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The use of algae in the process of heavy metal ions removal from wastewater

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ABSTRACT

This work presents the results of a study to compare the efficiency of Ni(II) and Zn(II) ions removal from wastewater and from the model solution using a live algal culture in laboratory and a mixed algal population obtained from a water reservoir. The scope of this study included initiating the metal biosorption process with the use of pure and mixed culture through the administration of metal ions to the model solution and entering the population to wastewater containing the metals. The process was controlled by assessing the rate of metal biosorption in comparison with control samples after the following exposure times: 1, 5, 10, 20, 40, 60 and 120 min. The presented results of this study confirm the effectiveness of chlorophyta in the process of zinc and nickel biosorption. Algal cultures used in the experiments displayed high affinity to the removal of Zn ions (90%) and lower for Ni (25%–46%).

Keywords: Algae; Heavy metals; Zinc; Nickel; Sorption; *Raphidocelis subcapitata*

1. Introduction

Environment pollution with heavy metal ions is the result of contamination of air, water and soil by dusts, industrial gases, waste and wastewater. The production of large amounts of industrial wastewater containing environmentally harmful metals is connected with many technological processes carried out in various plants. The wastewater mostly comes from chemical, tanning, automotive, paper, oil refining, dying, metallurgy and mining industries [1,2].

Along with the development of human activity and civilization, the level of heavy metal pollution has also raised. This phenomenon has become especially intensive in inland surface waters, coastal waters and shallow groundwaters. Water pollution is particularly important because of the role waters play in the circulation of elements in various environments.

Heavy metals that occur in water ecosystems may be dissolved (metals bonded with ligands, ions and ion complexes) or in the molecular form (e.g., colloids). Ions of heavy metals, such as Pb, Hg, Zn, Mn, Cu, Cd, Ni, Cr and Co are able to accumulate on or in living organisms. Due to their toxic and cancerogenic properties, they are a sanitary and ecological threat to ecosystems [3,4]. Acceptable concentration levels of ions of different toxic metals in wastewater are legally regulated. In Poland, pursuant to the Regulation of the Minister of Environment [5], the highest acceptable metal concentrations in wastewater are as follows: Hg, 0.06–0.2 mg/dm^3; Cd, 0.05–0.4 mg/dm^3; Zn, 2.0 mg/dm^3; Cr(VI), 0.05–0.5 mg/dm^3; total Cr, 0.5–1.0 mg/dm^3; Co, 0.1–1.0 mg/dm^3; Cu; Ni; and Pb, 0.1–0.5 mg/dm^3.

The aim of sustainable development policy is to achieve physicochemical parameters of treated wastewater that would be better than water parameters in the place it would naturally go. In order to meet this assumption, wastewater treatment plants usually apply multi-stage processes of treatment, combining the advantages of mechanical, chemical and biological methods.

The need to protect the environment and the related economic reasons has made the issue of heavy metal ions removal and recovery an extremely important practical matter and the subject of many research works. The major conventional methods of heavy metal ions removal from waters are chemical precipitation, ion exchange, adsorption, electrochemical processes and reversed osmosis. The majority of

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those methods are troublesome, expensive and they generate hazardous waste [6]. Therefore, solutions are sought which would be both safe for the environment and effective in the function of purifying waters polluted with heavy metals.

Many studies focus on biological methods of inorganic pollutants removal, especially biosorption and bioaccumulation processes. These methods involve binding metals from water solutions by dead or live biological material [7]. The process takes advantage of the ability of organic matter to accumulate ions of heavy metals through the processes of metabolic or physicochemical uptake [8,9]. The biosorption process allows for concentration of metals in low volumes and is one of the cheapest methods of eliminating metals from contaminated waters. It is characterized by high efficiency and short time of reaction [10].

The concept of using microorganisms as biosorbents of heavy metals deserves special attention due to their biological origin and much lower costs of obtaining and use than in the case of ionites or filtration membranes. Moreover, heavy metals removal using microorganisms is a very quick process. Research has proved that the sorption of 85%–90% of all the removed metal takes about 10–15 min, and a considerable part of it is bound within less than 20 s [11].

