ENVIRONMENTAL-FRIENDLY RECOVERY: BIO-ACCUMULATION OF RARE EARTH ELEMENTS

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Abstract.

The ERDF funded Interreg project REEgain focuses on developing new eco-friendly methods to recycle and recover REEs from Waste from Electric and Electronic Equipment (WEEEs) with the help of microorganisms. The project partners aim to develop a practicable recycling technology in collaboration with regional industry, making the technology available to businesses. The preliminary results indicate that bio-accumulation is dependent on the incubation time of the cells as well as the atomic weight of the elements in question, showing a direct influence on separation. The overall retrieval rate was determined to be 83.5% for this experiment. Further research needs to be directed, to distinguishing the correlations between separation, pH, growth, and atomic parameters.

Keywords: Rare earth elements, lanthanides, ICP-OES, bio-accumulation

1 INTRODUCTION

At a time when electric cars and smart devices are becoming more and more present, the supply of rare earth elements (REEs) is crucial and therefore represents a limiting factor for the production of the aforementioned products. [1, 2] From smaller enterprises to big tech companies, everyone depends on the flow of these precious metals, while only few know of their importance. [4] Scarce resources getting progressively difficult to obtain due to an increase in demand, in contrast to the difficulties of ore exploitation, in addition to the harsh conditions needed for metal extraction, draw an alarming picture. [3,4] Independently, the return in form of recycled REEs observed is incredibly low. The regeneration of lanthanides from electronic supplies (i.e. microchips) is difficult, due to the low concentrations obtained, while highly concentrated products (i.e. neodymium magnets) stay in use for an extended period of time before again being introduced to recycling procedures. [3, 5–7]

REEs consist of the group of Lanthanides (6^{th} Period of the Periodic Table of Elements) including Scandium and Yttrium. [8] These elements manifest very similar chemical properties. [3, 8] Except for Europium and Cerium, they are usually found in a trivalent form and decrease their ionic radius with increasing atomic number, also known as “lanthanide contraction", which might be one reason for the complexity of their separation and purification. [3, 9, 10] REEs are not particularly rare in terms of abundance, but for many years remained rarely separated from each other, as well, owing to their similar chemical characteristics. [11] REEs are often divided into LREEs (light rare earth elements) consisting of Lanthanum up to Europium or Gadolinium, and HREEs (heavy rare earth elements) from Gadolinium or Terbium to Lutetium. [8, 10] Some sources even introduce MREEs (medium rare earth elements), incorporating Samarium, Europium and Gadolinium. [13–17]

According to the findings of Herrmann *et al*. 2016, Lanthanides can be detected in nearly all biota, usually following the Oddo-Harkins rule. [18–20] Although they were thought to be inert to biological life, several studies since have found that REEs influence the enzymatic activity of certain proteins and can even make up the active site of some enzymes like alcohol dehydrogenases. [10, 21] It also could be proved that the growth rate of the microorganisms, as well as the enzymatic activity of proteins, might be influenced by the lanthanides present, with a preference for LREEs. [10]

These kinds of discoveries might shine a new light on the possibilities for the biological take-up of lanthanides since bioleaching and biosorption are considered environmental-friendly processes to separate and recover REEs from end-of-life materials. [8]

2 METHODS

The methods used are targeted towards the detection of bio-accumulation and biologically aided separation of REEs from liquid matrices. The strains used have been chosen due to their mesophilic character in favour of ease-of-use, and to diminish any additional risks that might be associated with extremophiles or genetically modified organisms. Promising bacterial strains were grown in LB medium and transferred to different (buffered) complex media or defined minimal media for bioaccumulation testing.

2.1 BACTRAC AND BIO-ACCUMULATION TESTING

To get insights into bacterial growth with REEs the BacTrac (Sylab) measuring device was used, which is based on an Impedance Splitting technology. The measuring cycle is automatic and the results are recorded permanently (all 10 minutes) allowing to monitor according growth curves.

For all proof of concept experiments, a standard (Rare earth element mix for ICP, TraceCert ®) containing 50mg/l each: Sc, Y, La, Ce Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu in 2% nitric acid is used. Negative controls with medium, 2% nitric acid and REE standard, as well as positive controls, are performed for each setup. All experiments are inoculated from o/n cultures (LB, 30°C, 120rpm). The BacTrac vials are filled to 10ml and cultured at 30°C for 24 hours. The starting OD_{600} for samples and positive controls in LB Medium is 0.1. The end concentration of 2.5ppm REEs was accomplished by introduction of boli into growing cultures and negative controls at 3, 6 or 9 hours accordingly (all triplicates).

