



Pb(II) and Cd(II) biosorption on *Chondracanthus chamissoi* (a red alga)

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ABSTRACT

Chondracanthus chamissoi is an efficient biosorbent for Pb(II) and Cd(II). The sorption efficiency increases with pH and reaches an optimum around pH 4. Maximum sorption capacity reaches 1.37 mmol Pb g⁻¹ and 0.76 mmol Cd g⁻¹. The biosorbent has a marked preference for Pb(II) over Cd(II), though insufficient for separating these metals by a simple sorption step. The uptake kinetics is controlled by the resistance to intraparticle diffusion with a limited impact of particle size, metal concentration and sorbent dosage. In the present case, grinding the biomass does not improve sorption capacity and uptake kinetics. The sorption of metal ions is probably due to their interaction with carrageenan (one of the main constituents of the biosorbent): sulfonic groups (on the sulfated polysaccharide) have a higher affinity for Pb(II) than for Cd(II) according to HSAB rules.

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1. Introduction

The regulations concerning wastewater discharge to the environment are becoming more and more drastic in order to recycle waste streams and optimize the use of water resources. Effluents containing metal ions processing from mining, metallurgy activities are important sources of contamination of water bodies. Conventional processes for metal recovery include precipitation [1], solvent extraction [2], sorption on ion exchange, extractant impregnated and chelating resins [3,4]. Though these processes are globally efficient, they frequently face economical and/or technical limitations. Indeed, they may be non competitive for the treatment of low-concentration effluents (resins, solvent extraction), not capable of reaching requested levels of decontamination (precipitation). They may have serious environmental drawbacks since they can produce huge amounts of contaminated sludge (precipitation) or toxic compounds release (solvent extraction). The thermal degradation of synthetic resins at the end of their life cycle can also produce hazardous sub-products [5]. These are some reasons that can explain the interest of research community for developing alternative processes such as biosorption.

Biosorption consists in using materials of biological origin for the sorption of target molecules (metal ions, dyes, etc.) through interactions that mimic those involved in metal binding on ion exchange and chelating resins. Though most of the studies focus

on living or non-living biomass (bacteria, fungi, yeast, etc.), sub-products from agriculture, marine industry have also been frequently cited as biosorbents [6,7]. Brown and green algae have retained most of the attention in the field of metal biosorption [8–14]. The presence of alginate in their cell wall may explain their high efficiency for metal uptake through complexation or ion exchange on carboxylic acid groups (guluronic and mannuronic acids). However, red algae may have also significant potential for sorption [15–18]. These algae are characterized by the presence of other polysaccharides like carrageenan. Actually, the term carrageenan recovers a number of different linear sulfated galactans. They are composed of alternating 3-linked β-D-galactopyranose (G-units) and 4-linked α-D-galactopyranose (D-units) or 4-linked 3,6-anhydro-α-D-galactopyranose (DA-units): these associations form the disaccharide repeating unit of carrageenan. Different carrageenans exist corresponding to different units, different arrangements and different proportions (Fig. AM1, in the Additional Material section) [19–21]. Carrageenan is used for its gelling properties in cosmetics, food industry, for coagulation and flocculation in environmental applications, for encapsulation in biotechnology. The sulfonic groups of the biopolymer are responsible for metal binding [22]: actually, the efficiency of the polymer depends on its degree of sulfatation.

Red algae can be considered as potential marine resource and in many countries of South America alga farming is considered a competitive activity for the production of carrageenan: *Chondracanthus chamissoi* has been cultivated for the extraction of this biopolymer [23,24]. The ability of this biomass for sorbing metals should be investigated not only for the potential of these biosorbents but

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also for evaluating how these biosorbents could be at the origin of a contamination of carrageenan sources (for applications in food, cosmetics and health).

This study evaluates *C. chamissoi* for the sorption of Pb(II) and Cd(II). These metal ions are frequently found in wastewater from mining, metallurgy industries and may contribute to contaminate marine environment and local fauna and flora [25,26]. FT-IR spectrometry was used for characterizing the biopolymers extracted from the alga and the spectrum was compared to the spectra of ι - and κ -carrageenan. After investigating the impact of pH on metal sorption, the sorption isotherms were determined at optimum pHs and experimental curves were modeled using the Langmuir equation. Finally, the influence of a series of experimental parameters (particle size, sorbent dosage, and metal concentration) on uptake kinetics was investigated using the models of resistance to film diffusion and to intraparticle diffusion and the pseudo-second order rate equation for simulating kinetic profiles.

2. Materials and methods

2.1. Materials

Lead acetate trihydrate ($\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$, Carlo Erba) and cadmium chloride ($\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$, Merck) salts were used for the preparation of stock solutions. Other solutions were prepared by dilution using Milli-Q demineralized water.

The red alga was collected in the Bahía de Chancay (Province of Huaral, Péru) in August 2009. It was identified as *C. chamissoi* (C. Agardh) Kützinger. The material was abundantly rinsed with tap water and finally with demineralized water. The clean biomass was then dried at room temperature before being ground and sieved at the following sizes:

$80 \mu\text{m} < \text{PS1} < 125 \mu\text{m} < \text{PS2} < 250 \mu\text{m} < \text{PS3} < 500 \mu\text{m} < \text{PS4} < 710 \mu\text{m}$.

