Adsorptive behaviour of mercury on algal biomass: Competition with divalent cations and organic compounds

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ABSTRACT

Biosorption processes constitute an effective technique for mercury elimination.

Sorption properties of native and acid-treated *Sargassum muticum* have been studied. Effect of pH, initial mercury concentration and contact time studies provided fundamental information about the sorption process. This information was used as the reference values to analyse mercury sorption under competition conditions. Saline effect has shown little influence in sorption, when only electrostatic modifications took place upon salt addition. On the contrary, if mercury speciation dramatically changed owing to the addition of an electrolyte, such as in the case of chloride salt, very large modifications in mercury sorption were observed. Competition with other divalent cations or organic compounds has shown little or none effect on mercury, indicating that a different mechanism is taking place during the removal of these pollutants.

Finally, continuous flow experiments have clearly shown that a reduction process is also taking place during mercury removal. This fact is not obvious to elucidate under batch sorption experiments. Scanning Electron Microscopy analysis of the surface of the materials show deposits of mercury(I) and metallic mercury which is indicative of the reduction process proposed.

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1. Introduction

Mercury is considered a harmful metal, extremely toxic, even at low concentration, which can cause neurological damage and other human diseases [1,2]. Monomethyl mercury is the most dangerous species for human health, but in aquatic environment this metal is also present as complexes of the inorganic divalent cation Hg(II). This species constitutes the main pollutant of mercury present in natural waters [3]. The maximum mercury uptake recommended by World Health Organization is 0.3 mg/week and 1 μg/L in drinking water [4]. This is the main reason why it is necessary to find a technology to remove these compounds, especially from wastewaters.

Sorption has been employed as a technique for heavy metal elimination using as sorbents different types of materials [5]. Many studies have been developed using activated carbons with chemical modifications and also exchange resins obtaining high mercury uptakes [6–8]. Good capacities of metal elimination were observed in adsorption process with this type of materials but there is also an alternative developed in recent years which is the use of low cost materials. Any sorbent is considered as a low cost material if it is easily obtained and abundant in the environment, such as bracken

fern [9,10], sugar beet pulp [11], chitin [12] or agro-industrial materials [13]. Algae are considered to be very good low cost sorbents, as many works have demonstrated high uptake capacities, specially brown algae [5,14–16] but also green algae species [17]. *Sargassum muticum* is a brown macroalga that belongs to "Fucales" order which is one of the most important algae orders from the point of view of biosorption [14]. This type of algae is abundant in nature, in addition *S. muticum* is considered to be an invasive species in Europe [18]. Previous studies have also shown high heavy metals and organic compounds elimination with this alga [19,20]. Moreover, *S. muticum* effectiveness as mercury sorbent has also been proved especially compared to other type of biomaterials [21]. All these characteristics render this brown alga a good low cost material for mercury removal from wastewaters.

In this work, it is demonstrated that the brown alga *S. muticum* and its chemically modified form are good sorbents for mercury elimination. It is remarkable the high alga capacity of mercury uptake, even in binary mixtures with divalent cations and organic compounds. Kinetic and equilibrium studies were carried to complete biosorption optimum conditions in batch mode operation. Moreover, pH dependence and salt addition at different concentrations were studied.

A continuous process was performed to obtain mercury uptake results with *S. muticum* treating higher volumes of polluted wastewaters. SEM analyses allow the characterization of the reduction process of mercury on the alga surface.

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2. Experimental

2.1. Biomass

Brown alga *S. muticum* was collected in Galician coast (NW Spain). First, the biomass was washed with tap water, once with deionised water and then was oven-dried at 60 °C during 24 h. The dried alga was ground with an analytical mill and sieved to collect the size fraction particles of 0.5–1 mm diameter. The biomass was stored in polyethylene bottles until use in the experiments.

A portion of the biomass was chemically modified through a treatment with HCl following a similar procedure describe elsewhere [16,19]. 5 g of *S. muticum* were treated with 250 mL of HCl 0.1 M during 2 h, the mixture was shaken at 175 rpm. This process was repeated three times and the biomass was finally washed with deionised water until constant conductivity was attained. Protonated alga was oven-dried at 60 °C. This process was done in order to remove interchangeable cations present in native alga and to saturate the biomass with hydrogen ions, obtaining protonated biomass.

2.2. Reagents

Reagents used were NaOH p.a. (pro analysis; Merck KGaA, Darmstadt, Germany) and HNO$_3$ Suprapur from Merck to adjust the pH of solution in concentration 2 mol/L and 1 mol/L respectively. NaNO$_3$ and NaCl from Merck to adjust the ionic strength of the media. 1-Propanol from Panreac (Panreac Quimica S.A. Barcelona, Spain) is used to prepare 4,4′-bis(dimethylamino)-thiobenzophenone solutions. 4,4′-Bis(dimethylamino)-thiobenzophenone from Merck is a complexing agent used in the spectrometric determination of mercury. Mercury, cadmium, copper, lead and calcium salts, namely HgCl$_2$, Cd(NO$_3$)$_2$·4H$_2$O, Cu(NO$_3$)$_2$·3H$_2$O, Pb(NO$_3$)$_2$ and Ca(NO$_3$)$_2$·4H$_2$O, were obtained from Merck. Methylene blue and Acid Blue 25 from Panreac and phenol and 4-chlorophenol (4-CP) from Aldrich were used as organic compounds to study the competition with metal elimination. All solutions were prepared with deionised water.

