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Praseodymium(III) Removal from Aqueous Solutions Using Living and Non-Living *Arthrospira platensis* Biomass

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Abstract: Praseodymium, the sixth-most abundant rare-earth element, is widely used in the aircraft industry for the elaboration of refractory substances, coloring materials, lighting equipment, and fiber optical cables. Living and non-living *Arthrospira platensis* biomass was applied for Pr(III) removal from aqueous solutions. In bioaccumulation experiments, the effect of Pr(III), introduced into the medium in a concentration range of 10–30 mg/L, on biomass productivity, biochemical composition, and antioxidant activity was assessed. The biomass showed high accumulation capacity (more than 99%) toward Pr(III). Supplementation of the cultivation medium with Pr(III) led to a decrease in carbohydrate and lipid content, but it did not significantly influence biomass productivity or the content of proteins and pigments. In experiments with non-living biomass, the effect of pH, Pr(III) concentration, temperature, and contact time on the efficiency of metal removal was investigated. The maximum uptake of Pr(III) was achieved at pH 3.0 after 3.0 min of interaction. The equilibrium data were explained using the Langmuir and Freundlich models, while the kinetics of the process was described by applying pseudo-first-order, pseudo-second-order, and Elovich models. The maximum sorption capacity of *Arthrospira platensis* biomass calculated from the Langmuir model was 99.3 mg/g. According to the thermodynamic calculations, the process of Pr(III) removal was spontaneous and exothermic in nature. The obtained data can be used for the development of environmentally-friendly technology for Pr(III) recovery from wastewater as well as to understand the effect of Pr(III) on aquatic organisms.

Keywords: praseodymium; biosorption; bioaccumulation; spirulina

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1. Introduction

Rare earth elements (REEs) are a group of 15 lanthanides, as well as Sc and Y, which are categorized into light (La, Ce, Pr, Nd, Pm, and Sm) and heavy (Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y) REEs [1,2]. Owing to their chemical, metallurgical, optical, catalytic, magnetic, and electronic properties, REEs are intensively applied in the chemical industry, metallurgy, medicine, electronic device production, petroleum refining [1–4], nuclear technologies, the production of fertilizers, telecommunications, and security systems [5].

Recently, China has become the leading producer of REEs [2,3] and the strict norms introduced by the state on REEs' export in 2011 significantly affected the global market through a reduction in REEs' availability and an increase in their price [1,3].

Under the current conditions, a viable alternative to cover the need for REEs is their recovery from industrial waste, including wastewater, and electrical and electronic compounds [3,5]. In addition, the recovery of REEs is determined by possible contamination of the environment, which might have a negative impact on aquatic organisms and even human health [3,6]. The toxic effects induced by REEs on soil, water organisms, as well as human health, are described in detail in several review papers [6–8].

Different technologies, including precipitation, ion exchange, electrochemical processes, flocculation, solvent extraction, and adsorption, have been routinely applied to recover REEs [1–3,9]. The mentioned techniques allow for high efficiency of REE recovery to be achieved; however, often, they have severe drawbacks, among which high costs, low selectivity and purity of the extracted elements, high consumption of reagents and energy, the creation of large volumes of sludge [2], and the use of materials derived from non-renewable resources can be mentioned [10]. These limitations do not allow us to consider the traditional techniques as environmentally-friendly approaches which correspond to green engineering principles.

Application of microbial biomass can be regarded as an alternative, cost effective approach for REEs' recovery from wastewater [11]. Among the biological approaches, biosorption and bioaccumulation have received special attention [10]. When looking at differences between processes, it should be highlighted that biosorption assumes REEs' removal mainly by using non-living biomass, while bioaccumulation uses only living organisms [12,13]. The biosorption process mainly occurs on the cell surface and includes several mechanisms of interaction: physical adsorption, complexation, ion exchange, and precipitation [14]. The bioaccumulation process is associated with metal ions transport across the cell membrane and accumulation inside the cells. Thus, the process is dependent on microorganisms' properties as well as the level of their adaptations and metal toxicity [12]. Biosorption in comparison with bioaccumulation does not require nutrients and energy sources and higher removal capacity can be achieved; in addition, the process is rapid and the biomass can be regenerated. Bioaccumulation is a more intricate and pricey process, which can be applied for bioremediation of large polluted territories, as well as to describe the mechanism of metal ions action on living organisms [12,13].

Microorganisms are actively applied for REEs' biosorption and bioaccumulation from aqueous solutions [11,15–18]. Among microorganisms, cyanobacteria have shown promising bioremediation properties for heavy metals, including REEs, which enable them to be used for bioremediation and metal recovery on an industrial scale [18–22]. However, according to the published information, there are no data on cyanobacteria use for Pr(III), a REE with numerous industrial applications, recovery from aqueous solution.

The basic aim of the present research was to assess the removal capacity of living and non-living *Arthrospira platensis* (*A. platensis*) biomass toward Pr(III). To achieve the goal of the study, the effect of different Pr(III) concentrations on living *A. platensis* biomass productivity, biochemical composition, and antioxidant activity was investigated. In the case of experiments with non-living biomass, the impact of Pr(III) concentration, pH, contact time, and temperature on biosorption capacity was monitored. In addition, to understand the mechanisms of Pr(III) adsorption, kinetic, equilibrium, and thermodynamic studies were performed.

2. Materials and Methods

2.1. Experiments with Living A. platensis Biomass

In experiments with living biomass (bioaccumulation), cyanobacteria *A. platensis CNMN-CB-02* from the collection of non-pathogenic microorganisms (IMB TU, Chisinau, Moldova) was cultivated in SP-1 medium [23]. Cultivation was performed using 100 mL Erlenmeyer flasks at pH 9–10, a temperature of 25–28 °C, and illumination of ~50 μM photons/m^2/s. On the first day of biomass cultivation, Pr(III) in concentrations of 10, 20, and 30 mg/L by metal was introduced to the medium, and the biomass was grown for six days.

On the sixth day, biomass separated by filtration was used for biochemical tests. Theconcentration of Pr(III) in the medium (at the beginning and end of the experiment) was determined using a inductively coupled plasma-atomic emission spectrometer (ICP-OES PlasmaQuant PQ 9000 Elite spectrometer, Analytik Jena, Jena, Germany).

