

The use of algae to remove zinc and lead from industrial wastewater

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ABSTRACT

The work presents the results of a study whose aim was to compare the assessment of effectiveness of removal of zinc and lead ions from the solution with the participation of two algal populations: *Raphidocelis subcapitata* cultured in laboratory conditions and a mixed population of chlorophyta coming from a natural water reservoir. The experiment assumed carrying out a model study involving the initiation of the process of biosorption of metal ions with the participation of both populations through dosing the ions of Pb(II) and Zn(II). In the second stage, the process was repeated with the participation of wastewater coming from battery manufacture. The process was controlled by assessing the rate of metal biosorption in comparison to the control sample after the assumed exposure times. The presented results of the study confirm the effectiveness of chlorophyta in the process of zinc and lead biosorption.

Keywords: Algae; Heavy metals; Zinc; Lead; Biosorption; *Raphidocelis subcapitata*

1. Introduction

The applicable standards of acceptable pollution rates in treated wastewater discharged to waters or sewage systems force battery manufacturers to use effective and tested technologies of wastewater treatment. Rational water and sewage management in chemical plants is connected with proper water management, the use of appropriate manufacture technologies, and methods of sewage treatment that are as environment-friendly as possible. The manufacture of batteries involves the generation of relatively large amounts of wastewater containing very high concentrations of heavy metal ions, especially ions of zinc and lead (even several thousand mg/dm³). Post-manufacture wastewater may also contain other metals, that is, copper, nickel, cadmium, and very high amounts of sulfates, even exceeding ten thousand mg SO₄²⁻/dm³. Ensuring rational water and sewage management in such plants is often a necessary condition for the proper functioning of industrial sewage treatment plants, which should result in the plant meeting the required

pollution rates in treated wastewater introduced into waters or sewage systems.

The methods of treating wastewater containing high concentrations of zinc and lead ions used by the manufacturing plants are usually based on physical, physicochemical, electrochemical, or chemical processes (Tables 1 and 2).

These methods are often very effective and ensure the removal of high proportions of metal ions. However, their application involves the use of chemical substances that are harmful for the environment; they also generate large amounts of waste after the treatment process, and high financial costs. Therefore, researchers look for methods which are equally effective yet more economical, more environment-friendly and generate less waste. Biological processes of heavy metal ions removal from the water environment have been tested and studied for many years. Processes of biosorption, bioaccumulation, and phytoremediation are more environment-friendly, and if carried out with proper parameters, they can often compete with traditional methods.

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Table 1
Methods of treating wastewater containing lead ions

Item no.	Method	Initial concentration (mg/dm ³)	Process conditions		Metal removal (%)	Notes	Reference
			pH	Contact time (min)			
1	Electrocoagulation	9	–	30	96.7	Fe–Fe electrode	[1]
		9	–	40	93.8	Fe–Fe electrode	[1]
2	Electroflotation	50	7.8	15	>98	Using sulfates	[2]
		100	7.8	2	>99	Using a polymetallic solution	[2]
		100	7.8	15	>81	Using acetates	[2]
3	Electrodeposition	74	2.16	240	21.4	–	[3]
		74	1.89	240	35.1	–	[3]
4	Chemical precipitation	100	5	60	94.2	Pyrite as the adsorbent (3 g/dm ³)	[4]
		100	5	45	99.8	Synthetic iron sulfide as the adsorbent (3 g/dm ³)	[4]
5	Nanofiltration	250	5.8	–	99.1	–	[5]
		50	5.8	–	>99	Pressure 25 bar	[5]
		5	5.8	–	>99	Pressure 50 bar	[5]
		25	5.8	–	>99	Pressure 50 bar	[5]
		100	5.8	–	>99	Pressure 50 bar	[5]
		250	5.8	–	98.9	Pressure 50 bar	[5]
6	Ultrafiltration	320	9	–	99.9	–	[6]
		320	6	–	95.9	–	[6]

Biosorption is a process of concentrating metal ions on the surface of cells, which occurs irrespective of the biochemical activity of organisms. This phenomenon was first observed in the early 1970s, when accumulated ions of radioactive elements were found on algae in water reservoirs around a nuclear power plant. Initial research showed that the process can be a promising alternative to previously used technologies [18].

