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TECHNOLOGIES FOR THE EXTRACTION OF RARE EARTH ELEMENTS USING CYANOBACTERIA *ARTHROSPIRA PLATENSIS*

167.01. BIOTECHNOLOGY, BIONANOTECHNOLOGY

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CONCEPTUAL LANDMARKS OF THE RESEARCH

Background and importance of the studied topic

Rare earth elements (REE) are becoming increasingly important for economy due to their unique chemical and physical properties. However, despite their widespread use in industry, the extraction and enrichment of REEs is a complex and expensive process due to the low metal content in the ore and the difficulties encountered in separating impurities. In addition, the extraction process poses a risk of environment pollution. The toxic effects of REEs on soil, aquatic organisms, and human health have been described in detail in several publications [1–3].

Currently, various physicochemical methods are used to extract and concentrate REEs, including: precipitation, solvent extraction, ion exchange, solid-phase extraction, etc. [4, 5]. However, traditional methods have a number of disadvantages, including high consumption of reagents and energy, low selectivity, and high operating costs. Therefore, it is necessary to develop cost-effective and environmentally friendly methods for REEs extraction from depleted ores and production waste.

In recent years, the attention of researchers has been focused on the use of biological methods for the extraction of metals. Among them, it is worth noting biosorption and bioaccumulation. Biosorption is an economically effective, fast, reversible, and environmentally friendly technology for REEs recovery [6]. Compared with traditional methods, biosorption has a number of advantages, such as: low operating costs, high efficiency of metal ion removal, even from wastewater with low elements concentrations, possibility of sorbent regeneration. Biosorption is more attractive for industrial applications due to the use of non-living biomass. Fungi, bacteria, yeast, algae, etc. are used as biosorbents.

Bioaccumulation is a more complex and expensive process that can be used for bioremediation of large contaminated areas, as well as for deciphering of the mechanism of action of metal ions on living organisms [7]. Bioaccumulation, combines both biosorption and intracellular uptake. The process depends on the type of microorganisms, as well as on their level of adaptation and toxicity of metals [8]. In case of bioaccumulation application for industrial purposes, it is necessary to provide conditions for the microorganisms' growth, which increases the cost of the process. It is also important to select microorganisms that are resistant to high concentrations of pollutants [9].

Cyanobacteria are polyextremophilic organisms that can cope with high alkalinity, temperature, salt concentrations and presence of various pollutants in the nutrient medium. Among cyanobacteria, *Arthrospira platensis* (*A. platensis*, *Spirulina platensis*, spirulina) attracts special attention due to its unique chemical composition, as well as high ability to accumulate metals [10].

Previous studies have demonstrated the effectiveness of spirulina in heavy metals and rare earth elements removal from solutions and wastewater. Among the REEs, La and Ce are the most studied, while only a small number of studies have been devoted to the extraction of Nd, Yb, Sm, Dy, and Tb [11–18]. A certain number of REEs remain poorly studied in terms of their recovery from wastewater, which prompted us to select for our study REEs that have not been previously used in research, including in relation to the cyanobacterium *Arthrospira platensis*. Such elements are yttrium (Y), praseodymium (Pr), europium (Eu), gadolinium (Gd) and erbium (Er). These REEs are widely used in various industries, in particular for the production of luminophores, magnets, lasers, metal alloys, glass and ceramics, and are also important components of neutron flux moderators, etc. At the same time, there is a confirmed danger of the compounds of these metals for living organisms; therefore, their extraction from wastewater is an extremely important task. [19, 20].

The aim of the study: Development of the effective technologies of Y, Pr, Eu Gd, and Er extraction from wastewater using the cyanobacterium *Arthrospira platensis* as a biosorbent and bioaccumulator.

Main objectives:

- to determine the optimal parameters for the sorption of Y, Pr, Eu Gd, and Er by *Arthrospira platensis* biomass;
- to identify the features of REEs bioaccumulation by *Arthrospira platensis* biomass;
- to evaluate changes in the biochemical parameters of spirulina biomass during REEs bioaccumulation;
- to develop the process flow charts for REEs biosorption and bioaccumulation from solutions.

The hypothesis of the research: Since cyanobacterium spirulina have high bioremediation potential toward heavy metal ions, it is assumed that the *Arthrospira platensis* CNMN-CB-02 can serve as an effective biosorbent and bioaccumulator of rare earth elements (Y, Pr, Eu Gd, Er) from solutions and can be used in the technologies for these and other REEs removal from various environments.

The synthesis of the research methodology and justification of the research methods: The methods used in the research are used in modern biotechnology and include a number of methodological techniques and analytical procedures optimized for the research object. To determine the elemental composition of the biomass, the neutron activation analysis (NAA) at the IBR-2 reactor (JINR), which allows for simultaneous determination of up to 45 elements, was used. The surface morphology of the cyanobacteria was determined using a Quanta 3D FEG scanning electron microscope (SEM) (FEI, Hillsboro, OR, USA), which has a resolution of up to 1.5 nm when operating in low vacuum mode. Functional groups on the surface of the cyanobacteria were determined using infrared spectrometry on a Bruker Alpha Platinum-ATR IR Fourier spectrometer (Bruker Optics, Ettingen, Germany).

The concentrations of REEs in experimental solutions were determined using an optical emission spectrometer with inductively coupled plasma (ICP-OES) PlasmaQuant PQ 9000 Elite (Analytik Jena, Jena, Germany). This method has a low detection limit and a high speed of elemental composition determination.

The amount of biomass was determined using a T60 Visible Spectrophotometer (PG Instruments Limited, United Kingdom) by measuring the optical density of the spirulina suspension and the quantitative calculation based on the calibration curve. Biochemical methods adapted for work with *Arthrospira platensis* were used to determine the biochemical composition of the spirulina biomass (protein, carbohydrates, lipids, water- and alcohol-soluble pigments, end products of lipid breakdown, antioxidant activity of the biomass) [21].

Classical models used in physical chemistry were used to describe the kinetics, equilibrium and thermodynamics of the sorption. Statistical tools were used to establish the reliability of the obtained experimental data.

The novelty and scientific originality: for the first time, the cyanobacterium *Arthrospira platensis* was used to treat wastewater containing rare earth elements (yttrium, praseodymium, europium, gadolinium, erbium). Sorption parameters which allow maximum efficiency of rare earth elements removal were determined. Unique data on the influence of the studied rare earth elements on the biochemical composition of Arthrospira platensis as a result of the accumulation of rare earth elements were obtained.

The theoretical importance of the work: the optimal physicochemical parameters (pH, time, temperature, element concentration) for the recovery of rare earth elements were determined. The nature of biosorption processes has been established. Information about the influence of rare earth elements on the life activity of *Arthrospira platensis* and its biochemical composition was obtained.

The applied value of the work: the developed approaches can be used for the treatment and post-treatment of wastewater from industrial enterprises containing rare earth metals in the production cycle, as well as the recovery of metals from concentrates of rare earth elements. Based on the data obtained, new technologies for the extraction of other metals can be developed.

1. PECULIARITIES OF EXTRACTION, APPLICATION AND PROCESSING OF REEs

Chapter 1 "Peculiarities of extraction, application and processing of REEs" is devoted to the analysis of the state of knowledge in the field of the research and includes data on the use of REEs, forms of their occurrence and reserves, methods of their extraction and processing. Information about the toxicity of these elements is presented as well. The literature review on the topic of the dissertation provided important theoretical support for the conducted research and allowed to identify gaps in modern knowledge, correctly select elements for research and formulate the purpose and objectives of the work.

2. MATERIALS AND METHODS

This chapter presents the object of study, materials and methods used in the research. The work was carried out in the Sector of Neutron Activation Analysis and Applied Research of the Frank Laboratory of Neutron Physics of the Joint Institute for Nuclear Research and the Phycobiotechnology Laboratory of the Institute of Microbiology and Biotechnology of the Technical University of Moldova. The strain of cyanobacterium *Arthrospira platensis* CNMN-CB-02 was chosen as the object of study. The SP-1 nutrient medium was used to cultivate the cyanobacterium.

The methods used to assess the quantity and quality of *Arthrospira platensis* biomass are described. A method for determination of elements concentrations in experimental solutions is presented, as well as procedures for determining the content of spirulina biomass and its biochemical composition.

Formulas for calculation of the efficiency of biosorption, determining the amount of element removed from the solution are given, and formulas for describing the equilibrium, kinetics and thermodynamics of the sorption process are also provided.

3. BIOSORPTION OF REE IONS BY CYANOBACTERIA *A. PLATENSIS*

This chapter presents the results of cyanobacterium *A. platensis* use as a biosorbent for the recovery of Y, Pr, Eu, Gd, and Er from model systems. The parameters influencing the biosorption efficiency, such as the initial pH, metal concentration, and solution temperature, as well as the contact time, were investigated. Equilibrium, kinetic, and thermodynamic models were calculated to understand the nature of the biosorption. Figure 3.1 shows the experimental design for studying the effect of various parameters on the biosorption of Y, Pr, Eu, Gd, and Er by *A. platensis* biomass.

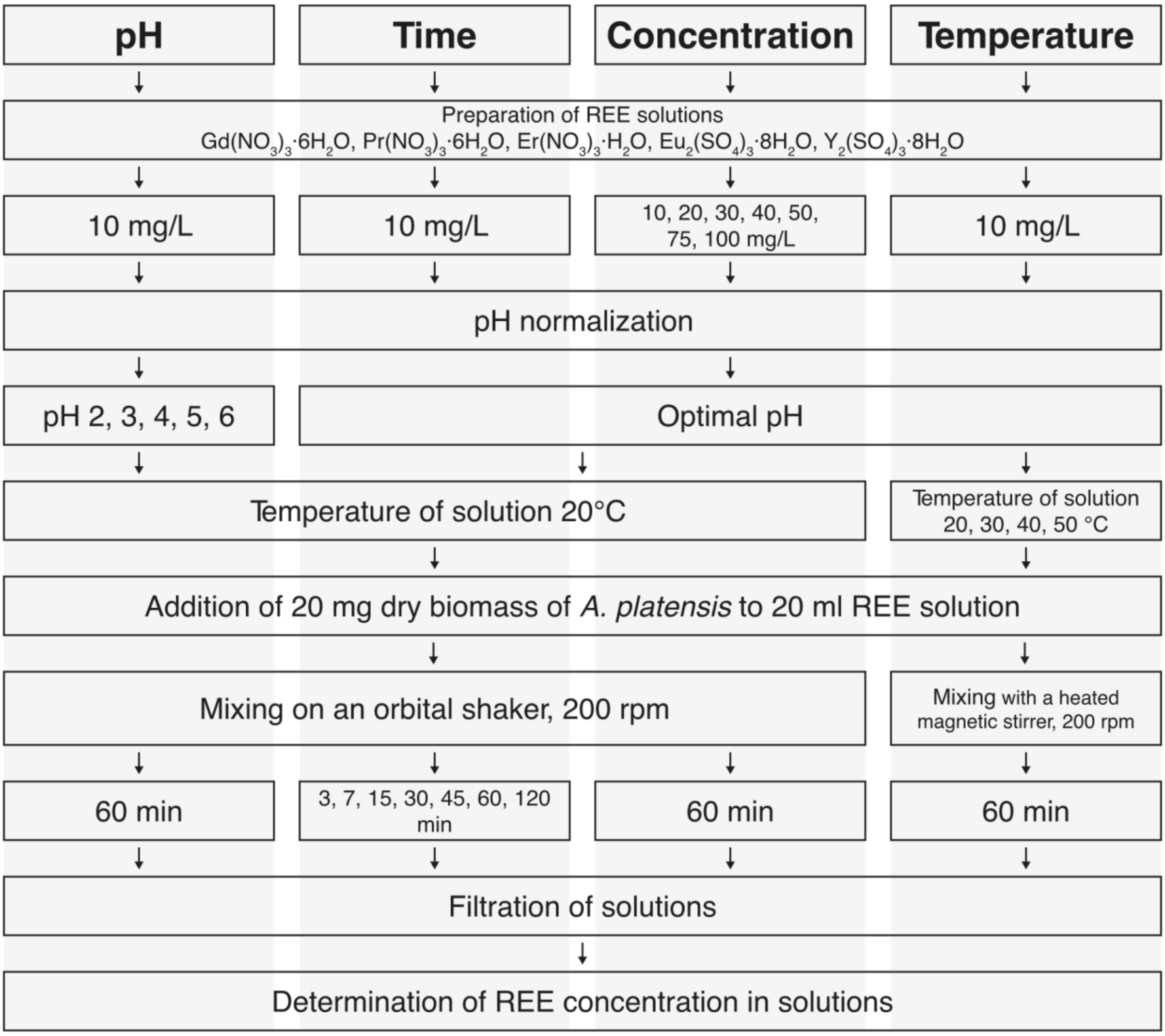

Figure 3.1. Scheme of experiments to assess the influence of various parameters on the biosorption of REEs by the biomass of *A. platensis*

3.1. Characteristics of the biosorbent

The cyanobacterium *A. platensis* used as a biosorbent was characterized using several analytical methods. Visualization of the biomass surface morphology was performed using a scanning electron microscope (SEM). The length of the cyanobacterial filaments was 20–30 µm, and the diameter was 1.5–2.5 µm. The cyanobacterial filaments were mostly intact, indicating minimal damage to the biomass during drying and homogenization. However, fragmentary inclusions were also observed in small quantities. Fourier transform infrared spectroscopy allowed identifying functional groups on the *A. platensis* surface that can participate in the binding of metal ions. These include –OH, –NH^2, –CH_3, –CO, –C–O, –C–C, –C–OH, –P–O, –S–O and –CH groups.

