



Study on bioaccumulation and biosorption of mercury by living marine macroalgae: Prospecting for a new remediation biotechnology applied to saline waters



Bruno Henriques^{a,*}, Luciana S. Rocha^a, Cláudia B. Lopes^a, Paula Figueira^a, Rui J.R. Monteiro^a, A.C. Duarte^a, M.A. Pardal^b, E. Pereira^a

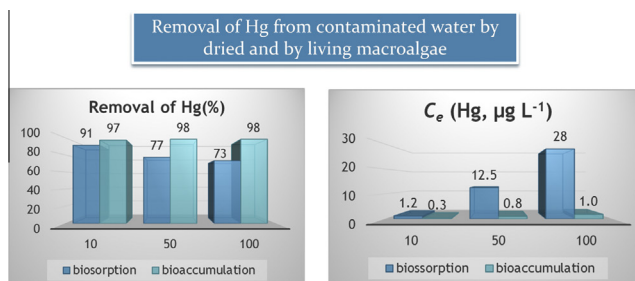
^a CESAM & Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

^b CEF & Department of Life Sciences, University of Coimbra, Calçada Martim de Freitas, 3000-456 Coimbra, Portugal

HIGHLIGHTS

- The removal of Hg from water by living algae was investigated at realistic levels.
- All seaweeds showed huge accumulation capabilities, reaching up to 209 $\mu\text{g Hg g}^{-1}$.
- *U. lactuca* achieved 99% of removal, leading to Hg levels in seawater below 1 $\mu\text{g L}^{-1}$.
- Bioaccumulation was more advantageous than biosorption in terms of efficiency.
- The volatilization of Hg or its conversion to organometallic forms was negligible.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 4 May 2015

Received in revised form 25 June 2015

Accepted 3 July 2015

Available online 9 July 2015

Keywords:

Mercury

Organo-metallic forms

Marine macroalgae

Biosorption

Bioaccumulation

Kinetic modeling

ABSTRACT

This study aimed to assess and explore the bioaccumulation capabilities of three different macroalgae species, *Ulva lactuca* (green), *Gracilaria gracilis* (red) and *Fucus vesiculosus* (brown), very common on temperate coasts and estuaries, for the removal of mercury (Hg) from contaminated waters (with high salinity), using environmentally realistic concentrations of metal (10–100 $\mu\text{g L}^{-1}$). Levels of Hg accumulated by all seaweeds ranged between 20.8 and 208 $\mu\text{g g}^{-1}$, corresponding to bioconcentration factors of c.a. 2000. A comparative evaluation of bioaccumulation (living biomass) and biosorption (dried biomass) was performed for *U. lactuca*, which had displayed the best performance in accumulating Hg. The removal conducted by the living seaweed ($m_{\text{macroalgae}}/V_{\text{solution}} \approx 500 \text{ mg L}^{-1}$), although slower, was more promising since all Hg levels were reduced by about 99%, fulfilling the European criteria for drinking water quality. Pseudo-second-order and Elovich models described quite well the experimental data, assuming a process essentially of chemical nature. Determination of total Hg content in algal biomass over time, allowed to confirm and to follow the uptake of this metal by the living organism. Volatilization of Hg or its conversion to organo-metallic forms (0.02–0.05%) was negligible during the decontamination process.

Overall, the results are a contribution for the development of an efficient and cost-effective water remediation biotechnology, based on the use of living macroalgae to promote the removal of Hg.

© 2015 Elsevier B.V. All rights reserved.

* Corresponding author.

E-mail address: brunogalinho@ua.pt (B. Henriques).

1. Introduction

Increasing industrialization, which allowed man to thrive and achieve high living standards, has resulted in the rise of the contamination levels in the environment at large-scale. Due to its high toxicity, temporal persistence, bioaccumulation and bioamplification along the trophic chain [1], mercury (Hg) has aroused a great concern worldwide [2].

In the aquatic environment, Hg is usually found as Hg^{2+} or as complexes of Hg^{2+} with different organic and inorganic ligands [3]. However, reduction of Hg^{2+} to elemental form Hg^0 may occur, as well as methylation of inorganic Hg, resulting in highly mobile-metallic species, such as methylmercury (MeHg^+), which is the most toxic form of Hg [4]. Organo-metallic species are more readily assimilated by organisms than inorganic forms [5], which enhances the risks associated with the entrance of Hg into the food chain – the main route of human exposure to this contaminant (mainly through the consumption of fish).

Alerted to the toxic effects of Hg, governmental institutions around the world have imposed increasingly tight limits for its concentration in industrial effluents. Recently European Union (EU) even brought a paradigm shift, ranking Hg as “priority hazardous substance” in the field of water policy, whose discharges should be ceased or eliminated progressively until 2021 [6]. So, instead of limits for wastewater discharges, legislation now considers environmental quality standards (EQS) for this metal in surface waters [7].

Physicochemical processes, conventionally used for metal removal, often have high operating costs, generate large amounts of sludge which require a proper disposal, or are ineffective when aim is to achieve very low residual levels [8,9]. The development of alternative treatment technologies is therefore essential. In this sense, methods based on the use of biomasses or organic wastes – biosorption [8], or even of live organisms – bioaccumulation [10], such as plants or macroalgae, largely available, may be the solution for reducing levels of Hg to acceptable limits, in a cost-effective and environmentally friendly way.