In biosorption, biomaterial, or biopolymer is used as the sorbent. The amount of bound material mostly depends on the chemical composition of cell envelopes, that is, the number and kind of ligands, their distribution in the cell wall, and affinity to the metal. Functional groups that improve the efficiency of the process are, that is, carboxyl group, sulfate group, hydroxyl group, amine group, and phosphate group. Research results show that in the biochemical process of metal ions removal from contaminated waters, dead (inactive) biomass can be more effective than live biomass. Dead biomass does not need food or any special conditions for growth. It can often be easily obtained and used multiple times. Researchers are still identifying and studying new sources of easily available and highly effective natural adsorbents (algae, fungi, bacteria, and agricultural waste) [19–21].

Research results show that if the experimental parameters are well chosen and if the applied adsorbent displays high affinity to the removed ion, the process of biosorption is usually very effective in removing low concentrations (up to several mg/dm³) of metals. However, natural adsorbents capable of removing high concentrations of metal ions

effectively have not yet been found. The aim of this study is to present the possibility of using chlorophyta to remove higher concentrations of zinc and lead ions from industrial wastewater produced after the washing of equipment used in the manufacture of batteries. Research was carried out using a model solution and wastewater.

2. Methodology and course of the study

The experiment was carried out using two populations of algae: one cultured in laboratory conditions and one collected from a natural water reservoir.

2.1. Origin of algae

Culture 1 was a population of *Raphidocelis subcapitata*, grown in laboratory conditions from a pure lyophilized culture. Those algae widely occur in eutrophicated fresh waters in moderate climate. They are used as a plant bioindicator in chronic toxicity tests. Culture 2 mostly included chlorophyta such as *Tetrasporales*, *Volvocales*, *Chlorococcales*, and *Chlorosarcinales*. A mixed population was obtained from the Poraj Dam Reservoir, located at 763.3 km of the Warta River in the southern part of Poland. The reservoir is strongly eutrophicated. Nearly every year, in the summer, algal blooms occur in its waters, whose lavish development leads to the alcalization of the environment through the process of photosynthesis. This promotes the precipitation of metal ions. The presence of metals such as nickel 15–59 mg Ni/kg, cadmium 1.5–2.3 mg Cd/kg, and copper 3.3–7.5 mg Cu/kg was found in the reservoir [22].

Table 2
Methods of treating wastewater containing zinc ions

Item no.	Method	Initial concentration (mg/dm ³)	Process conditions		Metal removal (%)	Notes	Reference
			pH	Contact time (min)			
1	Electrocoagulation	50	4	15	83	Al–Al–Al electrode	[7]
		250	5.5–5.7	50	96	Fe electrode, Cu, and Ni were also removed	[8]
		20.4	9.5	45	96	Cu was also removed	[9]
		20	–	60	>95	Fe–Fe electrode, Cu, and Ni were also removed	[10]
		1,000	>7	5	>99	Cu was also removed	[11]
		–	5	25	96.7	Al electrode	[12]
		3.2	–	30	95.2	Fe–Fe electrode	[1]
		3.2	–	40	93.3	Fe–Fe electrode	[1]
2	Electroflotation	2	5.5	–	98.6	Using zeolites (chabazite)	[13]
		167	8–10	–	99.97	Using hexadecyltrimethylammonium bromide (CTS Br)	[13]
		50	6	–	99	Using zeolites	[14]
		50	9	–	96	Using zeolites	[14]
		50	4	–	>99	Using Lycheny-sin-A	[15]
		50	7–9	–	>99	Using sodium dodecyl sulfate (SDS)	[16]
		600	7.8	10	93	Using sulfates	[2]
		50	7.8	10	>99	Using sulfates	[2]
3	Electrodesorption	407	2.16	240	75.7	–	[3]
		407	1.89	240	77.8	–	[3]
4	Ultrafiltration	320	9	–	99.7	–	[6]
		320	6	–	99.1	–	[6]
		–	7	–	88.7	–	[17]
		–	7	–	78.1	–	[17]