Neutron activation analysis (NAA) was used to measure the content of 22 elements in the biomass of *A. platensis*, including macroelements Na, K, Ca, Mg, and Cl; microelements Fe, Zn, Se, Br, Cr, Ni, and I, which play an important role in the metabolism and vital activity of living organisms, and other elements such as Al, Sc, As, Rb, Sb, Ba, Cs, and U, which have no known biological function. The main source of these elements in the biomass can be considered the salts used to prepare the nutrient medium. It should be noted that the content of rare earth elements in the biomass of *A. platensis* was below the NAA detection limit of [22].

3.2. Effect of various parameters on REEs biosorption by *A. platensis* biomass

The influence of pH, contact time, initial concentration and temperature of the solution on the biosorption of REEs by the biomass of the cyanobacterium *A. platensis* was studied.

Among the factors influencing biosorption, acidity (pH) is one of the most important. Experiments were conducted in the pH range of 2.0–6.0 to determine the optimal pH at which maximum REEs removal from wastewater occur (Fig. 3.2).

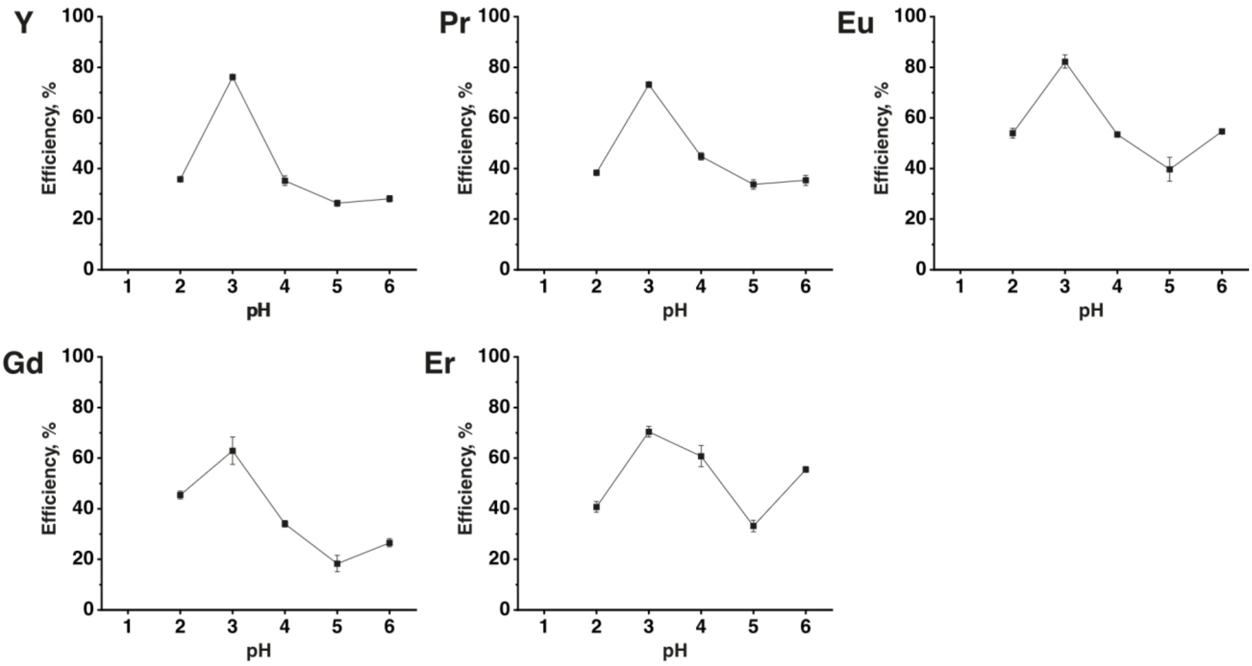

Figure 3.2. Effect of pH on the efficiency of REEs biosorption onto cyanobacterium *A. platensis*

In experiments on biosorption of REE ions, with an increase of pH from 2.0 to 3.0, the efficiency of biosorption of all metals increased and reached a maximum., At further increase of pH a decrease in sorption was noted. The maximum extraction was 76% for Y, 73% for Pr, 82% for Eu, 62% for Gd, and 70% for Er [22–26]. Since the maximum efficiency of REEs removal from solutions by dry spirulina biomass was achieved at pH 3.0, further experiments were carried out at this pH value.

The contact time has a significant influence on the biosorption process. The experiments were carried out in the range from 3 to 120 min. The experimental data are presented in Figure 3.3.

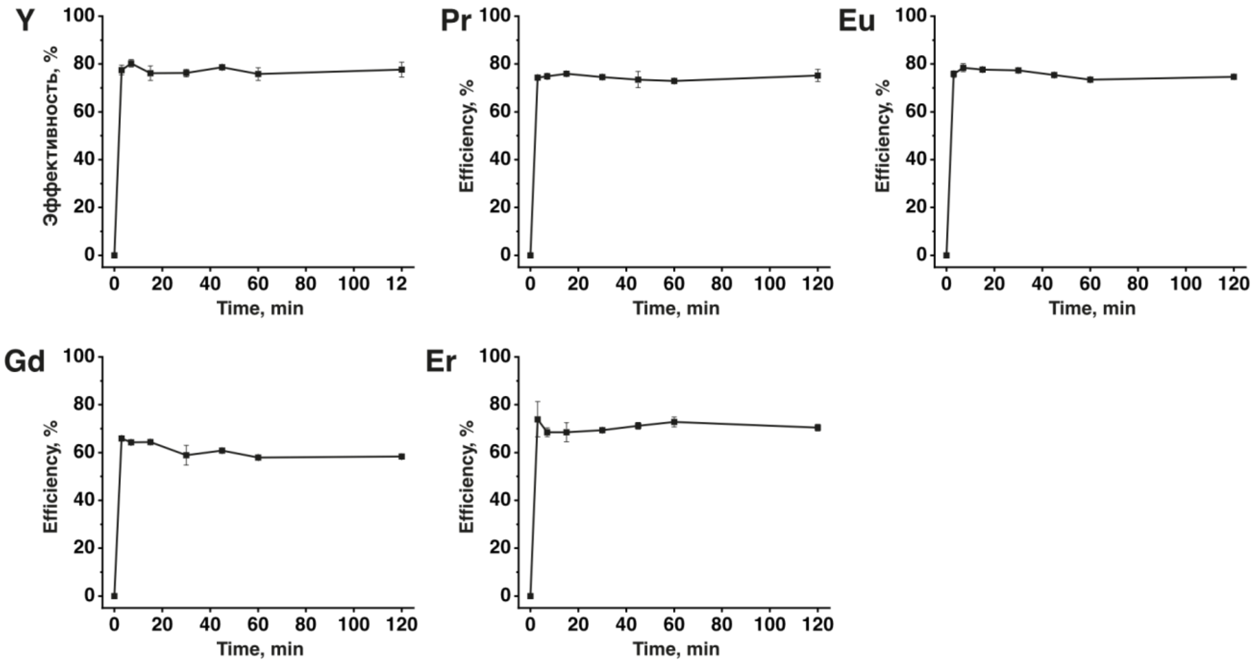

Figure 3.3. Effect of time on the efficiency of REEs biosorption by cyanobacterium *A. platensis*

The biosorption process was very fast. The maximum metal removal was achieved within 3–7 minutes of sorbent-sorbate interaction, after which equilibrium was established. Increasing the biosorption time up to 120 min did not have a noticeable effect on the *A. platensis* adsorption capacity. The maximum efficiency of Y, Pr and Eu removal was obtained after seven minutes of interaction and amounted 80, 74.8 and 78.4%, respectively [23–25]. In experiments with Gd and Er, the maximum removal (65.8 and 73.9%) was achieved after 3 minutes of interaction of the cyanobacterial biomass with the solution [22, 26]. Rapid adsorption in the first minutes of interaction can be explained by the abundance of functional groups on the surface of the biomass; a decrease in adsorption is usually associated with the saturation of the latter and the establishment of equilibrium.

Experiments on the effect of the initial solution concentration on biosorption were conducted in the concentration range from 10 to 100 mg/l. Figure 3.4 shows the content of REEs sorbed by biomass at different initial metal concentrations in solutions.

The sorption of Y by *A. platensis* biomass was directly proportional to its initial concentration in the solution; the adsorption capacity of 1.6 mg/g determined at a Y concentration of 10 mg/L increased to 16.7 mg/g at a concentration of 100 mg/L [23]. The highest adsorption capacity of spirulina for Pr (17.0 mg/g) was achieved at a concentration of 100 mg/L [24]. The biosorption capacity of *A. platensis* increased with increasing Eu concentration in solution from 0.8 to 7.25 mg/g [25]. Increase of the Gd concentration in the solution from 10 to 100 mg/L led to an increase in the biomass sorption capacity from 1.6 to 20 mg/g[26]. An increase in the initial concentration of Er ions led to an increase in the sorption capacity of the biomass from 1.0 to 12.1 mg/g [22].

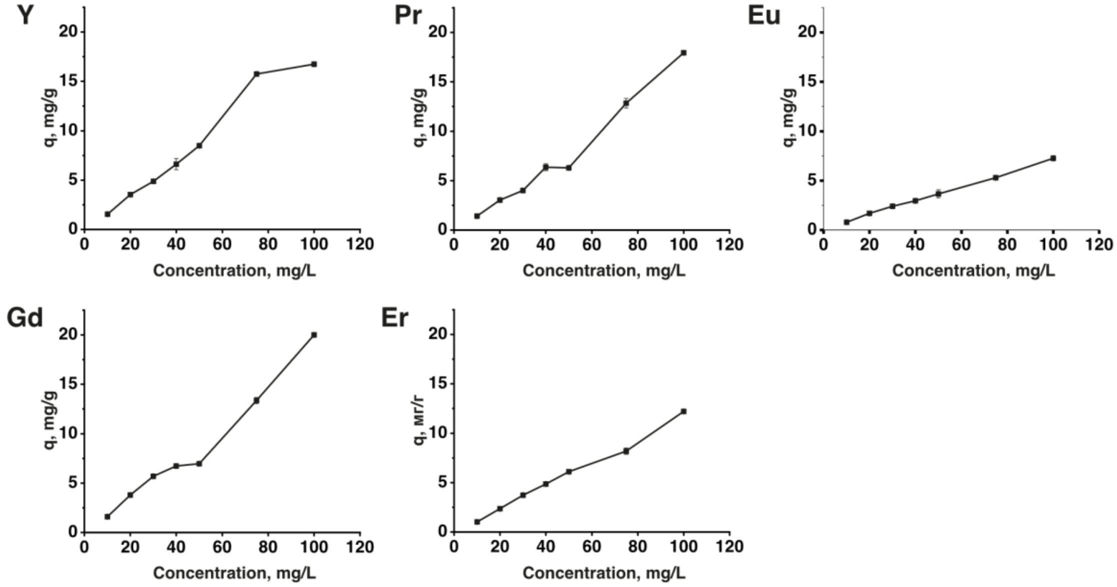

Figure 3.4. Effect of metal concentration in solution on REEs biosorption onto cyanobacterium *A. platensis*

Experiments on the effect of temperature on sorption were carried out within the temperature range of 20–50°C (Fig. 3.4).