Research shows that algae are a group of microorganisms that display one of the highest sorption capacities. In addition, they are very common and available in virtually unlimited amounts, which makes them a convenient biosorbent of heavy metal ions [12,13]. The biosorption process may occur with the use of live and dead biomass. The use of live biomass is more beneficial because of the constant multiplication of microorganisms and simultaneous bioaccumulation. However, dead biomass is also often used to take up metal ions [14,15].

Many algae species which display resistance to heavy metals are used in experiments aimed at biological wastewater treatment (e.g., *Spirogyra*—the removal and recovery of mercury from wastewater) or recovery of metals from contaminated waters (e.g., mining wastewater) [16]. The advantages of algae include virtually non-limited number of binding sites, high affinity to ions of various metals and the possibility of recovery. Biological methods using biomass are also characterized with simple waste disposal, for example, by burning [16,17].

The aim of the research was to determine the efficiency of removal of Ni(II) and Zn(II) ions from wastewater and the model solution using a live algal culture bred in laboratory conditions and a mixed algal population obtained from a water reservoir.

The population of algae cultured in laboratory conditions was algae *Raphidocelis subcapitata* (class—*Chlorophyceae*, family—*Selenastraceae*) classified as colonial organisms, which usually occur as unicellular organisms in the culture. Cells of *R. subcapitata* have the shape of 8–12 μm long crescents. Those algae are a common element of phytoplankton of temperate climate freshwaters. They occur in eutrophicated waters [18]. They are used as plant bioindicators in chronic toxicity tests Algaltoxkit F™.

The mixed algal population was sampled from the Poraj dam reservoir located at 763.3 km of the Warta River (from the point where it flows into the Oder). Mass algal bloom is observed every year in the reservoir waters, which causes increased photosynthesis process and alkalization of the environment. The increase of pH promotes the precipitation of heavy metals from the depths to the sludge. Reaction measurements in the summer showed that pH daily volatility ranged from 4.4 to 12.9 [19,20]. The presence of ions of heavy metals such as nickel (15–59 mg Ni/kg), cadmium (1.5–2.3 mg Cd/kg) and cuprum (3.3–7.5 mg Cu/kg) was found in the sludge from the reservoir [21].

2. Methodology and course of the study

2.1. The origin of algae

In the experiments, we used algae from two cultures. Culture 1 included *R. subcapitata* algae from a lyophilized pure culture, bred in laboratory. Although the culture medium used for multiplication of *R. subcapitata* was sterilized, various kinds of other chlorophyta scarcely occurred in the culture, with the dominance of *Scenedesmus quadricauda*. Those algae are commonly found in surface waters, usually fresh ones.

Culture 2 was a mixed population of algae, mainly chlorophyta (orders *Chlorococcales*, *Volvocales*, *Tetrasporales* and *Chlorosarcinales*) obtained from the Poraj dam reservoir.

2.2. The 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: NH_4Cl, 1.5g; $MgCl_2 \times 6H_2O$, 1.2g; $CaCl_2 \times 2H_2O$, 1.8g; $MgSO_4 \times 7H_2O$, 1.5g; and KH_2PO_4, 0.16g.
- Solution II: $FeCl_3 \times 6H_2O$, 0.08g and disodium edetate (Na_2EDTA) × $2H_2O$, 0.1g.
- Solution III: H_3BO_3, 0.185g; $MnCl_2 \times 4H_2O$, 0.415g; $ZnCl_2$, 0.003g; $CoCl_2 \times 6H_2O$, 0.0015g; $CuCl_2 \times 2H_2O$, 0.00001g; and $Na_2MoO_4 \times 2H_2O$, 0.007g.
- Solution IV: $NaHCO_3$, 50g.

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 dm^3. The solutions were sterilized. The basic solutions were kept in dark bottles at 4°C.

2.2.2. Preparation of the culture medium

A total of 10 cm^3 of basic solution I was entered into a 1 dm^3 volumetric flask, and then 1 cm^3 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 dm^3.

2.3. Origin of wastewater

The wastewater used in the experiment came from battery production industry, more specifically from the washing of equipment used in production technology. The sewage had the following parameters: pH 6.1 and contained the following heavy metal ions concentrations: Cd, 6.5 mg/dm^3;

Ni, 9.7 mg/dm^3; Zn, 10.2 mg/dm^3; Cu, 17.5 mg/dm^3; and Pb, 12.4 mg/dm^3. Sewage samples were collected in plastic containers. The sampling took place just after the process of washing of the equipment, directly from the outlet to the treatment plant.

