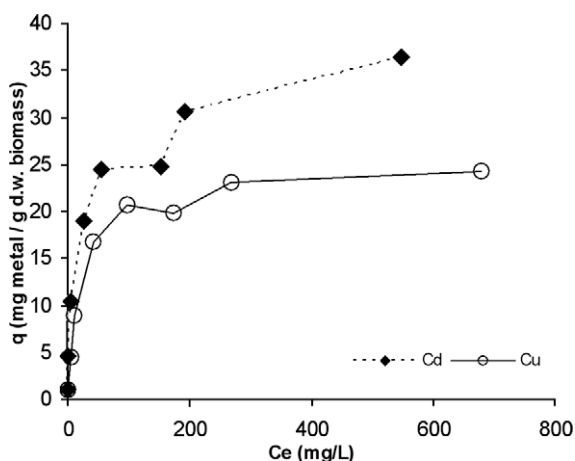


Fig. 3. Adsorption isotherms for Cu and Cd onto microalgal/bacterial biomass from the secondary treatment stage of the Lavrio wastewater treatment plant (dH₂O conditioning, pH 4.0 and 25 °C). The q values are expressed in mg metal /g d.w. biomass and the residual metal concentration C_e in mg/L.

Preliminary biosorption experiments with dH₂O-conditioned beads (immobilized biomass), using 100 mg/L copper solutions at different initial pH (i.e. 3.0, 4.0 and 5.5) verified that under flow-through conditions maximum biosorption was achieved at pH 4.0 ($p < 0.05$). Additionally, two different flow-rates were tested i.e. low f.r. = 44 mL/h and high f.r. = 136 mL/h. These trials demonstrated that metal removal is dependent on the flow-rate, as at the low f.r. max copper adsorption q (200 mg Cu²⁺/g d.w. immobilized biomass) was significantly higher ($p < 0.05$) than that at the high f.r. (circa 150 mg Cu²⁺/g d.w. immobilized biomass) (Fig. 4). This is a usual trend related to the adsorption equilibrium, the micro-porous tight structure of the Ca-alginate, and diffusion limitations of the solute into the pores of the biosorbent at higher flow-rates (Guibal et al., 1998; Vijayaraghavana et al., 2005). Nevertheless, since a higher flow-rate is preferable in order for a biofilter to be useful in practice, it was decided that the high flow should be used for both metals in all biosorption column experiments.

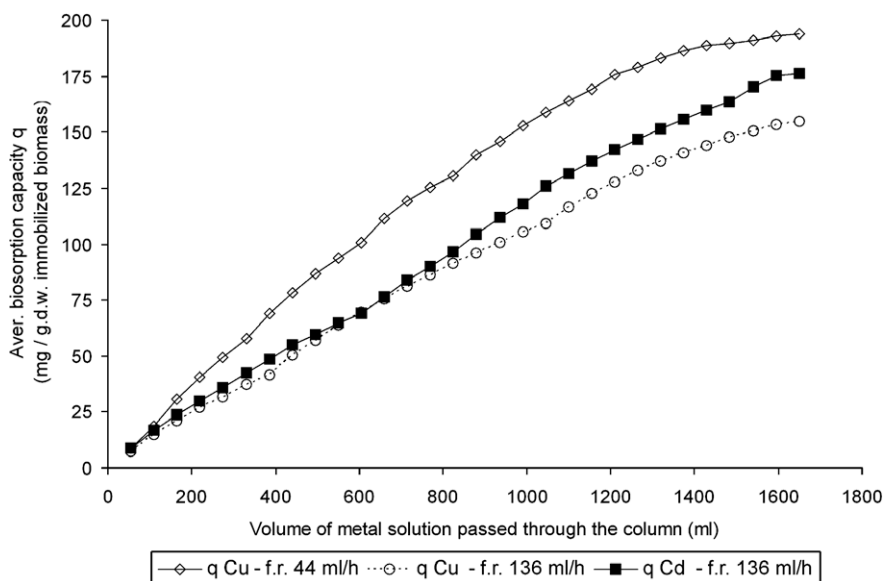


Fig. 4. Flow through column experiments showing the average Cu²⁺ and Cd²⁺ adsorption capacity (q) onto biomass/alginate beads (mg metal /g d.w. immobilized biomass) from 100 mg/L metal solution using different flow-rates of 44 mL/h and 136 mL/h. The observed differences were statistically significant ($p < 0.05$).