The biomass used as the control was cultivated under the same conditions but without adding Pr(III) to the medium.

2.2. Experiments with Non-Living A. platensis Biomass

Experiments with the non-living biomass (biosorption experiments) were performed in order to define the influence of contact time, temperature, initial Pr(III) concentration, and pH on *A. platensis* biosorption efficiency. To prepare the Pr(III) solutions, $Pr(NO_3)_3 \cdot 6H_2O$ (Sigma Aldrich, Darmstadt, Germany) of analytical grade, soluble in water, and with strong mineral acids was dissolved in distillated water. For the biosorbent, *A. platensis* biomass grown in SP-1 medium [23] for six days was used. At the end of the cultivation cycle, the biomass was separated from the medium by filtration, washed several times with distillated water to remove the remnants of salt, dried at 105 °C, and homogenized. For the characterization of *A. platensis* using scanning electron microscopy and Fourier-transform infrared spectroscopy, the neutron activation analysis is presented in [24]. The zeta potential of the biomass was measured using Zetasizer Nano ZSP (Malvern).

To assess the influence of pH on Pr(III) removal, 0.1 g of dry biomass was mixed with 20 mL of solution containing Pr(III) in a concentration of 10 mg/L for 60 min. The pH of the experimental solutions was adjusted to the required values, 2.0–6.0, using 0.1 M HNO_3 or NaOH. To study the kinetics of the process, the samples were withdrawn at predetermined time intervals (3–120 min), maintaining the pH (3.0), the Pr(III) concentration (10 mg/L), the biosorbent dosage (0.1 g), and the temperature (22 °C) constant. To describe the thermodynamics of the process, the temperature of the solution changed from 20 to 50 °C, while the other parameters were kept constant: pH 3.0, Pr(III) concentration 10 mg/L, and time 60 min. In the equilibrium experiments, the concentration of Pr(III) changed from 10 to 100 mg/L, at a fixed pH (3.0), contact time (60 min), and temperature (22 °C). All experiments were performed in 50 mL Erlenmeyer flasks. The experimental solutions were mixed using a rotary shaker at 200 rpm, and at the end of experiment, the solution was filtered using 5–8 μm "White Ribbon Filter" (Sigma-Aldrich, Darmstadt, Germany), and the Pr(III) concentration was determined using the ICP-OES technique.

The adsorption capacity on *A. platensis* biomass and the efficiency of Pr(III) removal were determined using Equations (1) and (2):

$$q = \frac{V(C_i - C_f)}{m} \quad (1)$$

$$R = \frac{C_i - C_f}{C_i} \times 100 \quad (2)$$

where V is the volume of the Pr(III) solution, L; C_i and C_f are the initial and final Pr(III) concentrations in mg/L, respectively; and m is the weight of the *A. platensis*, g.

2.3. Biomass Productivity and Biochemical Tests

The biomass productivity, in g/L, was determined by recording the absorbance of the suspension at a wavelength of 750 nm based on the relationship between the cells' density and absorbance at the aforementioned wavelength. The cell density was transposed into weight based on an experimentally established calibration curve.

For the biochemical tests, the biomass was standardized at a concentration of 10 mg/mL and subjected to freezing–thawing three times. The content of protein was determined using Folin–Cioalteu reagent [23]. The protein content was calculated using a calibration curve for bovine serum albumin and expressed in % of biomass. The content of carbohydrates was determined based on the formation of hydroxymethylfurfural under the interaction

of carbohydrates with the Anthon reagent in acid medium [23]. The carbohydrate content was calculated using a calibration curve for glucose and expressed in % of biomass. The phycobiliproteins content was determined by measuring the absorbance of the supernatant at 620 nm for c-phycocyanin and 650 nm for allophycocyanin [23]. The lipid content was determined spectrophotometrically using phosphovanilinic reagent [25]. Calculation of the lipid content was performed according to the calibration curve based on oleic acid. The degree of lipid oxidation, the content of malondialdehyde (MDA), was determined based on reactive products of thiobarbituric acid, while the content of β-carotene and chlorophyll α was measured spectrophotometrically [23].

2.4. Statistical Analysis

The experiments were performed in three replicates. The biochemical tests included three measurements for each repetition. The values in the manuscript are presented as the average ± standard deviation. One-way analysis of variance (ANOVA) and Student's *t*-test were applied.

2.5. Data Analysis

The kinetics of the Pr(III) biosorption was described using three kinetics models (Equations (3)–(5)).

The pseudo-first-order model:

$$q_t = q_e\,(1 - e^{-k_1 t}) \tag{3}$$

The pseudo-second-order model:

$$q = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{4}$$

The Elovich model:

$$q_t = \frac{1}{\beta}\ln(1 + \alpha\beta t) \tag{5}$$

where q_t is the content of adsorbed Pr(III) (mg/g); t is time (min); k_1 (1/min) and k_2 (g/mg·min) are the pseudo-first-order and the second-order reaction rate equilibrium constants, respectively; and α (mg/g·min) and β (g/mg) are the constants of the Elovich model.

The equilibrium data are described using the Langmuir and Freundlich isotherm models (Equations (6) and (7)).

$$q_m = \frac{q_m\, bC_e}{1 + bC_e} \tag{6}$$

$$q_m = K_F C e^{\frac{1}{n}} \tag{7}$$

where C_e is the Pr(III) concentration at equilibrium (mg/L), q_m is the maximum adsorption capacity (mg/g), b(L/mg), and K_F and n are the Langmuir and Freundlich equation constants.

The separation factor R_L was estimated from Equation (8).

$$R_L = \frac{1}{1 + bC_i} \tag{8}$$

A $R_L < 1.0$ adsorption is favorable and $R_L > 1.0$ adsorption is unfavorable.

The thermodynamic parameters such as the standard free energy (ΔG°, kJ/mol), enthalpy change (ΔH°, kJ/mol), and entropy change (ΔS°, J/mol·K) were estimated from Equations (9) and (10):

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{9}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{10}$$

The distribution coefficient K_d was estimated from Equation (11):

$$K_d = \frac{(C_i - C_e)V}{mC_e} \quad (11)$$

where R is the universal gas constant (8.314 J K^{-1} mol^{-1}) and T is the temperature (K).

