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## INFLUENCE OF PREPARATION METHOD OF *Spirogyra* sp. ALGAE ON THEIR SORPTION CAPACITY

### WPLYW SPOSOBU PREPAROWANIA PRÓBEK GLONÓW *Spirogyra* sp. NA ICH POJEMNOŚĆ SORPCYJNĄ

**Abstract:** The influence of the preparation method of samples on the zinc ions sorption parameters in *Spirogyra* sp. algae was analysed. The Zn<sup>2+</sup> sorption process from the salt solutions of this analyte was carried out in static conditions. The carried out analyses results show that the method of algae samples preparation for analyses (thermal drying, freeze drying, samples conditioning in demineralised water) and storage period influence their sorption capacity. On the basis of the carried out research of the metal sorption kinetics in live and prepared algae samples, it was found that the equilibrium is achieved after approximately 30 min. In the experiment conditions, 56% of metals are sorbed in live algae during the first 15 min. Approximately 17 and 65% of zinc ions present in the dilution accumulated in thermally dried and freeze dried algae samples respectively after 30 min of the process. It was confirmed that conditioning of the algae samples in demineralised water, prior to the sorption process, increases its efficiency. In order to define sorption capacity of freeze dried *Spirogyra* sp. algae, the Langmuir isotherm model was applied. It was found out that algae absorb heavy metals in proportion to their content in a solution, in which they were immersed. The sorption capacity of freeze dried *Spirogyra* sp. algae and zinc, defined with the use of the Langmuir isotherm, shows considerable imprecise result. Evident influence of hydrogen cations on zinc concentrations in algae and in the solution in the state of equilibrium was found out.

**Keywords:** zinc, the algae *Spirogyra* sp., preparation of the algae, the Langmuir isotherm model, sorption capacity

## Introduction

The studies of heavy metals sorption processes both in dried and live algae have been carried out for many years. The objective of these studies was to assess the possibility to use algae biomass, *eg* in water fitoremediation [1-4], sewage treatment processes [5, 6] and in surface waters contamination biomonitoring [7-18].

The differences in sorption properties of different types of algae are emphasised, caused by physiological and morphological structure of thallus, the location of the sample taking and the method of algae preparation for the analysis [19]. The equilibrium and sorption process kinetics of algae are the most frequently measured parameters, *eg* [2].

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The studies of heavy metals sorption kinetics show that the time necessary to achieve dynamic equilibrium depends on, among others, the types of algae and biomass shredding level. Biomass of sea algae *Ecklonia maxima* with thallus size of 1.2 mm achieved equilibrium during sorption of Cu, Pb and Cd after approximately 60 min, whereas when the shredded thallus was the size of 0.075 mm, the equilibrium was achieved after approximately 10 min [20]. It was found out that cosmopolitan algae *Chlorella vullgaris* and fresh water *Scenedesmus quadricauda* absorb 90-95% of Cu during the first 15 min of the experiment (equilibrium was achieved after approximately 2 h) [21], sea algae *Padina* sp. absorb 90% of Cd during 35 min (equilibrium was achieved after approximately 60 min) [22].

Considerable differences have been registered in the case of assessing algae sorption capacity. For example, the defined values of sorption capacity of two algae types: *Cladophora glomerata* and *Spirogyra* sp. in reference to copper ions are respectively 15.0 mg g<sup>-1</sup> d.m. [23] and 133.3 mg g<sup>-1</sup> d.m. (d.m. - dry mass) [2]. It seems that, aside from the variety of types, the main factors are the method of algae preparation, experiment conditions and the interpretation method of the studies results.

Various models, among other isotherm models by Freundlich [24, 25], Langmuir [26-28], Redlich-Peterson [1] and Koble-Corrigan [1] are used to describe the equilibrium status of the heavy metals sorption process in algae. The models are the basis for defining, among others, the sorption capacity of algae and the affinity levels of metals and algae thallus. Frequently, the best correlations between individual experimental and calculation data is obtained by the use of the Langmuir isotherm model [29-31].

The results of laboratory studies of kinetics and equilibrium of heavy metals in algae in static conditions have been obtained from numerous algae types, prepared in different ways to the analyses. These results are quite controversial, as there is no reliable methodology for preparing biomass to the tests. It is hard to specify whether the observed differences in sorption parameters result from the algae preparation method or their sorption characteristics.

