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# Batch desorption studies and multiple sorption-regeneration cycles in a fixed-bed column for Cd(II) elimination by protonated *Sargassum muticum*

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**ABSTRACT**

The protonated alga *Sargassum muticum* was employed in batch desorption studies to find the most appropriate eluting agent for Cd(II)-laden biomass regeneration. Eleven types of eluting solutions at different concentrations were tested, finding elution efficiencies higher than 90% for most of the desorbents studied. Total organic carbon and biomass weight loss measurements were made. The reusability of the protonated alga was also studied using a fixed-bed column. Eleven consecutive sorption-regeneration cycles at a flow rate of 10 $mL \cdot min^{-1}$ were carried out for the removal of 50 $mg \cdot L^{-1}$ Cd(II) solution. A 0.1 M $HNO_3$ solution was employed as desorbing agent. The column was operated during 605 h for sorption and 66 h for desorption, equivalent to a continuous use during 28 days, with no apparent loss of sorption performance. In these cycles no diminution of the breakthrough time was found; although, a relative loss of sorption capacity, regarding the found in the first cycle, was observed. The slope of the breakthrough curves experiments a gradual increase reaching its maximum value for the last cycle tested (40% greater than for the first one). The maximum Cd(II) concentration elution peak was achieved in 5 minutes or less, and the metal effluent concentration was always lower than 0.9 $mg \cdot L^{-1}$ after 1h of elution. The maximum concentration factor was determined to be between 55 and 109.

**Keywords:** *Sargassum muticum*, fixed-bed column, Cd(II), sorption-desorption.

## 1. INTRODUCTION

In the last decade biosorption, the passive removal of contaminants by biological materials, has been greatly developed as an alternative or complementary technique for wastewaters treatment. Marine macroalgae have been chosen, among many biosorbents, due to their high binding ability and low cost. Moreover, an adequate reinforcement of seaweeds can provide an increase in their adsorption capacity, stabilization and attrition characteristics, making this biomass suitable for practical uses [1].

The raw algal biomass is stabilised by the main cations present in seawater, such us, $Na^{+}$, $K^{+}$, $Ca^{2+}$ and $Mg^{2+}$. As a result of simple physical treatment with acid, protons substitute these ions bound to active sites, and then, an increase in the maximum adsorption capacity for Cd(II) ion and an improvement in the biomass stability are obtained [2-4]. Furthermore, the use of acid-treated biomass reduces the percentage of algal weight loss in more than 50% and the total organic carbon (TOC) measurement around 40%, in batch experiments, with respect to raw alga. These results, obtained in a previous paper [2], encouraged further studies focusing on the suitability of the protonated *Sargassum muticum* for an eventual new Cd(II) recovery process.

The application of biosorption as a viable commercial technique implies the recovery of bound metals and the subsequent recycling of the biosorbent [5,6]. For this reason, several eluting agents were evaluated in batch, studying the percentage of metal desorption and the biomass damage during the elution cycle. However, the fact that the desorbed metal remains in the batch difficults its complete desorption, not avoiding the possibility of residual metal uptake. Moreover, the data are not applicable to most treatment systems where contact time is not sufficient for the attainment of equilibrium, and then, dynamic sorption studies must be developed for process applications [7]. Fixed-bed column is one of the most effective configuration for cyclic sorption-

desorption, allowing better efficiency use of the biosorbent, as a consequence of the enhanced use of the metal concentration difference between solution and biomass. At the influent, the biosorbent is in contact with a relatively high concentration of metal solution, attaining high uptake values, whereas at the effluent, the solution pass through fresh biomass, achieving very low final metal effluent concentrations [5]. Therefore, the present work also studies the possible reusability of the *S. muticum* algae in several sorption-regeneration cycles in a packed-bed column, analysing the effluent concentration versus time curves. These plots are usually referred to, as breakthrough curves for adsorption and as elution curves for desorption. Despite the importance of these studies, only a few current papers can be found in the literature regarding the metal removal by seaweed, employing a fixed-bed column in sorption-desorption cycles [8-11]. Therefore, this work may contribute to improve the knowledge of this kind of systems.

## 2. MATERIALS AND METHODS

### 2.1. Biomass

Samples of the brown marine alga *Sargassum muticum* were collected from the coast of A Coruña (Galicia, NW Spain). The alga was washed with tap and deionised water to eliminate impurities, oven dried at 60 ºC overnight, crushed with an analytical mill, sieved (size fraction of 0.5-1 mm) and stored in polyethylene bottles until its use.

This raw biomass were acid-treated in order to transform the alga into its fully protonated form by soaking and shaking it in a 0.2 $mol \cdot L^{-1}$ $HNO_3$ (Merck p.a.) solution in a rotary shaker (175 rpm) for 4 h, at a biomass concentration of 10 $g \cdot L^{-1}$. Afterwards, the material was rinsed thoroughly with deionised water until pH 4.5 was attained. Following filtration, treated biomass was dried in an oven at 60 ºC overnight.