2.3. Batch experiments

Batch sorption experiments were carried out putting in contact 0.1 g of native or protonated alga with 40 mL of mercury solutions with different metal concentrations. These mixtures were shaken for 24 h at 175 rpm. pH was controlled periodically and adjusted by addition of the necessary volumes of concentrated solutions of HNO$_3$ or NaOH. Typically, acid or base volumes were added in a μL range.

In pH dependence experiments, mercury concentration was 0.25 mmol/L and the pH of solutions was adjusted between 1 and 7.

Mercury isotherms at 25 °C were determined for native and protonated alga. Mercury was used in a concentration range from 0.25 mmol/L to 5 mmol/L. The mixtures of 40 mL metal solution and 0.1 g of biomass were shaken during 24 h. pH was adjusted to the optimum value for mercury sorption according to previous experiment.

Kinetic studies were performed with both types of *S. muticum* and an initial mercury concentration of 0.5 mmol/L. The experiments were performed by adding 0.25 g of biomass to 100 mL of mercury solution. The mixtures were placed in a thermostated cell at 25.0 ± 0.1 °C and pH was adjusted to the optimum value during all the kinetic process. Moreover, with native alga, kinetic studies were completed at different mercury concentrations (0.1, 0.25, 0.5, 1 and 2.5 mmol/L) under the same experimental conditions. In order to ensure that the equilibrium was reached, all the kinetic experiments were carried out during 24 h.

The influence of saline media in mercury sorption was carried out using NaCl and NaNO$_3$, adjusting the ionic strength of the solution in a concentration range from 0.001 mmol/L to 1 mmol/L. Two different Hg(II) concentrations were used in these experiments, 0.5 mmol/L and 2.5 mmol/L.

Competition with divalent cations was carried out with salts of cadmium, lead, copper and calcium. Binary mixtures were prepared, fixing mercury concentration to 0.5 mmol/L and at several cations concentration, 0.5 mmol/L, 1 mmol/L and 5 mmol/L. Experiments with mercury concentration of 2.5 mmol/L and equimolar concentration of the other metal cations were also performed.

The influence of organic compounds in mercury adsorption was determined with two dyes solutions, the cationic Methylene blue and the anionic Acid Blue 25, and two phenolic compounds, phenol and 4-chlorophenol. Two different concentrations of mercury were used, 0.5 mmol/L and 1 mmol/L, bringing into contact with a solution of the organic compound in a concentration of 0.5 mmol/L.

Phenol and 4-CP present a maximum absorption at ultraviolet wavelength of 270 and 280 nm, respectively. But it was found that alga biomass releases different compounds into the solution that absorb at the same wavelength, so phenols concentration could not be determined.

On the other hand, dyes are very visible in water, even at low concentration and MB is the most commonly used compound in textile industry [22].

Mercury concentration was measured by colorimetric determination using Michlerĭs thioketone method in all the experiments [23]. Moreover, spectrophotometric mercury results were compared to cold vapour atomic absorption spectroscopy measurements and the results obtained with both techniques are in close agreement. Dye concentration was also determined through spectrophotometric measurements. Methylene blue shows an absorption peak with a maximum at 665 nm, and Acid Blue 25 has the maximum of absorption at 602 nm.

2.4. Column experiments

Mercury sorption capacity of *S. muticum* in continuous process was also studied in order to prove the material behaviour for industrial application in metal removal, based on the good results obtained in batch experiments.

First, a column with native biomass was analysed. A glass column of 3 cm internal diameter was filled with 30 g of biomass. The biomass was wetted with deionised water and a bed depth of 27 cm was reached due to the swelling of the native material. The top of the bed was covered with a layer of glass beads to avoid the loss of material and ensure a packed arrangement. A porous sheet or geotextile was attached at the bottom of the column to support the biomass and to achieve a good liquid distribution and a uniform flow inside the column, some of the glass beads were also put over the porous sheet at the bottom to support it and avoid biomass losses.

A mercury solution of 0.5 mmol/L was fed through the column in up-flow mode at 8 mL/min flow rate with a peristaltic pump (Watson-Marlow). With this flow rate, the bed depth and the internal diameter of the column, 23.8 min of residence time were attained. Continuous flow experiments were also carried out with protonated brown alga. The same experimental conditions were used but the acid treated material showed less swelling and the bed depth was 17 cm for 30 g of biomass. The flow rate was diminished to 5 mL/min to reach a similar residence time as in the previous column.

In both experiments, mercury samples were collected periodically at the top of the column and metal concentration was
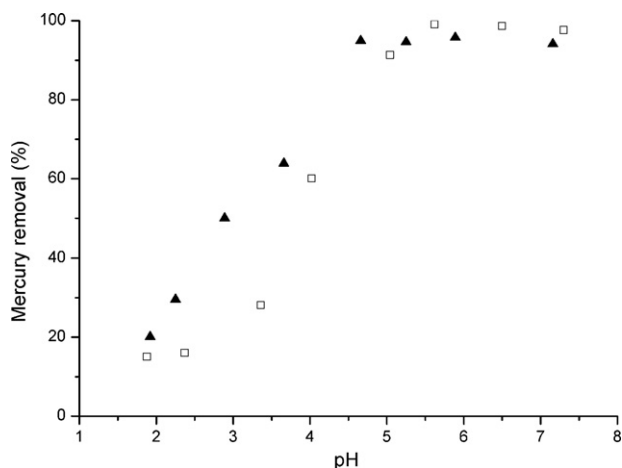
Fig. 1. Effect of pH on mercury sorption onto native *S. muticum* (squares) and protonated *S. muticum* (triangles). Initial mercury concentration of 0.25 mmol/L. Alga dosage 2.5 g/L.

determined in order to obtain the corresponding breakthrough curves.

