Journal of Hazardous Materials 178 (2010) 243–248

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Studies on sorption, desorption, regeneration and reuse of sugar-beet pectin gels for heavy metal removal

Y.N. Mata, M.L. Blázquez*, A. Ballester, F. González, J.A. Muñoz

Department of Materials Science and Metallurgical Engineering, Complutense University of Madrid, Ciudad Universitaria s/n 28040 Madrid, Spain

ARTICLE INFO

Article history:
Received 22 July 2009
Received in revised form
28 November 2009
Accepted 13 January 2010
Available online 18 January 2010

Keywords:
Beta vulgaris
Pectin xerogel
Biosorption–desorption cycles
Regeneration
Heavy metals

ABSTRACT

This work reports the effectiveness of sugar-beet pectin xerogels for the removal of heavy metals (cadmium, lead and copper) after multiple batch sorption–desorption cycles, with and without a gels regeneration step. Metals were recovered from xerogel beads without destroying their sorption capability and the beads were successfully reused (nine cycles) without significant loss in both biosorption capacity and biosorbent mass. Metals uptake levelled off or increased after using a 1 M $CaCl_2$ regeneration step after each desorption. Calcium, as a regenerating agent, increased the stability and reusability of the gels repairing the damage caused by the acid and removing the excess protons after each elution providing new binding sites. Because of their excellent reusability, pectin xerogels are suitable for metal remediation technologies.

1. Introduction

The treatment of effluents charged with highly dilute heavy metal concentrations is becoming an important issue because of environmental and sanitary problems, and increasingly restrictive legislations. Such effluents pose serious problems for the industry due to the high cost of metal decontamination using conventional technologies. Biosorption is a cost effective alternative for the purification of effluents containing low metal concentrations. Certain types of biomass (biosorbents) can passively bind metals and other pollutants such as dyes or organic compounds on chemically active sites or functional groups [1].

Different materials under different conditions have different metal uptake capacities and metal affinities. Recently, attention has been focused on byproducts or wastes of biological origin produced in large scale industrial or agricultural operations [2]. These biomass are characterized by their availability, high efficiency, easy handling and low cost. Among these, sugar-beet pulp (obtained from *Beta vulgaris*), a residue from the sugar industry has shown biosorption potential [3]. Moreover, biomass in its native state is generally inconvenient for biosorption applications due to its small particle size, low density, and lack of mechanical resistance. In this way, xerogels made from sugar-beet pectins extracted from the pulp are an interesting alternative.

Compared to other pectins obtained from other sources, like citrus, apple and sunflower pectins, sugar-beet pectins have the advantage that the raw material is already dried and does not depend on seasonality. There are previous studies characterizing sugar-beet pectin xerogels as a biosorbent [4]. Furthermore, cost reduction for industrial applications of a biosorption system requires that the biosorbent has an adequate mechanical stability, permeability and metal uptake in a series of sorption–biosorption cycles. In previous experiments, xerogel pectin beads have shown adequate stability at different solution pH and stirring conditions [4].

Once the biosorbent is exhausted, the metal-loaded biomass is in the form of residual muds. A decision has to be taken about the priority of removing a polluting or toxic substance from effluents and/or water that could be used for drinking or agricultural purposes, and about the problems that arise from the handling of exhausted biomass from the biosorption process. In this sense, desorption and reutilization of the biosorbents in adsorption–desorption cycles could help in reducing these residues. Desorption can be carried out by proton exchange using acids, chelating agents (EDTA) or exchange with other ions (i.e. $CaCl_2$) [5,6]. An efficient eluant is one that desorbs the metal completely without deteriorating the biomass. After elution, a metal concentrated solution is obtained from which metals can be recovered using electrochemical or other conventional techniques. In the case of cadmium, lead and copper desorption from sugar-beet pectin xerogels, previous studies have shown that HNO_3 is more effective than other inorganic acids (HCl or H_2SO_4) [4].

* Corresponding author. Tel.: +34 91 3944335; fax: +34 91 3944357.
E-mail address: mlblazquez@quim.ucm.es (M.L. Blázquez).

0304-3894/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2010.01.069

After metal desorption with acids, a regeneration step can be used to prevent biomass deterioration or loss of biosorption capacity. The choice of regenerating agent depends on the kind of biosorbent used and the metals adsorbed which determines the type of metal ion interaction with the solid material. In some cases, a simple wash with distilled water has been used [6,7]. In the present study the regeneration step of the biosorbent was carried out with the original gelling solution of the sugar-beet pectin gels, 1 M $CaCl_2$.