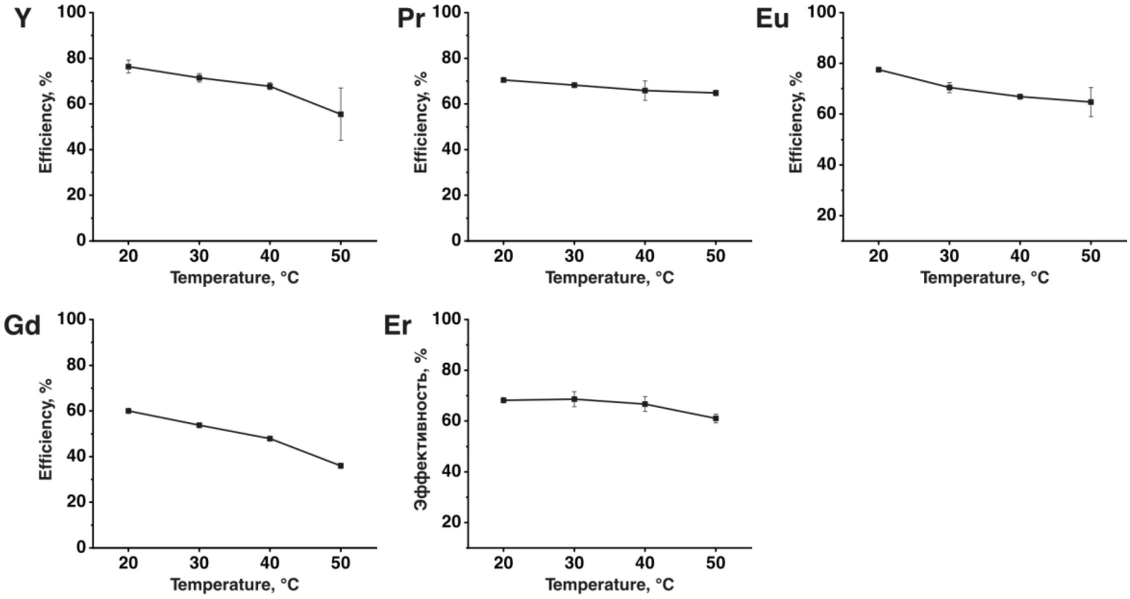

Figure 3.5. Effect of temperature on the efficiency of REEs biosorption by cyanobacterium *A. platensis*

The maximum biosorption efficiency was achieved at 20°C and was 79.4% for Y, 70.5% for Pr, 77.5% for Eu, 60% for Gd and 68.2% for Er. [23–25]. A decrease in the adsorption capacity of *A. platensis* toward REE ions with temperature increase indicates the exothermic nature of the process.

3.2. Description of experimental data

Kinetic, equilibrium and thermodynamic models were used to describe the experimental data and explain the nature of biosorption.

Models of adsorption kinetics correlate with the rate of absorption of dissolved substances, thus, these models are important in development of wastewater treatment methods, including REEs recovery. Pseudo-first-order (PFO), pseudo-second-order (PSO) and Elovich models were used. The parameters of the applied models obtained for experimental data are given in Table 3.1. The experimental data obtained for all five REEs are better described by the pseudo-first-order kinetic model, which assumes that the adsorption rate on functional groups is proportional to the number of free functional groups on the sorbent.

Table 3.1. Kinetics of REEs biosorption by spirulina biomass [22–26]

Element	PFO			PSO			Elovich model		
	q_e, mg/g	k_1, 1/min	R^2	q_e, mg/g	k_2, g/mg·min	R^2	α, g/mg·min	β, g/mg	R^2
Y	1,53	1,79	0,99	1,53	–2,54	0,99	$1{,}15·10^{43}$	69,4	0,99
Pr	1,43	2,13	0,99	1,43	26,5	0,99	$3{,}96·10^{-43}$	75,2	0,99
Eu	0,99	1,79	0,99	0,99	$2{,}83·10^{44}$	0,99	$1{,}07·10^{44}$	108	0,99
Gd	1,24	19,8	0,98	1,24	–0,6	0,97	$2{,}98·10^{-43}$	86,29	0,97
Er	2,5	0,67	0,99	2,5	1,18	0,98	$1{,}19·10^{-43}$	90,9	0,99

Langmuir and Freundlich models were used to study equilibrium of the biosorption. The calculated constants of isotherm are given in Table 3.2.

Table 3.2. Isotherms of REEs biosorption by *A. platensis* biomass [22–26]

Element	Langmuir model			Freundlich model		
	q_m, mg/g	b, L/mg	R^2	K_F	n	R^2
Y	719	0,0002	0,97	0,17	0,99	0,97
Pr	99	0,0019	0,95	0,06	1,2	0,99
Eu	89	0,0009	0,99	0,09	1,06	0,99
Gd	101	0,0081	0,97	0,09	0,84	0,98
Er	30	0,006	0,96	0,1	0,87	0,98

The Freundlich model fits well the data on REEs biosorption by the cyanobacterium *A. platensis*, since the determination coefficients were higher than 0.97. The applicability of the Freundlich model suggests that adsorption occurs on heterogeneous surfaces as multilayer adsorption. In the case of Pr and Eu, the values of the coefficient *n* greater than 1.0, indicated that chemisorption may be the main mechanism of these metals biosorption [27]. The maximum adsorption capacity of Y calculated using the Langmuir model was 719.8 mg/g, which significantly exceeds the values obtained for other metals (Table 3.2).

To assess the feasibility of the process and confirm the nature of the adsorption process, thermodynamic constants, namely, the free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°), were calculated.

Negative ΔG° values obtained for all REEs indicate the spontaneity of the biosorption process and points at physical nature process [28]. A negative ΔH° value indicates an exothermic type of sorption. Since ΔH° were less than 25 kJ/mol, sorption can be considered physical [29]. Negative ΔS° values observed for Y, Eu, and Gd indicate a decrease in randomness at the solid/solution interface, while a positive ΔS° value for Pr and Er indicates randomness at the solid/solution interface [22–26].

4. BIOACCUMULATION OF REEs IONS BY CYANOBACTERIA *A. PLATENSIS*

Chapter 4 "Bioaccumulation of REEs ions by the cyanobacterium *Arthrospira platensis*" is devoted to the assessment of the efficiency of bioaccumulation of REEs ions by spirulina. The experiments were carried out at REEs concentrations in the nutrient medium of 10, 20 and 30 mg/L. Figure 4.1 shows the scheme of the experiment on the bioaccumulation of Y, Pr, Eu, Gd, and Er by the biomass of *A. platensis*.

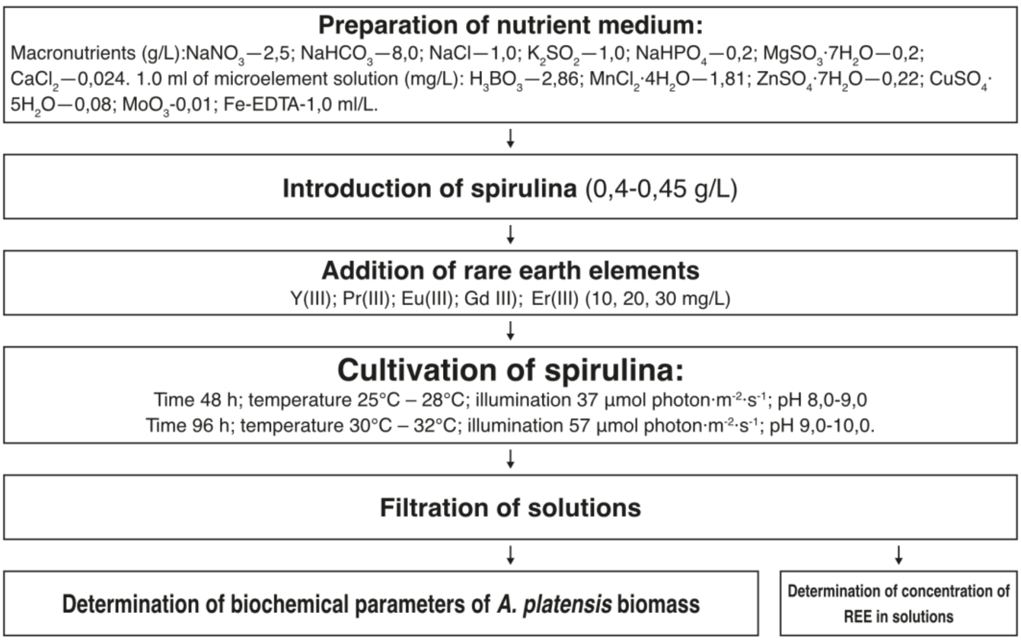

Figure 4.1. Scheme of experiments on bioaccumulation and assessment of the influence of REEs on the biochemical composition of *A. platensis* biomass

4.1. Efficiency of REEs bioaccumulation by *A. platensis* biomass

In bioaccumulation experiments, the effect of REEs on the efficiency of their accumulation by the cyanobacterium *A. platensis* was assessed. The results are presented in Figure 4.2.

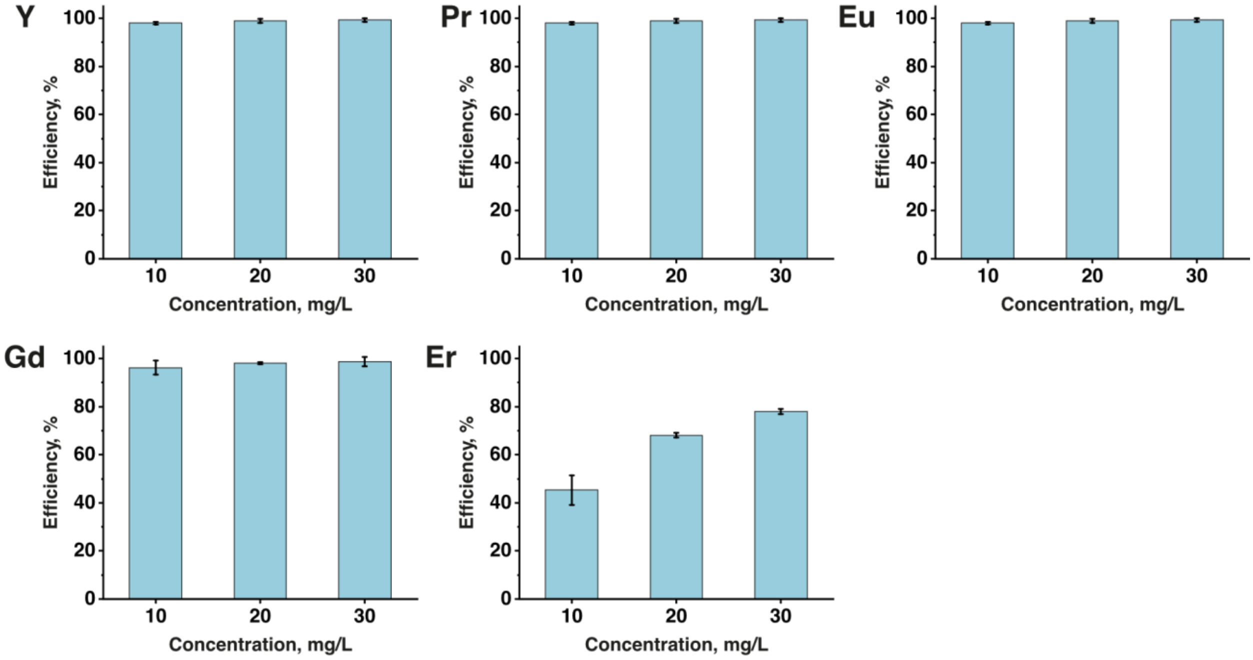

Figure 4.2. Efficiency of REEs bioaccumulation by cyanobacterium *A. platensis* depending on the element concentration

When *A. platensis* was exposed to Y ions, the lowest removal efficiency of 29% was obtained at Y concentration of 10 mg/L. At higher concentrations, the Y removal efficiency was approximately 60–70%. At the same time, regardless of the concentration used, the efficiency of Pr accumulation by the biomass exceeded 99% [24]. The removal efficiency of Eu was 98–99% at all studied concentrations [25]. The cyanobacterium *A. platensis* accumulated 96–98% of Gd ions [26]. The addition of Er resulted in the accumulation of 45–78% of ions from the solution [22].

