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Study of selected metals biosorption by *Arthrospira platensis* using neutron activation analysis

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ABSTRACT

The cyanobacterium *Arthrospira platensis*, previously called spirulina, is a well-studied biological entity with a wide range of possible physiological, biochemical, genetical, biotechnological and ecological uses. This study assessed the efficiency of zinc, iron, copper, cobalt and chromium ions biosorption by *Arthrospira platensis* biomass in single- and multi-component systems through the use of epithermal neutron activation analysis. The affinity of biomass for studied elements in single- and multicomponent system was Cu(II) > Zn(II) > Co(II) > Fe(III) > Cr(IV) and Cu(II) > Co(II) > Zn(II) > Fe(III) > Cr(IV), respectively. Additionally, alterations in the elemental content of spirulina biomass under metal loading were observed. *Arthrospira platensis* biomass can be efficiently applied to remove metal from complex industrial effluents.

Keywords: Elemental content; Metals; Neutron activation analysis; *Arthrospira platensis*; Biosorption

1. Introduction

Heavy metals represent a group of chemicals whose toxicity is a problem of increasing significance for ecological, evolutionary, nutritional and environmental reasons [1]. Metal compounds are widely applied in mining, electronics, metallurgical, electroplating, petrochemical, nuclear, chemical and textile industries, and paint production [2]. Living organisms require trace amount of heavy metals such as iron, zinc, copper and cobalt which are involved in a wide range of biochemical reactions. However, these elements become toxic at excessive amounts. Other elements such as mercury and cadmium have no biological function and even in trace amounts, they can cause serious disturbances in living organisms. Sometimes they act as a pseudo-element of the cell while at certain times they may even interfere with metabolic processes [1]. Therefore, it is important to remove metal ions from industrial effluents before their discharge in natural water bodies.

Since the microorganisms require metals for vital activity they have developed several mechanisms of metal recovery from aqueous solutions. First stage of these processes – biosorption occurs in the presence of different functional groups: hydroxyl, phosphate, amino, carboxyl, sulfhydryl associated with cell wall components such as peptidoglycans, teichuronic acids, teichoic acids, polysaccharides and proteins [3]. Formation of complexes between metal ions and functional groups on the cell surface permits to uptake metal ions to the amounts 10-fold higher than in control cells.

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Cyanobacteria belong to the organisms, which can be used as sorbents [4]. Cyanobacteria are a large and morphologically diverse group of phototrophic prokaryotes, which are found in a diverse range of habitats oceans and fresh water, bare rock and soil, hot springs and hydrothermal vents, and even in the Arctic under ice [5]. Among cyanobacteria, *Arthrospira platensis* has drawn more attention because of high nutritional content [6,7]. *Arthrospira platensis'* ability to accumulate chemical elements in high concentration and convert them into nontoxic organic form gives an opportunity to obtain biomass enriched with the essential elements [8–11]. Additionally, due to *A. platensis'* high sorption capacity, its biomass is increasingly used to develop new biosorbents for metal removal from batch solutions and complex industrial effluents. Seker et al. [12] studied the biosorption of lead(II), cadmium(II) and nickel(II) ions from aqueous solution by *A. platensis* biomass. The effect of pH, contact time, temperature, concentration of copper and dry biomass on copper biosorption by *Spirulina platensis* was studied by Al-Homaidan et al. [13]. Zinicovscaia et al. [14–16] investigated zinc, chromium and nickel removal from aqueous solution as well as complex industrial effluent produced by electroplating industry. Interest for spirulina use as biosorbent is mainly associated with its high availability, easy growth conditions, rapid kinetics of heavy metal recovery and applicability for complex solution treatment [12,17]. Cyanobacteria play an important role in the treatment of aqueous solutions containing heavy metals in concentrations below 100 mg/L [14].

Numerous investigations have shown efficient application of *Arthrospira platensis* biomass for metal and radioactive ions (cations), uptake from single-metal systems [18,19]. At the same time, many toxic compounds in the environment are present as anions. Study of metal removal from complex solution is important, since in nature the metallic ions are rarely found in isolation.

In the present study, non-destructive epithermal neutron activation analysis (NAA) was used to investigate: (i) the potential of spirulina biomass for cations (Zn^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}) and anion ($Cr_2O_7^{2-}$) uptake from single- and multi-component systems; (ii) the changes in the elemental composition of cyanobacteria under studied metal ions loading. Selection of zinc, cobalt, copper, iron and chromium ions for this study was determined by their abundancy in industrial effluent from a wide range of industrial processes. Metal uptake by spirulina biomass was traced using high sensitive NAA. NAA is an analytical technique, characterized by high sensitivity, good selectivity, good accuracy, independence of matrix effects, non-destructive nature; possibility of simultaneously determining a large number of elements; independence of the results of the form of chemical compounds, easy samples preparation [20]. NAA has been found to be very useful in the determination of trace and minor elements in biological samples [7,9,16].

