



Communication

Evaluation of Holmium(III), Erbium(III), and Gadolinium(III) Accumulation by Cyanobacteria Arthrospira platensis Using Neutron Activation Analysis and Elements' Effects on Biomass Quantity and Biochemical Composition

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Abstract: Rare-earth elements are released into the aquatic environment as a result of their extensive use in industry and agriculture, and they can be harmful for living organisms. The effects of holmium(III), erbium(III), and gadolinium(III) when added to a growth medium in concentrations ranging from 10 to 30 mg/L on the accumulation ability and biochemical composition of *Arthrospira platensis* were studied. According to the results of a neutron activation analysis, the uptake of elements by cyanobacteria occurred in a dose-dependent manner. The addition of gadolinium(III) to the growth medium did not significantly affect the amount of biomass, whereas erbium(III) and holmium(III) reduced it up to 22% compared to the control. The effects of rare-earth elements on the content of proteins, carbohydrates, phycobiliproteins, lipids, β carotene, and chlorophyll α were evaluated. The studied elements had different effects on the primary biomolecule content, suggesting that holmium(III) and erbium(III) were more toxic than Gd(III) for *Arthrospira platensis*.

Keywords: rare-earth elements; *Arthrospira platensis*; holmium; erbium; gadolinium; neutron activation analysis



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1. Introduction

A collection of 17 elements known as rare-earth elements (REEs) includes 15 lanthanides (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yu, and Lu), as well as Sc and Y [1,2]. The increased use of REEs in agriculture, metallurgy, the nuclear and chemical industries, and the production of magnets, luminescent and laser materials, superconductors, batteries, smartphones, and electronics is determined by their unique chemical, electrical, magnetic, and optical properties [3–5].

The widespread use of REEs in various industries causes their release in soil, water bodies, and the atmosphere at concentrations that are frequently orders of magnitude higher than the natural background levels [6,7], resulting in environmental contamination, which may have a serious negative impact on human health [6]. Thus, it was reported that endomyocardial fibrosis, lung and bladder cancer, indigestion, diarrhea, abdominal distension, anorexia, weakness, fatigue, etc. were all linked to high concentrations of REEs in humans [8,9].

Depending on the element, its quantity, and the organisms exposed, REEs can have either harmful or stimulating effects on aquatic organisms. Eight doped lanthanide-based ceramic oxides were tested on crustaceans and duckweeds, and either very low acute toxicity or no toxicity were seen [10]. Bergsten-Torralba et al. [11] demonstrated the toxicity

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of La, Nd, Sm, and their combinations for algae, microcrustaceans, and fungi. Several studies have reported the toxicity of Ce in nanoform for microalgae [12,13].

Among the 17 REEs, the influence of La, Ce, Gd, and Y on aquatic organisms has primarily been researched [12,14–17]. Despite studies and review papers detailing the bioaccumulation of REEs by aquatic organisms, their uptake by and effect on cyanobacteria have scarcely been investigated. According to numerous studies [7,18–20], cyanobacteria, including *Arthrospira platensis*, have a high biosorption and bioaccumulation capacity for heavy metals. This makes them promising candidates for polluted water bodies and wastewater remediation.

In recent years, the cyanobacterium *Arthrospira platensis* has primarily been used as a biosorbent to recover REEs from solutions. Two strains of *Spirulina platensis* were applied to recover Nd from batch solutions. Both strains showed high adsorption capacity: 72.5 mg/g for the LEB-18 strain and 48.2 mg/g for LEB-52 [21]. Approximately 80% of Yb ions were adsorbed by spirulina from simulated mine wastewater [22], and 87.62% of the ions were absorbed from an aqueous solution [23]. Endemic and commercial strains of *Arthrospira platensis* were able to recover 18.1 and 38.2 mg/g, respectively, of Ce ions [24]. *Arthrospira platensis* showed a high adsorption capacity of 89.5 mg/g for Eu ions [25].