3. Results and Discussion

3.1. Praseodium Uptake by Living A. platensis and Its Effect on Biomass

Traditionally, from a biological point of view, REEs are considered non-essential elements since in most living organisms, they are not involved in the vital processes. The exceptions are some extremophile microorganisms for which some REEs, including Pr(III), are essential, with them being cofactors of homodimeric methanol dehydrogenase (MDH) [26]. At the same time, the biological activity of REEs is significant and is explained by the similarity (ionic radii and coordination numbers) with some essential elements, such as Fe, Zn, Ca, Mg, and Mn. In addition, REEs are characterized by the variability of ionic charges and the ability to form stable complexes with biomolecules, replacing essential metal ions. As a result of the action of REEs, the enzymatic activity and the functioning of membrane ion pumps can be altered [27]. REEs can act either as antioxidants or pro-oxidants, depending on the environment, the nature of the bonds in their compounds, and the concentration of the element [28]. Cyanobacteria and microalgae show a high affinity for REEs by accumulating them in significant amounts mainly due to their similarity with the elements essential for these organisms. Based on the above-mentioned information, it is assumed that *A. platensis* biomass has a high bioaccumulation capacity toward Pr(III), as well as certain changes in the biochemical composition of the biomass, especially in its antioxidant status. It is expected that these changes will follow a pattern similar to other lanthanides: La, Ce, Nd, and Sm. The results obtained in the present study partially confirmed the hypothesis.

A. platensis showed very high uptake capacity with respect to Pr(III). Regardless of the applied concentration, the efficiency of Pr(III) accumulation by the living biomass was higher than 99% (Figure 1).

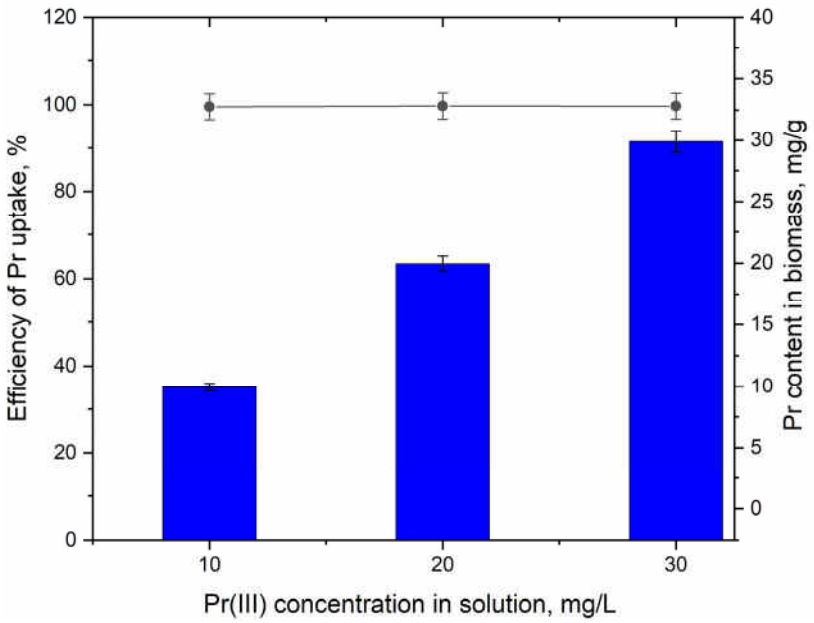

Figure 1. Efficiency of Pr(III) uptake by the living *Arthrospira platensis* biomass following its addition in the cultivation medium in concentrations of 10–30 mg/L.

Thus, following the introduction of 10 mg/L of Pr(III) into the medium, the efficiency of its uptake by the biomass constituted 99.6% (9.96 mg/g) and at concentrations of 20 and 30 mg/L—99.7% (19.9 and 29.9 mg/g, respectively). Pr(III) was not detected in the control biomass. It is considered that the phosphate groups of phospholipids, lipopolysaccharides, nucleic acids, polyphosphates, etc., play important roles in REEs' binding [29].

Through studying the influence of Pr(III) on biomass, it was observed that concentrations of 10 and 20 mg/L did not influence the biomass accumulated in the *A. platensis* culture during a growth cycle (Figure 2). At a metal concentration of 30 mg/L, a slight decrease in this parameter was observed. Although from a statistical point of view the amount of biomass decreased significantly, from a numerical point of view, this is an insignificant decrease, and the amount of *A. platensis* biomass was within the limits characteristic for this culture. The effect of Pr(III) on biomass was similar to that provoked by other REEs on the cyanobacterium *A. platensis*. Thus, it was demonstrated that Er, Eu, Sm, Tb, and Nd did not change the amount of *A. platensis* biomass produced during its growth in the medium supplemented with REEs [23–25,30].