2.2 ICP-OES ANALYTICS

The ICP-OES 5110 (Agilent) is used to measure the bio-accumulation of lanthanides in BacTrac samples after 24 hours growth. Both – supernatant and biomass are analyzed (centrifugation at 2500g for 45minutes at 4°C in a Beckman Coulter Allegra X-15R) after treatment with concentrated nitric acid at 60°C o/n and filled up to 10ml with ultrapure water, adjusting the samples to the standard's nitric acid concentration. For the ICP-OES calibration, a correlation coefficient of 0.99995 and 1.00000 was accepted, using 5 standards. The measurements were taken at least at 4 wavelengths and 3 replicates per element.

3 EVALUATION

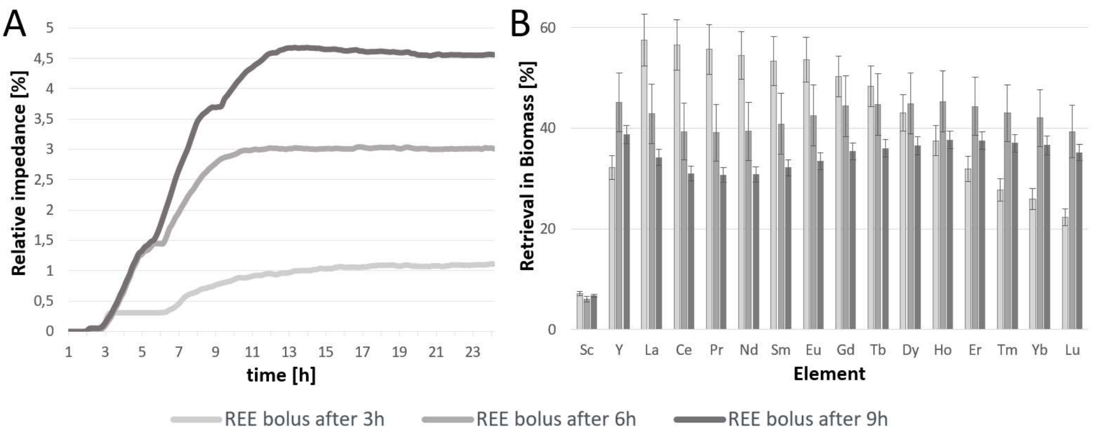

*Figure 1: **A** BacTrac measurements: Growth curve of E. coli with REE bolus [2.5ppm] at timepoints 3, 6 and 9hrs (normalized on acid control); **B** ICP-OES Analysis: Accumulation of REE bolus [2.5ppm] at timepoints 3, 6 and 9hrs, after 24hours growth in E. coli. The values indicate the REE content of the biomass fraction, which adds up to 100% with the supernatant (average recovery of 83.5%).*

The microorganisms in *Figure 1A* are comparable in growth up to the timepoint of bolus addition, where they seem to exert a decreased proliferation gradient. This might be mostly correlated to the induction of acidity originated from the Lanthanide-mix solution. The recovery phase again seems comparable for each sample after bolus donation.

In *Figure 1B*, a difference in relative uptake of lanthanide groups can be observed. Excluding Scandium and Yttrium from the equation, the light and medium REEs seem to be taken up more willingly in the samples with earlier bolus (longer induction time), while this trend is not as obvious with the later boli correlated to shorter incubation.

4 CONCLUSION

All in all, we were able to demonstrate bioaccumulation of rare earths in our experimental setup, as can be seen from the representative graphs (*Figure 1*), although it may be important to gain insight into the effects of pH, temperature, and biomass associated with said uptake. We were also able to detect differences in the uptake of certain lanthanides, which could be useful for future efforts. Another aspect to consider is that the methods used are only suitable for matrices with rare earths already dissolved, i.e., wastewater treatment, and that the harvesting of elemental particles is still subject to an acidic digestion process. The reference parameters of the used setups need to be further investigated before more accurate conclusions can be drawn.

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