The total q of cadmium onto the beads (using the established conditions) after processing 1,650 mL of metal solution was 180 mg Cd²⁺/g d.w. immobilized biomass, while for copper the q value was 160 mg Cu²⁺/g d.w. immobilized biomass. In general, apart from the initial stages of the experiment, q values of copper were always significantly ($p < 0.05$) lower than those of cadmium. However, after processing 1,650 mL of metal solution the columns just started to show evidence of saturation for both metals, so the final breakthrough point and their final performance could be higher.

The ability of the stand alone Ca-alginate beads to adsorb metal ions and their influence on the biosorption capacity of the immobilized biomass was tested by processing a 100 mg/L Cu²⁺ solution through columns containing beads with no biomass. These control experiments showed that Ca-alginate beads had a significantly ($p < 0.05$) lower biosorption capacity (max q 0.77 mg Cu²⁺/g d.w.) when compared to the immobilized biomass in Ca-alginate (max q 1.58 mg Cu²⁺/g d.w.).

Finally, our results show that the immobilization of biomass did not significantly improve the adsorption of copper compared to the batch experiments. Copper q values using an initial concentration of 100 mg/L was about 8 mg Cu²⁺/g d.w. biomass, which is significantly higher than the q value of the immobilized biomass i.e. 1.58 mg Cu²⁺/g d.w. immobilized biomass. This decrease may be attributed to the cross-linking of potential metal-binding sites with the alginate solution, thus masking potential active sites of the biomass that would otherwise be free (Saeed and Iqbal, 2006). Also, as demonstrated for other metals (Bai and Abraham, 2003), biosorption capacity of immobilized biomass is reduced compared to native biomass due to the formation of a physical barrier around the entrapped biomass material.

3.3. Biosorption followed by metal desorption and regeneration of columns

Copper biosorption-desorption experiments (Fig. 5) demonstrated that 0.2N HCl and 0.1N H₂SO₄ were the most efficient elution solutions (98–100%) using approximately 120 ml acid at a high flow-rate (approx. 142 mL/h). Elution with 0.1 N HCl was slightly less efficient but still more than 90%. Although significant difference was observed between the eluted percentages of Cu⁺² and

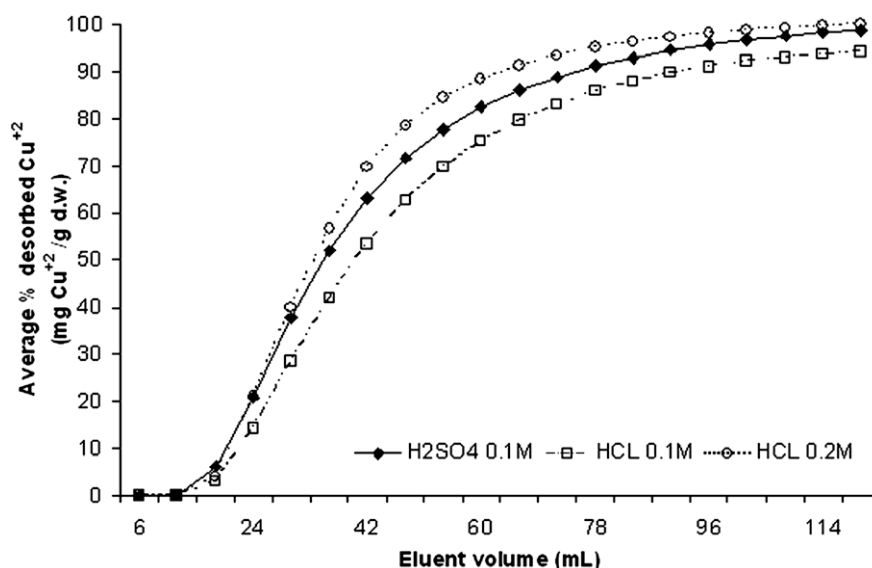


Fig. 5. Average percentage of copper eluted ions (mg Cu²⁺ / g d.w. immobilized biomass) after biosorption and desorption, using elution solutions of 0.1N H₂SO₄, 0.1N HCl, 0.2N HCl.

