



Antimony oxyanions uptake by green marine macroalgae



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ABSTRACT

The potential of green seaweeds, *Cladophora sericea* and *Ulva rigida*, to adsorb antimony(III) and antimony(V) from aqueous solution was studied in batch mode. The hydroxyl and carboxyl groups from the algae surface, responsible for Sb uptake, were quantified by potentiometric titration and a continuous model for the deprotonation of these sites was obtained. Kinetic studies using *C. sericea* as biosorbent were conducted using different initial Sb concentrations and solid/liquid ratios. A fast uptake process was observed with equilibrium being achieved in less than 2 h. Equilibrium studies show considerable adsorbed amounts for both Sb(III) and Sb(V). Maximum biosorption capacities, predicted by Langmuir model, were 2.1 mg/g, for Sb(III), and 3.1 mg/g for Sb(V), at pH 2 and 22 °C. A low influence of pH (range 2–8) and of ions typically present in natural waters were shown to be additional advantages of *C. sericea*, as a potential biosorbent for antimony.

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1. Introduction

Anthropogenic activities and industrialization have put increasing pressure on the environment [1]. Toxic metals and metalloids form a major class of environment contaminants and are commonly present in wastewaters. Biosorption, as a potential cost-effective remediation technique, can be a key technology. In the last decade, the biosorption of various toxic metal ions, especially the cationic ones, has been extensively investigated using biosorbents such as algae [2], fungi [3], moss [4], lichen [5], yeast [6] and other agro-industrial materials [7,8]. However, literature regarding the bioremoval of toxic metallic/metalloid oxyanions, especially antimony, is quite limited [9].

Antimony is a natural occurring metalloid, found in terrestrial surface and, despite of its low solubility, also found in water. Antimony compounds have multiple applications, such as in fire retardants, alloys for batteries, solders, as additive in glassware and ceramics and in ammunitions [9]. It is then especially introduced into environment by anthropogenic sources and expected to contaminate mining, copper smelters or power plant areas. The toxicity of this element is not still completely

documented, but damages in heart, lung, liver, and kidney have been reported following exposure [10].

Antimony has four possible oxidation states, but it mainly occurs as Sb(III) and Sb(V) in environmental samples [11]. Pentavalent form is less toxic than the trivalent one [12,13]. Antimony speciation in aqueous solution depends on the pH and electron activity. Clearly, in natural aqueous systems there are other variables that operate simultaneously, such as the presence of ligands. Antimony speciation in water is schematically presented in Fig. 1. The scheme was based on the pKa values reported in literature [14].

Many techniques are available for the removal of antimony from contaminated waters: coagulation/flocculation, phytoremediation or bioremediation, ion-exchange and adsorption, oxidation, electrochemical methods and membrane separation processes [9]. Adsorption has been noticed as a simple and relative low-cost process. The conventional adsorbents for water and wastewater treatment usually involve activated carbon (AC). Regarding the antimony removal, the literature has reported a limited performance, in addition to its disadvantageous high cost. A chemical modification of AC with iron(III) was however found to improve significantly its adsorption ability for Sb(III), reaching an adsorbed amount of approximately 3 mg/g, at pH 7 and Sb(III) concentration around 1 mg/L [15]. Several unconventional materials have been also studied as potential adsorbents for water treatment

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Sb(III)	Sb(OH) ₂ ⁺	Sb(OH) ₃	Sb(OH) ₄ ⁻
Sb(V)	Sb(OH) ₅	Sb(OH) ₆ ⁻	
	pH 1.4	pH 2.7	pH 11.8

Fig. 1. Predominant antimony species in aqueous solution, as a function of pH.

applications, such as natural diatomite [16], bentonite [17], freshwater cyanobacteria biomass [18], lichen [19], or green bean husk [20].

In this work, green marine macro algae (*Cladophora sericea* and *Ulva rigida*) were studied as biosorbents for Sb(III) and Sb(V) from aqueous solution.

2. Experimental methods

2.1. Chemicals

Biosorption of antimony was studied for the two Sb predominant oxidation states: Sb(III) and Sb(V). Adsorbate solutions were prepared by dilution of commercial standards: Sb(III) from K₂SbO₄·H₂O solution, 1000 ± 2 mg Sb(III)/L, in 2–5% HCl (*Carlo Erba*); Sb(V) from 1000 ± 2 mg Sb(V)/L, in 2–5% HNO₃ (*Chem Lab.*). The pH of the solutions was adjusted to the required values using diluted solutions of NaOH and HCl (for Sb(III)) or HNO₃ (for Sb(V)). These solutions were prepared from analytical grade chemicals: NaOH pellets (purity ≥99.0%, *Merck*), concentrated HNO₃ (65%) and concentrated HCl (37%). All solutions were prepared in distilled water.

Glassware and plastic material were acid-washed (soaked for 24 h in HNO₃ 20% solution) and rinsed with distilled water.