**2.2. Batch experiments**

Batch studies were conducted in order to test different desorbing substances for Cd(II) release from the algae biomass. The protonated *Sargassum* biomass was first loaded with Cd(II) in experiments conducted at fixed pH (4.5) and initial metal concentration (250 $mg \cdot L^{-1}$). The Cd(II) solutions were prepared by dissolving of $Cd(NO_3)_2 \cdot 4H_2O$ in deionised water. The experiments were performed in 100 mL conical flasks employing a biomass dose of 2.5 g of algae (acid-treated biomass) per liter of Cd(II) solution. The mixtures were agitated on a rotary shaker at 175 rpm for 3 hours. NaOH and $HNO_3$ were used for pH adjustment. After that, the algae biomass was filtered through a 0.45 μm pore size cellulose nitrate membrane filter and the concentration of Cd(II) in the filtrates was determined by differential pulse anodic stripping voltammetry (DPASV) by use of 757 VA Computrace (Metrohm) with a conventional system of three electrodes: hanging mercury drop electrode as working electrode, Pt auxiliary electrode and Ag/AgCl (3 M KCl) reference electrode.

The filtered Cd(II)-laden alga was dried in an oven at 60 °C overnight; this biomass was then placed in Erlenmeyer flasks containing 40 mL of the desorbing agent solution. The samples were stirred for 3 hours (at 175 rpm) in order to attain the desorption equilibrium and then the algal biomass was filtered and weighted again. Cd(II) ion concentration was analysed by DPASV. Eleven types of eluting solutions at different concentrations were selected and tested: $CaCl_2$ (0.01, 0.1 and 1 $mol \cdot L^{-1}$), $Ca(NO_3)_2$ (0.01, 0.1 and 1 $mol \cdot L^{-1}$), $CaCO_3$ (0.1 $mol \cdot L^{-1}$), NaCl (0.01, 0.1 and 1 $mol \cdot L^{-1}$), KCl (1 $mol \cdot L^{-1}$), KI (1 $mol \cdot L^{-1}$), $Na_2S_2O_3$ (0.1 and 1 $mol \cdot L^{-1}$), EDTA (0.01 and 0.1 $mol \cdot L^{-1}$), HCl (0.02 and 0.1 $mol \cdot L^{-1}$), $HNO_3$ (0.03 and 0.1 $mol \cdot L^{-1}$) and $H_2O$ (as reference). Biomass weight loss was determined after each experiment. It was evaluated

as the difference between the initial dry biomass weight and the filtered dry biomass weight after desorption. Moreover, the supernatant solution was analysed for the total organic carbon (TOC).

### 2.3. Column experiments

The column experiments were carried out in a glass column of 40 cm length and 1 cm of internal diameter initially filled with 5.8 g of dried protonated *S. muticum*. A porous sheet (pore size 0) was attached at the bottom of the column in order to support the algal bed and to ensure uniform inlet flow and a good liquid distribution into the column. The top of the bed was closed by a 10 cm height layer glass beads (1 mm in diameter), which avoid the loss of biomass and also ensure a closely packed arrangement.

A 50 $mg \cdot L^{-1}$ Cd(II) solution was fed through the bed in up-flow mode at 10 $mL \cdot min^{-1}$ flow rate with a peristaltic pump (from Watson Marlow) connected at the bottom of the column. Samples were collected periodically and filtered through a 0.45 μm pore size cellulose nitrate filter; the filtrate was analysed for the remaining Cd(II) ion concentration ($C_{Cd}$) by DPASV. Data presented constitutes average values from at least two replicates.

Operation of the column was stopped when the effluent metal concentration reached a constant value. Afterwards, the Cd(II) loaded biomass was regenerated using 0.1 M $HNO_3$; the acid was fed to the column at the same flux rate used in the adsorption cycle. Following elution, deionised water was used to wash the bed until the pH in the effluent achieved a value of approximately 5. This regenerated bed was employed in the next cycle of adsorption to investigate the possible reusability of the protonated *S. muticum* in multiple operation procedures. The pH of the effluent was periodically

recorded. In cycle number eleven, column operation was stopped, the biomass was oven dried and the algal weight loss was determined.

## 3. THEORY: DEFINITION OF OPERATION PARAMETERS

### 3.1. Adsorption curves

The sorption performance of packed bed is described through the concept of the breakthrough curve. The time until the sorbed species are detected in the column effluent at a given concentration (breakthrough point), and the shape of the concentration-time profile or breakthrough curve are very important characteristics of the curves. Moreover, experimental determination of these parameters is very dependent on column operating conditions [1].