The stability of the biomass was evaluated at different pHs (in the target pH range of the study; i.e., between 2 and 6.5). With some brown algae, some compounds may be dissolved during metal sorption causing potential “re-precipitation” phenomena [12]. In such a case a pre-treatment with calcium chloride is necessary. The biomass was stabilized at target pH values, the filtrate was recovered and mixed with metal solutions in order to verify the occurrence of precipitation. In the present case, the biomass was stable and could be used without any treatment.

In order to characterize the biomass, the biopolymers were extracted using the procedure described by Pereira et al. [21]. The treatment consists in rehydrating the biomass for 12 h in water before a treatment with a 1:1 acetone/methanol mixture. The biomass is digested in 150 mL of a 1 M NaOH solution at 80 °C under reflux for 3 h. Finally, the suspension is filtrated and the filtrate (containing the characteristic biopolymers) is precipitated by the addition of ethanol (96%). The precipitate was dried and analyzed by FT-IR spectrometry (FT-IR Bruker equipped with OPUS Software) after inclusion in KBr discs.

SEM-EDAX analysis was also performed on the biomass for observation and identification of binding localization. The dry sorbent was analyzed using an Environmental Scanning Electron Microscopy (ESEM) Quanta FEG 200, equipped with an OXFORD Inca 350 Energy Dispersive X-ray microanalysis (EDX) system.

2.2. Sorption experiments

The influence of pH was studied by contact for 48 h of the biosorbent (m : 20 mg of the biosorbent at the particle size PS3) with a

volume V (L) of 0.15 L of the metal solution (initial concentration, C_0 : 70 mg metal L^{-1}) at target pH values. For Pb(II), initial pH was set between 2.0 and 5.5 while for Cd(II) the pH was varied between 2.0 and 7.0. The pH was controlled using molar solutions of HCl and NaOH. After 2 days of agitation on a reciprocal shaker, the solution was filtrated using a 1–2 μm pore size filtration membrane and the filtrate was analyzed by ICP-AES for equilibrium metal concentration (C_{eq} : mg metal L^{-1} or mmol metal L^{-1}) using a Jobin-Yvon Activa-M (Jobin-Yvon, Longjumeau, France). The mass balance equation was used for calculating the sorption capacity q (mg metal g^{-1} , or mmol metal g^{-1}): $q = (C_0 - C_{\text{eq}})V/m$. The final pH was systematically monitored at equilibrium.

Sorption isotherms were performed at pHs 4 and 5 for Pb(II), and pH 4 for Cd(II). A given amount of sorbent (i.e., 20, 30 or 40 mg of biosorbent, PS3) was dropped into 150 mL of metal solution at the appropriate pH. The metal concentration was varied between 5 and 200 mg metal L^{-1} . The isotherms obtained with different amounts of biosorbent were merged. The suspension was maintained under agitation for 24 h using a reciprocal shaker at room temperature (i.e., 20 ± 1 °C). Finally, the suspension was filtrated and the residual concentration of metal was analyzed by ICP-AES. Similar procedure was used for the investigation of metal sorption in binary solutions.

Uptake kinetics was determined at room temperature mixing 1 L of solution with a fixed amount of sorbent. Samples were collected at different contact times, filtrated and analyzed by ICP-AES for the determination of the kinetic profile (plotting the relative concentration $C(t)/C_0$ versus time). The amount of sorbent (i.e., sorbent dosage, SD, g L^{-1}), the initial metal concentration and the particle size (PS1–PS4) were varied: relevant experimental conditions are extensively described in the caption of the figures.

The models used for the description of sorption isotherms and uptake kinetics are fully described in the [Additional Material section](#).

3. Results and discussion

3.1. Characterization of biosorbent

The biomass of *C. chamissoi* was treated by the alkaline procedure for carrageenan extraction [21] and the FT-IR spectrum of the extract was compared to the spectra of κ - and ι -carrageenan (Table 1 and Fig. AM2 in the [Additional Material section](#)). The most interesting wavenumbers for carrageenan identification range between 1400 and 700 cm^{-1} [19]. The bands appearing on the spectrum of the alkaline extract are consistent with those identified on κ - and ι -carrageenan and reported by Pereira et al. [19]. The peak at 801 cm^{-1} is typical of ι -carrageenan (also reported for θ -carrageenan). This peak did not appear on the spectrum of the alkaline extract of *C. chamissoi*. This probably means that the alga is mainly constituted of κ -carrageenan (or its precursor μ -carrageenan). This is consistent with the levels (molar fraction of κ -carrageenan) reported for several species of *Chondracanthus* algae (50–82 mol%) [27] and more specifically for *C. chamissoi* (82 mol%) [28].

The SEM analysis of the sorbent showed different structures such as tubular forms and more massive shapes. The surface of the biosorbent is quite irregular (stripped forms). The cross-sections of the tubes show irregular or heterogeneous aspects. The SEM-EDX analysis allows identifying the presence of major elements (Fig. AM3, [Additional Material section](#)). The most representative elements are alkaline and alkaline earth metals, the sulfur element (sulfated polysaccharides) and the target sorbed metals (i.e., Pb and Cd). Actually, it was not possible detecting significant variations in the distribution of S and Pb (or Cd) for the different samples. The biosorbent can be roughly considered as a homogeneous material in terms of metal sorption.

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