The objective of the carried out studies was to assess the influence of preparation method and storage time of fresh water *Spirogyra* sp. algae samples on their sorption capacity, versus Zn<sup>2+</sup> ions. The method of preparation of algae to analysis was optimised, in order to receive the samples with sorption characteristics comparable to live algae.

In order to define sorption capacity of freeze dried *Spirogyra* sp. algae, the Langmuir isotherm model was applied. The unreliability of measurements was assessed at the analysis and interpretation of the tests results stage.

## Experimental

*Spirogyra* sp. algae from the Large Turawa Lake located in the south-western Poland (PL) were used for the tests. Algae samples were cleaned from biological impurities by rinsing with demineralised water. Cleaned samples were tested or further prepared. Concentration of zinc naturally present in the algae:  $c_{(a,0)}$ , amounted to:  $c_{Zn(a,0)} = 0.021 \pm 0.002$  mg g<sup>-1</sup> d.m.

## The research method

The research was carried out on live and prepared algae. The research on the live algae was carried out immediately after cleaning. The algae were freeze dried at the temperature of 223 K for 20 h and by water evaporation at the temperature of 323 K (24 h) and 353 K (12 h).

The algae samples with mass of approximately  $0.50 \pm 0.02$  g d.m. were placed in a perforated container of approximately 15 cm<sup>3</sup> capacity and immersed in 200 cm<sup>3</sup> of zinc salt solution. Dried algae were immersed for 30 min in demineralised water, prior to experiment. The solution was thoroughly mixed by a magnetic agitator. The solution was regularly taken from the container in order to determine zinc concentration (AAS). The process was carried out for 40 min.

Conductivity and pH values were measured during the zinc sorption process in algae biomass.

The research of equilibrium parameters in a static system was carried out parallel to the process kinetics research. The process was carried out with freeze dried algae and only the initial zinc ions concentrations were altered.

## Equipment and reagents

The absorbing atomic spectroscope iCE 3000, made by Thermo Electron Corporation, USA, was used to determine zinc. For zinc, the detection (*IDL*) and determination (*IQL*) limits of the equipment are, respectively, 0.0033 and 0.010 mg dm<sup>-3</sup>. The highest concentration of the model (made by: ANALYTIKA Ltd. (CZ)) used for calibration (5 mg dm<sup>-3</sup>) was assumed as the limit of the linear dependence of the signal from the concentration.

The conductivity and pH of the solutions, in which algae were immersed, were measured with the equipment made by Elmetron Sp.j. from Zabrze (PL): pH meter CP551 and conductivity meter CC551, which absolute measurement error was  $\Delta\text{pH} = 0.02$  and  $\Delta\kappa = 0.1 \mu\text{S cm}^{-1}$ , respectively.

MERCK reagents were used to prepare the solutions.

## Quality control

The quality control of measurements was assured by test analyses of the BCR 414 *plankton* and BCR-482 *lichen* reference materials from the Institute for Reference Materials and Measurements in Belgium. The obtained results are summarized in Table 1.

Table 1  
Measured and certified values of Zn concentration in the BCR 414 *plankton* and BCR 482 *lichen* reference material

BCR 414 plankton					BCR 482 lichen				
Certified value	±Uncertainty	AAS		<i>D</i> *	Certified value	±Uncertainty	AAS		<i>D</i> *
		Mean	±SD				Mean	±SD	
	[mg kg <sup>-1</sup> d.m.]			[%]					[%]
112	3	103	4	-8.0	100.6	2.2	93.9	2.5	-6.7

\* Deviation - a difference between a measured value and a certified value, divided by the certified value

### Biosorption isotherm model

The Langmuir isotherms model is valid for monolayer adsorption on to surface containing finite number of identical sorption sites which is described by the following equation [31]:

$$c_{(a,1)} = (c_{(a,max)} \cdot K \cdot c_{(s,1)}) \cdot (1 + K \cdot c_{(s,1)})^{-1} \quad (1)$$

where:  $c_{(a,1)}$  - equilibrium concentration of a given metal in algae [ $\text{mmol g}^{-1} \text{ d.m.}$ ],  $c_{(s,1)}$  - equilibrium concentration of this metal ions in solution [ $\text{mmol dm}^{-3}$ ],  $c_{(a,max)}$  - sorption capacity of algae [ $\text{mmol g}^{-1} \text{ d.m.}$ ],  $K$  - constant.