The area below the adsorbed metal concentration versus time plot, obtained through numerical integration, can be used to find the quantity of Cd(II) retained in the column. Dividing this value by the mass of alga in the bed ($m_s$), the maximum uptake capacity of the biomass ($Q_{Cd,max}$) was obtained, as it is shown in the following equation:

$$Q_{Cd,\max} = \frac{0.06 \cdot F}{m_s} \int_{t=0}^{t=t_e} (C_i - C_{Cd}) \cdot dt \qquad (1)$$

where $F$ is the flow rate (mL·min$^{-1}$), $C_i$ the feed Cd(II) concentration and $C_{Cd}$ the effluent Cd(II) concentration (mg·L$^{-1}$). The numerical parameter was included for unit concordance ($t$ is expressed in hours).

The efficiency in the overall use of algae in columns is indicated in the length of the transfer zone, which is reflected on the step character of the breakthrough curve. The breakthrough point ($t_b$) was defined as the time when the effluent Cd(II) concentration reached a value of 0.02 mg·L$^{-1}$ (breakthrough concentration), which is around ten times lower than the recommended limits for effluents from industrial processes in European Union (83/513/CEE directive); nevertheless, the quality objectives fixed in this directive

indicated that the concentration of dissolved Cd(II) in territorial waters, internal coastal waters, etc, that will be measured sufficiently close to the point of discharge, must not exceed 0.0025 $mg \cdot L^{-1}$.The bed exhaustion time ($t_e$) was selected as the time when the effluent concentration achieved a constant value ($C_{Cd,e}$), although the bed was not fully saturated. The time period from $t_b$ to $t_e$ ($\Delta t$) represents the sorption zone. Moreover, other important parameters that describe the geometry of the curves, such as the stoichiometric time ($t^*$) and the length of unused bed (LUB), were also calculated.

The stoichiometric time corresponds to the time at which the effluent concentration is one half of the feed concentration ($C_{Cd} = 0.5 \cdot C_i$) for a symmetric curve. Nevertheless, this can not be applied for unsymmetrical shapes and, in this case, $t^*$ was calculated from the following equation:

$$t^* = \frac{1}{C_i} \int_{t=0}^{t=t_e} \left( C_i - C_{Cd} \right) \cdot dt \qquad (2)$$

The LUB can be defined as the section of the bed that is required to account for spreading of the concentration front. It measures the unused portion of the sorption zone, employing the following equation:

$$LUB = D \cdot \left( 1 - \frac{t_b}{t^*} \right) \qquad (3)$$

where $D$ is the bed height (13 cm).

### 3.2. Desorption curves

The elution curve is the equivalent to the breakthrough curve but referred to the desorption step. It normally has an unsymmetrical frequency distribution shape, with a rapid increase of the released metal concentration followed by a flatter diminution. This produces the appearance of a peak that provides two important parameters: $C_p$, the maximum concentration peak, which measures the eluted Cd(II) concentration at this

point, and $t_p$, the time passed until the effluent concentration peak reached its maximum value (it gives an idea of the elution rate).

The elution curves can be described by the elution efficiency ($E$). This parameter was obtained dividing the metal mass desorbed ($m_{Cd,d}$) by the metal mass bound to the biomass in the previous adsorption step ($m_{Cd,ad}$):

$$E\,(\%) = \frac{m_{Cd,d}}{m_{Cd,ad}} \times 100 \qquad (4)$$

where $m_{Cd,d}$ is calculated from the numerical integration of the regeneration curves from $t$= 0 to $t_e$', with the following equation:

$$m_{Cd,d} = 0.06 \cdot F \int_{t=0}^{t=t_e'} C_{Cd} \cdot dt \qquad (5)$$

where $t_e$' is the time passed until residual Cd(II) concentration (lower than 0.02 mg·L$^{-1}$) were found in the effluent.

## 4. RESULTS AND DISCUSSION

### 4.1. Batch desorption studies

Efficient elution of adsorbed metals, with simultaneous regeneration of the biosorbent for later reuse, is extremely important for any potential application of a biosorbent. Other aspects like process kinetics, desorbent cost, pollution or selectivity, must also be taken into account [12].

Several eluants were tested in batch studies and evaluated according to their effectiveness to release Cd(II) from the metal-laden biomass; i.e., estimating the percentage of metal desorbed and the biomass damage during the elution cycle, calculated by measurements of biomass weight loss and total organic carbon (TOC) (Table 1).

