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The effect of increase in concentration of Na(I) ions on biosorption of Cr(III) ions by *Enteromorpha prolifera* and *Spirulina* sp

Research Article

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Abstract: In this study, the effect of the increase in the initial concentration of Na(I) ions in the solution during biosorption of Cr(III) ions by two edible algae: marine macroalga – *Enteromorpha prolifera* and microalga – *Spirulina* sp. was investigated. During biosorption, essential elements are exchanged with alkali and alkaline earth metal ions (*e.g.* Na(I) ions), which are naturally bound with the biomass. The goal of this study was to investigate the effect of the increase in concentration of Na(I) ions on biosorption performance. The equilibrium of the process is described by Langmuir equation. It was found that with the increase in the initial concentration of NaCl (from 132 to 7331 mg L^{-1}), there was a lower biosorption capacity of *Enteromorpha prolifera* (from 85.8 to 51.0 mg g^{-1}) and *Spirulina* sp. (74.2 to 20.7 mg g^{-1}) towards Cr(III) ions. It was also possible to determine the number of times the solution used in the biosorption process can be recycled and yet mantain high biosorption capacity. The determined numbers were: 16 for *Enteromorpha prolifera* and 19 for *Spirulina* sp.

Keywords: *Biosorption capacity • Cr(III) ions • Na(I) ions • Enteromorpha prolifera • Spirulina sp*

1. Introduction

Due to increasing concern about environmental impact of agriculture, a new generation of mineral feed additives, based on algal biomass, has been introduced as the substitute for the presently used inorganic salts. Enriched with microelements, the biomass offers a solution to modern agriculture. Applications of such a product could solve a problem of increasing amount of microelements accumulated in soil and, at the same time, improve the quality of the livestock production, in particular in highly intense breeding systems [1,2].

The proposed mechanism of binding of metal ions to cell surface is based on ion exchange, in which microelements from the solution are exchanged for other cations bound with cells. As a consequence of taking up microelement ions by the algal biomass, other ions are released [3]. As a result, the concentration of alkali and alkaline earth metal ions in the solution after the process of biosorption is higher than in the solution before the biosorption. The proposed technology of the production of feed additives assumes that the biosorption solution will be recycled in order to minimize water consumption (closed water cycle) and to reduce environmental impact. Therefore it is necessary to determine how many times the solution can be recycled [1,4,5,6].

The solution that remains after the separation process is recycled back to the reactor, where it can be used once again in the subsequent biosorption process (Fig. 1). The same solution can be used several times; however, the concentration of alkali and alkaline earth metal ions will increase in every biosorption cycle [7]. Therefore, it is necessary to determine the effect of the increase in concentration of alkali and alkaline earth metal ions (Na(I), K(I), Ca(II) and Mg(II)) on the biosorption performance. It is assumed that the possible number of recycles is limited since increase in concentration of these ions will affect the biosorption process. It is important to study

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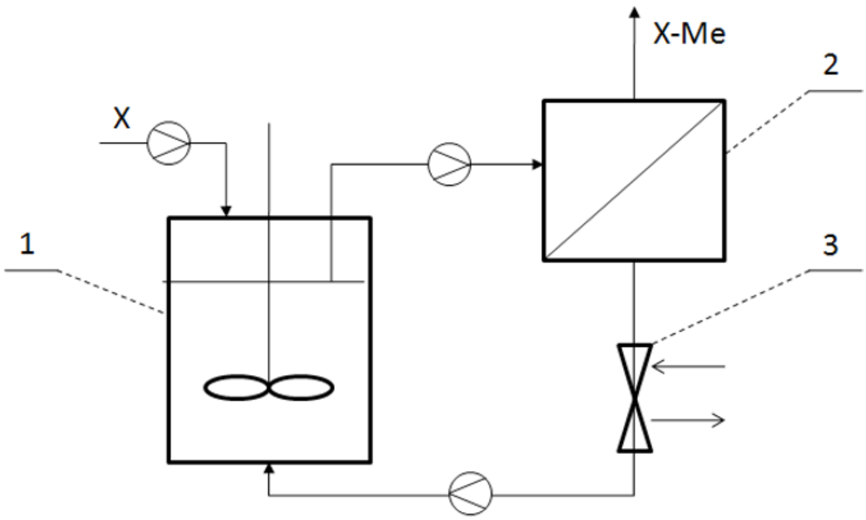