2. Materials and methods

2.1. Materials

2.1.1. Reagents

For the batch experiments, Merck (Darmstadt, Germany) reagents: $ZnCl_2$, $CuSO_4{\cdot}5H_2O$, $FeCl_3$, $CoCl_2{\cdot}6H_2O$ and K_2CrO_4 of analytical grade were used.

2.1.2. Biosorbent preparation

We have used, *A. platensis* CNMN – CB-11 (strain from National Collection of Nonpathogenic Microorganisms, Institute of Microbiology and Biotechnology of the Academy of Science of Moldova). Cells of *A. platensis* were cultivated in an open-type tank with a volume of 60 L in the SP-1 nutritive medium [21] at 32°C–35°C, 37–55 μmoles of photons/m^2/s, pH 8–9 and at constant mixing. On stationary growth phase (6th day of cultivation), the cyanobacteria biomass was separated from the culture medium by vacuum filtration and rinsed with distilled water. Obtained wet biomass was used in biosorption experiments.

2.1.3. Biosorption experiments

Biosorption experiments were performed for copper(II), cobalt(II), zinc(II), iron (III) and chromium (VI) ions in both single- and multi-metal systems. Experiments were carried out in batch mode, at equal salt concentrations 100 mg/L at 23°C, pH 6.3 (single-metal systems) and pH 6 (multi-metal system), and biomass amount of 1 g. The biosorption experiments were conducted in Erlenmeyer flasks containing 100 mL of metal solutions and spirulina biomass in 250-mL glass flasks on a rotary shaker set at 200 rpm. The contact time of 30 min was evaluated for *A. platensis* biomass based on our previous research [14–16].

After the experiments were conducted, the biomass was filtered, washed and dried until the constant weight. The resulting samples were packed in polyethylene bags and aluminum cups for NAA.

The biomass separated from culture medium, washed and re-suspended in distilled water served as the control. All the experiments were conducted in triplicate and the averages of the measurements for each treatment were used.

2.1.4. Neutron activation analysis

To determine the elemental content of the *A. platensis* biomass, NAA at the pulsed fast reactor IBR-2 (FLNP JINR, Dubna, Russia) was used. The description of the irradiation channels and the pneumatic transport system REGATA of the IBR-2 can be found in the Frontasyeva review [20].

To determine short-lived isotopes (Ca, Cl, Mg, Cu, Mn), samples were irradiated for 3 min under a thermal neutron fluency rate of approximately 1.6×10^{13} n cm^{-2} s^{-1} and measured for 15 min. In the case of long-lived isotopes (As, Ba, Br, Cr, Co, Fe, K, La, Na, Rb, U, Sr, Zn), the samples were irradiated for 4 d under a thermal neutron fluence rate of approximately 5×10^{11} cm^2 s^{-1} and their activity was then measured in 4 and 20 d, respectively. γ-Ray spectra were measured using a large-volume high purity germanium detector with a resolution of 1.96 keV for the 1,332.4-keV line of ^{60}Co.

National Institute of Standard and Technology (NIST, Gaithersburg, MD, USA) certified reference materials: SRM 1633b (constituent elements in coal fly ash), SRM 2709 (San Joaquin soil), and NIST certified reference materials SRM 1570a (spinach leaves) and SRM 1575a (pine needles) were used to calibrate the NAA measurements. The difference between certified and measured content of elements of the certified material varied between 1% and 10%.

3. Results and discussion

Biosorption depends on pH, metal concentration, interaction time, etc. pH of the solution is an important parameter for both chemical properties of metals and surface characteristics of biosorbent. At low pH values, H^+ ions competed with metal ions for the biosorption sites, thus the biomass biosorption capacity for cations is usually very low. However, this biosorption capacity increases at higher pH (from 4.0 to 6.0), because increasing of negative charges on the cells surface creates more metal binding sites [22]. In several studies it was shown that 4–6.5 pH range is optimal for metal biosorption [17,22,23]. The pH in studied system was not adjusted to certain values. It was in the range 6.0–6.3 after dissolving of metal salt and addition of spirulina biomass.

Experiments were carried out in six systems – five single-component ones (for each metal) and one multi-component. The results in Fig. 1 show the biosorption of zinc, iron, cobalt, copper and chromium ions by spirulina biomass from single- and multi-component solutions during 30-min experiments.