Eleven types of eluting solutions at different concentrations were selected and tested. Their efficiency were based on two general principles that can operate in conjunction: on one hand, the competition between cations from acids ($HNO_3$, HCl) or salts ($CaCl_2$, $Ca(NO_3)_2$, $CaCO_3$, NaCl, KCl and KI) and the heavy metal ions bound to active sites, which will be released if eluant concentration is high enough and there is no steric impediment. On the other hand, the complexation of Cd(II) in solution with a chelating agent (EDTA) that will decrease the free ion concentration, causing a release of metals from biomass to solution.

Around 25 $mg \cdot L^{-1}$ of Cd(II) remained in solution when adsorption equilibrium was attained. This implies that the alga was able to retain approximately 225 $mg \cdot L^{-1}$ of this metal, which was tried to be desorbed with different agents. This result is in good argument with others batch Cd(II) adsorption studies where the same alga was employed [2,13].

Figure 1 shows the percentages of Cd(II) desorption for protonated *S. muticum* biomass. These results illustrate elution efficiencies higher than 90% for most of the desorbents tested, if their optimal concentration is used. Deionised water control demonstrated negligible metal desorption (lower than 0.5%).

No significant differences were found between the two acid desorptions, both giving percentages around 100% at pH 1. The acid wash releases significant quantities of organic carbon, being one of the most aggressive for the stability of the cell structure, with a 13% of weight loss (Table 1). The dissolution of polysaccharides with Cd(II) binding sites would also contribute to release metal back into solution.

The desorption performance of $Ca(NO_3)_2$ and $CaCl_2$ solutions was tested at three different concentrations. Both eluants displayed the highest elution efficiencies for 0.1 $mol \cdot L^{-1}$ concentrations at a final pH of around 3.5. Moreover, it can be observed a

decrease in the biomass weight loss, around 50%, with respect to acid elution and a very low value for TOC measurements, comparable with those obtained in the water control. Similar results were found with $Na_2S_2O_3$ that released 95% of the metal at the same concentration; however, the TOC values were markedly high. Other salt solutions (KI, NaCl and KCl) only stripped comparable values of Cd(II) at very high concentrations (1 $mol \cdot L^{-1}$).

The desorption effectiveness of the chelating agent, EDTA, was also examined in the concentration range from 0.01 to 0.1 $mol \cdot L^{-1}$, finding a release of about 100% for the highest concentration studied, with a biomass weight loss comparable to deionised water control.

The results suggest that the use of calcium salts leads to the best desorption efficiencies with the lowest values of TOC and biomass weight loss. Ca(II) ion stabilize the algal biomass by binding to alginate and converting it to the gel state [14]. It can also be observed that there are no significant differences between chloride and nitrate salts of calcium. The application of $CaCO_3$ solution resulted in only limited metal desorption due to the high pH value reached (6.2), which lead to a calcite precipitate.

Furthermore, HCl and $HNO_3$ were found to be very powerful metal-desorbing agents, although, their use may have damaging effects for the alga as it was demonstrated by the high TOC and biomass weight loss values. The selection of the most appropriate desorbent agents also depends on the previous state of the algae. As an example, if we use protonated biomass, desorption with acid could be more advantageous, since the release of metal and regeneration of the alga can be achieved just in one step, diminishing the overall process cost. Although calcium salt desorption was suggested as the best desorbing agent, the fact that the affinity of the *Sargassum* biosorbent towards Ca(II) ion is greater than towards Cd(II) ion [15], implies that Ca(II)

ion is more difficult to be removed from the binding sites than the protons, when Cd(II) is adsorbed. So that, we chose $HNO_3$ acid as desorbent agent in column sorption-desorption studies with the protonated alga *Sargassum muticum*.

### 4.2. Column studies

#### 4.2.1. Adsorption cycles

The column operation parameters, such as flow rate and bed height, were selected based on a previous paper, where the influence of these process variables on metal biosorption in column was studied [16].

Eleven Cd(II) adsorption-desorption cycles were completed in a continuous way. Figure 2 shows these breakthrough curves obtained for the adsorption cycles. It can be observed that from the first cycle the curves are practically identical, with a stepper character reflected in the increase of their slopes (Table 2). The adsorption-desorption performance of a column is directly related to the shape and length of the breakthrough curve, so characterisation of these parameters may be significant.

The column operating parameters are presented in Table 2. The obtained values for the second cycle constitutes an exception, as it is explained below, due to the earlier anomalous desorption step, and they were not taken into account.

The breakthrough time ($t_b$) was found to remain practically constant during the eleven sorption cycles (Table 2), and only a little increase can be found in the last cycle. This is of great importance for the practical application of the algae as metal biosorbent, since it implies the continuous use of the biosorbent with no apparent loss of sorption performance. Moreover, as it was expected, the length of the mass transfer zone ($\Delta t$), which is described by the difference between exhaustion and breakthrough times, did not change considerably during the process. This implies that the overall sorption zone

remains approximately constant during the cycles. Different behaviour for breakthrough time, as cycles were incremented, can be observed in the literature for metal sorption-desorption in column by seaweeds [8-11].