2.2. Culture medium

The culture medium was prepared in accordance with the applicable regulation (Commission Directive No. 92/69/EEC of 31/07/1992). Composition of basic solutions:

- Solution I was: NH₄Cl – 1.5 g; MgCl₂ × 6H₂O – 1.2 g; CaCl₂ × 2H₂O – 1.8 g; MgSO₄ × 7H₂O – 1.5 g; KH₂PO₄ – 0.16 g.
- Solution II was: FeCl₃ × 6H₂O – 0.08 g; Na₂EDTA × 2H₂O – 0.1 g.
- Solution III was: H₃BO₃ – 0.185 g; MnCl₂ × 4H₂O – 0.415 g; ZnCl₂ – 0.003 g; CoCl₂ × 6H₂O – 0.0015 g; CuCl₂ × 2H₂O – 0.00001 g; Na₂MoO₄ × 2H₂O – 0.007 g.
- Solution IV was NaHCO₃ – 50 g.

2.2.1. Preparation of basic solutions

Weighted amounts of relevant salts were entered to each of four volumetric flasks and complemented with distilled water up to the volume of 1 dm³. The solutions were sterilized. The basic solutions were kept in dark bottles at 4°C.

2.2.2. Preparation of the culture medium

Ten cubic meters of basic solution I was entered into a 1 dm³ volumetric flask, and then 1 cm³ samples of the remaining basic solutions (II, III, and IV) were added; finally, it was complemented with deionized water up to the volume of 1 dm³.

2.3. Origin of wastewater

In the experiment, wastewater coming from the washing of battery manufacture equipment was used. The wastewater had the pH of 4.5 and the following concentrations of the studied ions: 84.1 mg Zn/dm³, 98.4 mg Pb/dm³, 11.7 mg Cd/dm³, 36.2 mg Cu/dm³, and 72.4 mg Ni/dm³. The samples were collected to PCV containers directly from the outlet leading to the treatment plant.

2.4. Determination of metal ions in algae and the culture medium – model study

Samples of the culture medium containing algae (50 cm³ each) were entered into a number of bioreactors. The culture

medium was the standard solution. Appropriate amounts of heavy metal ions were introduced into the solution. After the assumed time of contact, the samples were centrifuged with the speed of 6,000 rpm for 5 min, and then, the medium was separated from the biomass.

The obtained standard solution was filtered through a qualitative filter, acidified with concentrated nitric acid up to pH of approximately 2 and kept at 4°C until the moment of determination with the flame atomic absorption spectroscopy method (AAS) in accordance with the standard PN-81/C-04570/01.

The biomass was dried to solid mass, ground and weighed (0.2038–0.2241 g); then, it was mineralized in the presence of aqua regis (hydrochloric acid 38% and nitric acid 65%, 3:1). Then, the samples were filtered through qualitative filters, placed in tight, sterile containers, and kept at 4°C until the determination of heavy metal ions with the AAS method.

2.5. Determination of metal ions in algae and wastewater

Algal biomass had to be isolated so that it could be introduced to wastewater samples. For this purpose, a number of 50 cm³ samples collected from both cultures were centrifuged, the medium was separated from the biomass, and the biomass was washed with doses of redistilled water and entered into previously prepared reactors containing wastewater. After the assumed exposure time, the samples were centrifuged for 5 min at 6,000 rpm and then the wastewater and the biomass were separated.

Further procedure was the same as in the case of preparing the model solution and biomass (section 2.4 (Determination of metal ions in algae and the culture medium – model study)) in the model study.