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

Before the collection of algae samples from the tanks, the cultures were mixed thoroughly to homogenize them. Then, appropriate amounts of heavy metal ions were entered into a series of 50 cm^3 samples. After the assumed exposure time, the samples were centrifuged for 5 min at 5,000 rpm, and then the medium and the biomass were separated.

2.4.1. Determination of metal ions in the model solution

A 30-cm^3 sample was collected from the decanted medium after centrifugation and filtered through a qualitative filter. The filtrate was placed in tight, sterile 100 cm^3 containers, and then acidified with concentrated nitric acid up to pH of approximately 2 and kept at 4°C until the determination with the flame atomic absorption spectroscopy (AAS) method in accordance with the standard PN-81/C-04570/01, using a MOVAA 400 spectrometer from Analityk Jena (Germany).

2.4.2. Preparation of biomass

The obtained biomass was transferred to a quartz vaporizer. Then, it was dried up to dry matter at 105°C. After the drying and grinding down in a mortar, the algal dry matter was weighed (0.1883–0.2752 g), transferred to mineralizer reaction vessels and flooded with 12.5 cm^3 of aqua regis (hydrochloric acid 38% and nitric acid 65%, 3:1). Then, mineralization was carried out in accordance with PN–EN 14084:2004 in a VELP DK20 mineralizer at three temperature ranges. Stage 1 (20 min) at 70°C, Stage 2 (40 min) at 100°C, Stage 3 (30 min) at 140°C. After the mineralization, the samples were filtered through qualitative filters (65 g/m^3) to measuring cylinders and complemented with distilled water up to 50 cm^3. Samples prepared this way were placed in tight, sterile containers and kept at 4°C until the determination of heavy metal ions with the AAS method. The experiment was performed in duplicate. Whenever the findings were not consistent, for some samples, the experiment was repeated.

2.5. Determination of metal ions in algae and wastewater

Before the collection of algae samples from the tanks, the cultures were mixed thoroughly to homogenize them. Next, a number of 50 cm^3 samples were separated and centrifuged for 5 min at 5,000 rpm. Then, the medium and the biomass were separated. The culture medium was removed, and the biomass was washed with redistilled water and entered into previously prepared reactors containing wastewater (43 cm^3) to obtain samples of 50 cm^3. After the assumed exposure time, the samples were centrifuged for 5 min at 5,000 rpm and then the wastewater and the biomass were separated.

Further procedure was the same as in the case of preparing the model solution (Section 2.4.1) and biomass (Section 2.4.2) in the model study.

2.6. Algal culture

Culture 1 *R. subcapitata* was initially multiplied in 1 dm^3 round-bottomed flasks closed with cotton wool stoppers. The freshly prepared medium was aerified for 30 min, and then the pH was adjusted to the value of 8.3 ± 0.2, following which a graft of clean *R. subcapitata* culture was introduced. So as to prevent the precipitation of salts included in the medium, the flasks were located on magnetic stirrers working in low gear. After obtaining 6 dm^3, the culture was moved to a water tank for further multiplication.

Culture 2, which was a mixed population of algae, was collected from a natural standing water reservoir.

Both cultures were kept at the temperature of 24°C (±2°C) and continuously lit with cool white fluorescent lights L36W/840.

The control of the process involved systematic measurements of the number of algae occurring in the culture medium. The number of algae (specimens) was determined with the use of a microscope and a Sedgwick-Rafter Counting Cell. After obtaining the culture with the density of 2,400,000 specimens in 1 cm^3 of the medium, the experiment began.

2.7. Procedure of the experiments

2.7.1. Model study

So as to compare the model study with the experiment performed for wastewater, the concentrations of metals entered into the model solution were determined on the basis of the contents of heavy metals in the wastewater. The study described in the work only presents the assessment of the efficiency of sorption of Ni(II) and Zn(II) ions, but to ensure similar process conditions, the ions of all five metals found in the wastewater were entered into the model solution.

A total of 50 cm^3 samples of culture medium grafted with *R. subcapitata* were entered into 200 cm^3 glass bioreactors (Culture 1). The medium pH was adjusted to 6.1. Then, solutions of metal compounds in amounts corresponding to wastewater concentrations of those ions were entered (Section 2.3). Nickel was entered in the form of $NiCl_2 \times 6H_2O$ salt in the amount corresponding to 9.8 mg Ni/dm^3, and zinc in the form of $ZnCl_2$ in the amount of 10 mg Zn/dm^3. The reactor was designed as a control solution containing the culture medium and *R. subcapitata* algae without metals.