In the literature there is a considerable number of studies reporting the successful application of several biomasses in metal removal [8,11,12], although less have been devoted to Hg [13,14]. Furthermore, oddly the majority of works deals with synthetic water or freshwater, although most industrial effluents ends into estuaries or coastal areas [15], which are complex dynamic systems rich in salts. The focus on the removal of a particular contaminant in unrealistic and overly high concentration may also be pointed as a failure of most research works [13].

In the last years, marine macroalgae have gained special attention in the field of water remediation [16–18], due to their remarkable ability to bind metals, which is attributed to the structure and chemical composition of their cell walls, offering different metal-binding sites [18,19]. However, almost all of those studies concern the use of non-living biomass, neglecting the potential advantages of bioaccumulation, such as metal intracellular binding, which may lead to lower residual concentrations [10].

The study of metal accumulation by living organisms has been limited to microalgae [20] and other microorganisms [12], or relates with field studies [21,22]. Comparison between bioaccumulation and biosorption of metals by macroalgae is also virtually non-existent in the literature [20].

There is a need for laboratory studies, performed under controlled conditions, discussing metal bioaccumulation kinetics [12,23], since most works only reports initial and final concentrations of metal [9] or present data as a function of time, discarding the mathematical modeling of the results, which relate to short exposure periods [24,25].

Marine macroalgae may be divided into brown algae (Phaeophyta), red algae (Rhodophyta) and green algae

(Chlorophyta), with differences in the cell wall, which may dictate the binding to a particular metal. Carboxyl and sulfate are the predominant functional groups in brown algae cell walls, which are mainly composed by cellulose, alginic acid and sulfated polysaccharides [18]. Besides cellulose, red and green algae contain, respectively, agar and carragenates, rich in sulfated polysaccharides, and glycoproteins, which comprise amino, carboxyl, sulfate and hydroxyl groups [18]. In addition, intrinsic growth rate and potential production of exudates [1,15] may also influence Hg removal by each macroalgae specie. A better understanding of the mechanisms and kinetics of Hg accumulation by macroalgae is essential to develop a full-scale biotechnology, to be applied to water remediation.

Thus, the main objective of this study was to evaluate and compare the uptake and accumulation of Hg by three different living macroalgae, *Ulva lactuca*, *Gracilaria gracilis* and *Fucus vesiculosus* from Hg spiked saline waters, using environmentally realistic concentrations. In addition, for the macroalgae with best performance, the study and comparison of biosorption and bioaccumulation processes (in terms of removal efficiencies and kinetics), as well as the assessment of potential Hg methylation during removal were also addressed.

2. Materials and methods

2.1. Material and chemicals

All chemical reagents used in this work were of analytical reagent grade, obtained from chemical commercial suppliers and were used without further purification. The certified Hg standard stock solution, containing $1001 \pm 2 \text{ mg L}^{-1}$ of Hg(II) in nitric acid 0.5 mol L^{-1} , was purchased from Merck. All working solutions, including standards for the calibration curves, were obtained by diluting the stock solution. All material used in the experiments was previously washed in Derquim 5% rinsed in Milli-Q water ($18 \text{ M}\Omega \text{ cm}^{-1}$), soaked in 25% HNO_3 for at least 24 h and subsequently rinsed with Milli-Q water.

2.2. Macroalgae collection and maintenance

The *U. lactuca* (Chlorophyta), the *G. gracilis* (Rhodophyta) and *F. vesiculosus* (Phaeophyta) were collected in the Mondego estuary (Figueira da Foz, Portugal, $40^\circ 08' \text{N}$, $8^\circ 50' \text{W}$) and transported to the laboratory in isothermal plastic bags containing some local water. After rinse with seawater to remove debris and epibionts a small part of the algae was immediately freeze dried for subsequent quantification of the natural (baseline) concentrations of total and organo-metallic Hg. Until the beginning of the experiments the macroalgae were maintained in aquariums (filled with filtered seawater enriched with Provasoli stock solution [23]) under natural light (approximately 12L:12D), at room temperature of $20 \pm 2^\circ \text{C}$. Seawater needed for algae maintenance and for the experiments was collected at Portuguese coast ($40^\circ 33' \text{N}$, $8^\circ 46' \text{W}$), filtered through $0.45 \mu\text{m}$ pore size filters and stored in the dark at 4°C until further use.

A brief characterization of seawater, including pH, salinity, conductivity and multi-elemental analysis was carried out. The pH (8.0), salinity (35) and conductivity (55 mS cm^{-1}) were recorded on a WTW meter. Concentrations of major (Ca, K, Mg, Na and Si) and minor elements (Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Li, Mn, Ni, P, Pb, Sr, V and Zn), obtained by inductively coupled plasma spectroscopy, using a Jobin – Yvon JY70 Plus Spectrometer (data not show), were in line with those reported by Lopes et al. [14], which correspond to the natural levels in seawater at Portuguese coast. The concentration of Hg in the natural seawater was also

Download English Version:

<https://daneshyari.com/en/article/6584338>

Download Persian Version:

<https://daneshyari.com/article/6584338>

[Daneshyari.com](https://daneshyari.com)