Figure 1. Flowchart of the production of mineral feeds additives based on algal biomass. (1): Reactor/biosorber (here the biosorption process takes place), (2): Filter (here the separation of the biomass from permeate takes place), (3): Valve [13].

the light metal ions effect, since they might interfere with the biosorption process by shifting the equilibrium of biosorption process, which is based on the following ion-exchange reaction (*e.g.* Na(I) ions) (Eq. 1).

$$2R - Na + M^{2+} \leftrightarrow R_2M + 2Na^{+} \quad (1)$$

Schiewer and Volesky (1997) indicated that the presence of the light metal ions in the solution may interfere with the binding of target metal ions such as microelements – *e.g*. Cr(III), Co(II), Cu(II), Mn(II) and Zn(II). Sodium, as a typical "hard" ion, is electrostatically attracted to the negatively charged biomass and its presence in the solution can reduce the amount of other electrostatically bound ions [8].

Deng *et al*. (2007) indicated that industrial wastewater often contains other ions, such as Na(I), K(I), Mg(II) and Ca(II), which may interfere with the uptake of metal ions by biomass. However in their work it was shown that the effect of Na(I), K(I) and Mg(II) on adsorption of Pb(II) by green macroalga *Cladophora fascicularis* was very small. In contrast, the percentage of Pb(II) removal dropped with increase in concentration of Ca(II). The presence of Ca(II) at 10 mmol L^{-1} caused removal efficiency to drop by 26% [9]. Kaewsarn (2002) examined the effect of the presence of Ca(II), Mg(II), Na(I) and K(I) ions (one at a time - at a concentration of 10 mM) in the solution on Cu(II) uptake capacity by marine alga *Padina* sp. It was observed that the effect of Na(I) on Cu(II) uptake was negligible, and that K(I), Mg(II) and Ca(II) reduced the removal efficiency by 4%, 11% and 13%, respectively. Kaewsarn emphasized that this could give a significant advantage of algal adsorbents over commercially available ion exchange resins since the binding of Ca(II) and Mg(II) to these resins often reduces their efficiencies [10]. Nabizadeh et al. (2006) evaluated the effect of light metal ions on the biosorption of two toxic metal ions – Pb(II) and Cd(II) by macroalga *Sargassum* sp. It was found that the effect of Na(I) and K(I) on the Pb(II) uptake was insignificant even at 6 mmol L^{-1} concentration of these ions, but that Mg(II) and Ca(II) had affected the Pb(II) biosorption. The equilibrium capacity of Pb(II) biosorption, for the initial Mg(II) and Ca(II) concentration of 6 mmol L^{-1}, was reduced by 9 and 13%, respectively. The presence of Na(I), K(I), Mg(II) and Ca(II) in solution affected the biosorption of Cd(II) considerably, so that the equilibrium uptake of Cd(II) was reduced at the initial concentration of 0.5–6 mmol L^{-1} of Na(I), K(I), Mg(II) and Ca(II) by 1–11, 6–17, 7–35 and 12–56%, respectively [11]. Choi and Yun (2004) investigated the lead biosorption by waste biomass of *Corynebacterium glutamicum* for the following concentrations of Na(I) ions: 0.23, 230 and 468 mM. There was no significant effect of the change in concentration since the biosorption of lead was recorded as 121, 119 and 118 mmol g^{-1}, respectively [12].

The key issue in the technological process based on the biosorptive properties of algae biomass is the number of times the biosorption solution can be recycled without posing an adverse effect on the biosorption performance. It has been reported in the literature that not only the solution used in biosorption can be recycled, but it is also possible to reuse the biosorbent without any loss in its sorption properties [13]. Therefore the goal of this study was to examine to effluence of the increase in concentration of Na(I) ions on the biosorption process

Table 1. Model parameters for Langmuir isotherm for biosorption of Cr(III) ions by (a) *Enteromorpha prolifera* and (b) *Spirulina* sp. (C_S 1.0 g L^{-1}, pH 5, 25°C).