The Langmuir equation can be rearranged to linear form for the convenience of plotting and determining the Langmuir constants as below:

$$(c_{(a,1)})^{-1} = (c_{(a,max)} \cdot K \cdot c_{(s,1)})^{-1} + (c_{(a,max)})^{-1} \quad (2)$$

### Results and discussion

The research of zinc ions sorption by *Spirogyra* sp. algae was carried out in two stages, applying the methodology referred to in the previous chapter. During the first stage, the sorption process' kinetics was analysed, using live and prepared algae. The influence of the algae preparation methods on their sorption capacity was assessed. The second stage included research of equilibrium parameters, defined by the Langmuir isotherm model.

#### The influence of algae samples preparation method on zinc sorption kinetics

The kinetics research was carried out in static conditions, in order to estimate the time required to achieve equilibrium between the algae and the solution, in which they were immersed.

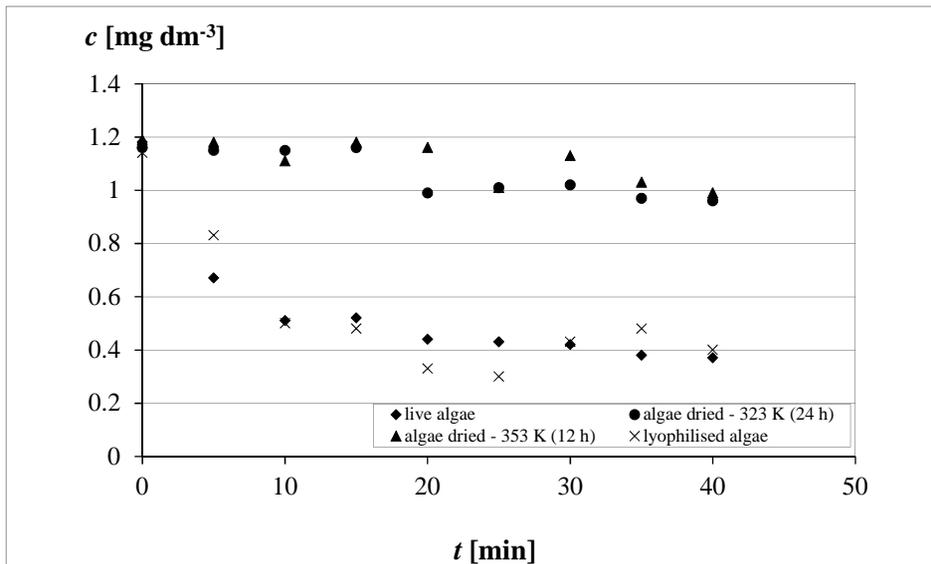


Fig. 1. Changes of Zn concentration in the solution, in which live and prepared *Spirogyra* sp. algae were immersed

Figure 1 presents examples of Zn concentration changes in the solution, in which algae were immersed. The process parameters: the solution initial concentration  $c_{Zn,0} = 1.14 \pm 0.05 \text{ mg dm}^{-3}$ , live algae wet mass approximately 8.0 g, after drying  $0.50 \pm 0.02 \text{ g}$ , dry mass of prepared algae  $0.50 \pm 0.02 \text{ g}$ .

The results of the carried out research show that the dynamic equilibrium during zinc sorption in *Spirogyra* sp. algae, both live and prepared, is achieved after approximately 30 min. During that time, approximately 69% of  $Zn^{2+}$  ions, present in initial solution, accumulate in live algae samples. During the first 15 min of the process, approximately 56% of  $Zn^{2+}$  ions is absorbed from the solution to biomass, in reference to their concentration accumulated in algae in equilibrium (for Zn -  $0.27 \text{ mg g}^{-1} \text{ d.m}$ ). In the prepared algae samples, compared to live algae, after 30 min of the process the following amounts accumulated respectively: the algae dried at 323 K - approximately 17%, the algae dried at 353 K - approximately 17%, the algae freeze dried - approximately 65% of zinc ions.