4.2. Effect of REEs on biomass productivity of *A. platensis*

The accumulation of biomass of the cyanobacterium *A. platensis* in a closed system during a cultivation cycle was monitored both under standard conditions (control) and when REEs in concentrations of 10–30 mg/L were added in the medium. The results are shown in Figure 4.3.

At Y concentration of 10 mg/L, no difference between the biomass productivity in the control and experimental samples was observed. A concentration of 20 mg/L caused an increase in the amount of biomass by 9.3%, and 30 mg/L caused a decrease by 4.6% compared to the control [23]. Concentrations of Pr 10 and 20 mg/L did not affect the amount of biomass accumulated in the *A. platensis* culture [24]. At a metal concentration of 30 mg/L, an insignificant decrease of this indicator was observed. In the case of Eu, the amount of biomass accumulated in the control and experimental samples was very close[25]. Gd did not inhibit the accumulation of *A. platensis* biomass, but, on the contrary, even enhanced its growth. Thus, at a concentration of 10 mg/L, the amount of *A. platensis* biomass was 23.4% higher than the control and then decreased, but still remained significantly higher than the control [26]. The applied Er concentrations did not affect the accumulation of *A. platensis* biomass [22]. The amount of biomass in all experimental variants was within the physiological norm characteristic for *A. platensis*.

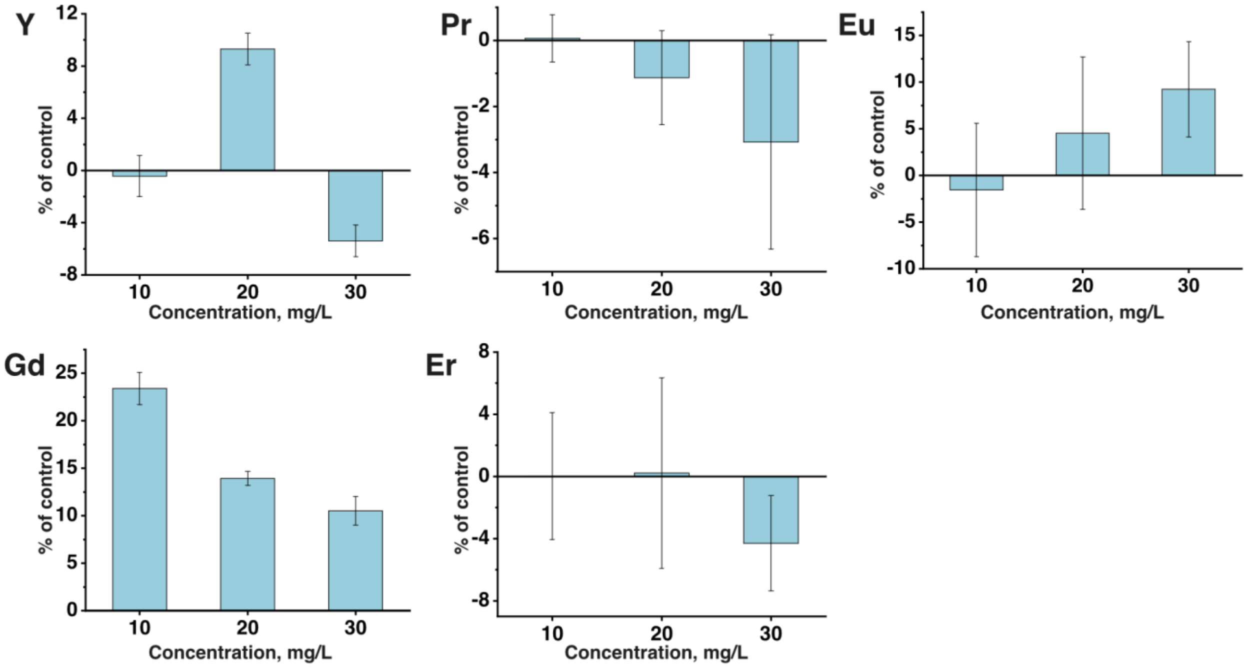

Figure 4.3. Effect of REEs in different concentrations on the amount of *A. platensis* biomass

4.3. Changes in the content of proteins and carbohydrates in the biomass of *A. platensis* under the influence of REEs

The biochemical composition of *A. platensis* biomass was altered by REEs ions. The effect of REEs on the protein and carbohydrate content of spirulina biomass was studied. Figure 4.4 shows the results of the experiment.

In the experiment with Y, the content of protein in the control biomass was 63.65% of the dry biomass, and in the experimental variants — 54.4–60.05%, which corresponds to a decrease of 5.7–14.5% compared to the control [23]. The presence of Pr in the nutrient medium did not affect the content of protein in the biomass of *A. platensis*, which ranged from 58.95 to 61.65%

of the dry biomass [24]. The toxic effect of Eu was directly proportional to the increase in its concentration in the medium and at 30 mg/L reached values close to the critical level for *A. platensis*. Thus, at an Eu concentration of 30 mg/L, the content of protein in the biomass was 50.7% of the biomass, which is 17.7% less than in the control [25]. In the case of Gd ions, a slight increase in protein content was observed — from 66.1% of dry biomass in the control sample to 70.2 and 69.3%, respectively, at concentrations of 10 and 20 mg/L. However, at a Gd concentration of 30 mg/L, the amount of protein was 56.6% of dry biomass [26]. The use of different concentrations of Er ions led to an insignificant change in the protein content in the biomass of *A. platensis* — 58.5–61.8%, while in the control sample this value was 61.65% of dry biomass [22].

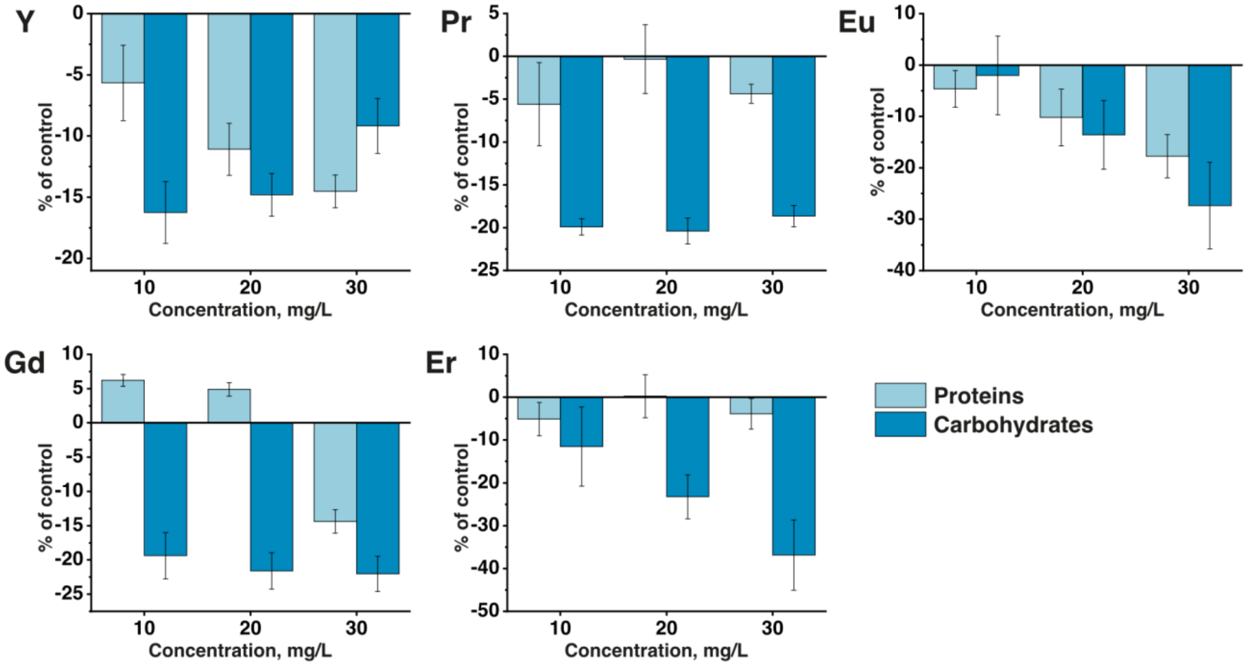

Figure 4.4. Effect of REEs in different concentrations on the content of proteins and carbohydrates in the biomass of *A. platensis*

The carbohydrate content in the biomass of *A. platensis* under the influence of Y varied from 13.18 to 11.03% and decreased by 17–16.25% compared to the control [23]. At the applied Pr concentrations, a decrease in content of carbohydrates by 18.7–20.4% compared to the control was observed [24]. At Eu concentrations of 10 and 20 mg/L, the carbohydrate content in the biomass of *A. platensis* did not differ significantly from the control value, and at 30 mg/L it decreased by 27.4% [25]. The amount of carbohydrates in the biomass of *A. platensis* grown on a medium with the addition of Gd in all experimental variants decreased compared to the control by 19.4–22.0% [26]. Concentrations of Er 10 and 20 mg/L did not affect the amount of carbohydrates in the biomass of *A. platensis*, and at a concentration of 30 mg/L this indicator decreased by 36.7% compared to the control [22].

4.4. Lipid and malondialdehyde (MDA) content in *A. platensis* biomass under the influence of REEs

A. platensis is an organism with a low content of lipids which are mainly found in membranes and provide overall cell function.

In experiments with the addition of Y and Gd to the nutrient medium at concentrations of 10 and 20 mg/L, the lipid content was on the level of control biomass, metals at a concentration of 30 mg/L led to an increase the lipid content by 30.7 and 12.9%, respectively (Fig. 4.5) [23, 26]. The amount of lipids in the biomass grown on a medium containing Pr, Eu and Er was significantly lower than in the control sample. The introduction of Pr led to a decrease in lipid content by 7.5–22.7% compared to the control [24]. Under the influence of Eu, the decrease was 24.2–36.9% [25]. In experiments with Er, signs of toxicity for *A. platensis* culture were observed. The lipid content in the control biomass was 4.4% of the dry biomass, while in the experimental variants it was slightly above one percent [22].

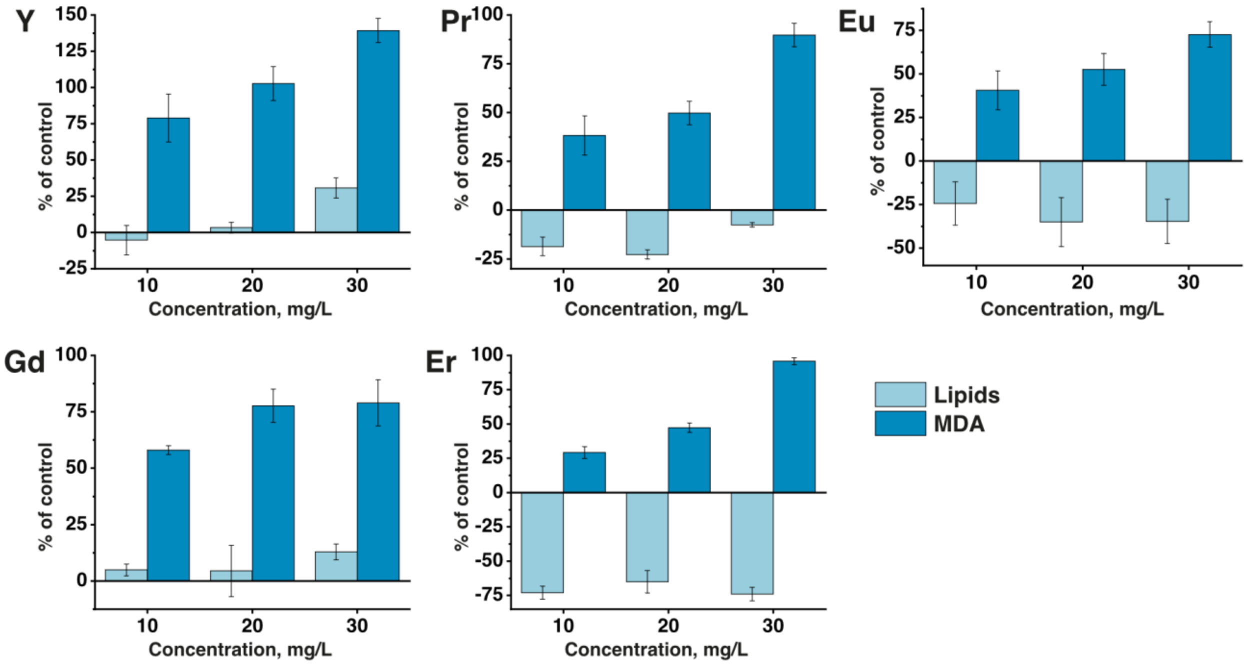

Figure 4.5. Effect of REEs in different concentrations on the lipid and MDA content in *A. platensis* biomass

In the experiments with Y, the amount of malondialdehyde in the control was 9.35 nmol/g dry biomass, while in the experimental samples the content of this oxidative stress marker was 1.78–2.38 times higher. A clear dose-effect relationship was obtained, which proved the toxic effect of Y on *A. platensis* [23]. The amount of MDA increased under the influence of

Pr by 38.2–89.8% compared to the control [24], and in the case of Eu and Gd by 41–73% and 58.0–79.0%, respectively [25, 26]. In the experiments with Er, the amount of MDA in the experimental variants was 1.3–2.0 times higher than in the control, which indicates a state of oxidative stress [22].