C_{NaCl} (mg L^{-1})	(a) *Enteromorpha prolifera* q_{max} (mg g^{-1})	(a) b (L mg^{-1})	(a) R^2	(b) *Spirulina* sp. q_{max} (mg g^{-1})	(b) b (L mg^{-1})	(b) R^2
132	85.8	0.0344	0.983	74.2	0.0104	0.996
162	78.3	0.0289	0.986	67.0	0.0144	0.995
194	77.8	0.0258	0.984	66.6	0.0125	0.975
227	69.9	0.0397	0.981	65.2	0.00637	0.993
567	62.5	0.0288	0.968	58.5	0.00843	0.991
1 005	54.7	0.104	0.981	41.1	0.0134	0.993
3 067	54.5	0.00734	0.999	26.9	0.0143	0.952
7 331	51.0	0.00976	0.986	20.7	0.0176	0.983

of Cr(III) ions performed by macroalga – *Enteromorpha prolifera* and microalga *Spirulina* sp. Since during a single biosorption process of Cr(III) ions by *Entermorpha prolifera* and *Spirulina* sp., the biomass released the highest amounts of Na(I) ions (as compared to K(I), Ca(II) and Mg(II)) to the solution, this ion was chosen as exemplary.

2. Experimental procedure

2.1. Sorbent preparation

The alga *Enteromorpha prolifera* was collected from the Baltic Sea (Niechorze – Poland). It was identified by the Department of Botany and Plant Ecology of the Wrocław University of Environmental and Life Sciences. The collected biomass of alga was washed several times with tap water to remove foreign matter and afterwards three times with deionized water. Then, the biomass was dried at 60˚C until the constant mass was reached. The biomass of dry alga was ground and used in biosorption experiments. A blue – green microalgae *Spirulina* sp. was obtained from SIGMA (USA) as a commercially available lyophilizate.

2.2. Batch biosorption experiments

The experiments were performed in Erlenmeyer flasks containing 20 mL of Cr(III) ions solution in thermostated water bath shaker at 150 rpm. The best conditions for biosorption (pH, temperature, initial solution concentration, adsorbent dose) of Cr(III) ions by *Enteromorpha prolifera* and *Spirulina* sp. were established in our previous studies, and were as follows: pH 5, 25°C, initial concentration of Cr(III) ions C_0: 10–300 mg L^{-1}, biomass concentration – C_S: 1 g L^{-1} [5,14-16]. The solutions of Cr(III) ions were prepared in NaCl solutions (by dissolving appropriate amounts of $Cr(NO_3)_3 \cdot 9H_2O$ (from POCh S.A. Gliwice, Poland)). The concentration of NaCl was as follows: 132, 162, 194, 227, 567, 1005, 3067, 7331 mg L^{-1}.

pH of the solutions was adjusted with a 0.1 M solution NaOH/HCl (from POCh S.A. Gliwice, Poland) and was measured with the Mettler–Toledo (Seven Multi, Greifensee, Switzerland) pH-meter equipped with the InLab413 electrode with compensation of temperature. The contact time, evaluated from kinetic experiments, was 4 h for *Enteromorpha prolifera* [14] and 1 h for *Spirulina* sp. [15].

Samples of the sorbent suspension were taken to determine the residual concentration of Cr(III) ions in the solution. Before the analysis, the samples were filtered through a medium paper filter. The concentration of the metal ions in the solution was determined directly by complexation with EDTA and measured spectrophotometrically by Varian Cary 50 Conc. Instrument (Victoria, Australia) [17]. ICP–OES (Inductively Coupled Plasma – Optical Emission Spectrometer – Varian VISTA-MPX ICP–OES (Victoria, Australia)) [2] was also used to confirm the obtained data. The analysis was performed in the laboratory of Multielemental Analyses at Wrocław University of Technology, which is accredited by the Polish Centre for Accreditation (No AB 696) and ILAC–MRA.

3. Results and discussion

The equilibrium between the metal ions adsorbed to the biomass and the metal ions in the solution at a given temperature was described by Langmuir equation: $q=q_{max}\,(bC_{eq}/(1+bC_{eq}))$, where: q_{max} – is the maximum possible quantity of metal ions adsorbed per gram of adsorbent (mg g-1), b – is the constant related to the affinity of binding sites for the metal ions (L mg^{-1}).