The maximum metal uptake resulted in a considerable reduction after the first desorption cycle and afterwards, the obtained values are practically constant with low variations in some cycles. The diminution in Cd(II) uptake capacity in the second cycle could be attributed to the effect of the prior acid desorption step. Although the biomass was previously acid treated, this first elution solubilised some part of the algal biomass, altering its structure and chemical composition, with the consequent loss or blockage of binding sites. On the other hand, it must be taken into account the diminution observed in algal mass was not considered in the calculations of Cd(II) uptake capacity, since it was related to the initial dry weight of biomass, and therefore, the values for metal adsorption from the first cycle are only apparent.

During the different cycles slight variations in flow rate and mass transfer conditions are possible, implying a possible change in the accessibility to the groups responsible for metal adsorption. As an example, in cycles three and six, a blockage in column that reduced flow rate around 15-20 % could be detected during the process. This could be a consequence of changes in physical properties, leaching or excessive swelling of the biomass, due to the large time that it is contacted with metal solution. So as not to influence the column operation we waited for desorption step, when the problem was solved due to the strong acid conditions employed. During this process the acid were able to sweep the rest of biomass that could block the flow, and clean the column.

As it was mentioned above, the geometry of the curves from cycle 2 to 11 is very similar. This is reflected in the constant values obtained for stoichiometric time ($t^*$) and LUB during these cycles (Table 2).

The slope of the breakthrough curves ($dC/dt$) may also be used to characterize the breakthrough curves. Table 2 shows the obtained values, which experimented a trend of increase, achieving its maximum for the last cycle tested (a 40% greater than for the first one), when the shortest adsorption zone was also found.

The effluent solution pH was frequently measured finding a decrease tendency as the Cd(II) was sorbed, from the initial value (between 4 and 5) to a constant value (approximately 3) when the bed was saturated. As the metal solution is contacted with the protonated biomass, an exchange between Cd(II) sorbed and protons released take place and therefore a pH decrease can be observed. When the bed was exhausted no more protons were liberate and then the pH tends to a constant value.

**4.2.2. Desorption cycles**

In order to regenerate the biosorbent material, an elution step was carried out after each adsorption cycle, when the column bed was saturated. The effective operation of the next sorption process is clearly related to the efficiency of the preceded desorption step. After each elution operation the column was washed with deionised water in order to eliminate the rests of acid in the bed, until a pH value between 4 and 5 was achieved in the effluent solution.

In the first desorption cycle the acid eluant solution was recycled throughout the column, so as to attain a higher efficiency of this desorbent agent. However, it did not produce the desire results. The acid solution (pH around 1.5) was fed to the column with the metal previously desorbed. This produced low Cd(II) gradient concentration in the

bed, which avoided the desorption of every metal bounded to the biomass. Moreover, it is not possible, in this way, to calculate very important parameters that define the elution performance, such as the quantity of metal desorbed, the elution efficiency or the concentration factor. In the other desorption cycles the eluted solution was not recycled.

As it was predicted in the previous batch studies, the first acid elution produced some loss of biomass material together with its corresponding binding sites, which produced an apparent uptake diminution in the followed sorption cycles. Nevertheless, this fact could be also beneficial, so several binding sites that were inaccessible due to structural limitations could be now available to metal uptake.

The desorption curves from cycle 2 to 11 showed a very similar unsymmetrical shape, with a rapid metal concentration increase, followed by a flatter diminution (Figure 3). One of the most important advantages of the acid elution is its high desorption rate, particularly in the first hour; moreover, it allowed to obtain elevated elution efficiencies in most of the regeneration cycles. Desorption was performed during 6 hours, giving very low residual Cd(II) concentrations ($C_{6h}$) (see Table 3). In only 5 minutes or less, the maximum concentration peak was achieved. When the elution reached to 1 hour ($C_{1h}$), the effluent concentration was always lower than 0.9 mg·L$^{-1}$. It is known that a long desorption time could cause the destruction of the biomass structure or, on contrary, a short elution process could be ineffective, so it is important to appropriate balance this procedure [1,17].

The elution efficiency provides information about the entire desorption curve, based on a previous adsorption step. Therefore, one must be aware of its significance and possible errors in its calculation. The narrow desorption peak make difficult to

exactly determine the area below it. Because of this, some uncertainty can be found in the metal mass desorbed calculations, which is reflected in the elution efficiency values.

The desorption efficiency was normally between 80-100% except for the cycle number two, where 120% was achieved. In the previous adsorption step the algae contained bound metal before the adsorption started, probably due to the failed first elution process; thus, the quantity of metal desorbed in the second cycle is greater than the adsorbed before, producing this apparent high percentage of elution. On the other hand, desorption efficiency for cycles 6 and 7 was atypically low. This can be attributed to changes in flow conditions due to the blockage of the column, channel and bubble formation, or to the error in the calculation of the area below desorption curves.