Cd²⁺ using 0.2N HCl, the percentage of cadmium was also high, approximately 96% for (Fig. 6). Similar high parentages of desorption are regularly reported in literature (Vilar et al, 2007; Bunluesin et al., 2007; Naiya et al. 2008).

Regeneration of the columns has been attempted by treating them with Na₂CO₃. During the regeneration process denaturation/chelation of the beads caused for the sodium alginate to leach from the beads, due to high solubilisation, and led to bead disintegration prohibiting the initiation of a new biosorption/desorption cycle. It has been reported that calcium alginate bonds are unstable in alkaline pH and dissolution occurs as a consequence of cation replacement or chelation. To overcome this problem a number of alternative non-toxic absorbing matrices (i.e. polysulfone-entrapped biomass, polyisoprene, PVA, or polyacrylamide-immobilized microbial biomass) were proposed (Bai and Abraham, 2003).

4. Conclusions

- The microalgal/bacterial biomass was sufficiently produced during the processing of the effluent from a municipal waste water treatment plant, with the additional benefit of reducing the phosphorus and nitrogen loading by 70–80% within four days.
- This dried biomass, in the batch experiments, was very efficient in removing copper (≈80%) and cadmium (≈100%) ions from metal waste, and the maximum removal rate was achieved within 5 min of contact time.
- The adsorption capacity *q* (mg of adsorbed metal/g biomass) was higher for cadmium than for copper ions, indicating a higher affinity of the microalgal/bacterial biomass for this metal.
- Reclaiming the metals through desorption with acids (0.2N HCl, 0.1N H₂SO₄) was successful reaching up to 100%

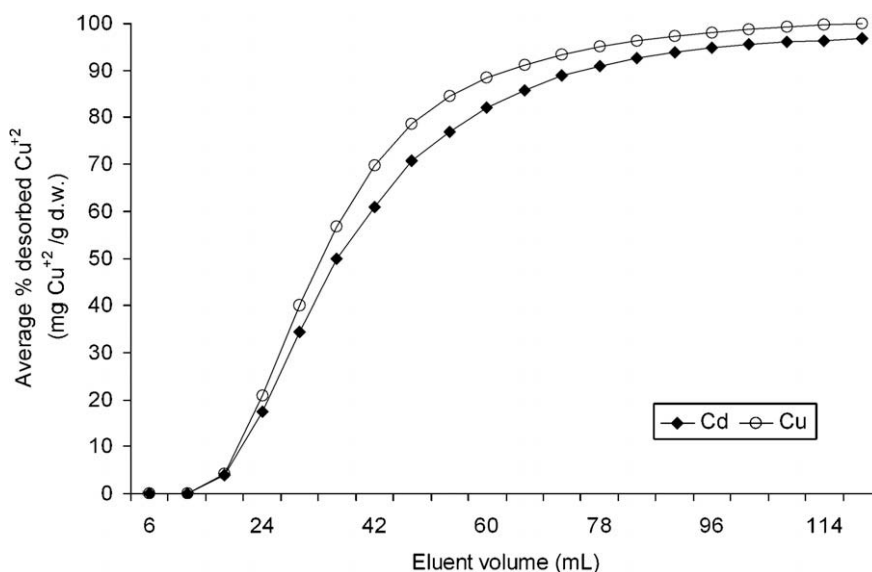


Fig. 6. Desorption of cadmium and copper ions (initial concentration 100 mg/L) with 0.2N HCl, at a flow-rate of 142 mL /h.

- Although the immobilization procedure with Ca-alginate contributed to the mechanical stability of the biomass, the biosorption efficiency was decreased compared to batch processes and it did not allowed for biomass regeneration due to denaturation of beads after treating with Na₂CO₃.

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