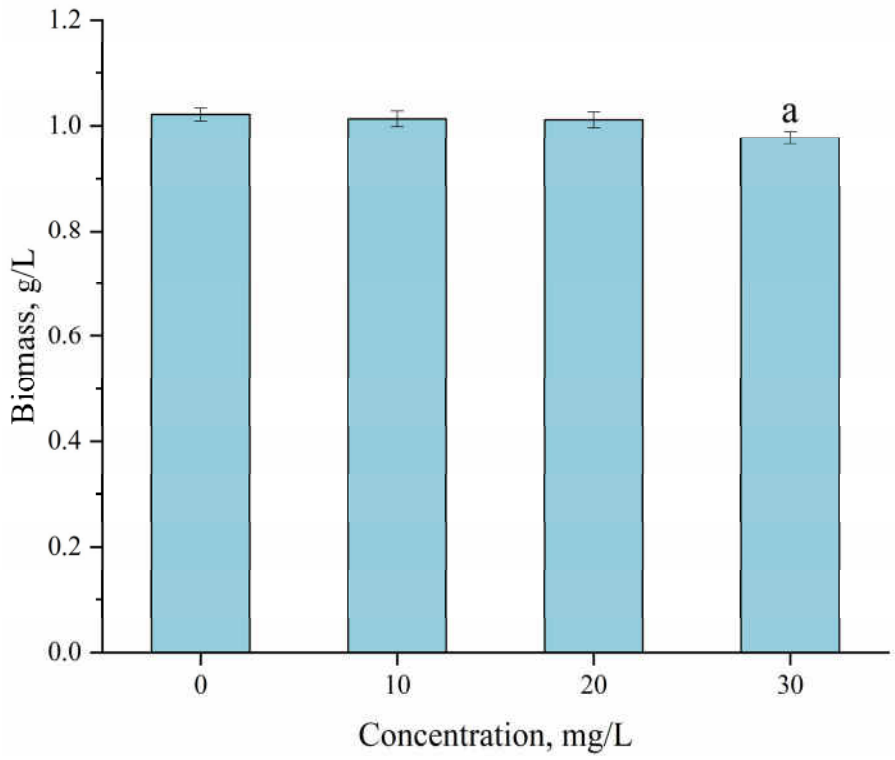

Figure 2. Effect of Pr(III) introduced to the cultivation medium in concentrations of 10–30 mg/L on the amount of *Arthrospira platensis* biomass (a—$p < 0.05$ for the difference between the sample and the control).

Very few studies have examined the effect of REEs on cyanobacteria, and frequently, the obtained results cannot be compared due to different experimental designs. Thus, in the case of Pr(III), there are only several publications that reflect its effects on photosynthetic microorganisms' growth and physiological processes. Goecke and co-authors [31], studying the modification of the lipid and pigments profiles of two microalgae, *Trachydiscus minutus* and *Parachlorella kessleri*, showed that 10 µM of Pr^{3+} did not cause a change in the cyanobacteria growth rate.

However, REEs are considered as elements with high biological activity toward microalgae and cyanobacteria. Their activity is determined by the REEs' properties (their ionic radius, coordination numbers, and ability to form stable complexes with biological molecules), which are very similar to those of some essential elements, such as Ca, Mn, Mg, Fe, and Zn [27]. In this regard, it is interesting to investigate Pr(III)'s impact on the biochemical composition of biomass and the content of its main components.

In Figure 3, the changes in the biochemical composition and antioxidant activity of *A. platensis* under the influence of Pr(III) introduced to the cultivation medium in different concentrations are presented.

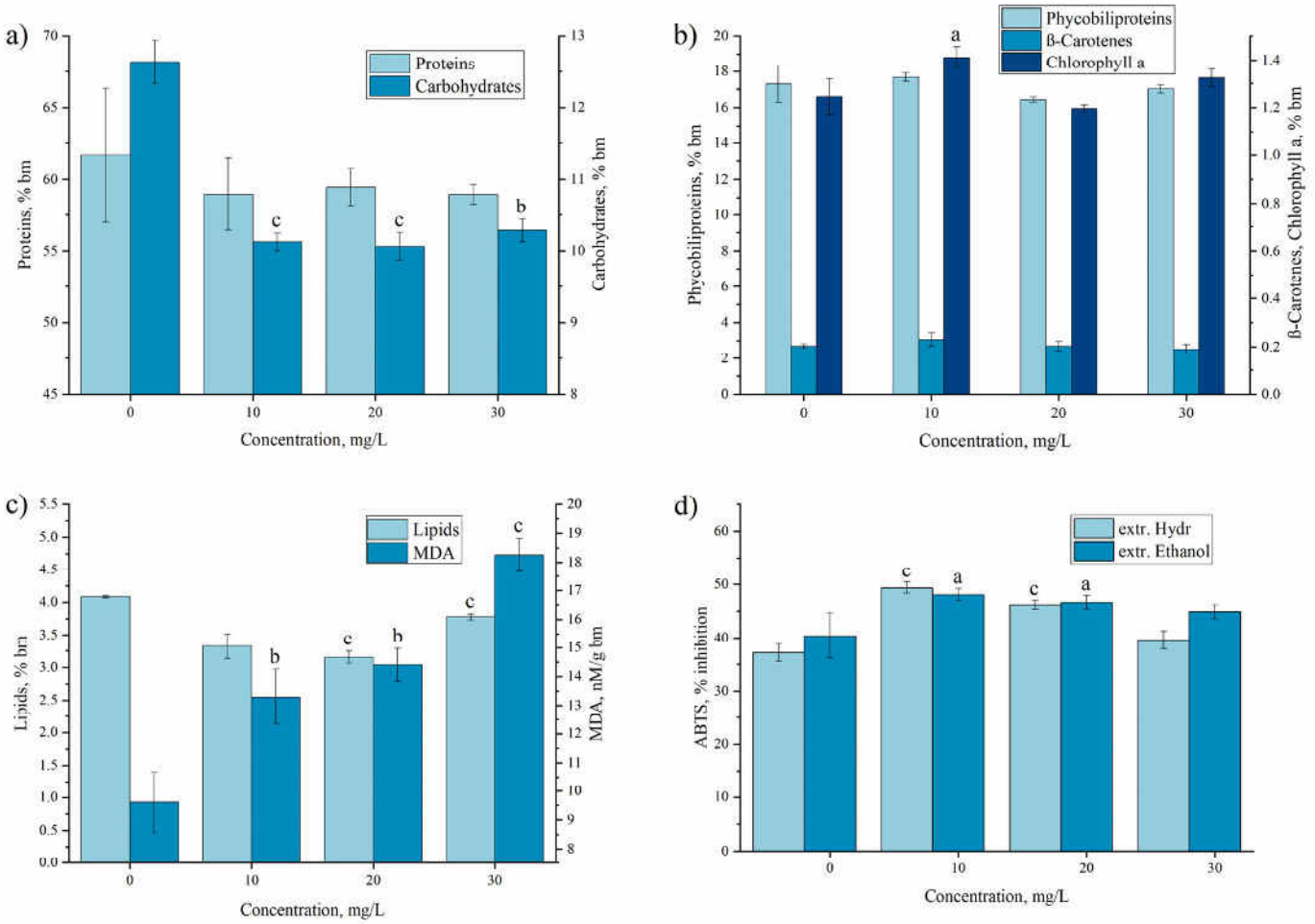

Figure 3. Effect of Pr(III) introduced to the cultivation medium in concentrations of 10–30 mg/L on the *Arthrospira platensis*: (**a**) content of proteins and carbohydrates (b—$p < 0.005$; c—$p < 0.001$ for the difference between the experiment and the control for carbohydrates); (**b**) content of phycobiliproteins, chlorophyll a, and β-carotene (a—$p < 0.05$ for the difference between the experiment and the control); (**c**) content of lipids and MDA (b—$p < 0.005$, c— $p< 0.0005$ for the difference between the experiment and the control); and (**d**) antioxidant activity of the extracts obtained from the biomass.