The process was carried out for six reaction times: 1, 5, 10, 30, 40, 60 and 120 min.

After the lapse of a specified incubation time, the contents of zinc and nickel ions were determined for the model solution and for algal biomass following the procedure described in Section 2.4.

Next, the same experiment was performed for algae coming from Culture 2, containing a mixed chlorophyta population. In order to obtain comparable results, the number of algae in both cultures was equalized before entering metal ions (in the same concentration as for Culture 1).

All the assays (including the control sample) were carried out twice. Whenever the findings were not consistent, for some samples, the experiment was repeated.

2.7.2. Experiment using wastewater

A total of 50 cm^3 samples of culture medium containing *R. subcapitata* were entered into 200 cm^3 glass bioreactors (Culture 1). The process was carried out for six reaction times: 1, 5, 10, 30, 40, 60 and 120 min. After the lapse of a specified incubation time, the contents of zinc and nickel ions were determined for the wastewater and for algal biomass following the procedure described in Section 2.5. Wastewater without algae was the control sample.

Next, the same experiment was performed for algae from Culture 2, containing a mixed chlorophyta population. Both cultures included a similar number of algae: approximately 2,400,000 specimens in 1 cm^3 wastewater.

All the assays (including the control sample) were carried out twice.

2.8. Mathematical description of the process

The biosorption capacity of the biomass was determined as follows:

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

where V is the volume of solution containing metal ions (cm^3), C_0 is initial metal concentration in the solution (mg/dm^3), C is equilibrium metal concentration in the solution (mg/dm^3), and m is 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:

$$\ln\left(q_{eq} - q\right) = \ln q_{eq} - k_I t \tag{2}$$

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

Second-order, expressed with the equation:

$$\frac{t}{q} = \frac{1}{k_{II} q_{eq}^2} + \frac{1}{q_{eq}} t \tag{3}$$

where k_{II} is constant of the speed of pseudo-second order model (g/mg·min).

3. Results and discussion

The biosorption process was controlled by determining the concentration of metal ions in the algal biomass and in the culture medium or wastewater after a specified incubation time. Assessment of the process efficiency was performed with reference to the control samples.

Before the experiment, the contents of nickel and zinc in both cultures were determined. The proportion of nickel both in *R. subcapitata* biomass and in the mixed population was below 0.01 mg Ni/$g_{d.m.}$, yet some nickel was detected. The content of zinc in the biomass from Culture 1 was also below 0.01 mg Zn/$g_{d.m.}$, and from Culture 2 was 0.017 mg Zn/$g_{d.m.}$. The presence of zinc in *R. subcapitata* biomass is justified. It is one of microelements and a component of the culture medium. Nickel, however, was probably entered accidentally. It probably happened as a result of slight (in terms of the number of the specimens entered) pollution of Culture 1 with *S. quadricauda.*

3.1. Model study

In the study of the dynamics of nickel ions removal, it is observed that the concentration of the element in biomass increased with the increasing exposure time, both for pure (Culture 1) and mixed (Culture 2) population (Fig. 1). The efficiency of nickel ions removal was much better when using mixed population than when using *R. subcapitata*, algae, in the case of which the biomass was maximally saturated very quickly. High sorption capacity was achieved in the 5th min of the process (0.32 mg/$g_{d.m.}$), whereas the maximum one was 0.35 mg/$g_{d.m.}$ (25.8% Ni removal from the model solution) and was achieved after 40 min of the experiment. Thus, incubation time longer than 5 min seems unnecessary to achieve visibly better effects of nickel ions removal in the case of Culture 1. The mixed population achieved the maximum sorption capacity (0.81 mg/$g_{d.m.}$) after 60 min (34.4% Ni removal from the model solution), and even after 20 min it was more than 50% more effective biosorbent of nickel ions than pure culture.

The efficiency of zinc ions removal was better when using Culture 2, especially in the initial stages of the process (Fig. 1). In the 40th min, both cultures achieved almost maximum sorption capacity, with the efficiency of Culture 2 was almost 10% better than of Culture 1. The rate of zinc ions removal from the culture medium was 88.1% (Culture 1) and 93.1% (Culture 2).