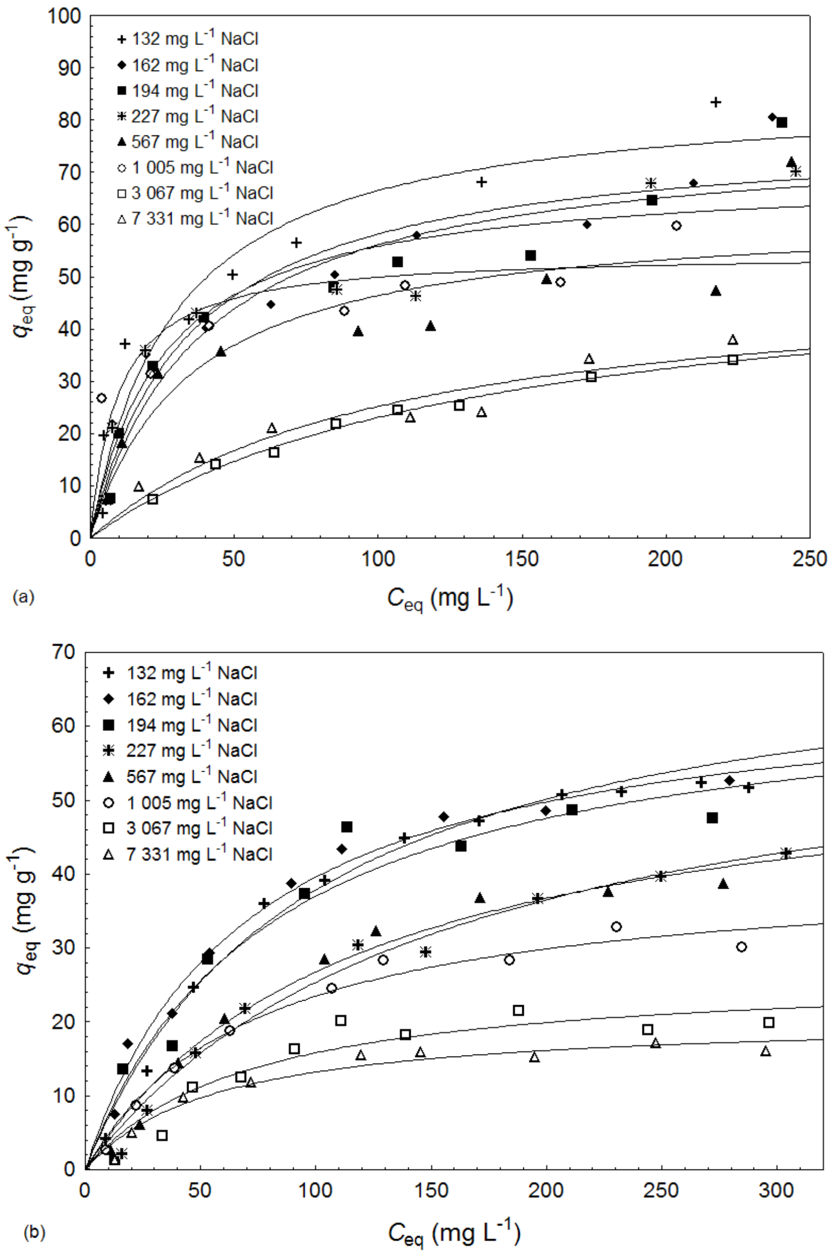

Figure 2. Langmuir isotherms for biosorption of Cr(III) ions by (a) *Enteromorpha prolifera* and (b) *Spirulina* sp. for different initial NaCl concentrations: 132 – 7331 mg L-1 (C_S 1.0 g L-1, pH 5, 25°C).

This model is simple and provides a good description of experimental behavior in a wide range of operating conditions [18]. The biosorption capacity at equilibrium (*q*eq) was calculated from the equation: $q_{eq}=C_0–C_{eq}/C_S$. The model parameters, determined by non-linear regression (*Mathematica v. 5.0.*), are presented in Table 1. It was found that with the increase in the initial concentration of NaCl in the solution, the maxiumum biosorption capacity of *Enteromorpha prolifera* and *Spirulina* sp. towards Cr(III) ions decreased. Also, the decrease in the affinity (*b*) of biosorbent to Cr(III) ions was observed with the increase of NaCl concentration. Langmuir isotherms are presented in Fig. 2.

Schiewer and Volesky (1997) indicated that Na concentration has no influence on Cd binding either if electrostatic effects are negligible (if ionic strength is very high, *e.g.* at a high concentration of Na or other ions) or if Na concentration is very low [8]. In the case of *Enteromorpha prolifera*, it was found that with the increase in the initial concentration of NaCl in

