Journal of Hazardous Materials 344 (2018) 531–538

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Research paper

Removal and recovery of Critical Rare Elements from contaminated waters by living *Gracilaria gracilis*

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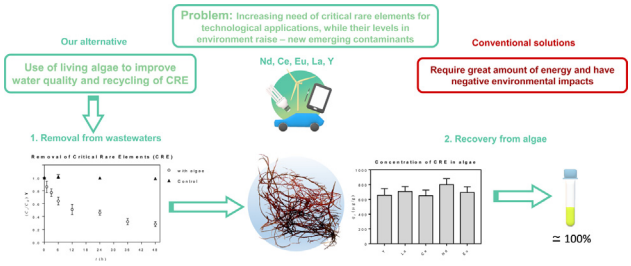
HIGHLIGHTS

- Living algae were applied to concentrate and recover critical rare earth elements.
- *G. gracilis* removed 70% of 500 μg L^{-1} solutions of Y, Ce, Nd, Eu and La in 48 h.
- In mixtures, selectivity was not observed although removal of lanthanides improved.
- Uptake of these emergent contaminants by algae followed the Elovich kinetic model.
- Nearly 100% of all elements were recovered in a 300-fold more concentrated solution.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 2 May 2017
Received in revised form 6 October 2017
Accepted 25 October 2017
Available online 27 October 2017

Keywords:
Rare earth elements
Macroalgae
Bioremoval
Recovery
Growth rate

ABSTRACT

The experiments performed in this work proved the ability of *Gracilaria gracilis* to concentrate and recover Critical Rare Elements (CRE) from contaminated waters. The importance of recycling these elements is related to their very limited sources in Nature and progressive use in technologies. Moreover, their mining exploitation has negative environmental impact, and recent studies point them as new emerging pollutants. To the best of our knowledge, this is the first report on the application of living macroalgae for the removal and recovery of CRE. *G. gracilis* (2.5 g L^{-1}, fresh weight) was exposed to mono- and multi-element saline solutions of 500 μg L^{-1} of Y, Ce, Nd, Eu and La. Removal was up to 70% in 48 h, with bioaccumulation following Elovich kinetic model. In multi-element solutions, selectivity was not observed although removal of lanthanides improved comparatively to single-element solutions. No mortality or adverse effect on growth was registered. The subsequent macroalgae digestion allowed collecting virtually 100% of all elements in a 300-fold more concentrated solution. The overall results suggest the application of living macroalgae as a simple and effective alternative technology for removing and recovering CRE from wastewaters, contributing to an improvement of water quality and CRE recycling.

1. Introduction

Rare earth elements (REE) include the lanthanide series (atomic number, Z, from 51 to 71) plus scandium (Z = 21) and yttrium (Z = 39) [1,2]. Although more abundant than precious metals, REE

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https://doi.org/10.1016/j.jhazmat.2017.10.054
0304-3894/

are often dispersed in ore deposits, which makes their extraction difficult [3]. Furthermore, due to their chemical similarities, individual separation of the elements is also problematic [1].

Recent reports of the European Commission [4–6] classify REE as Critical Raw Materials (CRM) due to their high supply risk, since more than 95% of the resources are provided by China, and difficulty of substitution by alternative materials in industrial applications [7–9]. Moreover, REE have a great strategic importance, being increasingly used in green and low-carbon technologies, such as hybrid and electrical cars, wind turbines, high performance batteries, and a vast range of electronic devices and catalysts in various industries [1,10]. Five of the most critical REE until 2025 are neodymium (magnets), europium and yttrium (phosphors and luminescence), and cerium and lanthanum (metal alloys, batteries, glass and catalysts) [11,12]. As the use of these elements is increasing, larger amounts of REE-containing wastes will end into the environment, posing environmental and human health risks [13,14]. Indeed, REE are already regarded as main environmental contaminants in China [15] and recent studies classified them as new emerging pollutants, pointing to the need of regulatory thresholds for REE concentrations and emissions to the environment [16,17].

Methods for the extraction of REE from ores, such as pyrometallurgy and hydrometallurgy have severe negative environmental impacts, besides being expensive [1,12]. Recovery and recycling of REE from electronic wastes, mine drainage and ore wastes, and other industrial wastewaters [3,18] provide a response to the dependence on a single and limited supply source, while mitigating environmental problems and slowing the depletion of natural resources [12,19]. However, recycling of REE is far from reaching its full potential since less than 1% was recycled in 2011, mainly due to the lack of incentives and technological constraints [2]. Various methods have been used in order to separate and pre-concentrate REE, such as liquid–liquid or solid-liquid extraction, precipitation and ion exchange [13]. However, these conventional methods present several disadvantages, such as generation of large quantities of contaminated water and requirement of high temperatures and/or high amount of chemicals [1,13]. To overcome these limitations, new biotechnological approaches for extracting and recovering REE have been proposed [9,18]. Biosorption has been described as an efficient method [20] and several biosorbents have been tested, namely, algae biomass, fungi, bacteria and plant and animal residues [7,21–24]. Among them, macroalgae have gained attention for water remediation and metal removal [25,26]. In recent works we have highlighted the potential of bioaccumulation of living marine macroalgae for the removal of toxic metals [27], showing in some cases higher removal efficiencies than the corresponding non-living biomass [28]. To the best of our knowledge, till date no work has been reported on the application of living macroalgae to remove, concentrate and recover REE from aqueous solutions.