Dividing the maximum concentration peak ($C_p$) by the initial influent metal concentration ($C_i$), the concentration factor ($CF_p$) is obtained (Table 3). This term expressed the factor by which the metal concentration is raised with respect to its initial concentration in the influent solution. Therefore, in order to desorb the maximum quantity of metal in a short time, which implies a low effluent volume, it is important that $CF_p$ was as high as possible. A constant concentration factor value around 95 was found from cycle 3 to 11, meaning that the overall capacity of biosorbent to concentrate the metal remains invariable during these cycles. The low value obtained for second desorption cycle was probably due to the previous anomalous step, as it was explained above.

The effluent solution pH was regularly measured during regeneration steps. The pH tendency was very similar to the observed in the desorption curves: a rapid increase in the first five minutes, followed by a continuing diminished towards constant values (around 1.5). The situation is opposite to the observed in adsorption cycles, the protons of the eluant were exchanged with the metal bound, which produces an initial augment

of the pH value up to the point of maximum Cd(II) released concentration in the effluent. As occurs in sorption cycles, this pH tendency supports the idea of ion exchange as the predominant mechanism in metal biosorption [18,19].

After the eleventh desorption cycle the biomass was oven dried and weighed, founding 4.3 g of algae remained, which correspond to a weight loss of 27% for the whole process.

## 5. CONCLUSIONS

Batch studies demonstrated the high efficiency of chloride and nitrate calcium salts as desorbing agents, for the released of the Cd(II) previously bound to protonated *S. muticum* alga, causing no structural damage in the biomass or even reinforcing it. $HNO_3$ and HCl were found to have similar eluant capacity. They were more aggressive for the stability of the algae; nevertheless, acid desorption contributed to sweep soluble biomass material, which could block a fixed-bed column employed in metal sorption-regeneration cycles. Moreover, the previous state of the biomass, among other factors, must be taken into account in the desorbent election.

The results obtained in the column studies demonstrated that the protonated macroalga *S. muticum* could compete with commercial biosorbents for the removal of Cd(II) from wastewaters in fixed-bed columns. The system tested was able to operate during 605 h for sorption, maintaining a Cd(II) effluent concentration lower than 0.02 $mg \cdot L^{-1}$ during at least 2 h in the eleven cycles tested. The metal desorption with $HNO_3$ acid was fast, with a maximum Cd(II) concentration peak obtained in 5 minutes or less, and a residual metal concentration lower than 0.9 $mg \cdot L^{-1}$, after 1 h of elution for all the cycles studied.

After an acid treatment, the invasive algae *S. muticum* was able to support an uninterrupted use during, at least, 28 days subjected to continuous Cd(II) sorption-desorption cycles in a fixed-bed column, with no apparent diminution of its sorption performance, despite the 27 % weight loss found for the whole process.

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**FIGURE CAPTIONS**

**Figure 1**

Percentage of cadmium released from protonated *S. muticum* biomass (2.5 g/L) in batch studies, employing several desorbing agents at different concentrations.

**Figure 2**

Multiple breakthrough curves for cadmium biosorption (50 $mg \cdot L^{-1}$) by protonated *S. muticum* biomass (5.8 g) at constant flow rate (10 $mL \cdot min^{-1}$).

**Figure 3**

Multiple elution curves for cadmium desorption at constant flow rate (10 $mL \cdot min^{-1}$), employing $HNO_3$ 0.1 M as eluant.

**TABLES**

**Table 1**

Total organic carbon and biomass weight loss found after the employment of different substances in batch studies, for the release of cadmium previously sorbed by protonated *S. muticum*.

| **Desorbed agents** | **TOC ($mg \cdot L^{-1}$)** | **Weight loss (%)** |
|---|---|---|
| $CaCl_2$ 0.1M | 6.3 ± 0.2 | 3 |
| $CaCl_2$ 0.05M+ HCl 0.004M | 5.4 ± 0.2 | 6 |
| $Ca(NO_3)_2$ 0.1M | 6.1 ± 0.6 | 2 |
| NaCl 1M | 15.5 ± 0.2 | 5 |
| HCl 0.1M | 13.1 ± 0.2 | 13 |
| $HNO_3$ 0.1M | 14 ± 0.3 | 13 |
| $H_2O$ | 5.8 ± 0.1 | 6 |
| $Na_2S_2O_3$ 0.1M | 27.2 ± 0.5 | 4 |
| EDTA 0.1M | n.a.* | 7 |

* Not available (the interferences in the measurements, due to the carbon presents in EDTA molecules, make the TOC value not reliable).