2.5. SEM and EDS

A sample of the biomass used in the column experiments was collected, dried and characterized by SEM (Scanning Electron Microscopy). These studies were done with a JEOL JSM 6400, equipped with an Oxford Inca Energy 200 system for EDS (Energy Dispersive X-ray Spectroscopy). Analyses were performed in order to determine if there were mercury deposits over the surface of the alga.

3. Results and discussion

3.1. Mercury uptake studies in the absence of other pollutants

3.1.1. Effect of pH

The effect of the pH on mercury adsorption was studied using both types of biomass and similar curves were obtained. It can be observed in Fig. 1 that maximum mercury removal values were reached at pH above 4.5, where a plateau in the curve was reached with both materials. These results render 5 as the optimum pH value to carry out all the sorption experiments with this alga avoiding metal precipitation at the same time. Moreover, acidic pH values can damage material structure. Different behaviour can be observed for values lower than 5, where protonated *S. muticum* showed higher adsorption capacity than the native alga, this pH values are close to natural ones for mercury solutions so it can help to keep pH constant during the adsorption process.

The shape of the curves obtained in the adsorption of mercury onto *S. muticum* is similar to the curve obtained previously for the mercury adsorption onto bracken fern [9] and is also similar to the behaviour found with other metals using different biomaterials in their elimination from solution [11,19].

In general, the effect of the pH in heavy metal removal is directly associated to the ionization state of the functional groups in biomaterials structure and also to the metal speciation in the solution. Taking into account the mercury speciation calculated with the MINEQL+ programme [24], the predominant metal compounds are $HgCl_2$, $Hg(OH)Cl$ and $Hg(OH)_2$. In the entire pH interval studied, the ionic form of mercury (Hg^{2+}) is never found, so the three neutral metal forms are the main species related with mercury elimination. Other metals such as cadmium appear as free cations at the working pH. In those cases metal removal is mainly associated to the

ionization state of the biomass groups, protonation or desprotonation of the cell wall, and electrostatic interactions can be assumed [18].

Adsorption process is more complex for mercury elimination. The behaviour of mercury has been explained previously based on similar results of its removal with bracken fern [9]. Three neutral species are presented in all the pH range where high mercury elimination was observed. At the pH selected for adsorption studies (pH 5) the neutral mercury forms appear in percentages 5% of $Hg(OH)_2$, 10.5% of $Hg(OH)Cl$ and 84.5% of $HgCl_2$, according to MINEQL+ calculations. Above this pH, where the plateau in the curve is observed and the maximum mercury elimination was registered, $HgCl_2$ percentage decreases and $Hg(OH)_2$ increases. Based on these results, it can be concluded that there is not a clear relation between metal sorption and one specific mercury species over pH.

15–20% of mercury elimination was observed even at pH around 2. This behaviour can be related not only to metal adsorption but also to mercury reduction process by oxidizable groups in the alga.

Moreover, the ionic state of the main functional groups on the material surface is clearly related to mercury removal. At high pH values, the increase in metal adsorption can be associated with the desprotonation of carboxylic groups making easier the sequestration of mercury species. These results support the mechanism previously explained in other papers [9,25] based on the interaction of neutral mercury species with carboxylate groups in the biomass surface.

Polysaccharides are the main content in the algae cell wall, especially alginates and fucoidans. The high selectivity of these molecules towards metal ions is related to their content in carboxyl, hydroxyl, sulphate and amino groups. Some of these groups not only are related to metal adsorption but also to reduction process because they are easily oxidized as it was reported [26]. *S. muticum* biomass has been characterized in previous studies made with these material and these functional groups were identified in the algae surface through FTIR analysis [21].

On the other hand, several metal cations dissolved in seawaters such as Na, K, Ca and Mg stabilize alga structure. These elements are substituted by protons with the acid treatment of the biomass, this fact can explain the difference between native and treated material found at pH interval 2–4. Protonated material improves metal removal at low pH making easier the access to binding sites and the exchange between mercury and proton [27].

pH plays a significant role in mercury sorption, affecting metal speciation and biomass functional groups behaviour.

3.1.2. Equilibrium and kinetic studies

Mercury adsorption onto brown alga *S. muticum* was studied with several initial mercury concentrations at 25 °C in order to obtain the maximum adsorption capacity of the native and modified alga. The value of mercury maximum adsorption capacity allows comparing both types of biomass between them and with other materials studied in the elimination of this metal. Langmuir–Freundlich model was used in order to fit equilibrium data.

$$q_e = Q_{max} \frac{(bC)^{1/n}}{1 + (bC)^{1/n}} \qquad (1)$$

where q_e is the uptake capacity at equilibrium, Q_{max} is the maximum uptake capacity, b is the adsorption equilibrium constant and C is the metal concentration in solution at equilibrium. n is a factor related to system heterogeneity.