4.5. Pigment content in *A. platensis* biomass under the influence of REEs

The influence of different concentrations of REEs on the content of the main photosynthetic pigments was assessed.

When 10 mg/L Y were added to the nutrient medium, the sum of phycobiliproteins in the control biomass was 17.93%, which was practically similar with the control value, and with an increase in concentration it decreased by 18–27% compared to the control (Fig. 4.6) [23]. In experiments with Pr, the content of total phycobiliproteins in the control biomass of *A. platensis* was 17.3% of the dry biomass, and in the experimental variants the values were 16.4–17.7% [24]. The applied concentrations of Eu changed the content of phycobiliproteins in the spirulina biomass by 5–10% of the dry mass [25]. The addition of Gd significantly reduced the pigment content (by 11.2–27.9% compared to the control) [26], while in experiments with Er no significant changes occurred under the influence of REE [22].

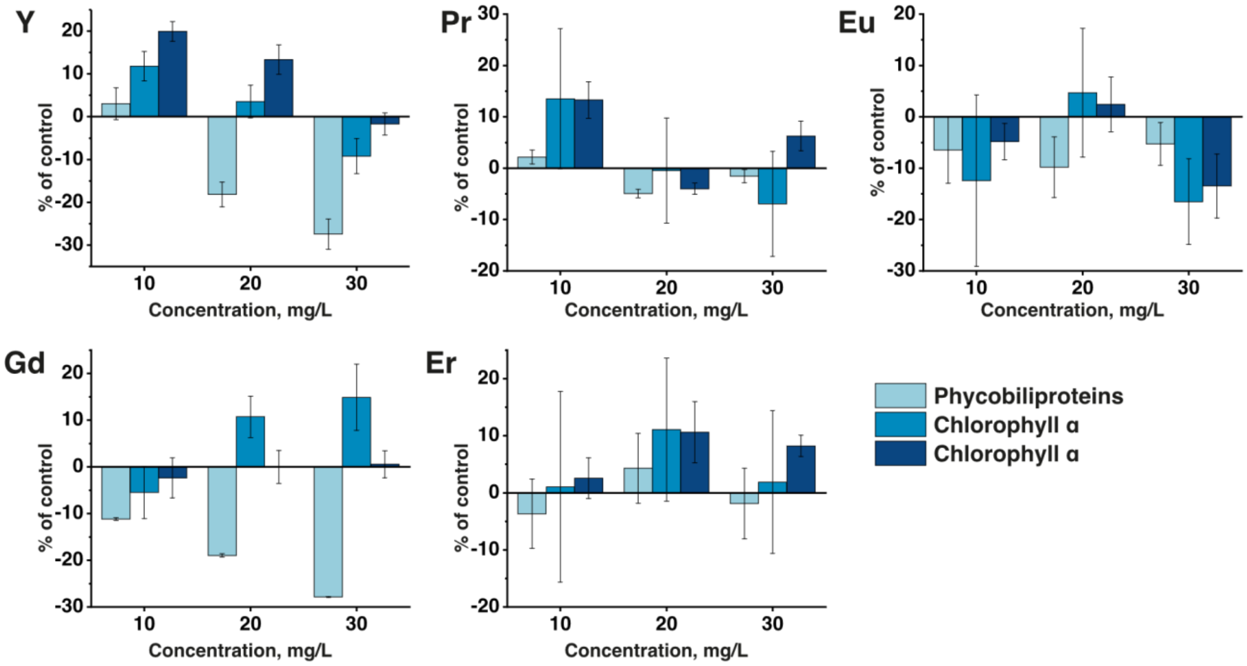

Figure 4.6. Effect of REEs in different concentrations on pigments content in *A. platensis* biomass

In the control samples, the α-chlorophyll content varied from 1 to 1.25% of the dry biomass. When Y was added to the nutrient medium, the chlorophyll α content in the experimental samples varied from 1.05 to 1.28% of the dry biomass [23]. The amount of chlorophyll α in the biomass of *A. platensis* increased by 13.2% compared to the control at a Pr concentration of 10 mg/L, while at other concentrations the value of this indicator did not change significantly [24]. The addition of Eu led to an increase in the concentration of chlorophyll α by 2.5–13.4% [25]. In the presence of Gd, the amount of chlorophyll α did not change [26]. Under the influence of Er, an increase in the pigment content from 2 to 10% was observed compared to the control [22].

The introduction of Y ions at concentrations of 10 and 20 mg/L in the nutrient medium of *A. platensis* resulted in an increase in the amount of β-carotene by 11.2 and 3.5%, respectively, while a concentration of 30 mg/L reduced its content by 9.2% compared to the control [23]. In experiments with Pr, the content of β-carotene did not change significantly [24]. A decrease in the amount of β-carotene was observed at a concentration of 30 mg/L of Eu and amounted to 16.4% of the control value [25]. In experiments with Gd, the amount of β-carotene in the control was 0.25% of the dry biomass, while with the introduction of the metal it varied from 0.24 to 0.29% [26]. In the case of Er, the pigment content in the experimental samples was close to the control values (0.24–0.27% of the biomass), which are characteristic physiological values for *A. platensis*.

The results obtained for photosynthetic pigments in the *A. platensis* biomass show that their content in spirulina cells remained at a level characteristic for the normal physiological state of the culture.

4.6. Antioxidant activity of *A. platensis* biomass extracts under the influence of REEs

The activity of ethanol and water extracts towards the $ABTS^{\cdot+}$ cation-radical obtained from *A. platensis* biomass grown on a medium with the addition of REEs was measured. Figure 4.7 shows the data of an experiment with the addition of REEs to the nutrient medium.

In the experiments with Y, the water extract obtained from the biomass grown on a medium with 10 mg/L Y was 19.97% more active against the $ABTS^{\cdot+}$ cation radical compared to the control. With an increase in the metal concentration, the activity of the extract increased. The alcoholic extracts in the experimental variants were 10.63–25.53% more active compared to the control [23]. In the experiments with Pr, both types of extracts had very similar antiradical activity. Aqueous extracts of Pr exceeded the control by 6.5–32.7% depending on the concentration. For alcoholic extracts, the same increase in activity by 11–18.8% was observed compared to the control [24]. The activity of the alcoholic extract was at the control level for all Eu concentrations. The activity of the water extract at Eu concentrations of 10 mg/L was 37.9%

higher than the control value and then decreased to the control level [25]. A significant increase in the activity of the aqueous extract was found under the influence of various concentrations of Gd. Thus, the maximum increase in the activity of the aqueous extract was 57.2% at 10 mg/L, and of the alcoholic extract by 32.1% at 30 mg/l Gd [26]. The activity of the alcoholic and aqueous extracts of *A. platensis* biomass grown in a medium containing Er was at the control level at all concentrations. To the best of our knowledge, this is the first rare earth element that does not cause a change in the inhibitory capacity of the ABTS$^{\cdot+}$ cation radical. Preservation of antioxidant activity at the level characteristic of the control biomass indicates the adaptation of *A. platensis* to Er [22].

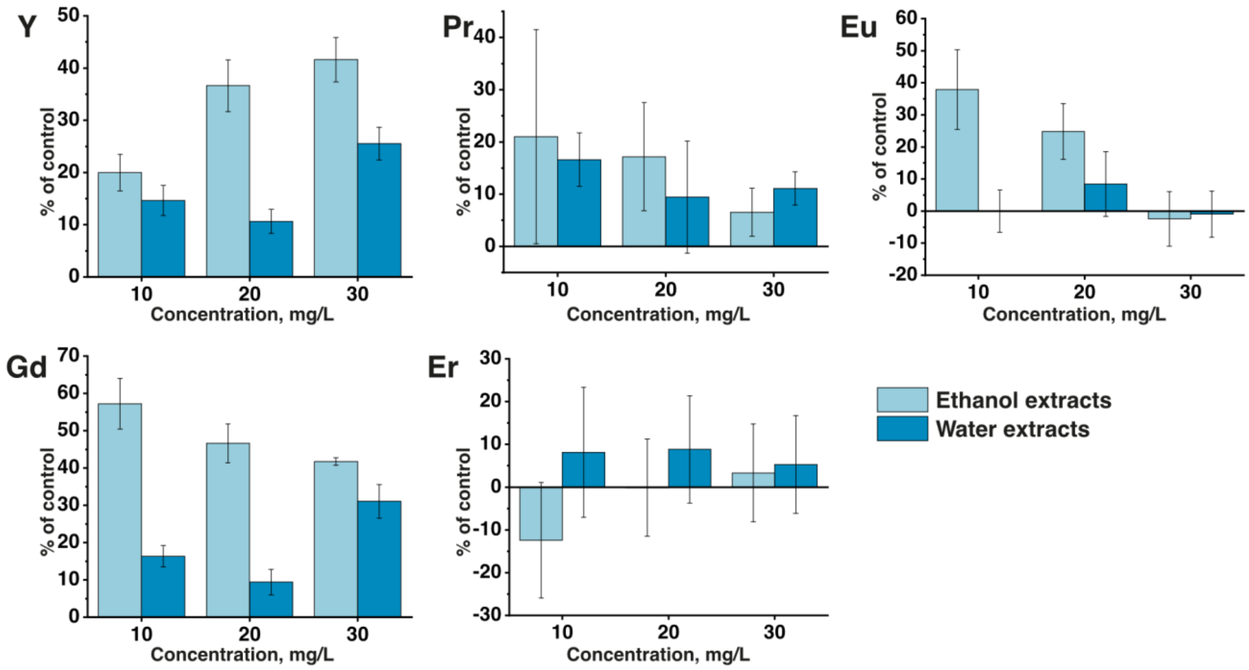

Figure 4.7. Effect of REEs in different concentrations on the antioxidant activity of *A. platensis* biomass extract

5. TECHNOLOGIES FOR REMOVING REEs FROM AQUATIC ENVIRONMENT USING CYANOBACTERIA *A. PLATENSIS*

In accordance with two mechanisms underlying REEs removal, biosorption and bioaccumulation, and based on the results described in Chapters 3 and 4, the studies were continued for the development of technologies of REEs removal by (1) biosorption on dry spirulina biomass and (2) bioaccumulation by living spirulina culture. The developed technologies include operational sequences of the complete process flow with a description of intermediate and final points of quality control and process efficiency.

5.1. Technology of REEs removal from liquid media using dry biomass of *A. platensis*

This technology is entirely based on the use of dry spirulina biomass as a sorbent. Thus, one of the main stages of the technology is sorbent production. This includes preparation of the nutrient medium, transferring it to the bioreactor, spirulina inoculating, spirulina growing (one cycle of growing of the culture in a closed system), collecting, standardizing and drying of the biomass. After this, the dry biomass is used to remove rare earth elements by the biosorption. Figure 5.1 shows the stages of technology implementation.

