Recovery of Rare Earth Elements from Luminophores using the Red Alga *Galdieria*

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Abstract
The red alga *Galdieria phlegrea* was used as an experimental organism to test the bioaccumulation of rare earth elements (REEs) from luminophores. Algal cells were cultured mixotrophically in a liquid medium with addition of glycerol as a source of carbon. Luminophores from two different sources (fluorescence lamps and energy saving light bulbs) were added into the medium in the form of a powder. The cell number was monitored to follow the growth of the algal culture. The content of single REEs in the luminophores, and the biomass, were determined using ICP-MS. The most abundant element in both luminophores was yttrium, representing about 90% w/w. The growth of cultures grown in the presence of both luminophores was comparable with the control. The total amount of accumulated REEs in biomass differed with the type and concentration of luminophore used. The most abundant element accumulated in the biomass was lanthanum. To conclude, *Galdieria phlegrea* can grow in the presence of luminophores and accumulate REEs. The enriched biomass is a promising template for biotechnological applications.
Keywords: rare earth elements; red algae; *Galdieria*; waste; luminophores

1. Introduction

The group of rare earth elements (REEs) includes scandium (Sc), yttrium (Y), and a series of 15 other elements from the lanthanide series. They exhibit very similar physical and chemical properties (Zhu et al., 2012). Due to their unique magnetic and catalytic properties, REEs are widely used in almost all electronic and clean energy technologies. They are also used as fertilizers in agriculture, in aquaculture, or as growth enhancers. REEs are considered as critical raw materials because of their high supply risk and above average economic importance in comparison with other raw materials (European Commission, 2017). With the increasing demand, the requirement for recycling of REEs from industrial waste rises. Research has recently focused on environmentally-friendly technologies of metal recovery from secondary resources (Sethurajan et al., 2018; Pollmann et al., 2018). Only a few studies of REE recovery by algae or cyanobacteria have been published e.g. the red alga *Galdieria sulphuraria* (Minoda et al., 2015) and the macroalga *Gracillaria gracilis* were effectively used to recover REEs from waste water (Jacinto et al., 2018). Biosorption of single REEs by the biomass of both microscopic and macroscopic algal species was studied (reviewed by Isildar et al., 2019).

The aim of this study was to examine the ability of the red alga *Galdieria* to accumulate REEs from luminophores obtained as powder mixtures from fluorescence lamps and energy saving bulbs containing a high concentration of REEs. In order to examine bio-absorption capacity and physiological effects of REEs, *Galdieria phlegrea* was cultivated mixotrophically in the presence of different types and concentrations of luminophores. As a comprehensive determination of the content of lanthanides accumulated in algal biomass, inductively coupled plasma mass spectrometry (ICP-MS) was used. The potential to use red algae for bio-recovery of REEs from luminophores was evaluated.

2. Methods

2.1 Experimental organism and culturing

The unicellular rhodophyte *Galdieria phlegrea* Nr. 613 was obtained from the Algal Collection of Dipartimento delle Scienze Biologiche, Section of Plant Biology, University "Federico II" of Naples, Italy (http://www.acuf.net/index.php?lang=en). Cultures were grown in photobioreactors in modified Galdieria-nutrient medium, pH 2 (Vítová et al., 2016) with addition of 1% glycerol at 39°C and a light intensity of 150 μmol photons m^{-2} s^{-1}. Biomass was harvested by centrifugation and freeze-dried.

2.2 Growth evaluation

Growth of the cultures was expressed as the number of algal cells mL^{-1}. It was followed by counting cells under transmitted light in a Bürker counting chamber using a BX51 microscope.

2.3 Quantitative analysis of REE content by ICP-MS

Samples of luminophores and algal biomass were digested with 67% HNO_3 and 30% H_2O_2 in a PTFE microwave oven at 250–600 W for 20 min. ICP-MS measurements were performed using an Elan DRC-e equipped with a concentric PTFE nebuliser and cyclonic spray chamber. Values were expressed as milligrams per kilogram (μg g^{-1}) of dry weight (Goecke et al., 2015).