During the experiment, spirulina biomass accumulated 55% of zinc from solution, and its content in biomass increased from 34 to 2,640 μg/g. Obtained results support previous study of zinc uptake by spirulina biomass at different concentration of zinc in solution [15]. The effectiveness of copper removal was 91%, (its content in biomass increased from 30 to 2,340 μg/g). This coincides with Al-Homaidan et al. [13] data, who showed that during 90 min 90.6% of copper was sorbed by *Spirulina platensis* biomass from the solution with

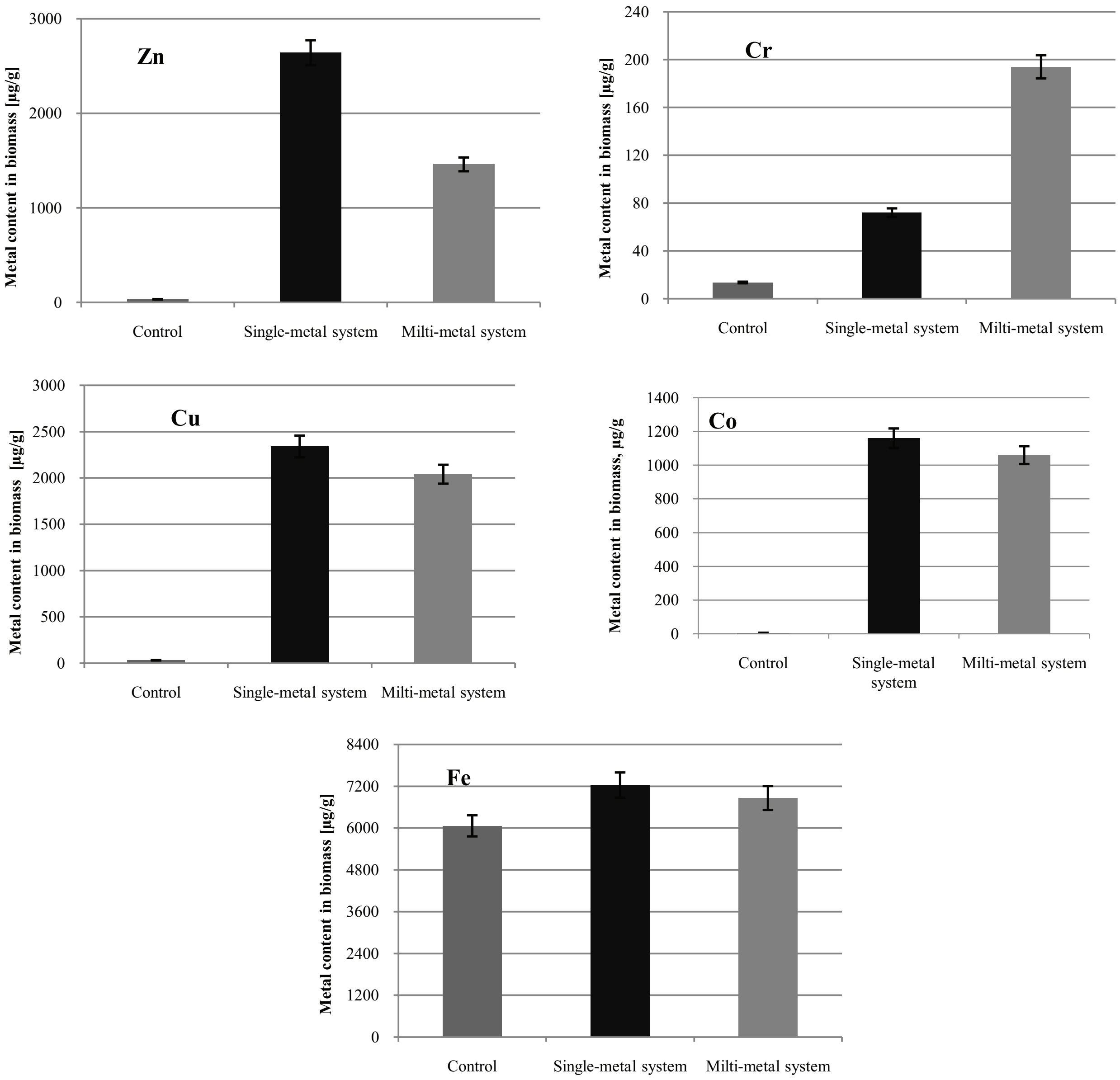

Fig. 1. Zn, Cr, Cu, Co and Fe content in *A. platensis* biomass as a result of biosorption (interaction time – 30 min, pH 6.3 [single-metal solutions], pH 6.0 [multi-component solution]).

copper concentration 100 mg Cu/L. High *S. platensis* affinity for copper ions was shown by Vannela and Verma [17]. Kiran and Thanasekaran [24] have shown that cyanobacterium *Lyngbya putealis* can be used for removal of copper from effluents discharged by electroplating industry that usually have up to 50 mg/L. In case of cobalt and iron their content in biomass increases by 46% and 34%, respectively, in comparison to the control. The efficiency of their uptake from solution was different whereas copper, zinc and cobalt at pH 6.3 are presented in solution in cationic forms.