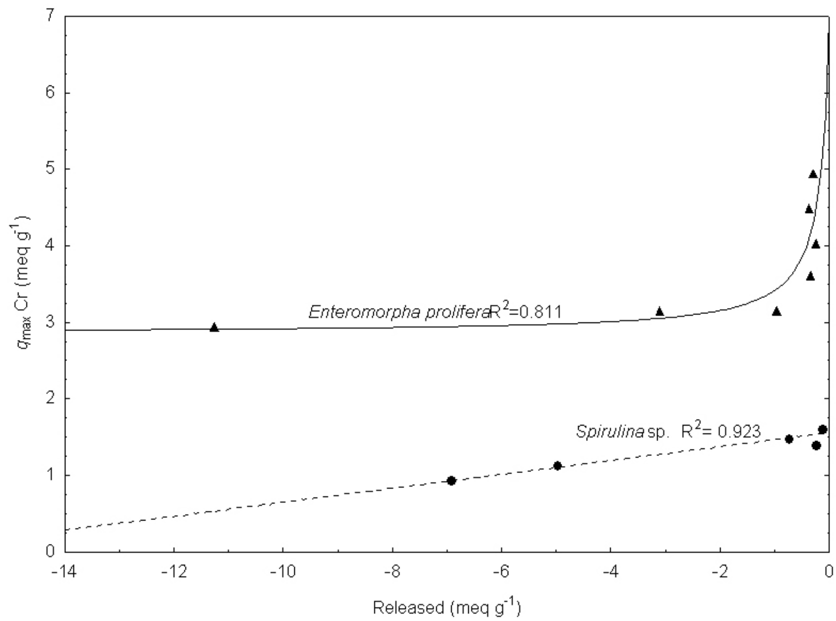

Figure 3. The dependence of q_{max} on the amount of released metal ions.

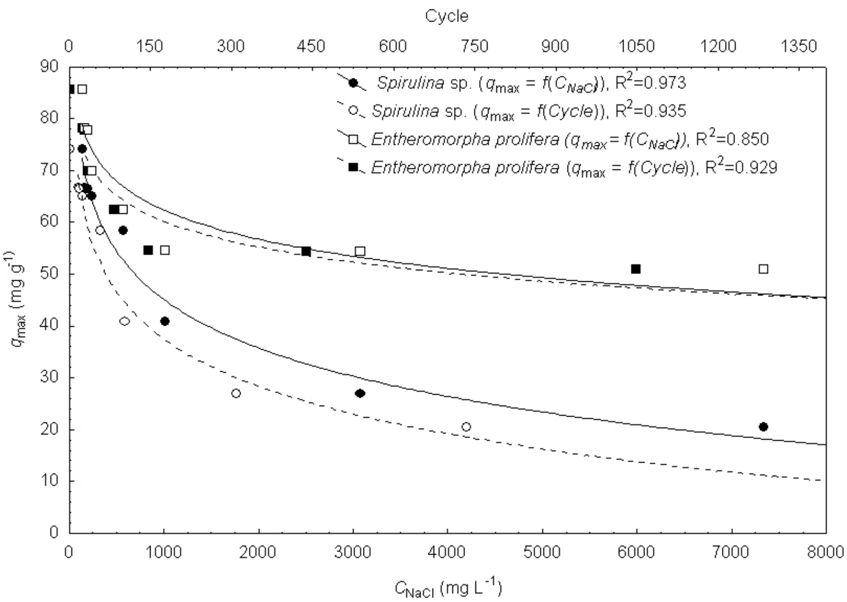

Figure 4. Decrease in q_{max} capacity of *Enteromorpha prolifera* and *Spirulina* sp. towards Cr(III) ions with increase in concentration of NaCl and the number of recycle cycles.

the solution (from 132 to 7331 mg L^{-1}), the maximum biosorption capacity of macroalga towards Cr(III) ions (from 85.8 to 51.0 mg g^{-1}) decreases. Similar results were also observed for *Spirulina* sp.; for the same range of NaCl concentration the maximum biosorption capacity decreased from 74.2 mg g^{-1} to 20.7 mg g^{-1}. From the obtained results it could be concluded that the increase in the concentration of NaCl did not influence significantly the biosorption capacity of macroalgae. For microalgae the effect was more significant.

The influence of released Na(I) ions on biosorption capacity of macro- and microalgae was presented on Fig. 3. It was found that the released Na(I) ions had a strong impact on biosorption capacity in the case of *Enteromorpha prolifera*, but above 1 meq g^{-1} of released Na(I) ions the biosorption capacity remains stable. In the case of *Spirulina* sp. such strong effect was not observed.