2.6. Algal culture

Cultures 1 and 2 were kept at the temperature of 24°C (±2°C) and continuously lit. The process was controlled using a microscope and a Sedgewick–Rafter chamber intended for counting of particles. After obtaining 2.5 million specimens per 1 cm³ in both cultures, the experiment began.

2.7. Procedure of the experiments

2.7.1. Model study

In order to allow the comparison of the model study with the experiment using the wastewater, the model study was carried out on the standard solution containing the ions of all the metals previously detected in the wastewater. The concentrations of metal ions (in accordance with the information in section 2.3 (Origin of wastewater)) and pH conditions were adjusted as needed.

Fifty cubic centimeters samples of culture medium grafted with *R. subcapitata* were entered into a number of bioreactors (culture 1). The pH was adjusted to 4.5, and then, solutions of metal ions (in concentrations provided in section 2.3 (Origin of wastewater)) were introduced. In the control reactor containing the medium with algae, only the pH was adjusted.

The process was carried out for six reaction times: 1, 10, 30, 60, and 120 min and 24 h. After the lapse of the proper

contact time of metals and biomass, the contents of zinc and lead ions were determined for the model solution and in the algal biomass, following the procedure described in section 2.4 (Determination of metal ions in algae and the culture medium – model study).

A similar experiment was carried out with the use of a mixed population of chlorophyta (culture 2).

2.7.2. Experiment using wastewater

Fifty cubic centimeters samples of wastewater were entered into a number of bioreactors. Then, algae in the concentration similar to the one use in the model study were entered. The process was carried out for the same reaction times as used in the model study. The contents of zinc and lead ions in the wastewater and the algal biomass were determined following the procedure described in section 2.4 (Determination of metal ions in algae and the culture medium–model study). Wastewater without algae was the control sample. The experiment was carried out using the algal population from both cultures. All the assays were done three times.

2.8. Mathematical description of the process

The biosorption capacity of the biomass was determined as follows:

$$q = \frac{(C_0 - C) \times V}{m} \quad (1)$$

where V is the volume of solution containing metal ions (cm³), C_0 is the initial metal concentration in the solution (mg/dm³), C is the equilibrium metal concentration in the solution (mg/dm³), and m is the mass of dry biosorbent (g).

The speed of the process and the parameters determining its speed were established using two kinetic models based on the biosorbent's sorption capacity:

- first-order, expressed with the Lagergren's equation:

$$\ln(q_{\text{eq}} - q) = \ln q_{\text{eq}} - k_1 t \quad (2)$$

where q_{eq} and q are the mass of metal ions adsorbed on the biosorbent at the state of balance and in time t , respectively [g], k_1 is the constant of the speed of pseudo-first-order model (1/min).

- second-order, expressed with the equation:

$$\frac{t}{q} = \frac{1}{k_2 q_{\text{eq}}^2} + \frac{1}{q_{\text{eq}}} t \quad (3)$$

where k_2 is the constant of the speed of pseudo-second-order model (g/mg min) [23].

3. Results and discussion

Before the experiment, the concentrations of zinc and lead ions in the standard solution and in both algal

populations were controlled. The contents of lead ions in both cultures were at the level of 0.01 mg/g_{dm} or lower. The content of zinc ions was slightly higher (not exceeding 0.2 mg/g_{dm}), which is understandable, because zinc is an element of the culture medium for the algae.

The pH of the model solutions was adjusted to the value of 4.5 so as to allow for comparison with the efficiency of the process carried out with the use of wastewater in similar conditions. The reaction of wastewater coming from the washing of battery manufacture equipment mostly depends on the applied technology, the amount of water and the kind and amount of the used cleaning agents. Because very high concentrations of sulfates (even several hundred thousand mg SO₄²⁻/dm³) often occur in post-production wastewater, the pH of that wastewater is low, close to 0. The reaction of wastewater produced after washing equipment may vary, but usually it is acidic or weakly acidic. The obtained wastewater had the pH of 4.5. The pH of the model solution was reduced to the value of 4.5 using the buffer solution. Metal concentrations were determined before and after adjusting the reaction in order to detect any potential precipitation of heavy metal ions. Zinc and lead ions were not precipitated.