Supplementation of nutrient medium with Pr(III) did not influence the content of protein in *A. platensis* biomass, which varied between 58.95 and 61.65% of the dry biomass in the control and experimental variants, respectively, without statistically relevant differences (Figure 3a). To our knowledge, there are no published data referring to the influence of Pr(III) on the content of protein in cyanobacteria and microalgae; therefore, the obtained data were compared with the values reported for other REEs. It has been shown that depending on the REE and its concentration in the medium, the amount of protein in the spirulina biomass can either increase, decrease, or remain unchanged. For example, at Nd, Y, and Eu concentrations of 30 mg/L, the content of proteins in the *A. platensis* biomass was lower than in the control; while at the Yb concentration of 20 mg/L, the Nd concentration of 10 mg/L, and the Dy concentration of 30 mg/L, the biomass contained more protein compared to the control. In case of Er, the content of proteins was similar to the control biomass [23,25,30].

In the *A. platensis* biomass grown on medium supplemented with Pr(III), the content of carbohydrates (Figure 3a) was significantly lower compared to the control. Thus, at the applied Pr(III) concentration, a decrease of 18.7–20.4% compared to the control was

observed without significant differences as a function of the element concentration in the culture medium. This phenomenon has also been observed for other REEs. For example, in the case of the medium supplemented with Eu, Er, Nd, or Yb, the *A. platensis* biomass accumulated 15.8–36.7% less carbohydrates compared to the control [23–25,30]. However, the phenomenon cannot be considered as a general one, since Sm, Tb, La, and Dy, on the contrary, significantly increased the level of carbohydrates in *A. platensis* biomass [30].

The content of total phycobiliproteins (Figure 3b) in the control biomass was 17.3% of the dry biomass, and in the experimental samples, these values oscillated between 16.4 and 17.7% (Figure 3b). Such behavior is less typical for *A. platensis* culture. As has been shown previously, only Eu and Er did not cause a reduction in the amount of phycobiliproteins in *A. platensis* [23,25], while other REEs (Nd, Yb, Y, La, Dy, Sm, and Tb) led to a reduction of their content by 11–50% compared to the control. This parameter is considered as a clear indicator of metals toxicity for *A. platensis* [30]. Phycobiliproteins are characterized by high antioxidant activity and the decrease in their content under the action of different REEs can be associated with their involvement in the inhibition of free radicals. At the same time, on the higher plants, it was demonstrated that the antioxidant effect of Pr(III) can inhibit the oxidative process generated by oxidative stress of a different nature [32,33]. On the other hand, Pr(III) can form with glutathione, a complex with high antioxidant activity [34], which possibly stops the consumption of other cellular antioxidants, including phycobiliproteins. It is very likely that the antioxidant properties of Pr(III) ensure the preservation of a normal level of phycobiliproteins in the spirulina biomass.

The amount of chlorophyll α in the *A. platensis* biomass rose by 13.2% compared to the control at the Pr(III) concentration of 10 mg/L, while at the other concentrations, the value of this parameter did not change considerably (Figure 3b). The stability of the chlorophyll α content was characteristic for *A. platensis* biomass grown in the presence of other REEs (Nd, Yb, La, Dy, Tb, and Er), and only some of them influenced it. Thus, depending on the concentration, Y can induce an increase in the content of chlorophyll α (up to 20%), while Sm and Eu can induce a significant decrease in its content [23,25,30]. The content of β-carotene in the native biomass was 0.203% of the dry biomass, and in the experimental samples, it varied between 0.189 and 0.230% of the dry biomass, with the differences being statistically insignificant. This is in line with previously performed studies [23–25,30].

In the case of other phycological species, such as *Trachydiscus minutus* and *Parachlorella kessleri*, Pr(III) has certain visible effects on the photosynthetic pigments, which differ depending on the species. For example, in *Trachydiscus minutus* under the influence of Pr(III), a slight increase in the amount of β-carotene and chlorophyll was observed, while the amount of other carotenoids decreased considerably. In contrast, in *Parachlorella kessleri*, the content of all monitored photosynthetic pigments decreased considerably in the presence of Pr(III) [31]. Thus, as in the case of the other components of the phycological biomass, the influence of REEs is determined by several factors—the species on which the REE is applied, the element, and its concentration in the medium.

The content of lipids in the biomass obtained on the medium supplemented with Pr(III) was significantly lower compared to the control (by approximately 8–23% depending on the concentration of the element) (Figure 3c). This phenomenon has also been observed in previous research. Most of the studied REEs caused a reduction in the amount of lipids in the *A. platensis* biomass (e.g., Tb, Dy, Yb, and Eu) or did not significantly change this parameter (e.g., Sm and Nd) [25,30]. The modification of the lipid profile in the biomass due to the action of Pr(III) was observed in the case of other phycological species as well. For example, in *Trachydiscus minutus* and *Parachlorella kessleri*, although the total lipid content did not change significantly, a quantitative displacement in the direction of the accumulation of saturated fatty acids and a reduction in the amount of polyunsaturated ones was observed [31].

The amount of MDA in *A. platensis* biomass, an important marker of oxidative stress, increased under the influence of Pr(III) by 38.2–89.8% compared to the control, with the effect having a pronounced dose-dependent character. The increase in the MDA levels

in *A. platensis* biomass grown on medium containing REEs has also been observed in other experiments. Thus, the content of MDA in *A. platensis* biomass increased under the influence of La, Dy, Sm, Nd, Yb, Eu, Er, and Y; in some cases, even doubling of the value of this parameter was observed [24,25,30].