**Table 2**

Breakthrough parameters for eleven sorption-desorption cycles, using a fixed-bed column for the removal of cadmium (50 $mg \cdot L^{-1}$) by protonated *S. muticum* biomass (5.8 g) at a flux rate of 10 $mL \cdot min^{-1}$, breakthrough concentration: 0.02 $mg \cdot L^{-1}$.

| Cycle | $Q_{Cd,max}$ ($mg \cdot g^{-1}$) | $C_{Cd,e}$ ($mg \cdot L^{-1}$) | $dC/dt$ ($mgL^{-1}h^{-1}$) | *LUB* (cm) | $\Delta t$ (h) | $t_b$ (h) | $t_e$ (h) | $t^*$ (h) |
|---|---|---|---|---|---|---|---|---|
| 1 | 98 | 43 | 1.0 | 11 | 41 | 2.2 | 46 | 19 |
| 2 | 60 | 46 | 1.2 | 12 | 39 | 0.8 | 40 | 12 |
| 3 | 72 | 42 | 1.1 | 11 | 40 | 2.1 | 42 | 14 |
| 4 | 71 | 44 | 1.1 | 11 | 39 | 2 | 41 | 14 |
| 5 | 70 | 42 | 1.2 | 11 | 36 | 2 | 38 | 14 |
| 6 | 66 | 43 | 1.2 | 11 | 38 | 2 | 40 | 13 |
| 7 | 69 | 42 | 1.3 | 11 | 36 | 2.2 | 38 | 13 |
| 8 | 56 | 44 | 1.2 | 11 | 38 | 1.8 | 40 | 11 |
| 9 | 60 | 44 | 1.2 | 11 | 36 | 2 | 38 | 12 |
| 10 | 56 | 46 | 1.3 | 10 | 36 | 2.2 | 38 | 11 |
| 11 | 65 | 43 | 1.4 | 10 | 33 | 2.7 | 36 | 13 |

**Table 3**

Regeneration parameters for eleven sorption-desorption cycles, using a fixed-bed column for the removal of cadmium (50 $mg \cdot L^{-1}$) by protonated *S. muticum* biomass (5.8 g) at a flux rate of 10 $mL \cdot min^{-1}$.

| Cycle | $C_p$ ($mg \cdot L^{-1}$) | $t_p$ (min) | $CF_p$ | $C_{1h}$ ($mg \cdot L^{-1}$) | $C_{6h}$ ($mg \cdot L^{-1}$) | $E$ (%) |
|---|---|---|---|---|---|---|
| 2 | 2755 | 5 | 55 | 0.78 | 0.010 | 120 |
| 3 | 4863 | 5 | 97 | 0.83 | 0.010 | 102 |
| 4 | 4563 | 2 | 91 | 0.51 | 0.018 | 81 |
| 5 | 5032 | 5 | 101 | 0.62 | 0.080 | 109 |
| 6 | 4336 | 3 | 87 | 0.51 | 0.040 | 71 |
| 7 | 4670 | 5 | 93 | 0.34 | 0.014 | 70 |
| 8 | 4415 | 5 | 88 | 0.66 | 0.010 | 99 |
| 9 | 5441 | 5 | 109 | 0.14 | 0.015 | 106 |
| 10 | 4567 | 5 | 91 | 0.24 | 0.011 | 95 |
| 11 | 5279 | 5 | 106 | 0.37 | 0.013 | 90 |