It is worth noting that little research has been done on their ability to bioaccumulate these elements. Thus, Zinicovscaia and co-authors [26] investigated the uptake of Dy, Sm, Tb, La, Nd, and Yb by spirulina biomass. The accumulation of Eu and Y ions by *Arthrospira platensis* and their effects on the biochemical composition of the biomass were reported in [25,27]. At the same time, the bioaccumulation technique, which allows the uptake of high levels of pollutants and their biotransformation into less harmful forms, is more appropriate for in situ remediation [28]. In this case, it is crucial to maintain the optimal level of biomass productivity and its biochemical composition in order to guarantee the excellent bioaccumulation potential of cyanobacteria.

In the current study, neutron activation analysis was used to examine the accumulation of gadolinium(III) (one of the most studied REEs), holmium(III), and erbium(III) (two less well-examined elements) by the cyanobacterium *Arthrospira platensis*. The effects of REEs on the biomass, biochemical composition, and antioxidant activity of *Arthrospira platensis* were evaluated. As far as we are aware, this is the first study to report the effects of the aforementioned REEs on *Arthrospira platensis*.

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References

 Goecke, F.; Zachleder, V.; Vítová, M. Rare Earth Elements and Algae: Physiological Effects, Biorefi Nery and Recycling. In Algal Biorefineries: Volume 2: Products and Refinery Design; Springer International Publishing: Berlin/Heidelberg, Germany, 2015; pp. 339–363, ISBN 9783319202006.