REEs can affect the stability, permeability, and function of cell membranes by blocking ion channels and binding to specific membrane proteins. The instability of cell membranes leads to intense oxidative degradation of the lipids that make up their composition. It is clear that the significant increase in MDA in the biomass of *A. platensis* under the influence of Pr(III) is due to the oxidation of lipids, primarily membrane lipids, but the exact mechanism of this phenomenon is not known. A possible explanation for this phenomenon could be the replacement of iron by Pr(III) and the release of ions capable of inducing lipid oxidation through Fenton and Haber–Weiss reactions. As a result, the amount of end products of lipid oxidative degradation, including MDA, increased.

The antioxidant activity of the ethanolic and water extracts obtained from biomass cultivated in the presence of Pr(III) can be seen in Figure 3d. Both types of extracts had very similar antiradical activity against the ABTS cation radical. The extracts of both types obtained from the biomass grown in the presence of 10 and 20 mg/L of Pr(III) were more active than those from the control biomass. The highest increase in the activity of the water extract compared to the control was attested at the Pr(III) concentration of 10 mg/L, with the extract being 32.7% more active against the ABTS cation radical. At the Pr(III) concentration of 20 mg/L, the water extract was 24.2% more active compared to the control, while in the case of the highest Pr(III) concentration, the value was comparable to the control. For the ethanolic extracts, the same change pattern was observed; however, the increase in its values compared to the control was more modest—by 18.8% at the concentration of 10 mg/L and by 15.4% at the concentration of 20 mg/L. The ABTS test values were inversely proportional to the MDA values. Under stress conditions, cells rapidly produce components with antioxidant properties, which determine the activity of biomass extracts. The more pronounced the state of stress, the more intensely the antioxidant compounds are consumed, and under severe stress, cells lose their ability to counteract this process.

In the previously performed studies, changes in the antioxidant activity of *A. platensis* grown on medium supplemented with REEs were also observed. Thus, addition of the Eu, La, Dy, Sm, and Tb resulted in the growth of antiradical activity, while Nb and Yb led to a considerable decrease in ABTS radical inhibition activity [23,30].

3.2. Praseodium Removal by Non-Living A. platensis Biomass under Different Experimental Conditions

Metal removal by non-living biomass, biosorption, is a complex process affected by several factors. Among them, pH is a critical parameter, since it influences the chemistry of the metals and the surface charge of the functional groups [35]. *A. platensis* had an isoelectric point at pH 2.85; this suggests that the positive charge of the cell surface was maintained until this pH value; then, the charge of the biosorbent surface became negative [36]. The results presented in Figure 4a confirm this fact. Thus, at pH 2.0, 38% of Pr(III) was removed from the solution. With a strong acidic pH in the solution, a high concentration of H^+ ions hampers Pr(III)'s removal due to competition for binding sites [37]. The increase in the pH from 2.0 to 3.0 resulted in the achievement of maximum Pr(III) removal of 73%, while a further increase in the pH value resulted in a continuous decrease in removal efficiency. The increase in the pH value and the decrease in concentration of H^+ ions facilitate interaction between Pr(III) and negatively charged functional groups on the *A. platensis* surface [23,25,37,38]. It is known that at pH values pH $\leq$ 5, lanthanides exist as Ln^{3+} [37]. A reduction in Pr(III) removal can be associated with the competition of OH and Pr(III) for binding sites as well as the formation of $Pr(OH)_3$ at pHs higher than 5.0.