As it can be observed in Fig. 2, adsorption capacity with the protonated material is higher than the value obtained with the native alga. The equilibrium data were fitted to Langmuir–Freundlich isotherm model and the parameters obtained are given in Table 1. Acid treated *S. muticum* reached a maximum of 1.2 mmol/g
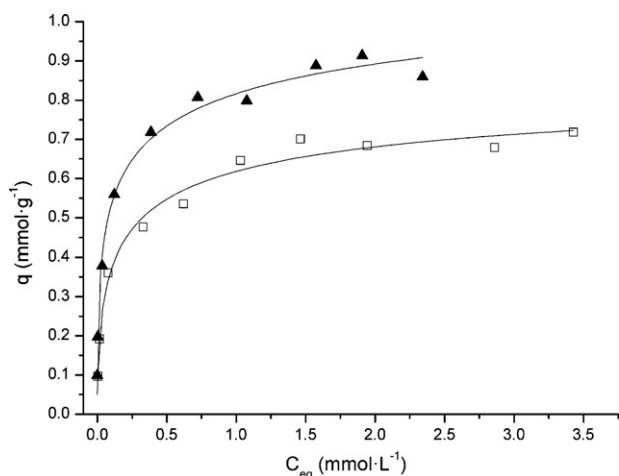
Fig. 2. Isotherm data for native alga (squares) and protonated material (triangles) at 25°C and pH 5. Solid line represents Langmuir–Freundlich model fitting curve.
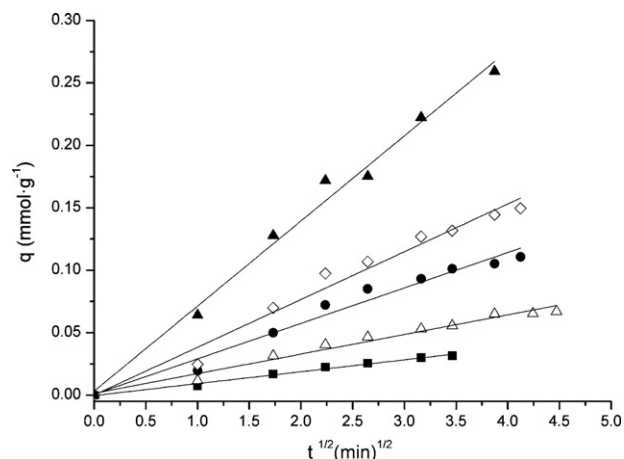

Fig. 3. Diffusion model fit of mercury sorption onto native *S. muticum*. Initial mercury concentrations 0.1 mmol/L (squares), 0.25 mmol/L (triangles), 0.5 mmol/L (circles), 1 mmol/L (diamond) and 2.5 mmol/L (solid triangles). pH 5.

(251 mg/g) and native *S. muticum* presented a sorption capacity of 0.9 mmol/g (181 mg/g). These results are comparable to mercury sorption capacities obtained previously with other natural materials such as brown alga *Cystoseira baccata* [25] or other modified sorbents [28]. On the other hand, *S. muticum* also presents adsorption capacities similar or even better than some activated carbons [7,29] and exchange resins [30]. The high capacity of this sorbent was previously demonstrated in a preliminary study of the biomass [21].

Kinetic studies were carried out to obtain the time necessary to reach the equilibrium in the mercury elimination process onto brown alga *S. muticum*. These experiments were performed adjusting solution pH at 5 during all the process. An analysis of mercury removal percentages vs. time shows short equilibrium times for both materials. In less than 100 min 80% of mercury elimination was attained for both materials. 150 min were required to obtain the maximum removal with the acid treated alga and equilibrium was reached in approximately 220 min with the native material. However, kinetics curves presented an initial sharp rise which indicates that mercury sorption is a fast process with both materials studied with little differences between them. In fact, high mercury elimination was obtained with both types of alga.

Native *S. muticum* kinetic studies were completed using different mercury initial concentrations. In the biosorption process of pollutants onto porous adsorbents three different stages can be described [31,32]:

- Transport of the adsorbate from the bulk of solution to the surface of the material (film diffusion).
- Intraparticle diffusion of the adsorbate into the pores of the adsorbent.
- Adsorption process onto internal surface of the material.

Different parameters in the adsorption process can be analysed in order to characterize the rate-limiting step such as solution concentration, size and structure of solute molecules, agitation speed or particle diameter of the adsorbent.

Previous studies have considered the diffusion as the rate-controlling steps in biosorption processes considering negligible the adsorption in the internal site [33,34]. Intraparticle diffusion process described by Weber–Morris model has been applied to the experimental data for mercury adsorption in order to determine the diffusion influence in the metal adsorption [32]. This model predicts a linear relationship between the uptake capacity (q_e) and the square root of time ($t^{1/2}$), according to the expression:

$$q_t = k_i t^{1/2} \tag{2}$$

where q_t (mmol g^{-1}) is the mercury uptake at time t (min), k_i (mmol g^{-1} min$^{-0.5}$) is the intraparticle diffusion constant. This kinetic constant was obtained from the slope of the plot of uptake capacity vs. square root of time. Intraparticle diffusion is considered to be the rate limiting step if the plot passes through the origin but it is assumed that not only this step contributes to the biosoption process but also film diffusion if small deviations from zero are registered.

Results of the diffusion model fitting for *S. muticum* are shown in Fig. 3 and intraparticle constant values are given in Table 2. A good linearization of data was observed and plots go through very close to the origin, which clearly indicates that intraparticle diffusion is the controlling rate step. It was observed that intraparticle diffusion constant increases with initial mercury concentration. This behaviour was reported before in other papers [35].

In the earlier stages of the adsorption process, considering t relatively small, intraparticle diffusion constant shows a linear relationship with the metal uptake according to the following equation:

$$k_i = \frac{6 \cdot D_i^{0.5}}{\pi^{0.5} r} q_e \tag{3}$$

Table 1
Results obtained from the fitting of equilibrium data at pH 5 with Langmuir–Freundlich model. Numbers after ± correspond to the standard error of each parameter obtained from the fitting.