3.1. Model study

The study of dynamics of lead ions removal indicates the increase in the content of that metal in biomass for both cultures (Fig. 1). *R. subcapitata* (culture 1) displayed relatively similar sorption capacity for the whole time of contact with lead ions. From the 10th min of the experiment, it was approximately 10 mg/g_{dm}. The maximum sorption capacity was obtained after 120 min, and it was 10.77 mg/g_{dm}. In the process, contact time longer than 10 min seems unnecessary to achieve visibly better effects of lead ions removal in the case of culture 1. Culture 2, which was a mixed chlorophyta population, displayed higher effectiveness of the process of lead removal from the solution at longer times of exposure to the metal (exceeding 60 min). After 120 min, lead ions concentration in the biomass was 12.72 mg/g_{dm} and was higher by 15% than the one obtained with the use of culture 1.

The dynamics of zinc ions removal was similar for both cultures (Fig. 2). The process trend was similar, but better effects of removing that element were obtained when using

a mixed chlorophyta population. The maximum sorption capacity was observed after 120 min of the process for both cultures. The effectiveness of *R. subcapitata* was nearly 10% lower than the effectiveness obtained with the use of a mixed population.

Comparing the dynamics of removal of ions of both metals from the model solution, better effectiveness of the process was found for the mixed algal population.

3.2. Experiment using wastewater

It was proved that during the 1st hour of exposure to lead, *R. subcapitata* algae display much higher effectiveness of removing ions of that metal from wastewater than the mixed chlorophyta population (Fig. 3). The difference in effectiveness may reach nearly 60% (the 10th minute). After 120 min of mixing, the mixed population achieves the maximum sorption capacity (9.2 mg/g_{dm}), whereas with the participation of *R. subcapitata* algae, the process stabilizes after 10 min (10.5 mg/g_{dm}). After one day of the process, the desorption of lead ions was observed.

The removal of zinc ions from wastewater (Fig. 4) for both cultures is similar to the removal of that element from the model solution (Fig. 2). The dynamics and trend of changes are similar. However, the process occurring in wastewater is more efficient, and the concentration of zinc ions in biomass is higher. Both populations achieved the

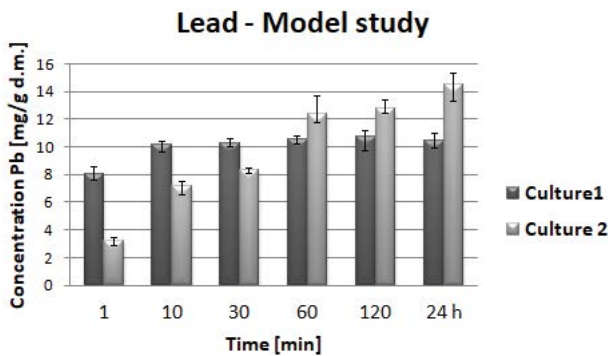


Fig. 1. Changes in lead concentrations in the algae biomass depending on the time of exposure.

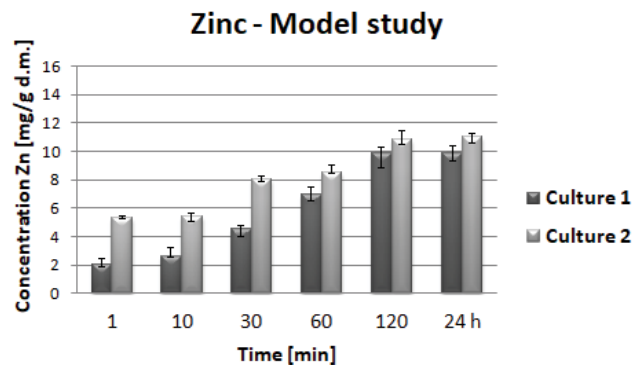


Fig. 2. Changes in zinc concentrations in the algae biomass depending on the time of exposure.