3. Results

3.1 Composition of luminophores

The luminophores collected from electrical waste (fluorescence lamps – FL, energy saving bulbs - CFL) in a form of the powder were analyzed for the REE content using ICP-MS. The most abundant element in both luminophores was Y (77592 and 160834 μg g^{-1} in FL and CFL, respectively) representing 89 and 90% of all REEs contained in luminophores. Yttrium was followed by Eu (5589.75 μg g^{-1} and 11354.5 μg g^{-1}), Gd, Ce, La, and Tb (Tab. 1, column 1, 3; respectively).

Table 1. Content of single rare earth elements in the luminophore (FL, CFL) and biomass of *Galdieria phlegrea* treated by luminophores (in μg g^{-1}).

Element	FL μg g^{-1}	Galdieria +FL50 μg g^{-1}	CFL μg g^{-1}	Galdieria +CFL100 μg g^{-1}
Y	77592	70.9	178649.5	1411.2
La	794.3	332.3	3144	654.9
Ce	1119.1	257.6	2048.6	424.8
Eu	5589.7	11.2	11354.5	156.1
Gd	1347.3	19.1	294.5	15.3
Tb	570	103.7	943.4	196.4

3.2 Algal growth in the presence of luminophore

Cultures of *G. phlegrea* of the same initial concentration ($1x10^6$ cells mL^{-1}) were cultivated mixotrophically in liquid mineral medium with the addition of 1% glycerol under continuous light. They were harvested after 3 days to obtain the biomass for elemental analysis. The luminophore powders (FL, CFL) were added at the beginning of the cultivation at concentrations of 25, 50, and 100 mg L^{-1}. The amount of produced biomass was monitored by counting the cell number per mL. When compared with the control culture (no luminophore added) the growth of cultures grown in the presence of both luminophores was comparable or even higher (Fig. 1). The control reached $6.35x10^6$ cells mL^{-1}, while the maximal value of treated cultures was $8.48x10^6$ cells mL^{-1} in the case of luminophore FL added at a concentration of 100 mg L^{-1}.

3.3 Accumulation of rare earth elements in biomass

To follow the accumulation of REEs by algal cells, the harvested biomass from these experiments was analyzed by ICP-MS for REE content. The total amount of accumulated REEs differed with type and concentration of luminophore used for treatment (Fig. 2).

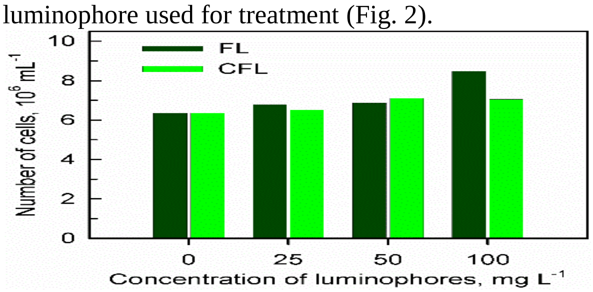

Figure 1. Cell number of *Galdieria phlegrea* grown in the presence of luminophores (FL, CFL) containing rare earth elements after 3 days of cultivation.

The algal biomass from cultures grown in the presence of luminophores contained La as the most abundant element (332 and 654.9 μg g^{-1} in FL and CFL, respectively) followed by Ce, Y, Tb, Gd and Eu (Tab. 1, column 2, 4; respectively). The main technical implication of this work is that use of the red alga *G. phlegrea* could provide an environmentally-friendly technology for recovery of REEs by bio-absorption from luminophores derived from industrial electrical waste. Mixotrophic growth using glycerol as a cheap source of carbon and energy would be a benefit for prospective commercial scale-up cultivation.

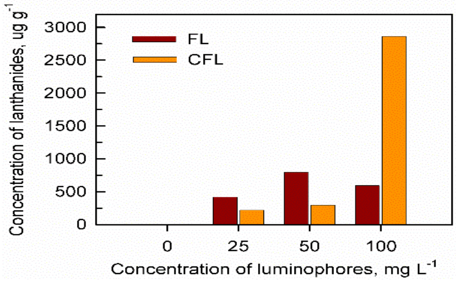

Figure 2. Total content of rare earth elements accumulated from luminophores (FL, CFL) by biomass of *Galdieria phlegrea*.

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