The aim of this work was to determine the effectiveness and resistance of sugar-beet pectin gels for the removal of Cd^{2+}, Pb^{2+} and Cu^{2+} from aqueous solutions in various batch adsorption–desorption cycles using 0.1 M HNO_3 as an eluant and with and without a 1 M $CaCl_2$ regeneration step. Published studies on metal binding with sugar-beet pectins are scarce and even less with calcium gels [4,8–10]. Studies concerning desorption, reuse and regeneration of metal-loaded biosorbents are also very rare and none of them addresses the use of pectins or their gels [11,12]. In recent reviews, Sud et al. [2] and Wang and Chen [13] pointed out that further research is needed in areas of metal desorption and biosorbent regeneration.

2. Materials and methods

2.1. Biosorbents

Azucarera Ebro Agrícola provided the sugar-beet pulp from the Toro plant in Zamora, Spain. The pulp was collected directly from the final drying line to ensure freshness. Sugar-beet pectin was extracted following the protocol proposed by Harel et al. [9]. The sugar-beet pulp was repeatedly washed with tap water and filtered with cheesecloth to remove the molasses. After that, a 5% pulp suspension in 0.3 M H_2SO_4 was heated during 4 h at 80 °C in a water bath. The solids were filtered and a solution of 95% ethanol was added to the remaining liquid causing pectin precipitation. The pectin was filtered and washed repeatedly with different ethanol solutions: twice with 70% ethanol and once with 85% and 95% ethanol successively. The remaining solid was dried in a stove at 35 °C and ground with an agate mortar.

The product of the extraction process, a highly methoxyl pectin, was demethylated in order to enable calcium gelation to produce adequate gels as described in a previous publication [4]. The demethylation method was adapted from the methods proposed by Harel et al. [9] and Le Cerf et al. [14]. A solution of 2% pectin in deionized water was stirred for at least 2 h, precipitated with 95% ethanol and filtered with cheesecloth. The pectin was cooled to 4 °C and a solution of 1 M NH_3 at the same temperature was added until a 2% pectin solution was obtained. This solution was stirred until homogenization and kept 12 h without stirring at 4 °C. Then, it was precipitated with a 70% ethanol solution, filtered and washed again twice with the ethanol solution. After three filtrations, it was kept stirred for 6 h in the 70% ethanol solution. Finally, it was filtered and resuspended in a 85% and then a 95% ethanol solutions. The remaining solid was dried in a stove at 35 °C and ground with an agate mortar.

The pectin gel beads were prepared by dropping a 1.5% pectin aqueous solution into a cooled 1 M $CaCl_2$ solution. The viscous solution was pressed through a syringe (internal diameter of 0.5 mm) to ensure bead uniformity. The beads were kept at 4 °C for at least 24 h in the same solution. The excess $CaCl_2$ was rinsed with distilled water. The hydrogel beads obtained had a diameter of 3 ± 0.2 mm and an average weight of 3.33×10^{-2} g. The beads were air dried at room temperature (23 ± 1 °C) to obtain xerogel beads of approximately 1.4 ± 0.2 mm of diameter and 1.11×10^{-3} g of weight (30 times lighter than the original hydrogels). On average, 1 mg of pectin yields 40 mg of hydrogels or 1.33 mg of xerogels. Xerogels contained approximately 73% of pectin and 27% of calcium.

2.2. Biosorption experiments

Biosorption experiments were carried out at room temperature (23 ± 1 °C) with monometallic 100 mg/l solutions (Cd^{2+}, Pb^{2+}, and Cu^{2+}) prepared from 1000 mg/l stock solutions using chemical reagents of analytical grade: $CdSO_4 \cdot 8/3H_2O$, $Pb(NO_3)_2$ and $CuSO_4 \cdot 5H_2O$. In the case of lead, nitrate instead of sulfate was used to avoid metal precipitation. Previous studies have shown that the effect of this anion is negligible [15]. The initial pH value of the metal solutions was adjusted with 1 M H_2SO_4 for Cd and Cu, 1 M HNO_3 for Pb, and 1 M NaOH as needed and based on previous optimum pH studies for the greatest metal binding capacity: pH 6 for Cd, 4 for Pb and 5 for Cu [4]. Special care was taken to select values below each metal's hydroxide precipitation pH for the metal concentrations used in this study, to ensure that metal uptake was only due to biosorption and not to chemical precipitation. The xerogel beads (0.05 g) were put in contact with the metal solutions (50 ml, 1 g/l biosorbent concentration) and liquid samples were removed at different times (0, 15, 60, 120, 240, 480 and 1400 min) for AAS analysis (PerkinElmer 1100B Flame Atomic Absorption Spectrometer) to ensure equilibrium concentration was reached in each biosorption. All the experiments were performed in duplicate and each point is the average mean of both results.