Comparing the removal of ions of both metals after 60-min exposure, the sorption of zinc ions was over 45% more effective than of nickel ions when using Culture 2 and almost five times more effective than when using Culture 1.

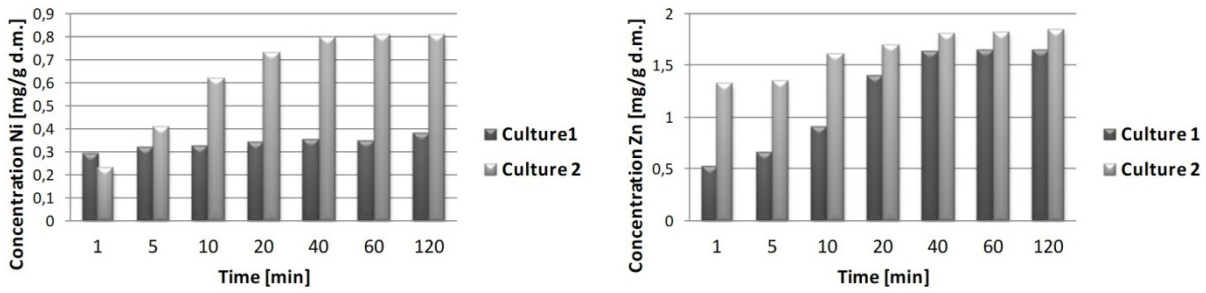

Fig. 1. Changes in nickel and zinc concentrations in the algae biomass depending on the time of exposure (model study).

It was found that mixed algal population from a natural environment was a better biosorbent of both nickel and zinc ions in the study of the model solution.

3.2. Experiment using wastewater

In the initial stages of the process, the efficiency of nickel ions removal from wastewater was comparable for both cultures and was 0.31–0.32 mg/$g_{d.m.}$ in the 1st min (Fig. 2). Beginning with the 20th min, the sorption of nickel by *R. subcapitata* algae proved to be approximately 20% more efficient than when using a mixed population. Both cultures achieved the maximum sorption capacity after 60 min (Culture 1, 0.74 mg/$g_{d.m.}$ and Culture 2, 0.59 mg/$g_{d.m.}$) and displayed 46.1% nickel removal from the wastewater in the case of pure culture and 35.9% in the case of mixed culture. After that time, desorption of nickel ions from biomass to wastewater was observed in both cultures.

The efficiency of zinc ions removal in the 1st minute was four times higher when using Culture 2 than when using Culture 1 (Fig. 2). Both populations achieved high saturation with zinc ions in the 60th min (Culture 1, 3.05 mg/$g_{d.m.}$ and Culture 2, 3.70 mg/$g_{d.m.}$) and similar percentage of Zn ions removal of 87.2% for pure population and 86.5% for mixed population.

To conclude, in comparison with nickel, after 1-h incubation the efficiency of zinc ions sorption was more than four times higher when using *R. subcapitata* and more than six times higher when using a mixed chlorophyta population.

It was proved that 1 h is the optimum time of contact both populations need for the most efficient removal of zinc and nickel ions, both from the model solution and from wastewater. The only exception is the use of *R. subcapitata* to remove nickel ions from the model solution, in which case the time of effective contact can be shortened to 5 min. Still, even in this case, 1 h is the time needed to achieve the maximum sorption capacity.

The study proved that the efficiency of zinc ions removal is high (around 86.5%–93.1%) regardless of the type of culture or the presence of other substances (Fig. 3). Theoretically, the mixed population should display higher efficiency of zinc ions biosorption, that is, due to the diversity of functional groups at the binding sites. But, the presented experiment shows high affinity of *R. subcapitata* chlorophyta to the removal of those ions.

The experiment showed that nickel displays a higher percentage of removal from wastewater than from the model solution. In addition, in the case of wastewater the efficiency of the process is higher when using pure culture than mixed population, which clearly proves better affinity of *R. subcapitata* to the removal of nickel (46.1%) in the presence in the wastewater of substances such as sulfates or surfactants used to wash equipment. In the case of the model solution containing only negligible amounts of salts being part of the culture medium and five entered metals, the mixed population proved to be a better biosorbent (34.3%) than the pure culture (25.8%), as expected. Generally, the efficiency of nickel ions biosorption in this concentration and these conditions is not high. Experiments with two-component systems have proved that zinc ions inhibit the sorption of nickel [22]. This fact may also cause the low percentage of removal of those ions.