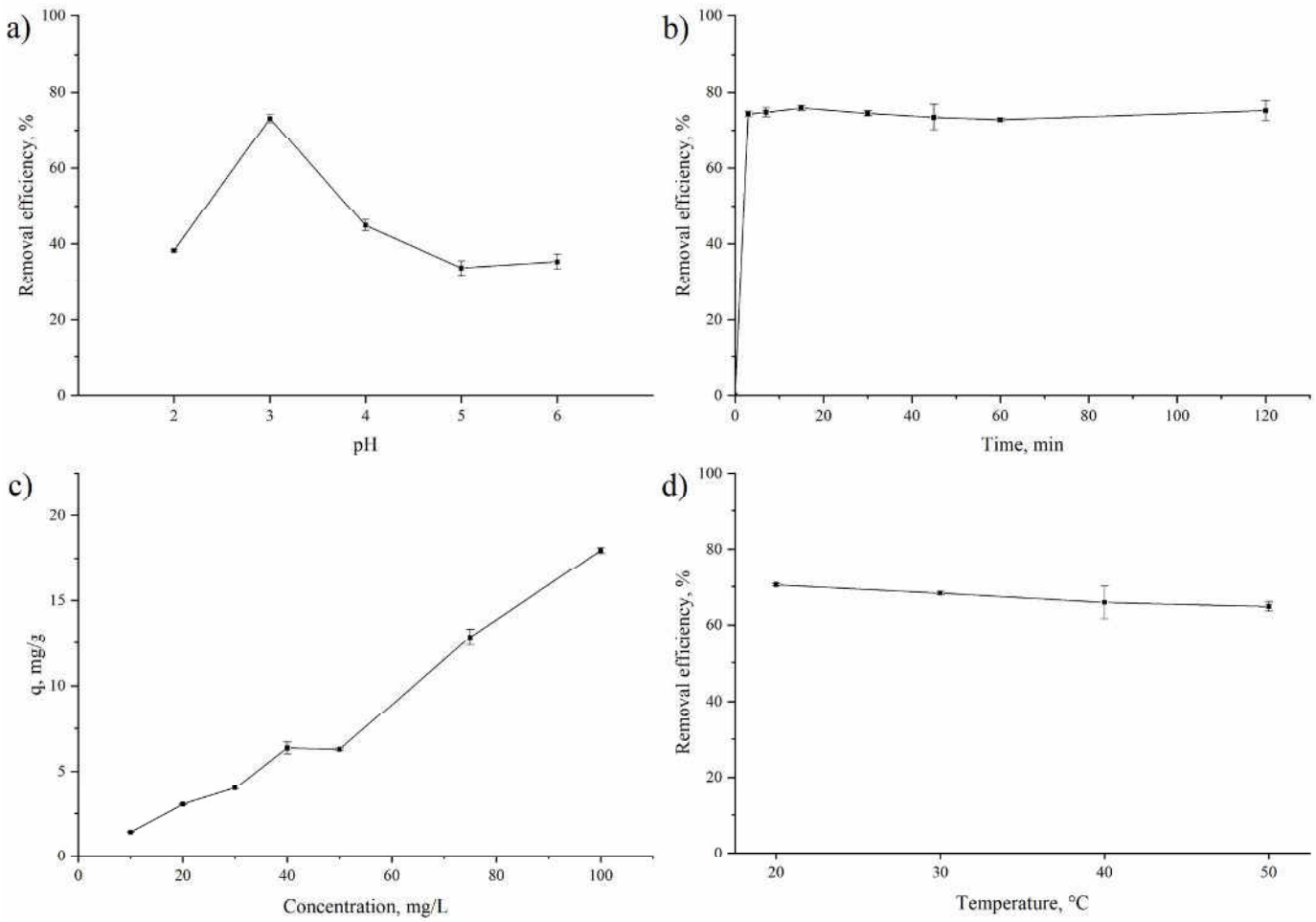

Figure 4. Effect of the experimental parameters on Pr(III) removal by *A. platensis*: (**a**) pH; (**b**) contact time; (**c**) initial Pr(III) concentration; and (**d**) temperature.

The maximum Pr(III) adsorption on the brown seaweeds Turbinaria conoides and Sargassum wightii [38] and green algae Ulva lactuca [39] was attained at pH 5.0, and this was accompanied by the replacement of some of the alkaline earth metals through the ion-exchange mechanism [38]. The maximum adsorption of Pr(III) on D72 resin was achieved at pH 3.0 [40], and on TVEX–PHOR resin, this was achieved at pH 3.5 [41].

Figure 4b shows the effect of the contact time on the efficiency of Pr(III) removal. The process of Pr(III) removal was very quick; 74% of the ions were absorbed from the solution in the first 3 min of the interaction, and then, equilibrium was attained. The biosorption of Pr(III) on Turbinaria conoides and Sargassum wightii with 90% of total biosorption took place within 20 min [38]. The rapid uptake of Pr(III) is explained by the availability of a large number of binding sites on the biomass at the initial stage of biosorption. Lowering of the process is usually associated with occupancy of the binding sites [40,42].

The kinetics of Pr(III) biosorption on *A. platensis* was analyzed using pseudo-first-order, pseudo-second-order, and Elovich models (Figure 5a, Table 1).

Table 1. The parameters of the kinetics models applied to describe Pr(III)'s biosorption on *A. platensis*.

Pseudo-First-Order			Pseudo-Second-Order			Elovich		
qe	**k_1**	**R^2**	**q_e**	**k_2**	**R^2**	**α**	**β**	**R^2**
1.43	2.13	0.999	1.43	26.5	0.998	3.96×10^{-43}	75.2	0.997

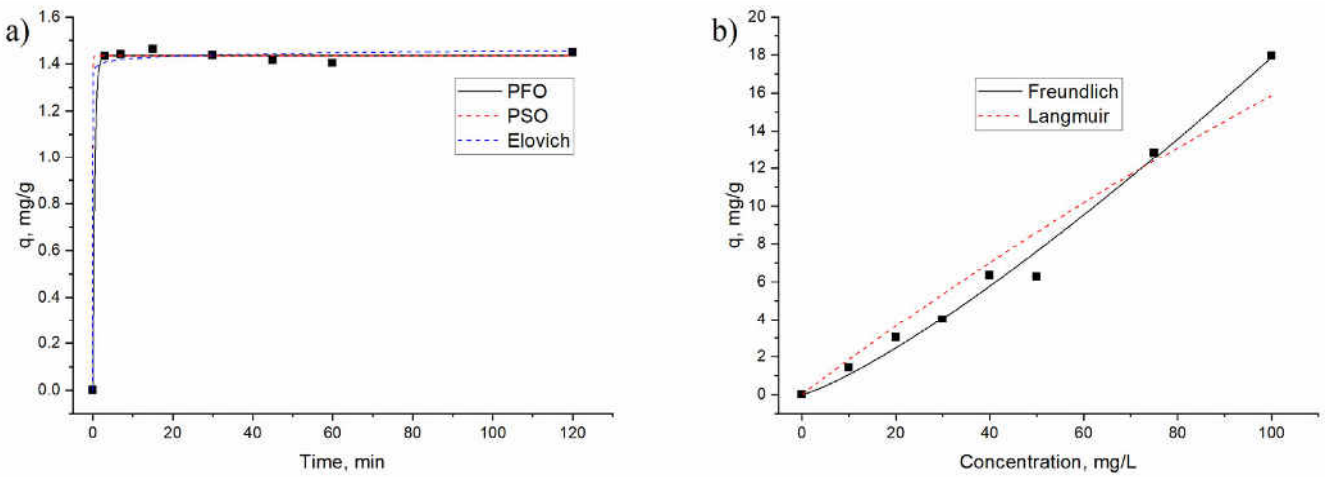

Figure 5. (**a**) Kinetics and (**b**) equilibrium of Pr(III) biosorption on *A. platensis*.

According to the R^2 values, all of the applied models can adequately describe the kinetics of sorption. However, the extremally low values of the coefficient α in the Elovich model shows its unsuitability for the description of the experimental data. The close values of the adsorption capacity (calculated and obtained experimentally) as well as the R^2 for the pseudo-first-order and pseudo-second-order models were very close indicates their relevance for explanation of the experimental data. However, according to the Akaike information criterion (AIC) test, the pseudo-first-order model was more appropriate to describe the kinetics data. The model suggests that the rate of adsorption is proportional to the number of unoccupied sites on the sorbent surface [43]. The model also assumes that the mass transfer controls the adsorption process due to a concentration difference between the adsorbent surface and the solution [44]. Furthermore, it is considered that in this case, chemisorption can inhibit the sorption kinetics due to the fact that chemical reactions and the diffusion of the liquid in the boundary layer can lead to resistance to mass transfer [43,45]. At the same time, the pseudo-second-order rate constant of 26.5 g/mg min for Pr(III) biosorption on *A. platensis* was considerably higher than the rate constant of the first-order kinetics (2.13 min^{-1}), suggesting that Pr(III) requires less time to achieve adsorption equilibrium [46].