The amount of metal ions adsorbed per gram of biomass (q_e, mmol/g of pectin) was obtained as follows:

$$q_e = \frac{C_o - C_e}{B} \quad (1)$$

where C_o is the initial metal concentration (mmol/l); C_e is the equilibrium (final) metal concentration (mmol/l); B is the biomass concentration (g/l).

2.3. Metal desorption and biosorbent regeneration

After adsorption, the metal-loaded gels were filtered, weighed and placed in contact with a 0.1 M HNO_3 desorption solution at a biosorbent concentration of 1 g/l. This acid was chosen from previous experiments as an effective eluant of cadmium, lead and copper from sugar-beet pectin gels [4]. Metal concentration was determined in samples removed at 2, 5, 10, 30 and 60 min to ensure that the equilibrium concentration had been reached in order to calculate the overall metal uptake in each cycle. In order to determine the reusability of pectin gels, the same beads were used in consecutive adsorption–desorption or adsorption–desorption–regeneration cycles. In each cycle, the xerogels were filtered and repeatedly washed with deionized water after each desorption to eliminate the excess of acid. In the regeneration step, the gels were soaked in a 1 M $CaCl_2$ solution for 12 h at 4 °C, filtered, and washed with deionized water before being reused in a new sorption–desorption cycle. The experimental set up for the adsorption–desorption–regeneration cycles is depicted in Fig. 1.

The stability of the xerogels was controlled by weighing the gels after filtration at the end of each cycle. Since xerogels were weighed prior drying, the calculation of the metal uptake capacity after each cycle was made taking into account the initial amount of biosorbent, that is, without considering possible biomass losses. In this way, heat and desiccation during the dehydration process would constitute an additional pre-treatment procedure that could alter the xerogel characteristics in the next biosorption–desorption cycle, adding an unnecessary step that would make the process less feasible.

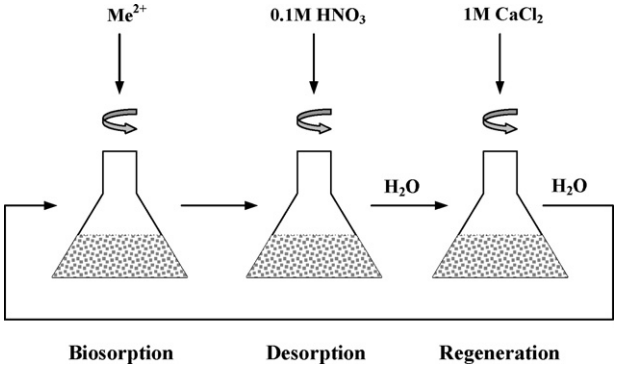

Fig. 1. Experimental setup for the metal adsorption–desorption–regeneration cycles with sugar-beet pectin xerogels.

After each biosorption, the final amount of metal adsorbed (Me_{ads}, mmol) was calculated with the following expression:

$$Me_{ads} = (Me_o + Me_{res}) - M_{ef} \quad (2)$$

where Me_o is the initial amount of metal in solution (mmol); Me_{res} is the residual amount of metal retained from the previous desorption, when applicable (mmol); Me_f is the final amount of metal in solution (mmol).

After each desorption, the desorption performance ($\%Me_{des}$) was determined as follows:

$$\%Me_{des} = \frac{Me_{des}}{Me_{ads}} \times 100 \quad (3)$$

where Me_{des} is the amount of metal in solution after each desorption (mmol).

The residual amount of metal retained per g of biosorbent at the end of each desorption experiment (Me_{res}/g, mmol/g) was:

$$\frac{Me_{res}}{g} = \frac{Me_{ads} - Me_{des}}{g\,\text{of biomass}} \quad (4)$$

3. Results and discussion

The following experiments were performed in order to evaluate the regeneration properties of 1 M $CaCl_2$ in multiple sorption–desorption cycles of cadmium, lead and copper with sugar-beet pectin xerogels:

- Five sorption–desorption cycles, washing the beads with deionized water after each 0.1 M HNO_3 desorption to remove the excess acid.
- Nine sorption–desorption–regeneration cycles, washing the beads with deionized water after each 0.1 M HNO_3 desorption and using 1 M $CaCl_2$ for 12 h as a regenerating agent.