To sum up, the efficiency of zinc ions removal, regardless of the type of culture (model solution, 88.1%–93.1% and wastewater, 86.5%–87.2%) was much higher than in the case of nickel (model solution, 25.8%–34.3% and wastewater, 35.9%–46.1%). These results confirm the experiments by other researchers, who have proved that microorganisms with biosorption ability can well be used to fully or partially treat wastewater containing dozens of milligrams of Ni and Zn ions per liter, achieving nickel removal of over 50%, and zinc removal of over 90% [23–25].

3.3. Biosorption kinetics

Pseudo-first order (Eq. (2)) and pseudo-second order (Eq. (3)) kinetic models were tested for both cultures so as to suit the experimental kinetics data (Table 1).

Pseudo second-order adsorption parameters q_{eq} and k_{II} were determined by plotting t/q_t vs. t (Figs. 4 and 5).

By comparing the obtained results, it can be concluded that the second-order kinetic model better describes the course of biosorption process for both cultures, regardless of the kind of the medium (model solution or sewage). This is indicated by higher R^2 correlation coefficients and q_{eq} values, which for the pseudo-second order model are much closer to

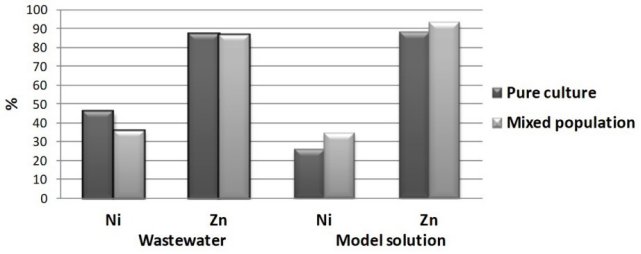

Fig. 3. Percentage removal of nickel and zinc ions after 60 min.

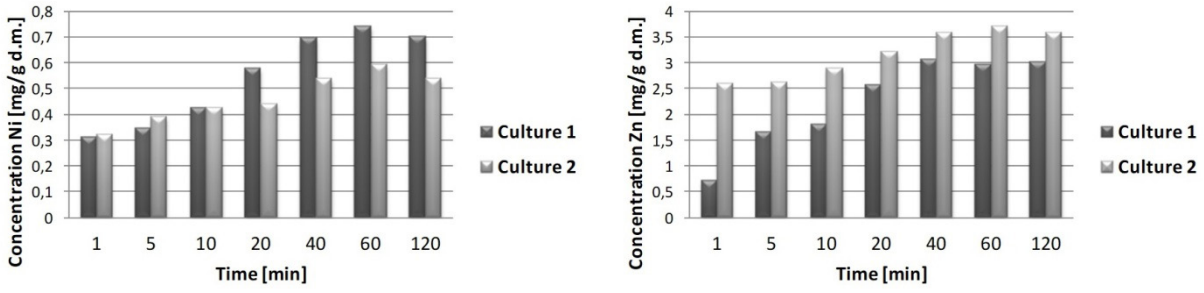

Fig. 2. Changes in nickel and zinc concentrations in the algae biomass depending on the time of exposure (wastewater).

Table 1
Kinetics parameters for the biosorption of Ni(II) and Zn(II)

	Pseudo-first order				Pseudo-second order		
	q_{exp} (mg/g)	q_{eq} (mg/g)	k_I (min^{-1})	R^2	q_{eq} (mg/g)	k_{II} (g/mg·min)	R^2
Nickel							
Model study—Culture 1	0.348	0.185	0.0659	0.6579	0.343	2.1060	0.9979
Model study—Culture 2	0.805	0.541	0.0498	0.7392	0.809	0.1213	0.9992
Wastewater—Culture 1	0.743	0.371	0.0541	0.4914	0.732	0.1878	0.9954
Wastewater—Culture 2	0.592	0.483	0.2125	0.8950	0.581	0.3622	0.9957
Zinc							
Model study—Culture 1	1.639	1.211	0.0059	0.7342	1.628	0.0611	0.9934
Model study—Culture 2	1.811	1.155	0.0850	0.6114	1.821	0.2405	0.9952
Wastewater—Culture 1	3.052	1.632	0.0062	0.5734	3.024	0.0272	0.9896
Wastewater—Culture 2	3.702	2.422	0.0325	0.7431	3.721	0.1028	0.9915