Biosorption of metal includes several processes: metal binding to functional groups, ion exchange and microprecipitation. The difference in metal biosorption can be explained by their preference for binding sites on the spirulina surface. From IR spectroscopy, analysis presented in our previous works it is known that spirulina contains OH, COO–, C=O, NH, CH, CC/CO, C–O–C and P=O groups in cell wall [14]. At pH 6.3 copper ions bind to carboxylate, amine and hydroxyl groups. Zn and Co ions bind predominantly to carboxyl groups [2,25]. However, Fe(III) and Cu(II) do not coordinate to the carboxylate groups. Gerlach et al. [26] have found that OH groups play the main role in iron ions binding. Low iron biosorption can be also explained by its presence at pH > 4 mainly in $Fe(OH)_3$ form and the amount of Fe^{3+} ion is very small [27]. Microprecipitation is also a possible mechanism of iron biosorption.

The lowest uptake (2%) was observed for chromium. Chromium was present in solution in anionic form. $Cr_2O_7^{2-}$ form is predominant in a low pH and high chromium concentration conditions, whereas CrO_4^{2-} is the most abundant forms at pH higher than 6.5 [28]. The amount of positively charged functional groups at pH 6 is negligibly small. Thus, the efficiency of chromium biosorption is very low.

In multi-component system, due to the presence of co-ions in the solution, the effectiveness of metal uptake changed. The cobalt content was approximately the same as in single-component system (1,060 μg/g), indicating high affinity of *Arthrospira platensis* cells toward cobalt ions. Zinc, iron and copper contents were reduced by 11%, 12% and 12%, respectively, compared with single-metal systems. At the same time, the content of chromium increased by 3.4%. In complex systems, the effectiveness of metal uptake depends on electronegativity, ionic radius, potential, redox potential of these metals, and preference for the ligand binding sites [29]. The reduction of metal uptake may be associated with preference of metal ions for the same binding sites onto the surface or by

Table 1
Content of macro- and microelement in metal-loaded spirulina biomass

Element	Control	Single-component systems					Multi-component system
		Zn-spirulina	Co-spirulina	Fe-spirulina	Cr-spirulina	Cu-spirulina	
	Concentration of macroelements, mg/g						
Na	17.6 ± 0.9	4.3 ± 0.2	2.5 ± 130	2.7 ± 0.1	2.6 ± 0.1	2.6 ± 0.1	2.4 ± 0.1
Mg	4.7 ± 0.1	4.6 ± 0.1	3.6 ± 0.1	3.5 ± 0.1	4.5 ± 0.145	4.1 ± 0.12	0.8 ± 0.02
Cl	6.3 ± 0.4	0.5 ± 0.03	0.2 ± 0.01	0.4 ± 0.02	0.3 ± 0.02	0.3 ± 0.02	0.3 ± 0.02
K	15.7 ± 1.4	8.3 ± 0.7	11.1 ± 1	11.1 ± 1	11.1 ± 1	10.2 ± 0.9	8.1 ± 0.7
Ca	20.7 ± 1	20.4 ± 1.1	17.8 ± 0.9	20.6 ± 1	22 ± 1.1	21.7 ± 1	13.7 ± 0.7
	Concentration of microelements, μg/g						
Cr	13 ± 1.5	13 ± 1.3	12 ± 1.7	16 ± 1.6	72 ± 3.6	17 ± 4.8	194 ± 9.7
Mn	183 ± 5.5	210 ± 6.3	166 ± 5	205 ± 6.1	198 ± 6	203 ± 6.1	1,120 ± 44.8
Fe	6,060 ± 303	6,930 ± 346	6,580 ± 329	7,230 ± 360	6,820 ± 341	6,660 ± 333	6,860 ± 340
Co	0.2 ± 0.02	3 ± 0.2	1,160 ± 58	0.7 ± 0.05	0.2 ± 0.02	0.3 ± 0.02	1,060 ± 40
Zn	34 ± 1	2,640 ± 132	177 ± 5.3	40 ± 1.2	38 ± 1.1	37 ± 1.1	1,460 ± 73
Cu	30 ± 2	n.d	n.d	n.d	n.d	2,340 ± 120	2,040 ± 100
As	0.3 ± 0.02	0.3 ± 0.02	0.3 ± 0.03	0.3 ± 0.02	0.3 ± 0.2	0.4 ± 0.03	0.3 ± 0.03
Br	2.3 ± 0.05	1.7 ± 0.03	1.5 ± 0.03	1.4 ± 0.03	1.4 ± 0.03	1.5 ± 0.03	1.3 ± 0.4
Rb	0.7 ± 0.2	0.3 ± 0.2	0.5 ± 0.4	n.d	0.7 ± 0.2	0.6 ± 0.2	n.d
Sr	318 ± 25	373 ± 30	381 ±3 0	344 ± 27	355 ± 28	362 ± 29	236 ± 19
Ba	37 ± 4	49 ± 7	171 ± 26	40 ± 5	46 ± 6	41 ± 5	46 ± 7
La	0.1 ± 0.04	0.1 ± 0.04	0.1 ± 0.04	0.08 ± 0.02	0.1 ± 0.04	0.08 ± 0.02	n.d.
U	0.04 ± 0.003	0.05 ± 0.002	0.06 ± 0.006	0.05 ± 0.002	0.05 ± 0.002	0.05 ± 0.002	0.05 ± 0.005