3.1. Cadmium

Fig. 2 shows the evolution of the cadmium uptake and desorption performance after five consecutive cycles of sorption and desorption without 1 M $CaCl_2$ regeneration. The general trend was a stabilization of the metal uptake, which was similar to the initial value (0.151 mmol/g) after five cycles (Fig. 2a). Another biosorbent, the green microalga *Chlamydomonas reinhardtii*, on the other hand, showed a progressive decrease in cadmium uptake after six sorption–desorption cycles using 0.1 M HCl as an eluant, a decrease that was also present after the fifth cycle [16]. In contrast to pectins, polysaccharides present in microalgal cell walls are rich in glycoproteins and could be responsible for that difference. Desorption performance decreased from 80% to 69% after the fifth cycle

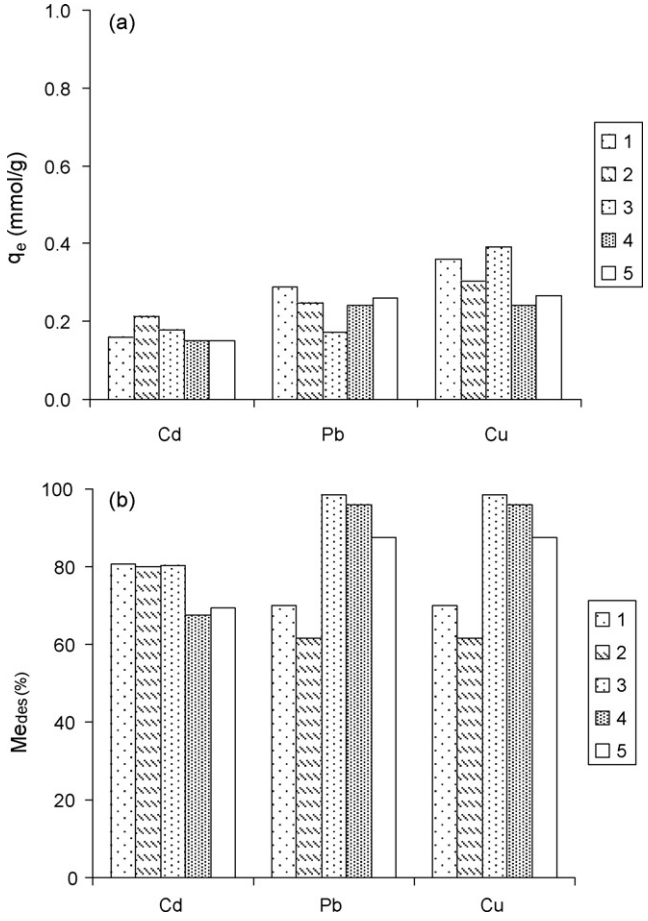

Fig. 2. Metal uptake (a) and desorption (0.1 M HNO_3) performance (b) of sugar-beet pectin xerogels after each adsorption–desorption cycle without a biosorbent regeneration step.

(Fig. 2b). Without regeneration, biosorbent mass decreased an average 20% after five sorption–desorption cycles (Fig. 3a). Besides the harmful effect of the acid during the desorption step, gel beads can become swollen during the experiments, which would be responsible for the small mass variations that were observed between the first and fifth cycles. After five cycles, however, there was a general biomass loss (Fig. 3a). The amount of metal retained in the biomass varied according to the desorption performance increasing progressively after five cycles (from 0.03 to 0.07 mmol/g) (Fig. 3b).

Fig. 4 shows the evolution of cadmium uptake and its desorption performance after nine cycles with a 1 M $CaCl_2$ regeneration step. Unlikely the experiments without regeneration in which metal uptake remained practically constant, the regeneration step, considerably increased cadmium uptake after five sorption–desorption cycles: from 0.151 to 0.329 mmol/g (Fig. 4a). Furthermore, even after completing nine cycles the metal uptake was two times higher than the initial value (increasing from 0.151 to 0.302 mmol/g). On the other hand, regeneration with $CaCl_2$ caused a higher decrease of the desorption performance than without regeneration (Figs. 2b and 4b). Biosorbent mass remained practically constant after five cycles and decreased only slightly after nine (10 mg), indicating a greater stability of the xerogels when using the regeneration step. The amount of metal retained after each elution is related with the desorption performance after each cycle and therefore remained low during experiments without regeneration but increased progressively in experiments with regeneration, suggesting a greater stability of the metal-biosorbent complexes (Figs. 3b and 5b).