- 2. Ramos, S.J.; Dinali, G.S.; Oliveira, C.; Martins, G.C.; Moreira, C.G.; Siqueira, J.O.; Guilherme, L.R.G. Rare Earth Elements in the Soil Environment. *Curr. Pollut. Rep.* **2016**, *2*, 28–50. [CrossRef]
- 3. Das, N.; Das, D. Recovery of Rare Earth Metals through Biosorption: An Overview. J. Rare Earths 2013, 31, 933–943. [CrossRef]
- 4. Gallardo, K.; Castillo, R.; Mancilla, N.; Remonsellez, F. Biosorption of Rare-Earth Elements From Aqueous Solutions Using Walnut Shell. *Front. Chem. Eng.* **2020**, *2*, 4. [CrossRef]
- Heilmann, M.; Breiter, R.; Becker, A.M. Towards Rare Earth Element Recovery from Wastewaters: Biosorption Using Phototrophic Organisms. Appl. Microbiol. Biotechnol. 2021, 105, 5229–5239. [CrossRef]
- 6. Malhotra, N.; Hsu, H.S.; Liang, S.T.; Roldan, M.J.M.; Lee, J.S.; Ger, T.R.; Hsiao, C.D. An Updated Review of Toxicity Effect of the Rare Earth Elements (REEs) on Aquatic Organisms. *Animals* **2020**, *10*, 1663. [CrossRef] [PubMed]
- 7. Piarulli, S.; Hansen, B.H.; Ciesielski, T.; Zocher, A.L.; Malzahn, A.; Olsvik, P.A.; Sonne, C.; Nordtug, T.; Jenssen, B.M.; Booth, A.M.; et al. Sources, Distribution and Effects of Rare Earth Elements in the Marine Environment: Current Knowledge and Research Gaps. *Environ. Pollut.* 2021, 291, 118230. [CrossRef] [PubMed]
- 8. Rim, K.T.; Koo, K.H.; Park, J.S. Toxicological Evaluations of Rare Earths and Their Health Impacts to Workers: A Literature Review. *Saf. Health Work* **2013**, *4*, 12–26. [CrossRef]
- 9. Brouziotis, A.A.; Giarra, A.; Libralato, G.; Pagano, G.; Guida, M.; Trifuoggi, M. Toxicity of Rare Earth Elements: An Overview on Human Health Impact. *Front. Environ. Sci.* **2022**, *10*, 1617. [CrossRef]
- 10. Blinova, I.; Vija, H.; Lukjanova, A.; Muna, M.; Syvertsen-Wiig, G.; Kahru, A. Assessment of the Hazard of Nine (Doped) Lanthanides-Based Ceramic Oxides to Four Aquatic Species. *Sci. Total Environ.* **2018**, *612*, 1171–1176. [CrossRef]
- 11. Bergsten-Torralba, L.R.; Magalhães, D.P.; Giese, E.C.; Nascimento, C.R.S.; Pinho, J.V.A.; Buss, D.F. Toxicity of Three Rare Earth Elements, and Their Combinations to Algae, Microcrustaceans, and Fungi. *Ecotoxicol. Environ. Saf.* **2020**, 201, 110795. [CrossRef]
- 12. Xiong, J.Q.; Ru, S.; Zhang, Q.; Jang, M.; Kurade, M.B.; Kim, S.H.; Jeon, B.H. Insights into the Effect of Cerium Oxide Nanoparticle on Microalgal Degradation of Sulfonamides. *Bioresour. Technol.* **2020**, *309*, 123452. [CrossRef] [PubMed]
- 13. Mahaye, N.; Musee, N. Evaluation of Apical and Molecular Effects of Algae Pseudokirchneriella Subcapitata to Cerium Oxide Nanoparticles. *Toxics* **2023**, *11*, 283. [CrossRef] [PubMed]
- 14. Cardon, P.Y.; Triffault-Bouchet, G.; Caron, A.; Rosabal, M.; Fortin, C.; Amyot, M. Toxicity and Subcellular Fractionation of Yttrium in Three Freshwater Organisms: Daphnia Magna, Chironomus Riparius, and Oncorhynchus Mykiss. *ACS Omega* **2019**, *4*, 13747–13755. [CrossRef] [PubMed]
- 15. Fujita, Y.; Walton, M.; Das, G.; Dohnalkova, A.; Vanzin, G.; Anderko, A. Impacts of Anthropogenic Gadolinium on the Activity of the Ammonia Oxidizing Bacterium Nitrosomonas Europaea. *Chemosphere* **2020**, 257, 127250. [CrossRef] [PubMed]
- 16. Herrmann, H.; Nolde, J.; Berger, S.; Heise, S. Aquatic Ecotoxicity of Lanthanum—A Review and an Attempt to Derive Water and Sediment Quality Criteria. *Ecotoxicol. Environ. Saf.* **2016**, 124, 213–238. [CrossRef] [PubMed]
- 17. Liu, S.; Wang, Y.; Zhang, R.; Guo, G.; Zhang, K.; Fan, Y.; Feng, C.; Li, H. Water Quality Criteria for Lanthanum for Freshwater Aquatic Organisms Derived via Species Sensitivity Distributions and Interspecies Correlation Estimation Models. *Ecotoxicology* **2022**, *31*, 897–908. [CrossRef]
- 18. Al-Amin, A.; Parvin, F.; Chakraborty, J.; Kim, Y.I. Cyanobacteria Mediated Heavy Metal Removal: A Review on Mechanism, Biosynthesis, and Removal Capability. *Environ. Technol. Rev.* **2021**, *10*, 44–57. [CrossRef]
- 19. Fischer, C.B.; Körsten, S.; Rösken, L.M.; Cappel, F.; Beresko, C.; Ankerhold, G.; Schönleber, A.; Geimer, S.; Ecker, D.; Wehner, S. Cyanobacterial Promoted Enrichment of Rare Earth Elements Europium, Samarium and Neodymium and Intracellular Europium Particle Formation. *RSC Adv.* **2019**, *9*, 32581–32593. [CrossRef]
- 20. Rakic, I.; Kevresan, Z.; Kovac, R.; Kravic, S.; Svircev, Z.; Djurovic, A.; Stojanovic, Z. Bioaccumulation and Biosorption Study of Heavy Metals Removal by *Cyanobacteria Nostoc* sp. *Chem. Ind. Chem. Eng. Q* **2023**, 29, 291–298. [CrossRef]
- 21. Lima, É.C.; Pinto, D.; Schadeck Netto, M.; Dos Reis, G.S.; Silva, L.F.O.; Dotto, G.L. Biosorption of Neodymium (Nd) from Aqueous Solutions Using Spirulina Platensis Sp. Strains. *Polymers* **2022**, *14*, 4585. [CrossRef]
- 22. Wenqiang, Z.; Qing, S.; Baoquan, X.; Wenqiang, Z.; Qing, S.; Baoquan, X. Study on Biosorption Characteristics of Spirulina to Rare Earth Ytterbium Ions in Simulated Mine Wastewater. *Nonferrous Met. Sci. Eng.* **2019**, *10*, 103–112. [CrossRef]
- 23. Shu, Q.; Liao, C.-F.; Zou, W.-Q.; Xu, B.-Q.; Tan, Y.-H. Recovery of Rare Earth Element Ytterbium(III) by Dried Powdered Biomass of Spirulina: Adsorption Isotherm, Kinetic and Thermodynamic Study. *Trans. Nonferrous Met. Soc. China (Engl. Ed.)* **2021**, 31, 1127–1139. [CrossRef]
- 24. Sadovsky, D.; Brenner, A.; Astrachan, B.; Asaf, B.; Gonen, R. Biosorption Potential of Cerium Ions Using Spirulina Biomass. *J. Rare Earths* **2016**, 34, 644–652. [CrossRef]
- 25. Yushin, N.; Zinicovscaia, I.; Cepoi, L.; Chiriac, T.; Rudi, L.; Grozdov, D. Biosorption and Bioaccumulation Capacity of Arthospira Platensis toward Europium Ions. *Water* **2022**, *14*, 2128. [CrossRef]
- 26. Zinicovscaia, I.; Cepoi, L.; Rudi, L.; Chiriac, T.; Grozdov, D.; Pavlov, S.; Djur, S. Accumulation of Dysprosium, Samarium, Terbium, Lanthanum, Neodymium and Ytterbium by Arthrospira Platensis and Their Effects on Biomass Biochemical Composition. *J. Rare Earths* **2021**, *39*, 1133–1143. [CrossRef]