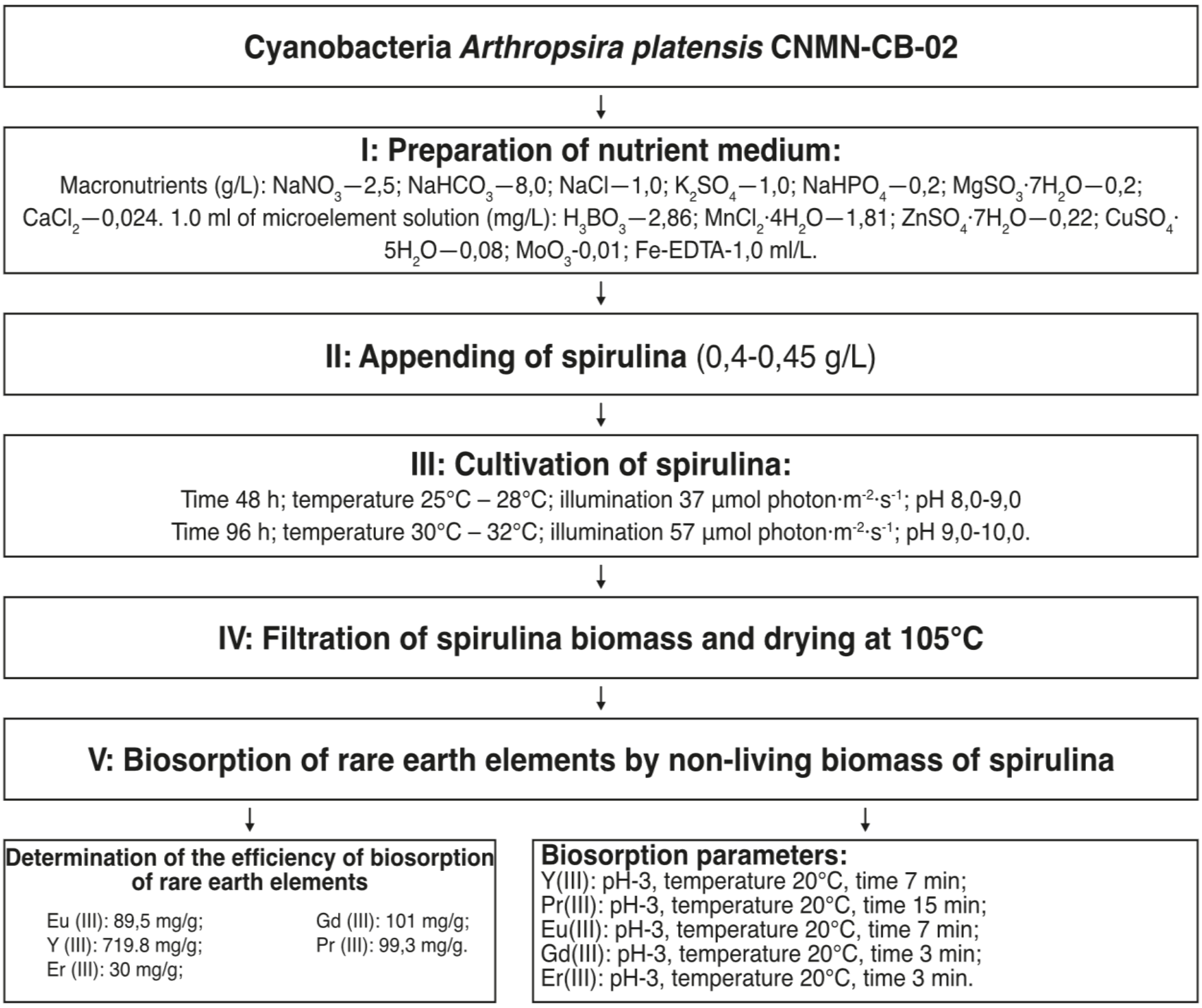

Figure 5.1. Technology of rare earth elements recovery by biosorption using dried *A. platensis* biomass.

The developed technology for REEs recovery showed high efficiency toward four studied elements (Y, Pr, Gd, Eu) and average efficiency for Er.

5.2. Technology of REEs recovery by bioaccumulation by *A. platensis*

The living culture of *A. platensis* has the ability to accumulate REEs due to mechanisms based on their similarity to elements essential for the culture of cyanobacteria. At the same time, the concentrations of these elements should be low to not affect the vital processes in the cells of spirulina. Thus, spirulina is a bioremediator that can be used in the processes of subsequent wastewater treatment, where the elements of interest are found in quantities that cannot be removed by traditional treatment methods. Based on the data described in Chapter 4, a technology for the bioaccumulation of REEs by spirulina was developed, including the adjustment of REEs-containing solutions to the needs of the *A. platensis* culture, cultivation of cyanobacteria under conditions as close as possible to the optimal ones for cyanobacterium, separation of spirulina biomass, and assessment of the efficiency of the bioaccumulation process. The stages of the implementation of the process flow chart are shown in Figure 5.2.

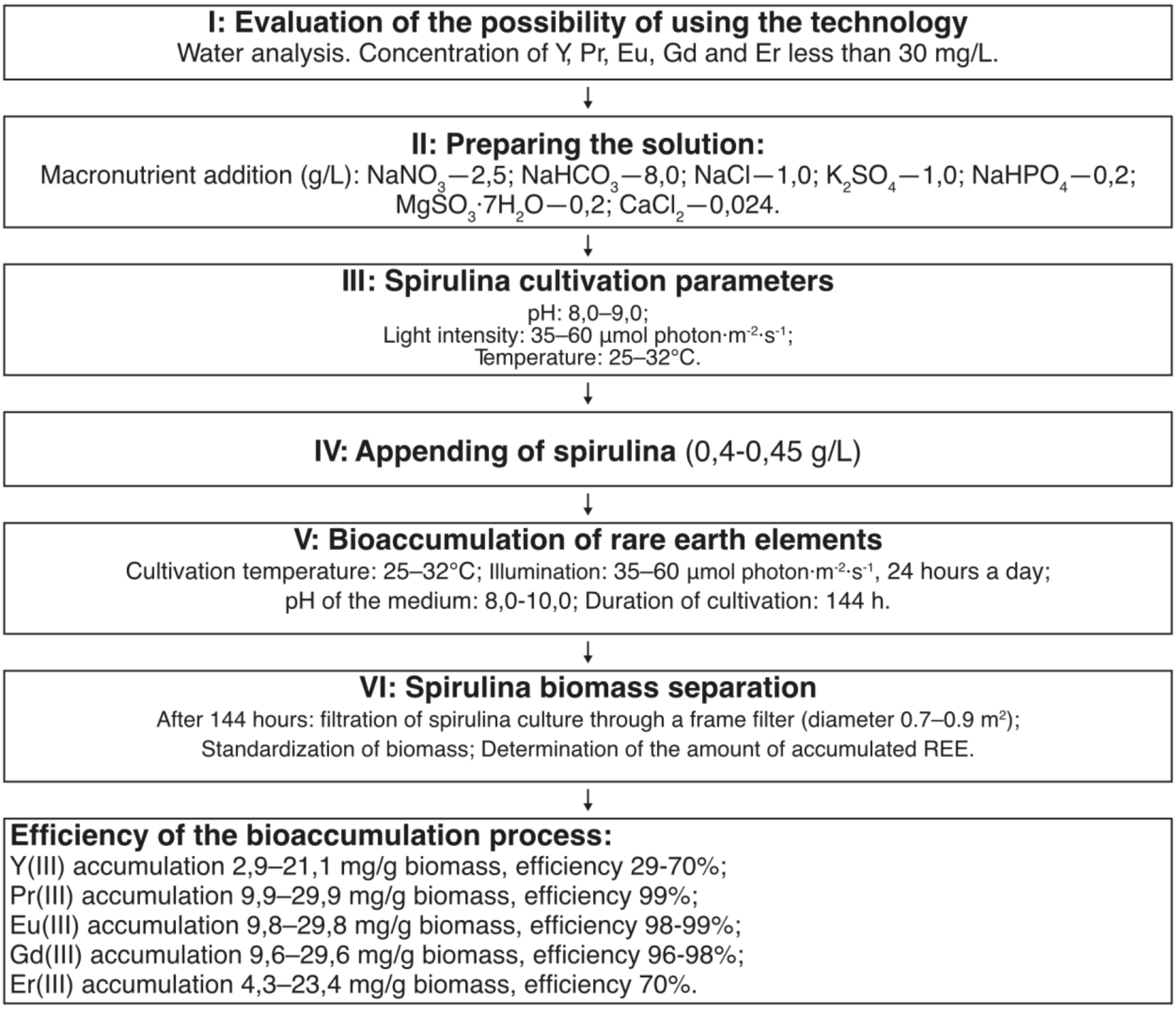

Figure 5.2. Technology of rare earth elements recovery from liquid media by bioaccumulation by *A. platensis*

5.3. Application of the developed technologies for other REEs — Dy and Tb

The developed technology was tested for other rare earth elements — Dy and Tb. Initially, the optimal conditions were identified, under which the process proceeds most effectively. To achieve the goal biosorption experiments were conducted. Maximum adsorption was attained at pH 3.0 for both metals: 50% Dy and 66% Tb [1, 2], while further increase of pH led to a decrease in the biosorbtion efficiency. The highest adsorption of Dy was achieved after 60 minutes of contact, reaching 66% [1]. With regard to Tb, the removal efficiency increased sharply in the first 3 minutes of sorbent interaction with the sorbate, reaching 60%, after which equilibrium was established [2]. The highest adsorption capacity of spirulina was achieved at Dy(III) concentration of 50 mg/lL (2.3 mg/g) and remained constant even with the increase of the metal concentration in the solution [1]. With an increase in the initial Tb concentration from 10 to 100 mg/l, the amount of adsorbed elements increased from 5.7 to 85.8 mg/g [2]. The efficiency of Dy biosorption in the temperature range of 20–50°C was 59% [1]. The efficiency of Tb removal reached a maximum of 56% at 20°C and decreased to 52% with increasing of the temperature [2].

The application of this technologies showed the following results for Dy and Tb in the biosorption experiment

: • The achieved sorption capacity for Dy was 3.24 mg/g (maximum removal efficiency was 66%);

• The achieved sorption capacity for Tb was 212 mg/g (maximum removal efficiency was 66%);

Thus, the developed technology for the removal of rare earth elements showed average efficiency toward Dy and Tb.

For Dy and Tb, the technological scheme of rare earth elements bioaccumulation was also applied (at metal concentrations of 10–30 mg/L). The results obtained were as follows:

• Accumulation of Dy varied from 8.9 to 25.5 mg/g of biomass depending on the element concentration in the medium, the efficiency of the process was 85–90% and increased with an increase of the metal concentration in the solution [3];

• Tb accumulation was on the level of 0.7–1.5 mg/g of biomass, the efficiency of the removal did not exceed 19% [3].

CONCLUSIONS AND RECOMMENDATIONS

The obtained results, which correspond to the aim and objectives formulated in the dissertation, allowed us to formulate the following general conclusions:

1. The optimal parameters for yttrium, praseodymium, europium, gadolinium and erbium biosorption by cyanobacterium *Arthrospira platensis* biomass were determined. The highest efficiency of metal ion removal was observed at pH 3, temperature of 20°C and sorption time of 3 minutes for Gd, Er, 7 minutes for Y, Eu and 15 minutes for Pr (Chapter 3).

2. The obtained thermodynamic parameters indicate that biosorption of the studied REEs is a spontaneous and exothermic process. The experimental data were better described by the pseudo-first order kinetic model which assumes that the adsorption rate on functional groups is proportional to the number of free functional groups of the sorbent. The applicability of the Freundlich equilibrium model indicates that adsorption occurs on a heterogeneous surface as multilayer adsorption (Chapter 3).

3. Bioaccumulation of the studied REEs was dose-dependent. The maximum accumulation efficiency varied from 70 to 99%, depending on the element and its concentration (Chapter 4).

4. The influence of rare earth elements on the productivity and biochemical composition of *Arthrospira platensis* biomass during their bioaccumulation was revealed. The introduction of REEs into the nutrient medium of cyanobacteria did not significantly affect the productivity of the biomass. At the same time, a toxic effect was observed, expressed in a decrease in the content of proteins, lipids and carbohydrates and increased levels of malondialdehyde. Nonetheless, the content of pigments allowed maintaining the vital activity of cyanobacteria at a normal level (Chapter 4).

5. According to the experimental data, during bioaccumulation, the recovery of the studied REEs from the solution was higher compared to biosorption experiments, which indicates the high efficiency of this process. However, due to the high value of *Arthrospira platensis* and the costs of its cultivation for industrial purposes, it is more appropriate to use biomass (waste from biotechnological production) as a sorbent (Chapter 3, 4).

6. Technological schemes for biosorption and bioaccumulation of rare earth elements from solutions were developed, allowing the described purification technologies to be introduced into the wastewater purification cycle of enterprises both for the elements studied in the work and for other REEs (Chapter 5).