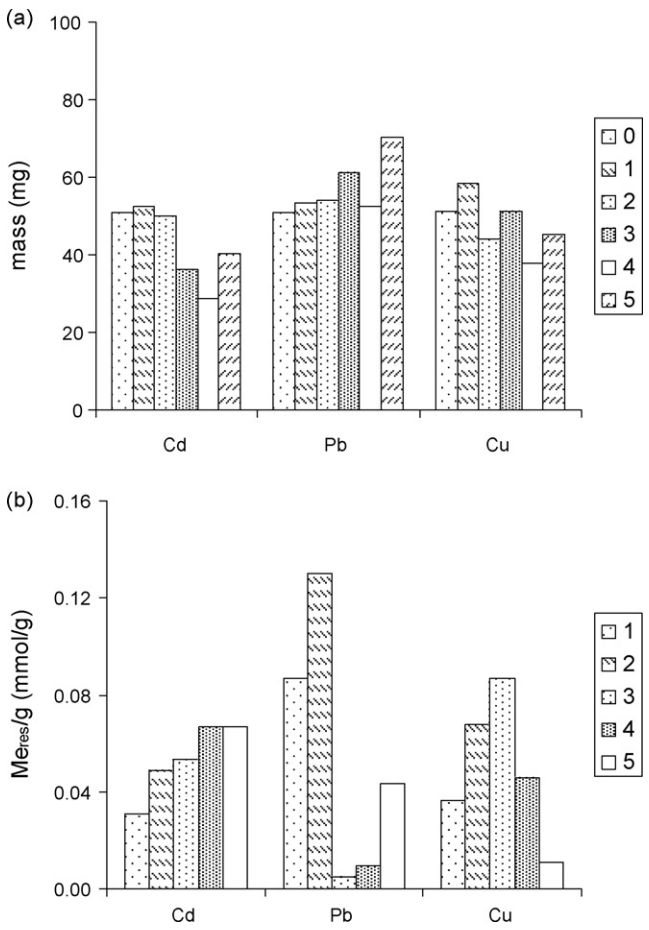

Fig. 3. Biosorbent mass (a) and amount of metal retained (b) after each adsorption–desorption (0.1 M HNO_3) cycle using sugar-beet pectin xerogels without a biosorbent regeneration step.

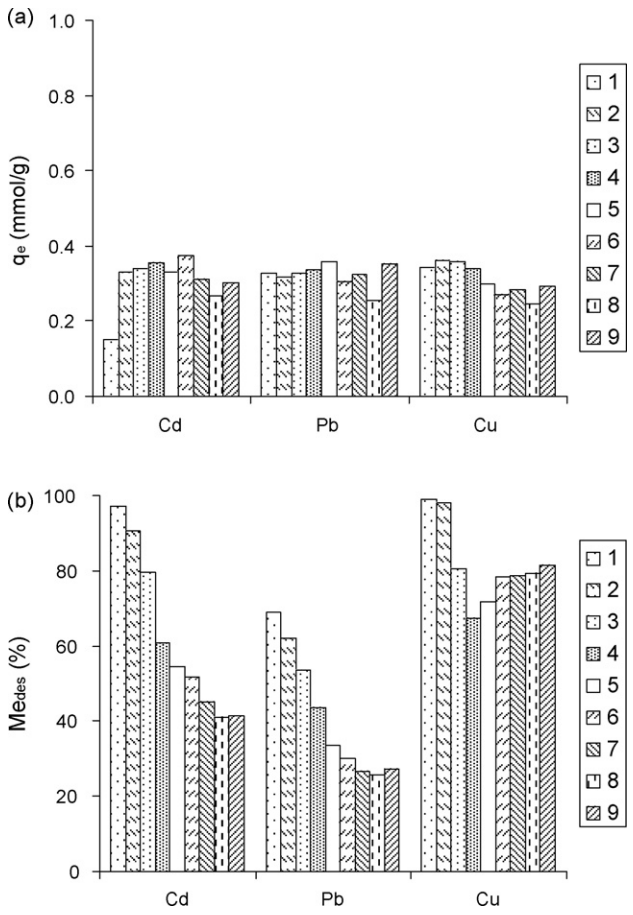

Fig. 4. Metal uptake (a) and desorption (0.1 M HNO_3) performance (b) of sugar-beet pectin xerogels after each adsorption–desorption cycle with 1 M $CaCl_2$ biosorbent regeneration step.

Similarly, Yan and Viraraghavan [12] observed that cadmium uptake levelled off or even increased after six adsorption–desorption cycles with *Mucor rouxii* using a 0.2 M NaOH regeneration step after each desorption with 0.05 M HNO_3. The mucopolysaccharide (glucosaminoglycan) cell wall of this fungus provides stability to this biomass. Additionally, Torres et al. [18] have shown that $Ca(OH)_2$ is less effective than $CaCl_2$ as a gelling agent. Therefore, $CaCl_2$ regeneration is one way to increase the stability of the gels that must withstand repeated sorption–desorption cycles.