The influence of Pr(III) concentration on *A. platensis* biosorption capacity was investigated in the range of 10–100 mg/L (Figure 4c). The adsorption efficiency increased as the concentration of Pr(III) in the solution grew, and the highest adsorption capacity of 17.0 mg/g was achieved at 100 mg/L. The high initial concentration of Pr(III) contributed to the higher number of Pr(III) ions in the aqueous solution, which led to a greater number of interactions between Pr(III) and the available binding sites. Additionally, a higher initial Pr(III) concentration may facilitate metal ions adsorption by enhancement of the mass transfer coefficient, along with providing the driving force to overcome the mass transfer resistances between the solid and liquid phases [47,48]. It should be mentioned that *A. platensis* maintained high removal efficiency at all studied Pr(III) concentrations.

The Lagmiur and Freundlich models were applied for studying the nonlinear adsorption of Pr(III) on *A. platensis* (Figure 5b, Table 2). The Freundlich model, according to the higher R^2 value, was shown to be more applicable for the description of the experimental data. The n value of 1.2 indicated heterogeneity in the biosorbent surface and the favorable adsorption of Pr(III) [36,40]. Since the Freundlich isotherm model suggests that adsorption takes place on heterogeneous surfaces as a multilayer adsorption [5,41], it can be expected that there is favorable adsorption of Pr(III) onto the heterogeneous surface of *A. platensis* with a variety of binding sites. In this case, the sorption process is not restricted to one specific class of sites [41]. A large number of the functional groups which can participate in Pr(III) biosorption, including C=O, C-C, C-O-C, P=O, CH_2, and NHC(O) have been identified on the surface of *A. platensis* [25]. Since these functional groups include nitro-

gen and/or oxygen, which aid in the formation of hydrogen bonds between Pr(III) and cyanobacteria surface, they can facilitate the biosorption process [46]. The sorption of Pr(III) is also possible through ion exchange between Pr(III) and Ca(II) as well as other cations including Na, K, and Mg [42].

Table 2. The parameters obtained by fitting the experimental data with the isotherm models used.

Langmuir			Freundlich		
q_m	b	R^2	K_f	n	R^2
99.3	0.0019	0.952	0.062	1.2	0.99

The lower values of R^2 obtained for the Langmuir model showed that it did not fit well to the adsorption data. The maximum theoretical predicted adsorption of Pr(III) onto *A. platensis* constituted 99.3 mg/g, and this is higher than the values reported for other sorbents: 57.8 mg/g for crab shell and 49.9 mg/g for orange peel [45] and 30.0 mg/g for Dowex 50WX8 resin [49]. The capacity was comparable with the values obtained for Laminaria digitate (110–120 mg/g) [50] and lower than the values obtained for D72 resin (294 mg/g) [40]. The separation factor values ranged from 0.84 to 0.98, pointing at favorable Pr(III) biosorption. The calculated maximal absorption capacity (Table 2) was greater than the experimentally obtained value (17 mg/g), suggesting that the biosorption of Pr(III) onto *A. platensis* might occur at higher concentrations of the element [46].

Thus, the mechanisms of Pr(III) biosorption by *A. platensis* may include electrostatic interaction between Pr(III) and the negatively charged functional groups on the *A. platensis* surface, ion exchange, or chemical biosorption [36,46].

The effect of temperature on the adsorption of Pr(III) on *A. platensis* has been examined at temperatures in the range of 20–50 °C. It was observed that the sorption of Pr(III) slightly decreased with the increasing temperature, from 70% at 20 °C to 65% at 50 °C (Figure 4d). Next, from the slope and intercept of the plot (Figure S1), the values of ΔH° and ΔS° were calculated, while ΔG° was evaluated from Equation (11). The obtained parameters are listed in Table 3.

Table 3. Thermodynamic parameters for metal biosorption on *A. platensis*.

Temperature K	ΔG° kJ/mol	ΔH° kJ/mol	ΔS° J/mol
293	−15.0	−7.0	27.4
303	−15.3		
313	−15.6		
323	−15.8		

As shown in Table 3, the values of ΔG° ranging from −15.0 to −15.8 kJ/mol suggest that adsorption is a physical process [41]. The negative value of ΔG° indicates the spontaneous and thermodynamical feasibility of the process. The negative value of ΔH° suggests the exothermic type of the sorption, and the value is typical for physisorption [9]. Positive values of ΔS° shows that Pr(III) biosorption is associated with the displacement of more than one water molecule as a result of the increase in entropy [9].

Application of *A. platensis* in the form of waste from different biotechnological processes will make the process of Pr(III) removal efficient and economically viable. The use of mineral and organic acids, as shown in our previous studies [51,52], will make it possible to regenerate the biosorbent and to apply it for several sorption–desorption cycles.

4. Conclusions

Living and non-living *A. platensis* biomass showed high affinity toward Pr(III). The high rate of Pr(III) uptake by the living biomass (9.96–29.9 mg/g) was accompanied by

a reduction in the amount of lipids and carbohydrates and overaccumulation of malonic dialdehyde. The biomass productivity and the content of proteins and pigments were maintained on the level of the control biomass. The changes observed in the Pr-supplemented biomass indicate a state of oxidative stress for the *A. platensis* culture, caused by the presence of Pr(III) in the medium. Pr(III) removal by the non-living biomass was a quick and pH-dependent process. The maximum biosorption of 99.3 mg/g was attained at pH 3.0 within 3 min of sorbent interaction with the sorbate. The pseudo-first-order and Freundlich models explained better te kinetics and equilibrium of Pr(III) biosorption. Thermodynamically, Pr(III) biosorption can be described as a spontaneous exothermic process. *A. platensis* biomass has great potential to be applied as a biosorbent and/or bioaccumulator for Pr(III) recovery from wastewater.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w15112064/s1. Figure S1: Plot of $\ln K_d$ versus 1/T.

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