In view of this, the aim of this study is to evaluate whether living *Gracilaria gracilis* is an efficient alternative to remove and pre-concentrate Y, La, Ce, Nd and Eu, herein referred as Critical Rare Elements (CRE), from contaminated saline water, towards the recovery of these elements through a simple, low-cost and environmental friendly procedure. This species of wide availability in Nature and well-established commercial production has several cartilaginous, cylindrical branches arising from perennial discoid holdfast, and internal tissue of large thin-walled cells, which contain cellulose, agar and carragenates, rich in sulfated polysaccharides [25].

2. Material and methods

2.1. Experimental design

The ability of living *Gracilaria gracilis* to remove CRE from saline water was assessed by exposing 2.5 g of biomass (fresh weight) to mono- and multi-element solutions of Ce, Eu, Y, La and Nd with element concentration of 500 $\mu g\,L^{-1}$. Experiments were conducted during 48 h in Schott© glass flasks of 1 L, under natural light (12 h light:12 h dark) at room temperature (20 ± 2 °C). Mono- and multi-element solutions were prepared by adding the required volume of certified reference solutions (1000 $mg\,L^{-1}$; Alfa Aesar Specpure®, plasma standard solutions for La, Y and Eu; Inorganic Ventures™, certified reference materials for ICP, for Nd and Ce) to saline water of salinity 15. Saline water was obtained by diluting filtered seawater with ultrapure water (18,2 MΩ cm). The pH was adjusted to 7.8 with NaOH (1 M) and all spiked solutions were left to pre-equilibrate during 12 h before the experiments. Kinetics of CRE uptake was studied by collecting 5–10 mL of water at pre-defined periods of time (0, 1, 3, 6, 12, 24, 36 and 48 h). Water samples were immediately acidified to pH <2 with HNO_3 65% Suprapur® and stored at 4 °C until quantification. The experiments were performed in triplicate with blanks (clean saline water in the presence of living macroalgae) and controls (saline water spiked with CRE in the absence of living macroalgae) running in parallel with the experiments. Solution pH was monitored during the essays (0, 6, 24 and 48 h). At the end of the experiments macroalgae biomass was weighted to evaluate their growth. *G. gracilis* used in the experiments was collected in Ria de Aveiro (Portugal, 40°34′58″N, 8°44′52″W), and brought to laboratory in isothermal plastic bags containing local water. To remove debris and epibionts, macroalgae were rinsed with filtered seawater and maintained in aerated aquariums until their use. Salinity, sunlight exposure and temperature were the same of the subsequent experiments. Before the experiments a sub-sample of the macroalgae was collected and freeze-dried for quantification of CRE baseline concentrations. To determine the dry/fresh weight ratio several pieces of the fresh macroalgae were blotted with paper, weighted and then dried at 40 °C until constant weigh. Seawater was collected at Ria de Aveiro (Portugal 40°38′39″N, 8°44′43″W) in high tide, filtered using Millipore™ 0.45 μm pore size filters and stored at 4 °C in the absence of sunlight, until further use [28].

2.2. Analytical procedures

Quantification of CRE in water samples was performed by inductively coupled plasma spectroscopy (ICP-MS), using a Thermo ICP-MS XSeries equipped with a Burgener nebuliser. Calibration curves were obtained using 9 standards within the concentration range of 0.1–100 $\mu g\,L^{-1}$ prepared by diluting a certified standard solution in 2% HNO_3. The limit of quantification of the method for all the elements was 0.1 $\mu g\,L^{-1}$, and the acceptable coefficient of variation among replicates was 5%. To avoid matrix interferences related with salinity, all samples were diluted 10 times in 2% HNO_3 prior analysis.

Contents of CRE in macroalgae biomass before and after exposure to spiked solutions were determined by ICP-MS, after microwave-assisted acid digestion. The freeze-dried biomass samples (150–200 mg) were weighed into acid-washed Teflon vessels, 2 mL HNO_3 (70%) were added, and a first microwave cycle (5 min raising temperature up to 170 °C and then held at 170 °C for 10 min) was run on a CEM Mars 5 microwave. Afterwards, 0.25 mL of H_2O_2 (30%) were added and the mixture was left to sit for 15 min to allow any vigorous oxidation to vent before the reaction vessels were tightened and placed in the microwave for a