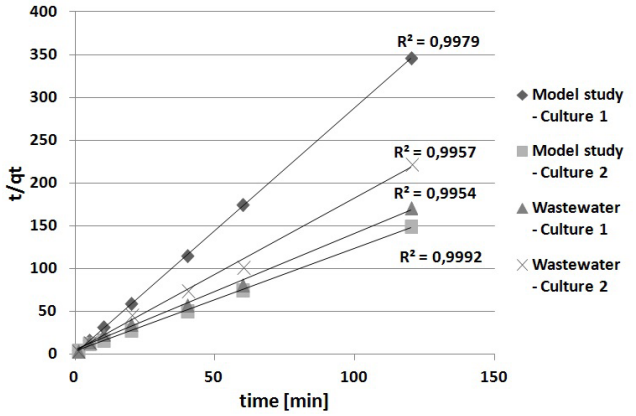

Fig. 4. Pseudo-second-order model for Ni(II) biosorption.

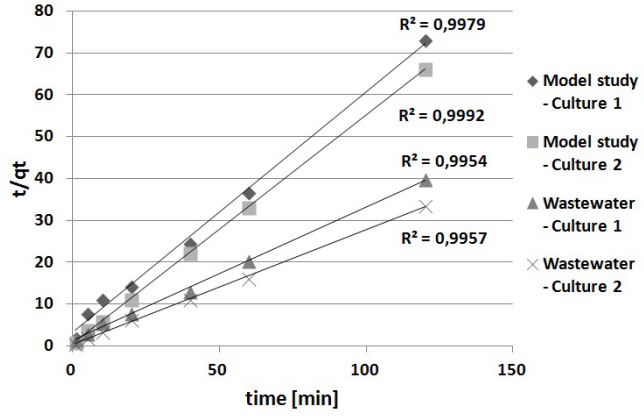

Fig. 5. Pseudo-second-order model for Zn(II) biosorption.

the experimental values (q_{exp}) than in the pseudo-first order model. Similar results were found by other scholars doing research with the use of different types of biosorbent. The pseudo-second-order kinetic model assumes that the speed of the biosorption process is limited with the speed of chemical reactions occurring between heavy metal ions and functional groups present in cell walls of biosorbents [4,12,26].

4. Conclusions

This study results proved that both a mixed population of chlorophyta and *R. subcapitata* culture were good biosorbents of Ni and Zn ions. Biosorption occurred with various intensity depending on the biosorbent and the time of contact between the biomass and the metal. Longer time of exposure improved the efficiency of metal ions removal from the solutions. In the assumed process conditions and selected metal concentrations, the best removal effect was achieved after 60 min of contact.

At the maximum saturation with metals, both algal cultures displayed high affinity to zinc ions removal at the level of approximately. 90%, and lower for nickel (25%–46%). In the model study, the mixed chlorophyta population was a more efficient biosorbent of both metals (nickel by approximately 20%, zinc by almost 3%), and *R. subcapitata* culture bred in laboratory displayed better efficiency of zinc and wastewater removal from wastewater (nickel by approximately 15% and zinc by approximately 2%).

In addition, it was proved that the pseudo-second-order model better describes the process kinetics.

The aim of this study was to compare the efficiency of Ni(II) and Zn(II) ions removal with the use of two bacterial cultures. Diverse, mixed chlorophyta population sampled from a natural water reservoir has for centuries been exposed to the presence of heavy metal compounds and other substances occurring in eutrophicated ecosystems. This fact has enabled the population to develop resistance mechanisms and tolerance to many toxic substances present in the environment, including heavy metals [27]. Still, despite the diversity of functional groups in cell walls, the efficiency of zinc ions removal by the mixed algal population was comparable with the efficiency of the process in the presence of *R. subcapitata* culture bred in optimum conditions and not exposed to stress. The presented experiment proved that in certain conditions the studied pure algal culture might well be used to remove zinc ions from waters polluted with organic and inorganic compounds. The population of *R. subcapitata* may be a great substitution to other algal cultures used in experiments for many years, such as *Scenedesmus* [28–30] or *Chlorella* [29–34].

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