3.2. Lead

Fig. 2 shows lead sorption uptake and desorption performance without 1 M $CaCl_2$ regeneration. The final lead uptake after the fifth cycle (0.261 mmol/g) was very similar to its initial value (0.290 mmol/g). On the other hand, lead desorption performance increased after the five cycles, from 70% to 88%. Pectin has shown greater cadmium than lead uptakes in previous studies which could explain this ease of elution [4]. A more progressive decrease of metal uptake was observed by Singh et al. [19] using the green alga *Pithophora oedogonia* in five cycles of lead sorption and 0.1 M HCl desorption. Conversely, Tuzun et al. [16] observed that lead uptake by *Chlamydomonas reinanhardtii* levelled off after five sorption and desorption cycles whereas cadmium uptake decreased as explained previously. Biosorbent mass remained practically constant after five cycles (Fig. 3a). The amount of metal retained decreased significantly after five cycles (Fig. 3b).

The effect of 1 M $CaCl_2$ regeneration on lead biosorption was similar to that observed for cadmium: better biosorption but worse desorption (Fig. 4). Final uptake values slightly increased after the fifth cycle (from 0.328 to 0.357 mmol/g) remaining practically constant after nine cycles (0.352 mmol/g), despite the 20% loss biosorbent mass (Figs. 4a and 5a). Desorption performance decreased until the fifth cycle (from 69% to 34%), after which remained practically constant (27% after nine cycles) (Fig. 4b). Like cadmium, the biosorbent mass remained practically constant after five cycles with regeneration, and a slight decrease was observed after nine cycles, indicating a greater biosorbent stability than without a regeneration step (Fig. 5a). The amount of lead retained increased progressively with increasing the number of cycles (Fig. 5b).

Similarly, Jalali et al. [11], using the brown alga *Sargassum*, rich in alginate polysaccharides, which are similar to pectins, observed similar lead uptakes and desorption performances after nine sorption and 0.1 M HNO_3 desorption cycles regenerating with 0.1 M $CaCl_2$. In the same way, fungal biomass of *M. rouxii* could resist five adsorption–desorption cycles without losing its lead uptake with an alkaline 0.2 M NaOH regeneration step [12]. This suggests that sugar-beet pectin xerogels and this fungus behave similarly during cadmium and lead adsorption–desorption cycles when a regeneration step was added.

Lead was difficult to elute showing performances lower than 100% with or without regeneration (Figs. 2b and 4b) and increasing the amount of lead retained after each sorption–desorption cycle (Figs. 3b and 5b). Unlikely without regeneration, the amount of metal retained increased progressively with regeneration, which

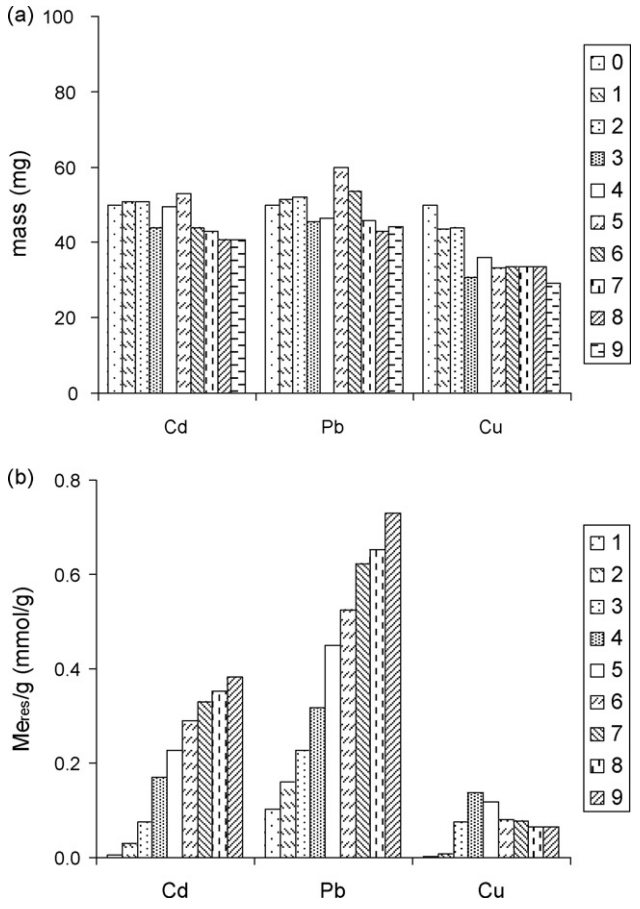

Fig. 5. Biosorbent mass (a) and amount of metal retained (b) after each adsorption–desorption (0.1 M HNO_3) cycle using sugar-beet pectin xerogels with 1 M $CaCl_2$ biosorbent regeneration step.

was related to the stability of the gels. The low lead desorption was also related to the stability of the biosorbent metal-complexes, which increased in the experiments with regeneration. In addition, the amount of lead retained after each cycle was greater with than without regeneration and with respect to cadmium and copper. In fact, previous experiments had shown that lead form more stable complexes with the xerogels than with cadmium and copper, as confirmed by its higher Langmuir affinity (64.1 l/mmol) than for the other two metals (1.75 l/mmol for cadmium and 8 l/mmol for copper) [4]. This greater equilibrium constant *b* indicates a stronger bond between metal and biomass [3].