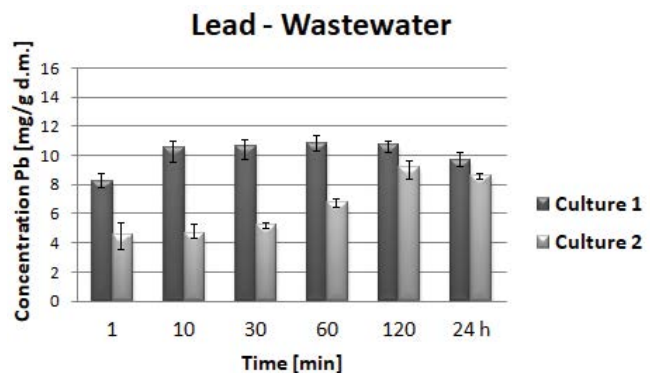


Fig. 3. Changes in lead concentrations in the algae biomass depending on the time of exposure.

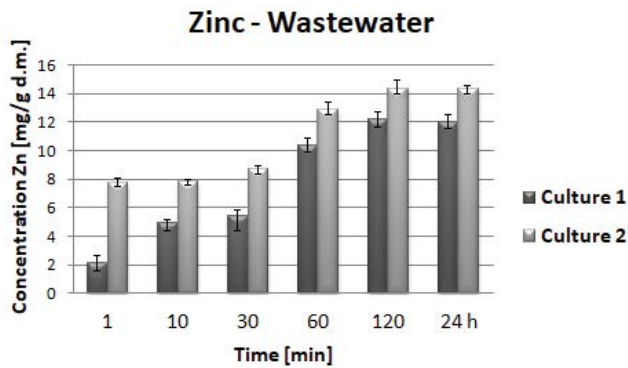


Fig. 4. Changes in zinc concentrations in the algae biomass depending on the time of exposure.

maximum sorption capacity after 120 min from the beginning of the experiment (culture 1: 12.3 mg/g_{dm}, culture 2: 14.3 mg/g_{dm}).

To sum up, it was found that the *R. subcapitata* population was a better biosorbent for lead ions, and the mixed population displayed higher effectiveness of the process for zinc ions.

In most cases, the optimum time of achieving the maximum sorption capacity for the populations used in the process was 120 min (Fig. 5). The experiment proved that after 120 min of exposure, the effectiveness of biosorption of zinc ions in wastewater was higher than that of lead ions. Lead was removed in 58% by the pure *R. subcapitata* population and in 48% by the mixed chlorophyta population, while the rate of zinc removal was 70% (culture 1) and 75% (culture 2). The model study displayed slightly higher effectiveness of removing lead ions (culture 1:58%, culture 2:68%) than zinc ions (culture 1:51%, culture 2:57%).

It was expected that as assumed theoretically, the mixed chlorophyta population would display higher effectiveness of biosorption of zinc and lead ions because of greater diversity of functional groups at the binding sites. The experiment confirmed that theory, but not in each case. The *R. subcapitata* population displayed high affinity to the removal of lead ions from wastewater than the mixed population. Perhaps this was caused by the presence of other substances in the wastewater, such as sulfates or surfactants, which displayed a synergy effect and intensified the process.