In order to increase  $Zn^{2+}$  sorption efficiency in thermally and freeze dried *Spirogyra* sp. algae, the biomass samples were prepared for 30 min in demineralised water, with conductivity of  $\Delta\kappa = 0.5 \mu\text{S cm}^{-1}$ . The graphs in Figure 2 show changes of zinc concentration in the solution, in which the prepared algae were immersed, and additionally activated in demineralised water.

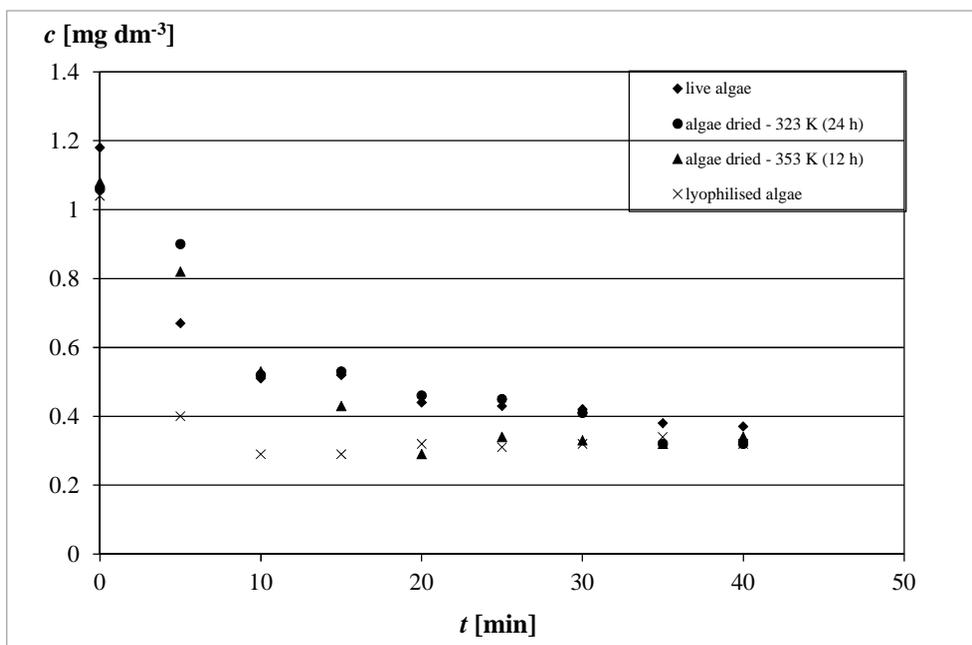


Fig. 2. Changes of Zn concentration in the solution, in which live and prepared *Spirogyra* sp. algae were immersed, activated in demineralised water

The results presented in the graph show that the prepared algae, in order to achieve the proper sorption parameters, should be immersed for approximately 30 min in demineralised water; then their sorption characteristics are comparable to those of live algae.

The graphs in Figures 3 and 4 present respectively the changes of conductivity during Zn sorption process, in live and prepared algae biomass.

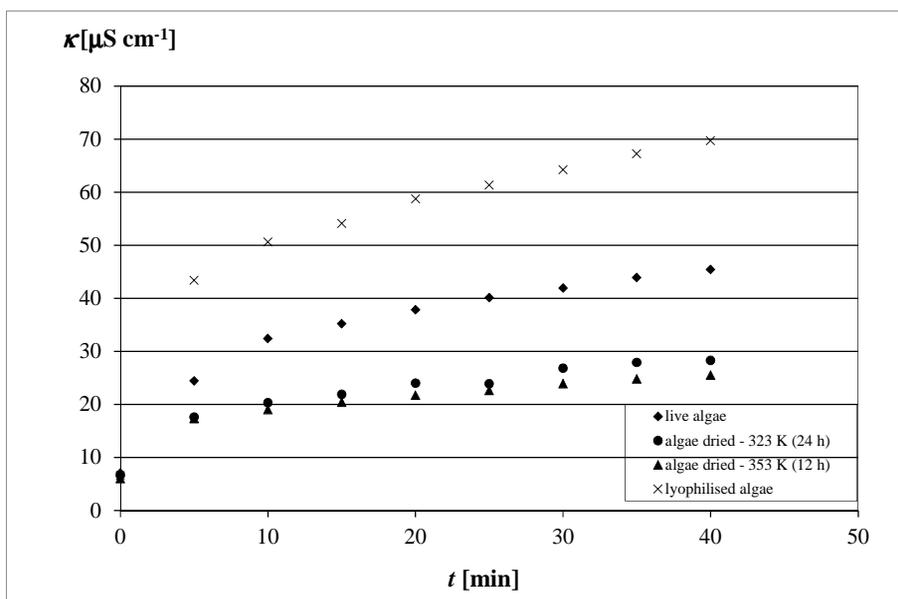


Fig. 3. Changes of conductivity in Zn solution, in which live and prepared algae were immersed, activated in demineralised water

