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Interaction of heavy metals with Ca-pretreated *Sargassum muticum* algal biomass: Characterization as a cation exchange process

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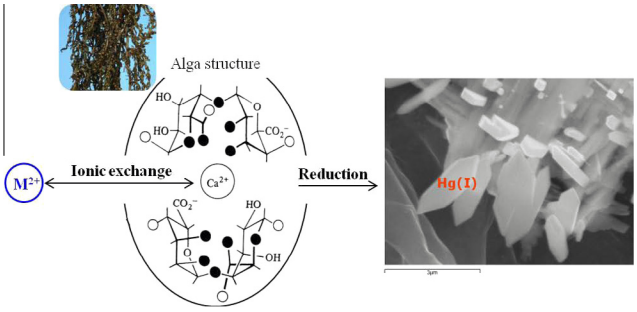
HIGHLIGHTS

- Ca-loaded biomass was used to analyse the elimination mechanism of different heavy metals.
- Cadmium and lead interaction with biomass is mainly ruled by an ion exchange mechanism.
- Mercury elimination by alga biomass is a complex process including adsorption and reduction.
- SEM/EDS analysis confirms mercury reduction after batch sorption experiments.

GRAPHICAL ABSTRACT



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ABSTRACT

The exchange mechanism taking place during elimination processes of different metal cations with natural biomass was analysed using the brown alga *Sargassum muticum* loaded with calcium. Sorption experiments varying initial metal concentration and kinetic studies have been performed. Cadmium and lead experiments have shown a 1:1 ratio between the amount of metal exchanged by the material and the calcium released back to the solution. This ratio was maintained for all metal concentrations. Based on the results it was concluded that cadmium elimination using the brown alga is mainly associated with an exchange process with calcium cations retained in the material structure. The analysis of kinetic data indicates that film diffusion is the rate limiting step in cadmium elimination process. On the other hand, the experiments carried out with mercury have shown varying ratios depending on the metal concentration, and more mercury was removed from solution than calcium was released back. Comparing mercury results with those of cadmium, it can be assumed that mercury elimination is not only associated with an exchange mechanism but also reduction is taking place. SEM and EDS analysis confirmed for the first time mercury reduction after batch sorption experiments.

1. Introduction

Algae constitute one of the most important biosorbents employed in elimination studies of heavy metals and organic compounds. This natural material is widely used in sorption studies, not only for its high capacity to remove pollutants from solution but also for its abundance in the environment. Their high capacity to retain pollutants can be associated with their content in polysaccharides in the cell wall. These polysaccharides are mainly associated with heavy metal binding [1].

In brown algae, the cell wall consists mainly of alginates and fucoidans; the alginic acid is composed by mannuronic and guluronic acid units and can constitute between 10% and 40% of the

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alga dry weight. Both mannuronic and guluronic acids contain carboxylic acid in their structures. This acidic moiety is the main functional group present in the brown algae and it is directly associated with the high capacity of this material to retain heavy metals [2,3]. Coordination capacity of carboxylic groups with divalent cations, such as calcium, stabilizes the internal structure of the alginates due to dimerization of guluronic acid chains leaving cavities where calcium cations are placed, resulting in the well-known "egg box" model [4,5]. The binding between different chains of this structure renders greater viscosity of alginate and it can even promote the formation of an alginate gel. This fact explains the relevance of cations such as calcium, magnesium, potassium or sodium in the algae structure and at same time in biosorption processes, due to the role of these species in the exchange mechanisms with heavy metal divalent cations. Simultaneously, the stabilized capacity of the biomass with cations such as calcium is associated with very low values of total organic carbon (TOC) in solution if the biomass is previously treated with calcium. This is an important characteristic for the use of these treated materials in column processes [6]. At the same time, the material loaded with calcium improves pH control which also benefits its use in continuous flow processes [7].

Therefore generally speaking, heavy metal adsorption by dead biomass can be associated with an ionic exchange mechanism, where heavy metal divalent cations replace other ions which are bound to the functional groups (i.e. carboxylic acids) on the material surface. This process has been previously studied, proving the exchange mechanism with different divalent cations [8–10] and analysing the role of protons in these equilibria [11,12]. It was also studied how to optimize the sorption capacity loading the material with cations such as calcium to facilitate the access to binding sites [13].