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27. Yushin, N.; Zinicovscaia, I.; Cepoi, L.; Chiriac, T.; Rudi, L.; Grozdov, D. Biosorption and Bioaccumulation Capacity of Arthrospira Platensis toward Yttrium Ions. *Metals* **2022**, *12*, 1465. [CrossRef]

- 28. Sayqal, A.; Ahmed, O.B. Advances in Heavy Metal Bioremediation: An Overview. *Appl. Bionics Biomech.* **2021**, 2021, 1609149. [CrossRef]
- 29. Cepoi, L.; Zinicovscaia, I.; Rudi, L.; Chiriac, T.; Rotari, I.; Turchenko, V.; Djur, S. Effects of PEG-Coated Silver and Gold Nanoparticles on Spirulina Platensis Biomass during Its Growth in a Closed System. *Coatings* **2020**, *10*, 717. [CrossRef]
- 30. Tsuruta, T. Selective Accumulation of Light or Heavy Rare Earth Elements Using Gram-Positive Bacteria. *Colloids Surf. B Biointerfaces* **2006**, 52, 117–122. [CrossRef]
- 31. Řezanka, T.; Kaineder, K.; Mezricky, D.; Řezanka, M.; Bišová, K.; Zachleder, V.; Vítová, M. The Effect of Lanthanides on Photosynthesis, Growth, and Chlorophyll Profile of the Green Alga Desmodesmus Quadricauda. *Photosynth. Res.* **2016**, 130, 335–346. [CrossRef]
- 32. Makhi, V.V.; Ahmad, A.; Chaugule, B.B. Effect of Bismuth, Gadolinium, and Cadmium Nanoparticles on Biomass, Carotenoid, and Lipid Content of *Dunaliella salina* (Dunal) Teodoresco. *Curr. Microbiol.* **2022**, 79, 30. [CrossRef] [PubMed]
- 33. Goecke, F.; Vítová, M.; Lukavský, J.; Nedbalová, L.; Řezanka, T.; Zachleder, V. Effects of Rare Earth Elements on Growth Rate, Lipids, Fatty Acids and Pigments in Microalgae. *Phycol. Res.* **2017**, *65*, 226–234. [CrossRef]

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