2.2. Adsorbent preparation

The green seaweeds were collected at Romanian shore of Black Sea in August 2014: *Cladophora sericea* in Costinesti and *Ulva rigida* in Mangalia. Algae were washed with tap and distilled water, in order to remove soluble salts, until the conductivity of the wash water reached 50 μS/cm. It was then dried and ground in fragments of approximately 5 mm, using an electric grinder (*GM-100 Retsch Knife Mill Grindomix*). The algae were dried again, at 60 °C, and stored in a desiccator until use.

2.3. Adsorbent characterization

2.3.1. Chemical analysis

The concentrations of metals in the virgin algae (Fe, Mn, Al, Cd, Cr, Zn, Pb, K, Mg, Na, Ca, Ni, Cu, Se, As, Sb) were measured after digesting 0.5 g (accurately weighed) of algae with 12.0 mL HCl 37%, 4.0 mL HNO₃ 65% (analytical grade acids) and 5.0 mL distilled water, in glass tubes at 150 °C for 2 h. Samples and blank digestions were performed in triplicate. After digestion, solutions were filtered, using cellulose acetate membranes (*Sartorius Stedim*, porosity 0.45 μm), and metal concentrations were measured by flame AAS (atomic absorption spectroscopy), or electrothermal AAS (for As, Sb and Se), using standard methods [21].

2.3.2. Fourier transform infrared analysis

Infrared spectroscopy (*Shimadzu FTIR, model IRAffinity*) was used to identify functional groups present on the raw algae surface. Infrared spectra were obtained in duplicate, with algae ground to finer particles, in a wavenumber range of 400–4000 cm⁻¹, 50 scans and with a resolution of 8.0 cm⁻¹. In addition, infrared spectra were obtained for *C. sericea*, after loading with Sb(III) and Sb(V).

2.3.3. Potentiometric titration

Acid-base potentiometric titrations were carried out for both green algae. A *Metrohm 702 SM Titrino* automatic system, equipped with a glass pH electrode pH (Profitrode 125 mm, *Metrohm 6.0255.100*), and coupled with a shaker module (*Metrohm, 728 stirrer*) was used. Calibration of the glass electrode was performed before each titration, with buffer solutions of pH 4.0, 7.0 and 10.0. The output data were processed through the software program *tiamo 1.3*.

The titration cell was filled with 50.0 mL of a 0.1 mol/L NaCl solution and 0.25 g of seaweed. The suspension was stirred (250 rpm) under nitrogen bubbling and acidified with 0.1 mol/L HCl solution until a pH 2.5 was achieved. Before titration, suspensions were equilibrated during 30 min. Titrations were carried out by stepwise addition of standardized 0.1 mol/L NaOH (increments of 0.02 mL). The drift rate was measured after each increment and pH readings were accepted for a drift rate less than 0.5 mV/min or for a maximum time of 30 min. All titrations were done under nitrogen bubbling, in order to eliminate the CO₂ interference and carried out in duplicate. A blank (electrolyte solution) was also titrated following a similar procedure.

2.4. Adsorption studies

2.4.1. Analytical procedures

The concentration of antimony in aqueous solution was measured by flame AAS (*GBC 932 plus*), using air/acetylene flame and deuterium background correction, using the following instrumental parameters: lamp current 10 mA, wavelength 217.6 nm and slit 2 nm. Calibration was performed daily (accepted for correlation coefficient R² > 0.995), in the linear range 1–40 mg/L. The limit of detection was calculated as 0.4 mg/L. Before AAS analysis, the samples were filtered using cellulose acetate membrane filters (0.45 μm porosity).

2.4.2. Screening tests

Preliminary assays were performed with *U. rigida* and *C. sericea*, in order to compare the biosorption ability of both species for Sb(III) and Sb(V). The experiments were conducted at constant temperature (22 ± 1 °C) and constant pH (pH 5.0 ± 0.5). Antimony (trivalent or pentavalent) solutions, with 25 mg/L concentration, were stirred after addition of virgin algae (dosage 10 g/L) in 100 mL capped Erlenmeyer flasks, under orbital agitation at 120 rpm (orbital rotator *GFL 3031*). The experimental conditions (pH, temperature and initial Sb concentration) were selected to be representative of possible real situations. After 4 h-contact time, samples were filtered and final Sb concentrations analysed. Removal percentages were calculated.

2.4.3. Effect of pH

The pH conditions were known to have a significant influence in the adsorption of metals and metalloids. In order to study the influence of this variable on the biosorption of antimony(III, V) by *C. sericea*, adsorption tests were conducted at different pH values. The experiments were carried out in duplicate, following a procedure similar to the one described in Section 2.4.2. The pH of the initial solution was adjusted to values between 2 and 8, and was regularly controlled throughout the contact time, in order to be approximately constant (±0.5).

2.4.4. Kinetic studies

The effect of contact time on the biosorption of Sb(III) and Sb(V) by *C. sericea* was studied in batch mode, at constant temperature (22 ± 1 °C) and pH (pH 7, for Sb(III), and pH 2, for Sb(V)). The experimental conditions were selected in order to evaluate the effect of initial adsorbate concentration (5, 10 and 25 mg/L, using

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