R. subcapitata are mostly used in toxicity tests. There are very few publications presenting studies of the sorption of metal ions with the use of those algae. Experiments with

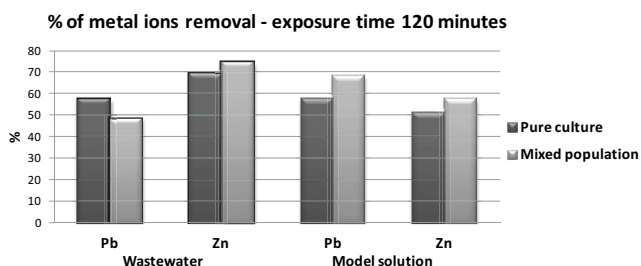


Fig. 5. Percentage removal of lead and zinc ions after 60 min.

the use of mixed algal populations are not frequent, either, because such biomass is difficult to reconstruct. However, for wastewater with chemically diverse composition, a mixed population may be a more effective biosorbent than a pure culture.

To sum up, with 84.1 mg/dm³ zinc concentration and 98.4 mg/dm³ lead concentration in the solution, the effectiveness of removing the ions of those elements is lower than when using lower concentrations of metal ions. There is a study concerning lower zinc concentrations (approximately 10 mg Zn/dm³) which reported the 86%–93% rate of removal of ions of that element using similar algal populations and times of exposure to the metal. Similar experiments carried out for lead (approximately 10 mg Pb/dm³) showed over 94% removal of Pb ions from the model solution and from the wastewater. The difference only occurred in the pH value, which in the presented study was 6.1 [24]. The selection of pH of 4.5 in the presented findings results from the need to adjust the pH of the model solution to the pH of the obtained wastewater. It was found that the attempt to adjust the pH of the wastewater to the nearly neutral reaction led to the precipitation of copper ions, which disturbs the natural character of the wastewater. Although a change in pH may have the key influence on the effectiveness of biosorption, many studies also confirm the gradual loss of effectiveness of biosorbents with growing concentrations of metal ions. The obtained results are probably caused by this fact.

The aim of the presented article was to compare the effectiveness of removing zinc and lead ions with the use of two algal cultures. The mixed chlorophyta population was collected from an eutrophicated water reservoir where algal blooms occurred almost every year. It can be supposed that the collected biomass, constantly exposed to the presence of heavy metal compounds and other substances occurring in similar ecosystems, managed to develop a number of mechanisms connected with resistance and tolerance to many toxic substances present in the environment, including heavy metals. The effectiveness of removing zinc and lead ions by the mixed chlorophyta population, which includes a variety of functional groups, was higher than in the presence of the population cultured in optimum conditions and not exposed to stress; however, that effect was weaker than expected.

3.3. Biosorption kinetics

Pseudo-first and pseudo-second-order kinetic models were tested for both cultures. Model parameters determined on the basis of Figs. 6 and 7 are presented in Table 3.

Pseudo-second-order adsorption parameters q_{eq} and k_2 were determined by plotting t/q_t vs. t (Figs. 6 and 7).

Pseudo-first and pseudo-second-order kinetic models were adjusted to kinetic experimental data [Eqs. (2) and (3)]. It was found that second-order kinetic models better fit the experimental values and better describe the course of the process. This is true for both cultures, regardless of the used medium. Pseudo-second-order models have higher correlation coefficients R and better fitting reaction quotient q . The pseudo-second-order kinetic model assumes that the speed of the biosorption process is limited with the speed of

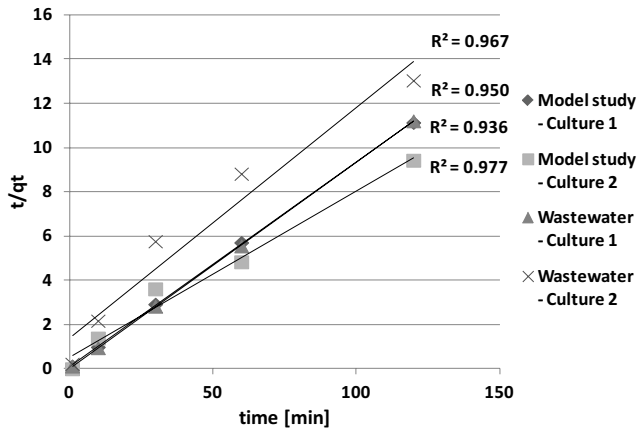


Fig. 6. Pseudo-second-order model for Pb(II) biosorption.