	Langmuir–Freundlich			
	Q_{max} (mmol/g)	b (L/mmol)	n	r^2
Native *S. muticum*	0.9 ± 0.1	4.8 ± 2.8	2.0 ± 0.3	0.98
Acid treated *S. muticum*	1.3 ± 0.2	4.7 ± 4.4	2.5 ± 0.4	0.99

Table 2
Results for diffusion model fitting kinetic data of mercury sorption onto native *S. muticum* at pH 5. Numbers after ± correspond to the standard error of each parameter obtained from the fitting.

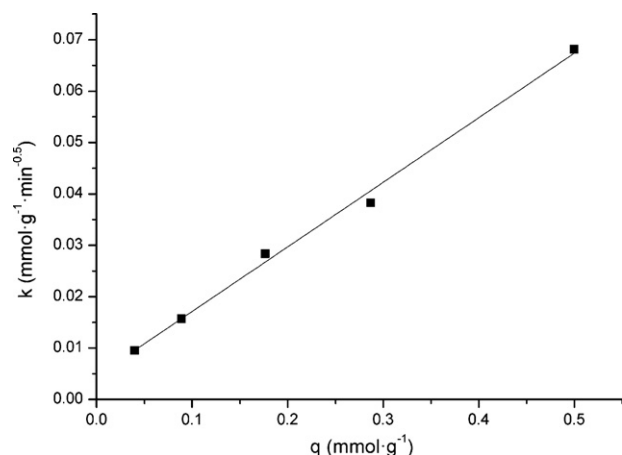| [Hg^{2+}] (mmol/L)	k_i (×10^{-2} mmol/g min$^{0.5}$)	r^2
0.1	0.95 ± 0.04	0.99
0.25	1.57 ± 0.08	0.97
0.5	2.84 ± 0.17	0.97
1	3.83 ± 0.21	0.98
2.5	6.82 ± 0.32	0.99

Fig. 4. Linear representation of intraparticle diffusion constant (k_i) vs. mercury uptake capacity (q_e) according to Eq. (3).

where D_i is the intraparticle diffusion coefficient and r is the radius assuming spherical particles with an average radius between the upper and lower size fraction (0.5–1 mm). The linear trend observed is shown in Fig. 4. Diffusion coefficient was calculated from the slope as 1.3×10^{-7} cm^2 s^{-1} considering the average radius as 7.5×10^{-2} cm.

This value can be compared with diffusion coefficients for ions at infinite dilution such as Pb^{2+} 0.95×10^{-5} cm^2 s^{-1} or Cu^{2+} 0.72×10^{-5} cm^2 s^{-1} [36] and for HgCl$_2$ 1×10^{-5} cm^2 s^{-1} [37]. The differences observed can be explained taking into account that experimental conditions are far away from infinite dilution but it should also be expected that mercury diffusion in the algal particle will be smaller than in water.

Diffusion model fits well experimental data and low errors in the parameters were obtained. Therefore a diffusion controlled mechanism is postulated as the mechanism governing the adsorption process.

3.2. Competition studies

3.2.1. Effect of salinity

The influence of salinity of the media in mercury sorption onto *S. muticum* was tested adjusting ionic strength of the solution with two different salts, NaNO$_3$ and NaCl.

Two initial metal concentrations (0.5 and 2.5 mmol/L) were used and the salt was added in concentrations 0.001, 0.01, 0.1 and 1 mol L^{-1}. This study was also carried out with both native alga and protonated material but similar results were obtained with both materials.

As it can be observed in Fig. 5, mercury removal is not affected by the presence of NaNO$_3$. High metal removal percentages were obtained even at high salt concentration. However, a significant decreased in metal adsorption was observed with an increased in NaCl concentration.

These differences can be related to the different counter ion present in the salts. NO$_3^-$ does not interfere in mercury sorption but Cl$^-$ forms mercury species with negative charge which interfere in the sorption process. Metal speciation in solution with nitrate salt does not change and metal removal proceeds through neutral species as it was mentioned previously. Speciation diagram changes significantly with high chloride concentration in solution; mercury species with negative charge such as HgCl$_3^-$ and HgCl$_4^{2-}$ are present at working pH and they do not contribute to metal elimination. A calculation made with MINEQL+ allows obtaining the fraction of neutral mercury species present in the aqueous phase at working pH for each chloride concentration. A linear correlation
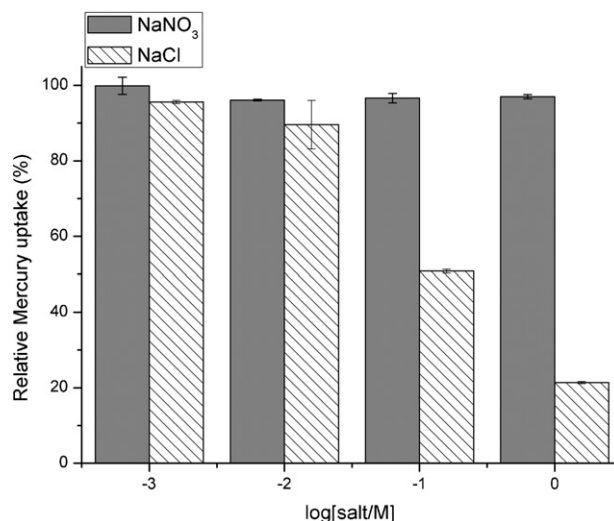

Fig. 5. Relative mercury elimination percentages with native *S. muticum* as a function of salinity. Addition of NaNO$_3$ and NaCl in a concentration range from 0.001 mol/L to 1 mol/L. Initial mercury concentration of 0.5 mmol/L. pH 4.5–5. Alga dose 2.5 mg/L. The reference value 100% represents the metal removal in the absence of added salt. Error bars show standard deviation for triplicate experiments.

between this fraction and the adsorption capacity obtained for each experiment was found which clearly indicate that mercury sorption is related to neutral species, $q = (7.5 \pm 0.9) + (0.30 \pm 0.01)N$, with a correlation coefficient of $r^2 = 0.99$, where N is the neutral specie percentage for each chloride concentration.