The obtained result, which contributed to the solution of an important scientific task proposed in this work, consists in the scientific substantiation of the applicability of the cyanobacterial strain *Arthrospira platensis* CNMN-CB-02 for the biosorption and bioaccumulation of yttrium, praseodymium, europium, gadolinium and erbium from aqueous solutions, which led to the development of new technologies for the purification of wastewater containing REEs.

In the theoretical aspect, new data on the efficiency and conditions of biosorption of yttrium, praseodymium, europium, gadolinium and erbium by the biomass of the cyanobacterium *Arthrospira platensis* have been accumulated. Optimal conditions for the removal of REEs were determined and the main mechanisms of sorption have been described. Also, for the first time, data on the effect of rare earth elements on the productivity of biomass, as well as on the level of their accumulation in the biomass during bioaccumulation were obtained. Changes in the biochemical composition, the content of oxidative degradation products of lipids and the level of antioxidant activity of the biomass during the accumulation of REE by cyanobacteria were assessed.

Recommendations:

1. It is recommended to use the cyanobacterium *Arthrospira platensis* CNMN-CB-02 for the treatment and post-treatment of industrial wastewater containing rare earth elements.

2. It is recommended to use the cyanobacterium *Arthrospira platensis* CNMN-CB-02 at enterprises processing secondary raw materials containing rare earth metals for their extraction and secondary use.

Suggestions for future research:

1. It is necessary to continue studying the efficiency of recovery of other rare earth metals, as well as to conduct experiments on the recovery of metals from multi-element wastewater.

2. It is necessary to continue experiments on development of wastewater treatment technologies using spirulina, which is obtained after medicinal and cosmetic products production, as a biological sorbent.

3. It is necessary to conduct experiments on biosorption in a fixed layer. The obtained data will allow to implement the proposed treatment method in the technological cycle of industrial enterprises.

REFERENCES

1. Malhotra, N. et all. An updated review of toxicity effect of the rare earth elements (REEs) on aquatic organisms. In: *Animals*. 2020, vol. 10, nr. 9, p.1663. ISSN 2076-2615.
2. Laveuf, C., Cornu, S. A review on the potentiality of rare earth elements to trace pedogenetic processes. In: *Geoderma*. 2009, vol. 154, nr. 1–2, pp.1-12. ISSN 0016-7061.
3. Brouziotis, A.A. et al. Toxicity of rare earth elements: An overview on human health impact. In: *Frontiers in Environmental Science*. 2022, vol. 10, p.948041. ISSN 2296-665X.
4. Dev, S. et al. Mechanisms of biological recovery of rare-earth elements from industrial and electronic wastes: A review. In: *J. Chem. Eng.* 2020, vol. 397. p.124596. ISSN 1385-8947.
5. Binnemans, K. et al. Recycling of rare earths: A critical review. In: *Journal of Cleaner Production*. 2013, vol. 51. pp.1-22. ISSN 0959–6526.
6. Chen, Qing: Study on the adsorption of lanthanum(III) from aqueous solution by bamboo charcoal. In: *Journal of Rare Earths*. 2010, vol. 28, pp.125-131. ISSN 1002–0721.
7. Filote, C. et al. Sustainable application of biosorption and bioaccumulation of persistent pollutants in wastewater treatment: Current practice. In: *Processes*. 2021, vol. 9, p.1696. ISSN 2227–9717.
8. Timková, I., Sedláková-Kaduková, J., Pristaš, P. Biosorption and bioaccumulation abilities of actinomycetes/streptomycetes isolated from metal contaminated sites. In: Separations. 2018, vol. 5, nr. 4, p.54. ISSN 2297–8739.
9. Chojnacka, K. Biosorption and bioaccumulation - the prospects for practical applications. In: *Environment International*. 2010, vol. 36, nr. 3, pp.299-307. ISSN 1873–6750.
10. Zinicovscaia, I. et al. Evaluation of biosorption and bioaccumulation capacity of cyanobacteria *Arthrospira* (spirulina) *platensis* for radionuclides. In: *Algal Research*. 2020, vol. 51, p.102075. ISSN 2211–9264.
11. Sadovsky, D. et al. Biosorption potential of cerium ions using Spirulina biomass. In: *Journal of Rare Earths*. 2016, vol. 34, nr. 6, pp.644-652. ISSN 1002–0721.
12. Lima, É.C. et al. Biosorption of Neodymium (Nd) from Aqueous Solutions Using Spirulina platensis sp. Strains. In: *Polymers*. 2022, vol. 14, nr. 21, p.4585. ISSN 2073–4360.
13. Paper, M. et al. Rare earths stick to rare cyanobacteria: Future potential for bioremediation and recovery of rare earth elements. In: *Frontiers in Bioengineering and Biotechnology*. 2023, vol. 11, p.1130939. ISSN 2296–4185.
14. Fritz, M. et al. High-resolution particle size and shape analysis of the first Samarium nanoparticles biosynthesized from aqueous solutions via cyanobacteria *Anabaena cylindrica*. In: *NanoImpact*. 2022, vol. 26, p.100398. ISSN 2452–0748.
15. Okajima, M.K. et al. Cyanobacterial polysaccharide gels with efficient rare-earth-metal sorption. In: *Biomacromolecules*. 2010, vol. 11, nr. 7, pp. 1773-1778. ISSN 1525–7797.
16. Koval, E., Olkova, A. Determination of the sensitivity of cyanobacteria to rare earth elements La and Ce. In: *Pol. J. Environ. Stud.* 2022, vol. 31, nr. 1, pp.985-988. ISSN 1230–1485.

17. Fischer, C.B. et al. Cyanobacterial promoted enrichment of rare earth elements europium, samarium and neodymium and intracellular europium particle formation. In: *RSC Advances*. 2019, vol. 9, nr. 56, pp. 32581-32593. ISSN 2046–2069.
18. Zinicovscaia, I. et al. Accumulation of dysprosium, samarium, terbium, lanthanum, neodymium and ytterbium by *Arthrospira platensis* and their effects on biomass biochemical composition. In: *Journal of Rare Earths*. 2021, vol. 39, nr. 9, pp.1133-1143. ISSN 1002–0721.
19. Barry, M.J., Meehan, B.J. The acute and chronic toxicity of lanthanum to *Daphnia carinata*. In: *Chemosphere*. 2000, vol. 41, nr. 10, pp.1669-1674. ISSN 0045–6535.
20. Vítová, M., Čížková, M., Zachleder, V. Lanthanides and Algae. In: Awwad N.S., Mubarak A. *Lanthanides.* IntechOpen. 2019, pp. 87-111. ISBN 978-1-78985-010-9.
21. Rudi, L. et al. Metode de analiză în ficobiotehnologie. Ghid metodic. Chisinău : S.n., 2020, (Tipogr. ”Artpoligraf”), 101 p. ISBN 978-9975-3462-9-0
22. Yushin, N. et al. Application of cyanobacteria *Arthospira platensis* for bioremediation of erbium-contaminated wastewater. In: *Materials*. 2022, vol. 15, nr. 17, p. 6101. ISSN 1996–1944.
23. Yushin, N. et al. Biosorption and Bioaccumulation Capacity of Arthrospira platensis toward Yttrium Ions. In: *Metals*. 2022, vol. 12, MDPI, nr. 9, p. 1465. ISSN 2075–4701.
24. Yushin, N. et al. Praseodymium(III) removal from aqueous solutions using living and non-living *Arthrospira platensis* biomass. In: *Water*. 2023, vol. 15, nr. 11, p. 2064. ISSN 2073–4441.
25. Yushin, N. et al. Biosorption and bioaccumulation capacity of *Arthospira platensis* toward europium ions. In: *Water*. 2022, vol. 14, nr. 13, p. 2128. ISSN 2073–4441.
26. Yushin, N. et al. Cyanobacteria *Arthospira platensis* as an Effective Tool for Gadolinium Removal from Wastewater. In: *Clean Technologies*. 2023, vol. 5, pp. 638–651. ISSN 2571-8797.
27. Cadogan, E.I., Lee, C.H., Popuri, S.R. Facile synthesis of chitosan derivatives and Arthrobacter sp. biomass for the removal of europium(III) ions from aqueous solution through biosorption. In: *International Biodeterioration and Biodegradation*. 2015, vol. 102, pp.286-297. ISSN 0964–8305.
28. El-Dessouky, S.I., El-Sofany, E.A., Daoud, J.A. Studies on the sorption of praseodymium (III), holmium (III) and cobalt (II) from nitrate medium using TVEX-PHOR resin. In: *Journal of Hazardous Materials*. 2007, vol. 143, nr. 1–2, pp.17-23. ISSN 0304–3894.
29. Anastopoulos, I., Bhatnagar, A., Lima, E.C. Adsorption of rare earth metals: A review of recent literature. In: *Journal of Molecular Liquids*. 2016, vol. 221, pp.954-962. ISSN 0167–7322.
30. Zinicovscaia, I. et al. The remediation of dysprosium-containing effluents using cyanobacteria *Spirulina platensis* and yeast *Saccharomyces cerevisiae*. In: *Microorganisms*. 2023, vol. 11, nr. 8. ISSN 2076–2607.
31. AL-BAGAWI, A.H. et al. Terbium removal from aqueous solutions using a In_2O_3 nanoadsorbent and *Arthrospira platensis* biomass. In: *Nanomaterials*. 2023, vol. 13, nr. 19 ISSN 2079–4991.

LIST OF PUBLICATIONS ON THE SUBJECT OF THE THESIS

2. Articles in scientific journals

2.1. in journals from the Web of Science and SCOPUS databases

1. **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(13), pp. 1-13. ISSN 2073-4441. DOI: 10.3390/w14132128.
2. **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(9), pp. 1-17. ISSN 2075-4701. DOI: 10.3390/met12091465.
3. **Yushin, N.**, Zinicovscaia, I., Cepoi, L., Chiriac, T., Rudi, L., & Grozdov, D. Application of Cyanobacteria *Arthospira platensis* for Bioremediation of Erbium-Contaminated Wastewater. *Materials*. 2022, 15(17), p. 6101. ISSN 1996-1944 DOI: 10.3390/ma15176101.
4. **Yushin, N.**, Zinicovscaia, I., Cepoi, L., Chiriac, T., Rudi, L., & Grozdov, D. Cyanobacteria Arthospira platensis as an Effective Tool for Gadolinium Removal from Wastewater. *Clean Technologies*. 2023, 5(2), pp. 638-651. ISSN 2571-8797. DOI: 10.3390/cleantechnol5020032.
5. **Yushin, N.**, Zinicovscaia, I., Cepoi, L., Chiriac, T., Rudi, L., & Grozdov, D. Praseodymium (III) Removal from Aqueous Solutions Using Living and Non-Living *Arthrospira platensis* Biomass. *Water*. 2023, 15(11), p. 2064. ISSN 2073-4441. DOI: 10.3390/w15112064.
6. Zinicovscaia, I., **Yushin, N.**, Grozdov, D., Peshkova, A., Vergel, K., & Rodlovskaya, E. The Remediation of Dysprosium-Containing Effluents Using Cyanobacteria *Spirulina platensis* and Yeast *Saccharomyces cerevisiae*. *Microorganisms*. 2023, 11(8), p. 2009. ISSN 2076-2607. DOI: 10.3390/microorganisms11082009.
7. Al-Bagawi, A. H., **Yushin, N.**, Hosny, N. M., Gomaa, I., Ali, S., Boyd, W. C., Kalil, H., Zinicovscaia, I. Terbium Removal from Aqueous Solutions Using a In_2O_3 Nanoadsorbent and *Arthrospira platensis* Biomass. Nanomaterials. 2023, 13(19), p. 2698. ISSN 2079-4991. DOI: 10.3390/nano13192698.