In the present work, the brown alga *Sargassum muticum* was treated with $CaCl_2$ to perform elimination studies of Hg(II), Cd(II), Pb(II) and Cu(II); thus, the mechanism that is taking place between these species and the biomass can be tested measuring simultaneously the amount of heavy metal retained by the material surface and the amount of calcium released into the solution. The novelty of this study is based on the analysis of different interactions metal-biomass with the divalent cations tested, specially the differences between cadmium and mercury. This calcium exchange study provided new information about the mercury elimination mechanism and also confirmed the metal reduction by alga biomass in batch sorption processes.

Two different types of experiments were carried out to develop this work: batch sorption experiments varying the initial concentration of divalent cations and kinetic experiments analysing cadmium and mercury adsorption at the same time that calcium is released into the solution.

2. Materials and methods

2.1. Biomass

S. muticum biomass was collected in Galician coast (NW Spain). First, the brown alga was washed with deionised water and was oven dried at 60 °C during 24 h in a forced air circulation oven. The dried material was ground with an analytical mill, selecting the particle fraction ranging from 0.5 mm to 1 mm which was used in all the experiments.

This biomass was loaded with calcium following the experimental procedure described next:

5 g of *S. muticum* were kept in contact with $CaCl_2$ 0.2 M (500 mL) during 24 h. The treated biomass was filtered and rinsed with deionised water to eliminate the calcium that was not bound to the material. Then the material was dried at 60 °C in a forced air circulation oven [14].

2.2. Reagents

Calcium solution ($CaCl_2 \cdot H_2O$) from Merck was used to treat the biomass. Mercury, cadmium, copper and lead salts namely $HgCl_2$, $Cd(NO_3)_2 \cdot 4H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$ and $Pb(NO_3)_2$ were obtained from Merck to prepared heavy metal solution. 4,4′-Bis(dimethylamino)-thiobenzophenone also from Merck was used as a complexing agent in the spectrometric determination of mercury. 1-Propanol from Panreac was used to obtain mercury complexing agent solution [15]. All solution were prepare with deionised water.

2.3. Sorption experiments

Sorption experiments were performed putting in contact 0.1 g of Ca-treated alga biomass with cadmium, lead, copper or mercury solutions at three different concentrations: 0.5, 1 and 2 mmol L^{-1}. These mixtures were stirred during 24 h to assure the equilibrium was reached. Then, calcium and heavy metal concentrations in solution were determined using different analytical techniques.

Mercury and calcium isotherms were determined following the experimental methodology described for sorption experiments but varying metal initial concentration from 0.1 to 6 mmol L^{-1}. Metal concentrations were measured after 24 h of contact between the biomass and the solution.

Kinetic studies were carried out for cadmium and mercury elimination. 0.25 g of *S. muticum* treated with calcium were put in contact with 100 mL of metal solutions at different initial concentrations (varying from 0.1 to 2.5 mmol L^{-1}). The mixtures were placed in a thermostated cell at 25.0 °C ± 0.1 °C and kept under magnetic stirring during 24 h.

Finally, 40 mL of binary mixtures with mercury and cadmium were put in contact with 0.1 g of alga biomass. Mercury, cadmium and calcium concentrations were determined after 24 h contact.

2.4. Desorption studies

The total amount of calcium retained by the brown alga surface was determined through desorption studies. 0.1 g of *S. muticum* were put in contact with 40 mL of HCl solution at three different concentrations: 0.1, 0.5 and 1 mmol L^{-1}. These mixtures were stirred during 48 h and calcium concentration was measured after 24 and 48 h.

2.5. Analytical techniques

Mercury concentration was determined through colorimetric measurements following the Michleŕs thioketone method describe previously [15]. Cadmium, lead, copper and calcium concentrations were measured using AAS.

2.6. SEM and EDS

Samples of Ca-loaded alga were characterized by SEM (Scanning Electron Microscopy) and EDS (Energy Dispersive X-ray Spectroscopy). These studies were performed with a JEOL JSM 6400, equipped with an Oxford Inca Energy 200 system for EDS. Not only *S. muticum* loaded with calcium, but also the same treated material after sorption process with cadmium and mercury was analysed in order to compare the biomass surface after and before heavy metal elimination. In addition, EDS analysis confirmed the metal presence in the alga surface.