Moreover, Na$^+$ does not affect to the metal binding to the biomass therefore electrostatic effect is not driving force in metal elimination. All these results support the idea that mercury sorption is associated with neutral species in solution. These conclusions are similar to previous works related to mercury removal onto bracken fern [9] or *C. baccata* [25].

3.2.2. Mercury uptake in mixtures with other pollutants

Four different cations were added to the mixtures of mercury and brown alga in order to observe the effect of these compounds in metal removal. Cd(II), Pb(II), Cu(II) and Ca(II) at three concentrations (0.5, 1 and 5 mmol L^{-1}) were put into contact with mercury solution (0.5 mmol L^{-1}) and both types of biomass, native *S. muticum* and protonated form of the alga. Moreover, the same experiments were carried out with 2.5 mmol L^{-1} of initial mercury concentration and the divalent cation solution in equimolar concentration. Mercury adsorption was studied controlling the pH in the range of 5–6.

Results for this study with native alga and mercury 0.5 mmol L^{-1} are shown in Fig. 6. It is remarkable that, in general, divalent cations do not interfere in mercury elimination from solution. High mercury removal percentages were attained which indicates that the metals studied do not compete with mercury for sorption sites. Adsorption mechanisms for those divalent cations and for mercury are different. Taking into account that all of these metals at working pH are present as free cations, M^{2+}, their interaction with the biomass can be related to electrostatic effects while mercury sorption was associated to neutral species as it is mentioned in the previous section.

It is remarkable a small decreased in mercury elimination with lead and copper at high concentration. Both heavy metals are "soft" elements and can bind to the biomass through covalent bonds and interfere with mercury sorption [38]. A slight decreased in mercury removal was also registered with calcium in solution. This fact can be associated to the high affinity of calcium for alga biomass and the
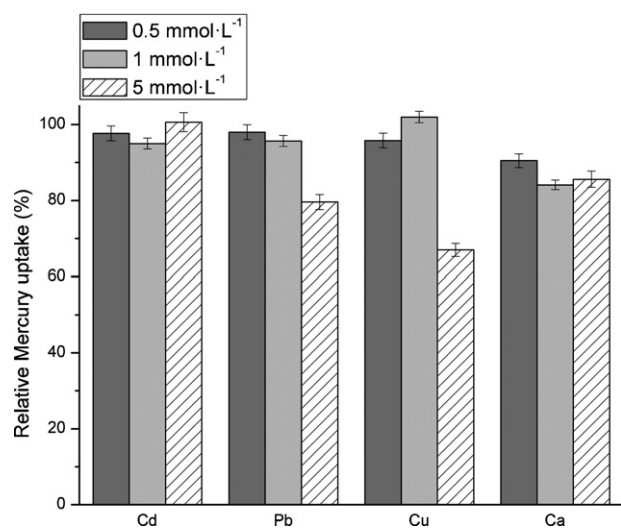
Fig. 6. Relative removal percentages of mercury onto native *S. muticum* in the presence of divalent cations in concentration 0.5 mmol/L, 1 mmol/L and 5 mmol/L. Initial mercury concentration of 0.5 mmol/L and pH 5. Alga dose 2.5 mg/L. The reference value 100% represents the metal removal in the absence of divalent cation. Error bars show standard deviation for triplicate experiments.

Fig. 7. Relative removal percentages of mercury sorption onto native *S. muticum*. Initial mercury concentrations 0.5 mmol/L and 2.5 mmol/L. Organic compounds in concentration of 0.5 mmol/L. pH 5–5.5. Alga dose 2.5 mg/L. The reference value 100% represents the metal removal in the absence of organic compounds. Error bars show standard deviation for triplicate experiments.

possible formation of the "egg box" structure between the calcium and the main functional groups present in the biomass surface [39].

In general, the same behaviour was found with both types of alga, but even higher mercury eliminations were obtained with protonated material. In all cases nearly 100% of metal removal was reached and the effects of lead, copper and calcium at high concentrations were not observed. Acid treatment makes easier the access to sorption sites presents in functional groups and the interchanges between metals and proton. When the initial mercury concentration was increased the mercury removed from solution reached values over 80% but a slight decrease in mercury sorption was registered with the four cations comparing the adsorption value in the absence of added divalent metal. This fact can be explained taking into account the different mechanism between ionic species in solution and the mercury neutral species. High affinity of alga biomass for ionic cations through electrostatic mechanism renders less sorption sites available for mercury sequestration when high concentrations of both species are present in solution.

A similar behaviour was observed in the competition of divalent cations in mercury sorption with other sorbents [9] and the same mechanism proposed based on pH dependence results can support the behaviour described in this section.

Competition with different organic compounds was also analysed. Generally, in wastewaters there are many types of pollutants, not only different heavy metals but also organic species which can interfere with mercury removal. Adsorption technique effectiveness was also proved with two types of chemical compounds to obtain pollutant free water.