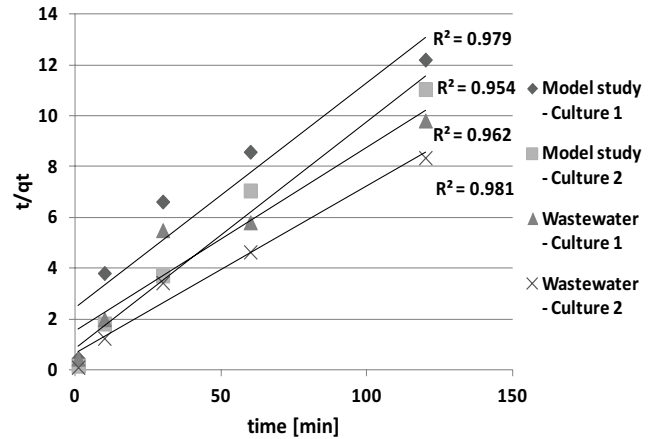


Fig. 7. Pseudo-second-order model for Zn(II) biosorption.

Table 3
Kinetics parameters for the biosorption of Zn(II) and Pb(II)

	q_{exp} (mg/g)	Pseudo-first-order			Pseudo-second-order		
		q_{eq} (mg/g)	k_1 (1/min)	R^2	q_{eq} (mg/g)	k_2 (g/mg min)	R^2
Lead							
Model study – culture 1	10.77	6.15	0.069	0.551	10.34	0.160	0.950
Model study – culture 2	12.72	9.51	0.049	0.742	12.68	0.113	0.977
Wastewater – culture 1	10.74	5.31	0.151	0.591	10.31	0.378	0.936
Wastewater – culture 2	9.25	8.43	0.212	0.910	9.04	0.462	0.967
Zinc							
Model study – culture 1	9.81	7.21	0.094	0.738	9.72	0.091	0.979
Model study – culture 2	10.84	7.15	0.085	0.681	10.25	0.275	0.954
Wastewater – culture 1	12.21	7.62	0.062	0.552	12.01	0.022	0.962
Wastewater – culture 2	14.37	10.42	0.132	0.774	14.21	0.118	0.981

chemical reactions occurring between heavy metal ions and functional groups present in cell walls of biosorbents.

4. Conclusions

Two algal cultures were used in the study: pure *R. subcapitata* culture and a mixed population of *Chlorophyta* coming from a highly eutrophicated natural water reservoir. As compared to the pure culture, the mixed algal population displayed better efficiency of zinc ions removal from the wastewater. In the case of lead ions, the situation was the opposite. However, for both metals, the differences did not exceed 10% after 2 h exposure to metal. The diversity of functional groups is probably one of the main advantages of the mixed population, which ensured such good efficiency of the process, although the biomass collected from the natural water reservoir was already partially saturated.

The presented results showed that both populations were good biosorbents for zinc and lead ions. Depending on the time of ions' contact with the algal biomass, the effectiveness of the process differed. At the time of the maximum saturation of the biomass with metals, 48%–57% removal of lead ions and 69%–75% removal of zinc ions from the wastewater

was obtained. The optimum time of saturation of biomass with metal ions was 120 min, except the removal of lead ions from the wastewater in the presence of a pure *R. subcapitata* population, when the maximum sorption capacity was obtained after 10 min. Usually, longer contact time caused higher effectiveness of the process.

In the author's opinion, the obtained effect of removal of metal ions from wastewater is not sufficient. The wastewater still contains too high concentrations of zinc and lead ions to be safely discharged without further treatment. Perhaps if the process was repeated with the introduction of new algae to preliminarily treated wastewater, the effects would be satisfactory.

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