3. Articles in conference proceedings and other scientific events

3.3. in the works of scientific events included in the Register of materials published on the basis of scientific events organized in the Republic of Moldova

1. **Yushin N.**, Zinicovscaia I., Cepoi L., Chiriac T., Rudi L., Grozdov D. Biosorption and bioaccumulation capacity of *Arthrospira platensis* toward yttrium ions. In: Abstract Book "Natural sciences in the dialogue of generations", national conference. The National

Conference with international participation, September 14-15, 2023, Chisinau, Republic of Moldova, p. 195. ISBN 978-9975-3430-9-1. 082 N 26 UDC: 582.232:591.5

2. **Yushin N.**, Zinicovscaia I., Cepoi L., Chiriac T., Rudi L., Grozdov D. Cyanobacteria *Arthospira platensis* as an effective tool for gadolinium removal from wastewater. In: Abstract Book "Natural sciences in the dialogue of generations", national conference. The National Conference with international participation, September 14-15, 2023, Chisinau, Republic of Moldova, p. 196. ISBN 978-9975-3430-9-1. 082 N 26 UDC: 582.232:628.16:546.662

3a. Theses in conference proceedings and other scientific events

3.2a. in the works of scientific events included in other databases accepted by NAAQES (ANACEC)

1. **Yushin N.**, Zinicovscaia I., Cepoi L., Grozdov D. Biosorption of europium by *Spirulina platensis* biomass. In: Book of Abstracts – RAD 2022 Conference (Spring Edition), June 13-17, 2022, Herceg Novi, Montenegro, p. 49. ISBN: 978-86-901150-4-4. https://doi.org/10.21175/rad.spr.abstr.book.2022.13.4
2. **Yushin N.**, Zinicovscaia I., Cepoi L., Chiriac T., Rudi L., Grozdov D. Cyanobacteria *Arthospira platensis* as an effective tool for gadolinium removal from wastewater. In: Fundamental Interactions & Neutrons, Nuclear Structure, Ultracold Neutrons, Related Topics, 30th International Seminar on Interaction of Neutrons with Nuclei (ISINN-30), 14 – 18 April 2024. Sharm El Sheikh, Egypt, p. 132. ISBN 978-5-9530-0613-2

3.3a. in the works of scientific events included in the Register of materials published on the basis of scientific events organized in the Republic of Moldova

3. **Yushin N.**, Zinicovscaia I., Cepoi L., Chiriac T., Rudi L. Europium bioaccumulation by *Artrospira platensis* and its effect on biomass. In: Abstract book Life sciences in the dialogue of generations: Connections between Universities, Academia and Business Community", national conference with international participation, September 29-30, 2022, Chisinau, Republic of Moldova, p. 199. ISBN 978-9975-159-80-7. CZU: 546.661:620.925
4. **Yushin N.**, Zinicovscaia I., Cepoi L., Chiriac T., Rudi L. and Grozdov D. Metal removal from erbium -containing wastewater using *Arthospira platensis*. In: International Scientific Conference on Microbial Biotechnology 5th edition, 12-13 October 2022, Chisinau, Republic of Moldova, p. 65. ISBN 978-9975-3555-6-8. – ISBN 978-9975-3555-7-5 (PDF). CZU:628.35:582.232 https://doi.org/10.52757/imb22.43

АННОТАЦИЯ

Юшин Никита, Технологии извлечения редкоземельных элементов с использованием цианобактерий *Arthrospira platensis*. Диссертация кандидата биологических наук, Кишинев, 2024

Структура диссертации: Аннотация (на русском, румынском и английском языках), введение, пять глав, выводы и рекомендации, библиография из 272 источников, 21 рисунка, 7 таблиц и 112 страниц основного текста. Результаты диссертации отражены в 13 научных публикациях, включая 7 статей в реферируемых Scopus и WoS журналах.

Ключевые слова: редкоземельные элементы, иттрий, празеодим, европий, гадолиний, эрбий, *Arthrospira platensis*, спирулина, биоремедиация, загрязнение; биосорбция, биоаккумуляция, кинетика, равновесие, термодинамика, биомасса, белки, углеводы, липиды, малондиальдегид, пигменты, антиоксидантная активность.

Цель работы: целью работы является разработка эффективных технологий извлечения иттрия, празеодима, европия, гадолиния и эрбия из сточных вод, используя в качестве биосорбента и биоаккумулятора цианобактерию *Arthrospira platensis*. Для достижения цели были поставлены следующие задачи: определить оптимальные параметры сорбции иттрия, празеодима, европия, гадолиния и эрбия биомассой *Arthrospira platensis*; выявить особенности биоаккумуляции редкоземельных элементов биомассой *Arthrospira platensis*; оценить изменения биохимических параметров биомассы *Arthrospira platensis* в процессе биоаккумуляции РЗЭ; разработать технологические схемы биосорбции и биоаккумуляции редкоземельных элементов из растворов.

Научная новизна и оригинальность исследования: впервые цианобактерия *Arthrospira platensis* была применена для очистки сточных вод, содержащих редкоземельные элементы (иттрий, празеодим, европий, гадолиний, эрбий). Были определены параметры сорбции, позволяющие достичь максимальной эффективности извлечения редкоземельных элементов. Получены уникальные данные по влиянию изучаемых редкоземельных элементов на биохимический состав *Arthrospira platensis* в результате аккумуляции редкоземельных элементов

Результат, который способствует решению научной проблемы: получены принципиально новые данные по биосорбции и накоплению редкоземельных элементов биомассой *Arthrospira platensis*. Предложены новые технологии извлечения редкоземельных элементов из загрязненных вод.

Теоретическая значимость работы: определены оптимальные физико-химические параметры (pH, время, температура, концентрация элемента) извлечения редкоземельных элементов. Установлена природа биосорбционных процессов. Собраны сведения о влиянии редкоземельных элементов на жизнедеятельность *Arthrospira platensis* и ее биохимический состав.

Практическая значимость работы: разработанные подходы могут быть использованы для очистки и доочистки сточных вод промышленных предприятий, содержащих редкоземельные металлы в производственном цикле, а также извлечения металлов из концентратов редкоземельных элементов. На основе полученных данных могут быть разработаны новые технологии извлечения других металлов.

Внедрение полученных результатов: полученные результаты были использованы для разработки технологий извлечения редкоземельных элементов из промышленных сточных вод, используя *Arthrospira platensis* в качестве сорбента. Технологии были внедрены в ООО «Ангениум».

ADNOTARE

Iushin Nikita, Tehnologii de recuperare an elementelor de pământuri rare cu utilizarea cianobacteriei *Arthrospira platensis*. Teză de doctor în științe biologice, Chișinău, 2024.

Structura tezei: Adnotare (în rusă, română și engleză), introducere, cinci capitole, concluzii şi recomandări, bibliografie din 272 surse, 21 figuri, 7 tabele şi 112 pagini ale textului principal. Rezultatele expuse în teză sunt reflectate în 13 publicații științifice, inclusiv 7 articole în reviste din bazele de date WoS și Scopus.

Cuvinte-cheie: elemente de pământuri rare, ytriu, praseodim, europiu, gadoliniu, erbiu, *Arthrospira platensis*, spirulina, bioremediere, poluare; biosorbție, bioacumulare, cinetică, echilibru, termodinamică, biomasă, proteine, carbohidrați, lipide, malondialdehidă, pigmenți, activitate antioxidantă.

Scopul și obiectivele tezei: scopul lucrării constă în dezvoltarea tehnologiilor eficiente de îndepărtare a ytriului, praseodimului, europiului, gadoliniului și erbiului din apele uzate, utilizând cianobacteria *Arthrospira platensis* ca biosorbent și bioacumulator. Pentru atingerea scopului, au fost specificate următoarele obiective: determinarea parametrilor optimi pentru sorbția ytriului, praseodimului, europiului, gadoliniului și erbiului de către biomasa *Arthrospira platensis*; evidențierea particularităților bioacumulării elementelor pământurilor rare de către biomasa *Arthrospira platensis*; evaluarea modificării parametrilor biochimici ai biomasei *Arthrospira platensis* în procesul de bioacumulare a EPR; elaborarea unor scheme tehnologice pentru biosorbția și bioacumularea elementelor pământurilor rare din soluții.

Noutatea și originalitatea științifică: pentru prima dată, cianobacteria *Arthrospira platensis* a fost folosită pentru tratarea apelor reziduale care conţin elemente de pământuri rare (itriu, praseodim, europiu, gadoliniu, erbiu). Au fost determinați parametrii sorbției, care permit îndepărtarea maximă a elementelor pământurilor rare. Au fost obţinute date unice cu privire la influența elementelor pământurilor rare studiate asupra compoziției biochimice a *Arthrospira platensis* ca rezultat al bioacumulării pământurilor rare.

Rezultatul obținut care contribuie la soluționarea unei probleme științifice importante: au fost obținute date fundamentale noi despre biosorbția și acumularea elementelor pământurilor rare de către biomasa *Arthrospira platensis*. Au fost propuse tehnologii noi pentru îndepărtarea elementelor pământurilor rare din apele poluate.

Semnificația teoretică a tezei: au fost determinați parametrii fizico-chimici optimi (pH-ul, timpul, temperatura, concentrația elementului) pentru îndepărtarea elementelor de pământuri rare. A fost stabilită natura proceselor de biosorbție. A fost studiat impactul elementelor pământurilor rare asupra activității vitale a *Arthrospira platensis* și a compoziției ei biochimice.

Valoarea aplicativă a tezei: abordările dezvoltate pot fi utilizate pentru tratarea și post-tratarea apelor reziduale de la întreprinderile industriale care conţin metale de pământuri rare în ciclul de producție, precum și extracția metalelor din concentrate de elemente de pământuri rare. Pe baza datelor obținute pot fi dezvolte tehnologii noi pentru extracția altor metale.

Implementarea rezultatelor științifice: rezultatele obținute au fost folosite pentru elaborarea tehnologiilor de îndepărtare a elementelor pământurilor rare din apele reziduale industriale folosind *Arthrospira platensis* ca sorbent. Tehnologiile au fost implementate de către. compania „Anghenium”.

ANNOTATION

Iushin Nikita, Technologies for the extraction of rare earth elements using cyanobacteria *Arthrospira platensis*. PhD thesis in biological sciences, Chisinau, 2024

Structure of the thesis: Abstract (in Russian, Romanian and English), introduction, five chapters, conclusions and recommendations, bibliography from 272 sources, 21 figures, 7 tables and 112 pages of main text. The results of the dissertation are reflected in 13 scientific publications, including 7 articles in peer-reviewed Scopus and WoS journals.

Keywords: REEs, yttrium, praseodymium, europium, gadolinium, erbium, *Arthrospira platensis*, spirulina, bioremediation, pollution; biosorption, bioaccumulation, kinetics, equilibrium, thermodynamic, biomass, proteins, carbohydrates, lipids, malondialdehyde, pigments, antioxidant activity.

The aim and objectives of the thesis: the purpose of the thesis is to develop effective technologies for the extraction of yttrium, praseodymium, europium, gadolinium and erbium from wastewater, using the cyanobacterium *Arthrospira platensis* as a biosorbent and bioaccumulator. To achieve the goal, it is necessary to complete the following tasks: to determine the optimal parameters for the sorption of yttrium, praseodymium, europium, gadolinium and erbium by *Arthrospira platensis* biomass; to identify the features of rare earth elements bioaccumulation by *Arthrospira platensis* biomass; to evaluate changes in the biochemical parameters of *Arthrospira platensis* biomass during the process of REEs bioaccumulation; and to develop technological schemes for the biosorption and bioaccumulation of rare earth elements from solutions.

The novelty and scientific originality: for the first time, the cyanobacterium *Arthrospira platensis* was used to treat wastewater containing rare earth elements (yttrium, praseodymium, europium, gadolinium, erbium). Sorption parameters which allow maximum efficiency of rare earth elements removal were determined. Unique data on the influence of the studied rare earth elements on the biochemical composition of Arthrospira platensis as a result of the accumulation of rare earth elements were obtained.

A result that contributes to the solution of a scientific problem: fundamentally new data on the biosorption and accumulation of rare earth elements by *Arthrospira platensis* biomass were obtained. New technologies for recovery of rare earth elements from polluted waters have been proposed.

The theoretical importance of the work: the optimal physicochemical parameters (pH, time, temperature, element concentration) for the recovery of rare earth elements were determined. The nature of biosorption processes has been established. Information about the influence of rare earth elements on the life activity of *Arthrospira platensis* and its biochemical composition was obtained.

The applied value of the work: the developed approaches can be used for the treatment and post-treatment of wastewater from industrial enterprises containing rare earth metals in the production cycle, as well as the recovery of metals from concentrates of rare earth elements. Based on the data obtained, new technologies for the extraction of other metals can be developed.

The implementation of the results: the obtained results were used to develop technologies for extracting rare earth elements from industrial wastewater using *Arthrospira platensis* as a sorbent. The technology was implemented at Angenium LLC.

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Rezumatul tezei de doctor în științe biologice

CHIȘINĂU, 2024

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Abstract of PhD thesis in biology

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