**FIGURES**

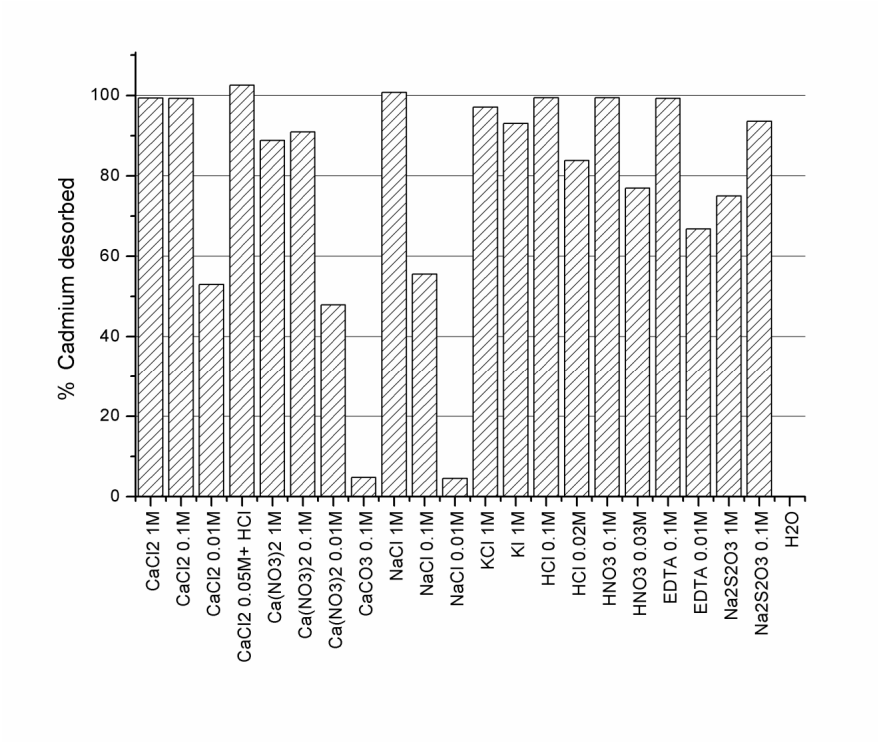


**Figure 1**

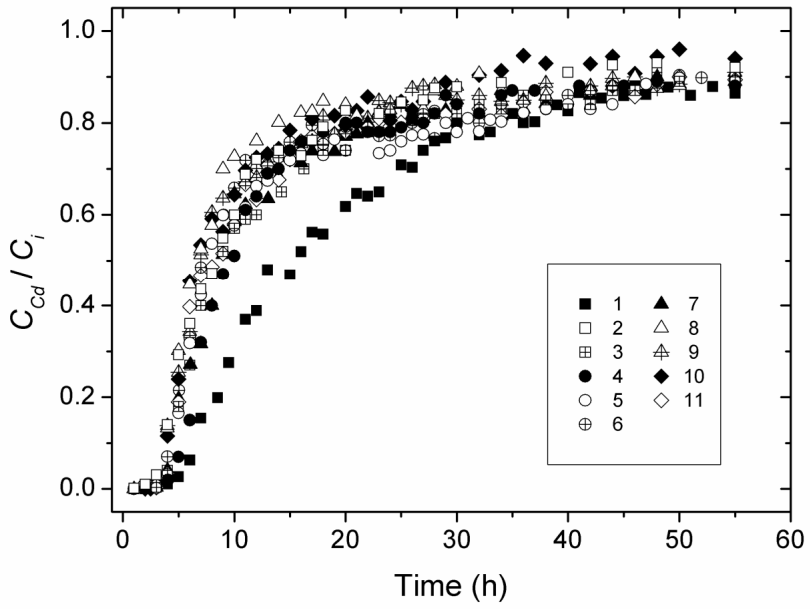


**Figure 2**

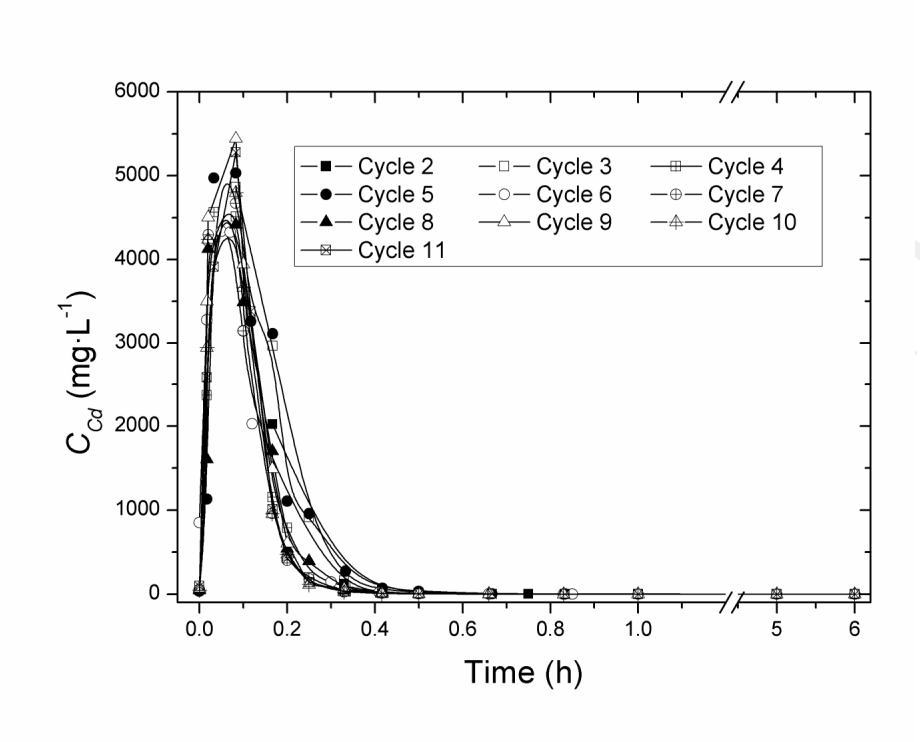


**Figure 3**