The study shows that it is possible to recycle the solution spent in the biosorption cycle. At NaCl

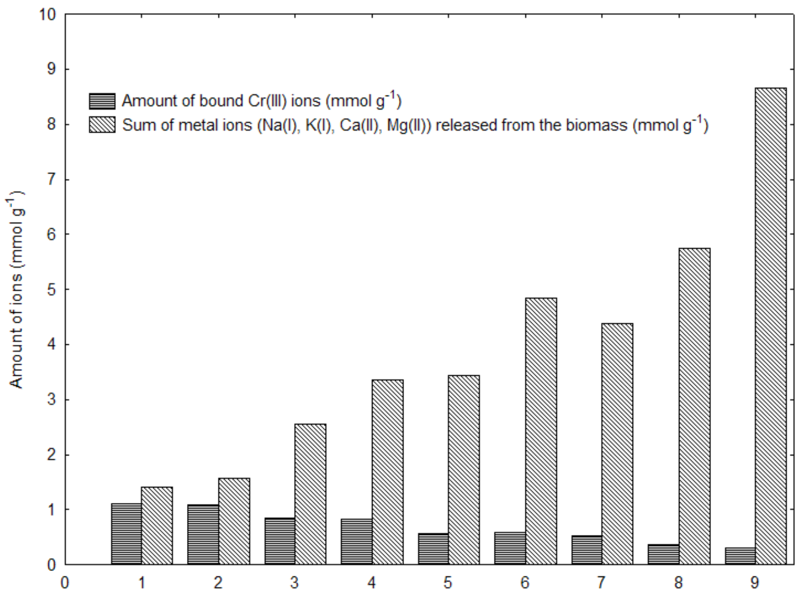

Figure 5. The effect of increase in concentration of light metal ions in the solution on biosorption capacity of *Enteromorpha prolifera* towards Cr(III) ions (25°C, pH 5, C_S 1.0 g L^{-1}, C_0 Cr(III) 300 mg L^{-1}).

concentration of 132 mg L^{-1}, macroalga released 7 mg g^{-1} of Na(I) ions to the solution while microalga released 10 mg g^{-1}. This means that in order to receive the total concentration of Na(I) ions in the solution at 7331 mg L^{-1}, the solution after the biosorption process could be recycled 1047 times when macroalga is used and 733 times when microalga, resulting in a 72% and 40% decrease of sorption performance for micro- and macroalgae, respectively. A significant decrease of sorption capacity was observed when the NaCl concentration was greater than 194 mg L^{-1} for macrolaga and 227 mg L^{-1} for microalga (Fig. 4).

During a single biosorption process of Cr(III) ions (initial concentration 300 mg L^{-1}) by *Entermorpha prolifera*, the biomass released the highest amounts of Na(I) inons to the solution, followed by Ca(II), Mg(II), and finally K(I) ions. Therefore, an experiment was conducted to check the biosorption properties of *Enteromorpha prolifera* towards Cr(III) ions (C_0 300 mg L^{-1}) with increasing concentration of all metal ions in the solution. Nine solutions were prepared, with the concentration of Na(I) ions ranging from 148 mg L^{-1} to 3996 mg L^{-1}, Ca(II) ions from 6.96 mg L^{-1} to 576 mg L^{-1}, Mg(II) ions from 7.0 mg L^{-1} to 593 mg L^{-1} and K(I) ions from 8.60 mg L^{-1} to 431 mg L^{-1} (the concentration of each metal ion in the prepared solutions increased proportionally to the amount of the metal cations released from the biomass). It was assumed that the total concentration of all metal ions should not exceed 7331 mg L^{-1} – the highest concentration of NaCl in the experiment, which simulated the influence of the increase in the concentration of Na(I) ions on biosorption of Cr(III) ions by *Enteromorpha prolifera* and *Spirulina* sp. It was found that with the increase of alkali and alkaline earth metal ions in the solution, the biosorption capacity of *Enteromorpha prolifera* towards Cr(III) ions decreased (Fig. 5).

4. Conclusions

The goal of this study was to analyze the possibility of recycling of the solution used in the biosorption process. The number of cycles used could be limited due to the increase in the concentration of light metal ions, which are responsible for reduction of the biosorption capacity of the biomass. Nowadays, any development of new technologies requires a design with closed water systems, which generate no liquid wastes. According to the obtained results it was possible to recycle the solution 16 times with only 10% decrease in biosorption capacity for *Enteromorpha prolifera* and 19 times for *Spirulina* sp., which corresponded to 155 mg L^{-1} and 195 mg L^{-1} of the initial solution concentration of Na(I) for *Enteromorpha prolifera* and *Spirulina* sp., respectively.

Acknowledgments

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