High mercury removal percentages were obtained in mixtures with phenols and dyes, values over 90% were found (see Fig. 7). These substances do not influence in metal adsorption onto *S. muticum* and the behaviour is similar to the influence of the divalent cations.

High MB eliminations were found even at high mercury concentration. Almost 100% of the dye was removed from solution with both native alga and protonated material. However, low AB 25 elimination was observed, about 50%. Both dyes present different structures, MB is a cationic substance while AB 25 shows an anionic form in solution. This fact can be directly associated with the different adsorption values onto *S. muticum*. It is remarkable that the sorption pH chosen for mercury removal is also adequate for MB
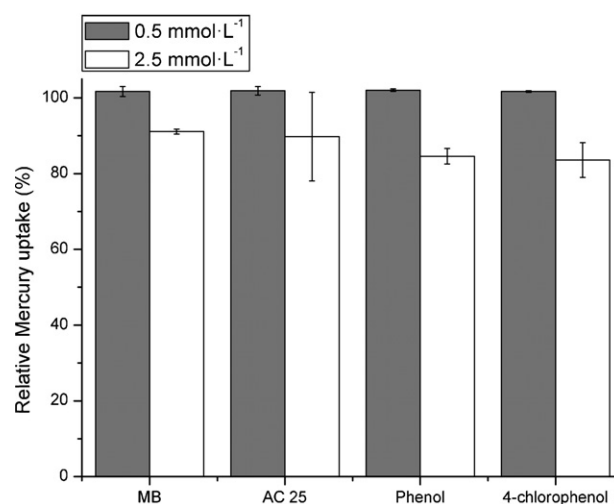
elimination, so the process is more favourable for the mixtures of both compounds. High MB sorption capacities onto this alga were found in previous works [20] and with different materials [22].

With this study it can be concluded that *S. muticum*, specially its protonated form, is a good material to remove not only high mercury quantities from solution but also MB dye from the same polluted water.

3.3. Continuous flow experiments

Continuous flow experiences were carried out in order to study the *S. muticum* properties for industrial application in mercury removal from wastewaters. These experiments were based on the results obtained in batch studies where high mercury elimination capacities and short equilibrium times were observed. Two different columns were performed using as sorbents native and protonated alga.

Breakthrough curves with both biomasses are shown in Fig. 8. The two columns were carried out adjusting the experimental conditions in order to have the same residence time in both processes
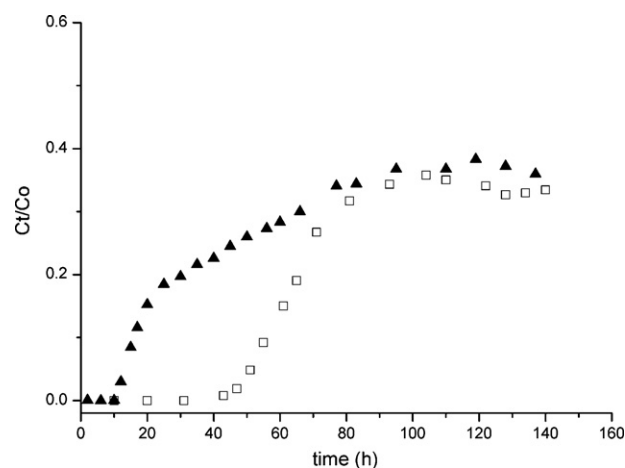

Fig. 8. Breakthrough curves for mercury adsorption onto native *S. muticum* (squares) and protonated biomass (triangles). Mercury initial concentration of 0.5 mmol/L. Bed depth 27 cm and flow rate 8 mL/min with native alga and bed depth 17 cm and flow rate 5 mL/min with acid treated alga.
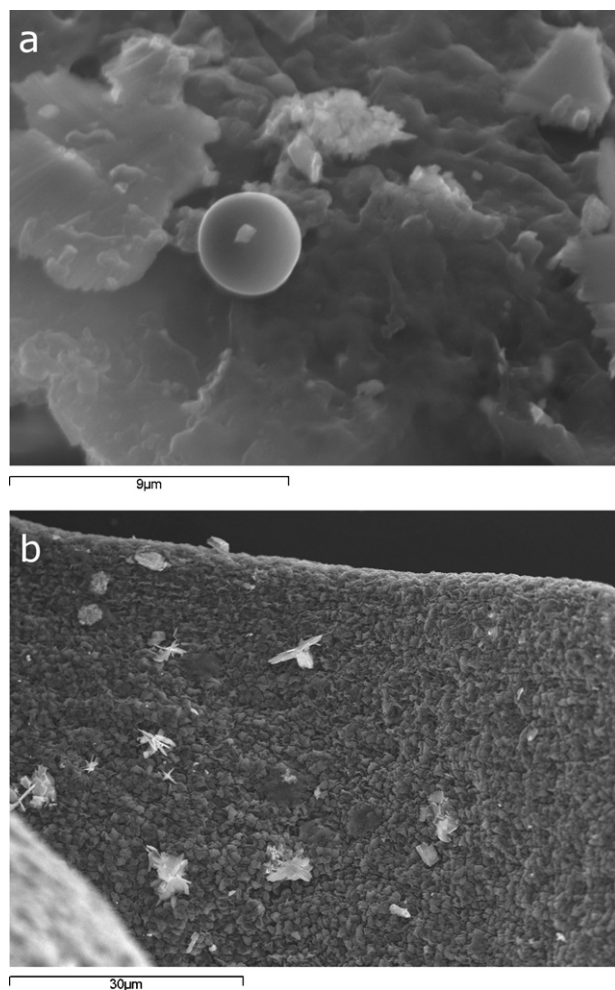
Fig. 9. Scanning electron micrograph of native (a) and acid treated (b) *S. muticum* surfaces after column experiments with mercury(II). Two parts of the alga surface are shown in the images which present different mercury deposits, drop of metallic mercury and crystalline precipitates.
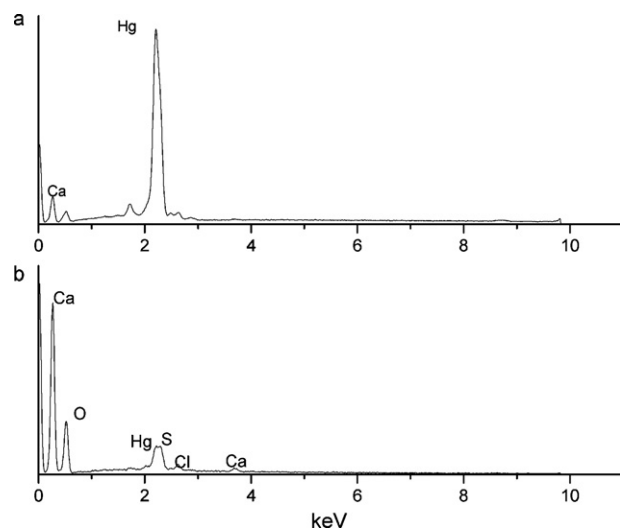