the phenomenon of negative cooperation. Increase of chromium content can be explained by pairing of chromium ions charge with charges of cationic forms present in the solution, thus decreasing the repulsion between the negative chromate ions adsorbed on the surface. The improvement of Cr(VI) ions adsorption onto lignin in the presence of zinc ions in the solution was shown by Albadarin et al. [30].

Vannela and Verma [17] studied the effect of Co^{2+}, Cu^{2+} and Zn^{2+} on the cross biosorption by *Spirulina platensis* in binary metal systems. In all systems, the metal cations competition for binding sites was observed and metal biosorption significantly decreased in comparison with single-element systems. Kuyucak and Volesky [31] studied the effect of co-ions K^+, Ca^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Fe^{2+}, Cr^{3+}, Pb^{2+} and UO_2^{2+} on the cobalt biosorption by *Ascophyllum nodosum* at different pH values. At pH near 4.5 many cations had an appreciable effect on the cobalt uptake capacity, except K^+, Ca^{2+} and Fe^{2+}.

Cyanobacteria cell walls are polyanionic in nature and effectively act as cation exchangers. NAA results presented in Table 1 supported this observation. NAA allowed the determination of five macroelements (Na, Mg, Cl, K and Ca) and 12 microelements (Cr, Mn, Fe, Co, Zn, As, Br, Rb, Sr, Ba, La and U) in spirulina biomass (Table 1). In particular, the profound decrease of macroelements Na, Cl and K content in metal-loaded biomass in both type of systems was noticed. The decrease of sodium content was more evident than in the case of other macroelements; thus Na(I) was claimed to be most involved in ion exchanging among cations naturally bound with surface functional groups. The chlorine content in all experiments decreased 12.6- to 31.5-fold. In the case of Ca and Mg, their decrease was noticed in the presence of Co(II) and Fe(III) cations and in the multi-metal system.

Data are supported by Dmytryk et al. [32] who studied Cu(II), Mn(II), Zn(II) and Co(II) ions biosorption by *Spirulina* sp. and *Spirulina maxima.* Cochrane et al. [33] showed that copper biosorption by *Fucus vesiculosus* was 77% due to ion exchange with calcium, magnesium, sodium and potassium ions. The concentration of some non-essential elements: Rb, La, U and As were in range of μg/g and did not change during the experiment. Trace amounts of these elements can appear in biomass with chemical reagents or water used to prepare nutrient medium.

4. Conclusions

The biosorption of the zinc, copper, iron, cobalt and chromium ions by *Arthrospira platensis* biomass occurs differently in single- and multi-component systems. In single-metal solutions, biosorption efficiency followed the order: Cu(II) > Zn(II) > Co(II) > Fe(III) > Cr(IV), while in the multi-metal system the following order was observed: Cu(II) > Co(II) > Zn(II) > Fe(III) > Cr(IV).

The highest rate of removal was obtained for copper and the lowest for chromium in both systems. The low rate of Cr(VI) anion biosorption can be explained by negative charge of the spirulina surface at pH near 6. The behavior of 17 macro- and some microelements, determined in spirulina biomass, support the fact that ion exchange is one of the mechanism of metal ion biosorption. The replacement of macroelements with sorbed metal ions was more pronounced in multicomponent system. Biomass of *A. platensis* can be used for the development of biosorbent for selective metal removal at fixed pH values.

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