3.3. Copper

Fig. 2 shows the variation of copper uptake and desorption performance after five adsorption–desorption cycles without 1 M $CaCl_2$ regeneration. Copper uptake decreased after five cycles (from 0.362 to 0.268 mmol/g) and desorption performance (90%) increased to 96% after the fifth cycle. Therefore, there was practically no metal retained after each cycle (Fig. 3a). Similarly, Lau et al. [20] observed a decrease of copper uptake but stable desorption performances after three adsorption and desorption (0.1 M H_2SO_4) cycles with the green alga *Ulva lactuca*. On the other hand, biosorbent mass was very unstable during the adsorption–desorption cycles, with an average 20% loss of mass (Fig. 3a). Singh et al. [19], using the green alga *Pithophora oedogonia*, also registered a decrease of copper sorption and biomass loss after five sorption–desorption cycles. Chen and Yang [21], using the brown alga *Sargassum* pretreated and non-pretreated with formaldehyde, observed a decrease of the copper uptake after five sorption–desorption cycles and weight loss, but the elution efficiency remained practically constant for the pretreated alga and decreased for the non-pretreated alga.

With $CaCl_2$ regeneration, copper uptake remained practically constant after five cycles (from 0.343 to 0.300) decreasing slightly after nine cycles (0.293 mmol/g) (Fig. 4a). Desorption performance decreased from 99% to 72% after five cycles, increasing slightly after the ninth cycle (82%) (Fig. 4b). Similarly to the other metals and in contrast to the results obtained without regeneration, with regeneration, biosorbent mass remained practically constant after five sorption–desorption cycles and decreased only 20% after nine, which could reflect an increase stability of the gels (Fig. 5a). There was also a slight increase in the amount of metal retained after each regeneration cycle when the regeneration step was introduced (Figs. 3b and 5b).

With regeneration, the amount of metal retained in successive cycles followed the order: Pb > Cd > Cu, suggesting that this phenomenon could also be related to ionic size and not only to the metal affinity constants. As a regenerating agent, $CaCl_2$ could repair the damage caused by the acid during the desorption process, remove the excess protons remaining from that step and form new cation bridges in the gel structure, re-stablishing sorption performance by exposing new binding sites [17]. In fact, after each adsorption cycle, there is an increase of uniformity and a visible decrease of coarse porosity of the gels, as shown in previous metal biosorption studies with pectin xerogels [4], and the adsorbed metals become part of the gel structure forming bridges similar to calcium, according to FTIR and EDS analysis also shown in the same study. This increase after each biosorption combined with the regeneration effect achieved with the $CaCl_2$ treatment, could prevent the desorption of part of the adsorbed metals in successive cycles. Without regeneration, the acid was able to strip practically all the metals retained in the gels.

Biosorption after $CaCl_2$ regeneration levelled off (lead and copper) or even increased (cadmium). This effect on the metal uptake compensates the decrease of the desorption performance observed with regeneration, which in turn increases the amount of metal retained in the gels. Since metal recovery, decontamination and biosorbent reusability were the main goals, the metal retained was not important as far as the adsorption capacity of the gels was maintained or increased. Anyway, metals retained after the reutilization process could be recovered from the exhausted gels by conventional techniques, including the destruction of the gel, such as pyrolisis or concentrated acid solutions.

4. Conclusions

Sugar-beet pectin hydro- and xerogels revalue an agricultural residue. Sugar-beet pectin xerogels are stable sorbents able to resist multiple sorption–desorption–regeneration cycles, using 0.1 M HNO_3 and 1 M $CaCl_2$ as desorbing and regenerating agents respectively. Despite an average 20% biomass loss due to biosorbent reuse in successive cycles, regeneration with 1 M $CaCl_2$ favored metal biosorption: increasing the metal uptake in the case of cadmium and levelling it off for lead and copper. Calcium, as a regenerating agent, increased the stability and reusability of the gels repairing the damage caused by the acid and removing the excess protons after each elution providing new binding sites. Because of their excellent reusability, pectin xerogels are suitable for metal remediation technologies.

Acknowledgements

The authors acknowledge the financial support received from the Ministry of Science and Technology of Spain and the European

Social Fund (Project REN 2002-02196). Y.N. Mata wishes to thank these institutions for the FPI scholarship she received through the same project.