Fig. 10. EDS analyses of two different deposits over sorbent surface corresponding to Fig. 9 micrographs. The peaks indicate the main elements found in those deposits over the alga after continuous flow experiments. (a) Metallic mercury drop and (b) crystalline precipitates on the surface.

and a different behaviour was observed. Native material presented a breakthrough time at 50 h, so 24 L of metal free solution were obtained. From 50 h to 90 h a steady increase in mercury concentration in the effluent was registered and then a plateau in the curve was observed at 35% of initial mercury concentration. However, with treated alga the breakthrough time was attained in 12 h of continuous process and only 3.6 L of clean solution were obtained. The curve shape is similar to the native material and a plateau was also reached at 37% of initial mercury concentration.

Different breakthrough times found in both curves were associated with a variation in the pH in the effluent solution. With treated *S. muticum* the solution pH decreased significantly down to 3, measured on the exit of the column. At this value, moderate removal capacities were found in batch experiments (see Section 3.1 and Fig. 1). However, the pH in the effluent of native alga column was around six which is an optimum range for mercury elimination.

In both continuous flow experiments inlet mercury concentration was never reached in the effluent solution. This is not the typical behaviour of a breakthrough curve for the adsorption of other heavy metals such as cadmium [40] onto different biomaterials where the maximum in the curve is coincident with the metal concentration in the feed solution. However, an analogous curve was previously reported for mercury elimination onto bracken fern [9]. This behaviour was related not only to the sorption mechanism but also to mercury reduction due to biomass functional groups.

3.3.1. SEM and EDS analysis

S. muticum SEM studies were done after the column experiments in order to prove if there was some mercury reduced onto the material surface due to continuous flow experiments.

In the acid treated material some deposits with metal shine were found, which could be observed even macroscopically. Moreover, the SEM and EDS studies allow analysing the composition of these deposits. As it can be observed in Fig. 9, there are different sediments over the material surface. Most of them are composed of metallic mercury or chloride and mercury in a 1:1 proportion which indicate that the metal has been reduced to Hg(I). There are other deposits where high percentages of S were measured in addition to Hg and Cl. It is remarkable that these three elements are mainly located at the same positions over the surface, so it can be assumed that reduced mercury is associated with chloride or sulphide.

The SEM images registered with the native biomass are very similar to the protonated alga. Many mercury drops were found over the surface of both materials. An EDS analysis of this type of deposits allowed determining that they are essentially composed of mercury (see Fig. 10). The EDS studies shown in this work correspond to the SEM microphotographs in Fig. 9, but different deposits all over the alga surface were analysed and in many of them crystalline deposits with equal proportions of Hg and Cl were also found. The shape and composition of both types of sediments demonstrate mercury reduction to metallic mercury and mercury(I).

4. Conclusions

Results obtained in this study have shown that *S. muticum* is a good adsorbent for mercury elimination even at high metal concentration. Batch sorption experiments have demonstrated a high influence of pH in the sorption process, a relatively fast kinetics with a diffusion controlled determining step, and high maximum metal uptake.

At the same time, competition studies showed that mercury removal performance is scarcely hindered owing to the presence of potential interferences. Salt addition showed that electrostatic effect has a negligible influence in mercury removal when a non-complexing electrolyte, such as sodium nitrate, is added to the solution. On the contrary, the addition of a salt which promotes changes in mercury speciation, like chloride that enhances the

appearance of negatively charged species of mercury, drastically diminishes metal removal by the sorbent materials. Competition with other divalent cations tested has been found to be small or insignificant, only lead and copper have shown some influence, which has been attributed to the softer character of these two cations. Even possible interference of four organic species tested, two phenols and two dyes, has not been observed. All this results support a mechanism for mercury removal totally different to the common sorption processes governing the removal of other pollutants analysed in sorption studies. In the case of mercury, results indicate that metal removal is taking place through neutral species of this toxic metal.

The continuous flow experiments allowed the identification of reduction of mercury(II) to mercury(I) and metallic mercury as a very important elimination process taking place during mercury removal from solution.

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