References

[1] G.M. Gadd, Biosorption: critical review of scientific rationale, environmental importance and significance for pollution treatment, J. Chem. Technol. Biotechnol. 84 (2009) 13–28.
[2] D. Sud, G. Mahajan, M.P. Kaur, Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions—a review, Bioresour. Technol. 99 (2008) 6017–6027.
[3] Z. Reddad, C. Gérente, Y. Andrés, M.C. Ralet, J.F. Thibault, P. Le Cloirec, Ni (II) and Cu (II) binding properties of native and modified sugar beet pulp, Carbohydr. Polym. 49 (2002) 23–31.
[4] Y.N. Mata, M.L. Blázquez, A. Ballester, F. González, J.A. Muñoz, Sugar-beet pulp pectin gels as biosorbent for heavy metals: preparation and determination of biosorption and desorption characteristics, Chem. Eng. J. 150 (2009) 289–301.
[5] F. Beolchini, F. Pagnanelli, L. Toro, F. Veglio, Biosorption of copper by *Sphaerotilus natans* immobilised in polysulfone matrix: equilibrium and kinetic analysis, Hydrometallugy 70 (2003) 101–112.
[6] K.C. Sekhar, C.T. Kamala, N.S. Chary, A.R.K. Sastry, T.N. Rao, M. Vairamani, Removal of lead from aqueous solutions using an immobilized biomaterial derived from a plant biomass, J. Hazard. Mater. 108 (2004) 111–117.
[7] K.F. Tan, K.H. Chu, B.S. Gupta, M.A. Hashim, Studies on fixed-bed biosorption and elution of copper using polyvinyl alcohol—immobilized seaweed biomass, J. Environ. Sci. Health Part A 37 (2002) 1621–1632.
[8] V.M. Dronnet, C.M.C.G. Renard, M.A.V. Axelos, J.F. Thibault, Characterisation and selectivity of divalent metal ions binding by citrus and sugar-beet pectins, Carbohydr. Polym. 30 (1996) 253–263.
[9] P. Harel, L. Mignot, J.P. Sauvage, G.-A. Junter, Cadmium removal from dilute aqueous solution by gel beads of sugar beet pectin, Ind. Crop Prod. 7 (1998) 239–247.
[10] M.T. Kartel, L.A. Kupchik, B.K. Veisov, Evaluation of pectin binding of heavy metal ions in aqueous solutions, Chemosphere 38 (1999) 2591–2596.
[11] R. Jalali, H. Ghafourian, Y. Asef, S.J. Davarpanah, S. Sepehr, Removal and recovery of lead using nonliving biomass of marine alga, J. Hazard. Mater. 92 (2002) 253–262.
[12] G. Yan, T. Viraraghavan, Heavy-metal removal from aqueous solution by fungus *Mucor rouxii*, Water Res. 37 (18) (2003) 4486–4496.
[13] J. Wang, C. Chen, Biosorbents for heavy metal removal and their future, Biotechnol. Adv. 27 (2009) 195–226.
[14] D. Le Cerf, F. Irinei, G. Muller, Solution properties of gum exudates from *Sterculia urens* (Karaya gum), Carbohyd. Polym. 13 (1990) 375–386.
[15] A. Hammaini, F. González, A. Ballester, M.L. Blázquez, J.A. Muñoz, Biosorption of heavy metals by activated sludge and their desorption characteristics, J. Environ. Manage. 84 (2007) 419–426.
[16] I. Tuzun, G. Bayramoglu, E. Yalcin, G. Basaran, G. Celik, M.Y. Arica, Equilibrium and kinetic studies on biosorption of Hg (II), Cd (II) and Pb (II) ions onto microalgae *Chlamydomonas reinhardtii*, J. Environ. Manage. 77 (2) (2005) 85–92.
[17] J.M. Lezcano, Efecto del pretratamiento de biomasa procedente de un hábitat eutrofizado sobre la bioadsorción de metales, PhD dissertation, Complutense University of Madrid, Spain, 2008.
[18] E. Torres, Y.N. Mata, M.L. Blázquez, A. Ballester, F. González, J.A. Muñoz, Gold and silver uptake and nanoprecipitation on calcium alginate beads, Langmuir 21 (2005) 7951–7958.
[19] A. Singh, D. Kumar, J.P. Gaur, Removal of Cu(II) and Pb(II) by *Pithophora oedogonia*: sorption, desorption and repeated use of the biomass, J. Hazard. Mater. 152 (2008) 1011–1019.
[20] T.C. Lau, P.O. Ang, P.K. Wong, Development of seaweed biomass as a biosorbent for metal ions, Water Sci. Technol. 47 (2003) 49–54.
[21] J.P. Chen, L. Yang, Chemical modification of *Sargassum* sp. for prevention of organic leaching and enhancement of uptake during metal biosorption, Ind. Eng. Chem. Res. 44 (2005) 9931–9942.