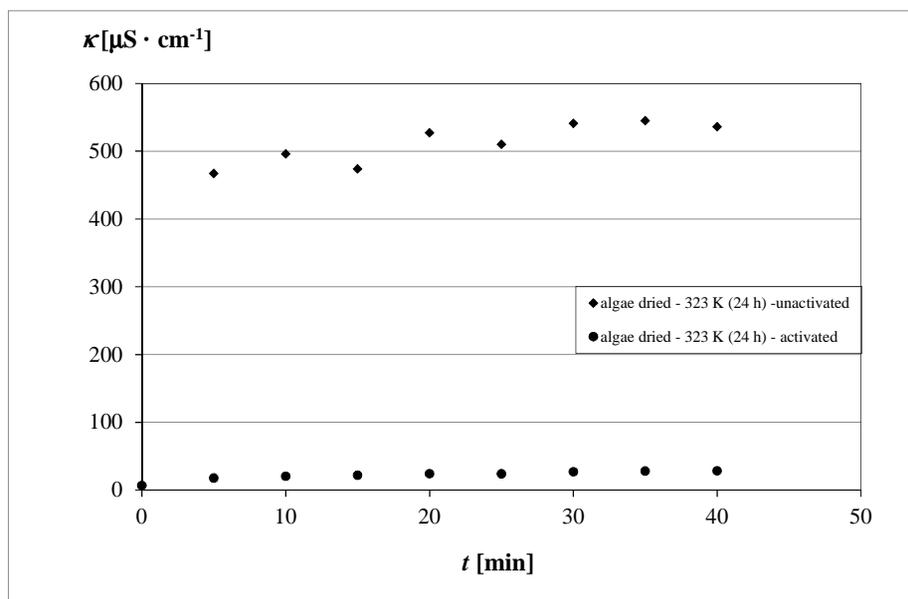


Fig. 4. Comparison of conductivity changes in zinc solutions, in which the prepared algae were immersed

During the zinc sorption process in *Spirogyra* sp., increase of conductivity was recorded (Fig. 3). It can be assumed that it was caused by the progressive and irreversible changes in the cellular membranes structure, which results in ions leaking from algae cells to the solution. This effect was observed during the tests of the influence of copper on lichens thallus. Potassium ions were released to the solution, in consequence of cells membrane destruction [32]. It was determined that (Fig. 4) conductivity of the solutions, to which the samples of algae not activated in demineralised water were introduced, was approximately 10 times higher than conductivity of the solution, in which the biomass previously conditioned in demineralised water was immersed. The presence in the solution of a large number of sodium, potassium, calcium and manganese ions introduced with an algae sample could have been the reason for the reduced sorption of metal ions.

The graphs presented in Figure 5 show that the process of  $Zn^{2+}$  ions sorption by algae biomass is accompanied by the sorption of  $H^+$  ions. This conclusion is confirmed by the tests of heavy metals sorption kinetics from the solutions with  $pH = 3.5$ .

0.1 M of hydrochloric acid was added in order to reduce pH of the zinc salt solution. Figure 6 presents the graph with results of the carried out analyses.

It was determined that the higher  $H^+$  ions concentration in the solution, into which algae were added, the higher their competitiveness versus metal ions. From the solution with the initial  $pH = 4.10$  and metal concentration  $c_{Zn,0} = 1.10 \text{ mg dm}^{-3}$ , more  $Zn^{2+}$  ions were absorbed ( $0.31 \text{ mg g}^{-1} \text{ d.m.}$ ) than from the solution with the same zinc concentration and  $pH = 3.50$  ( $0.23 \text{ mg g}^{-1} \text{ d.m.}$ ). This conclusion is confirmed by the result of the research carried out by other authors [33].

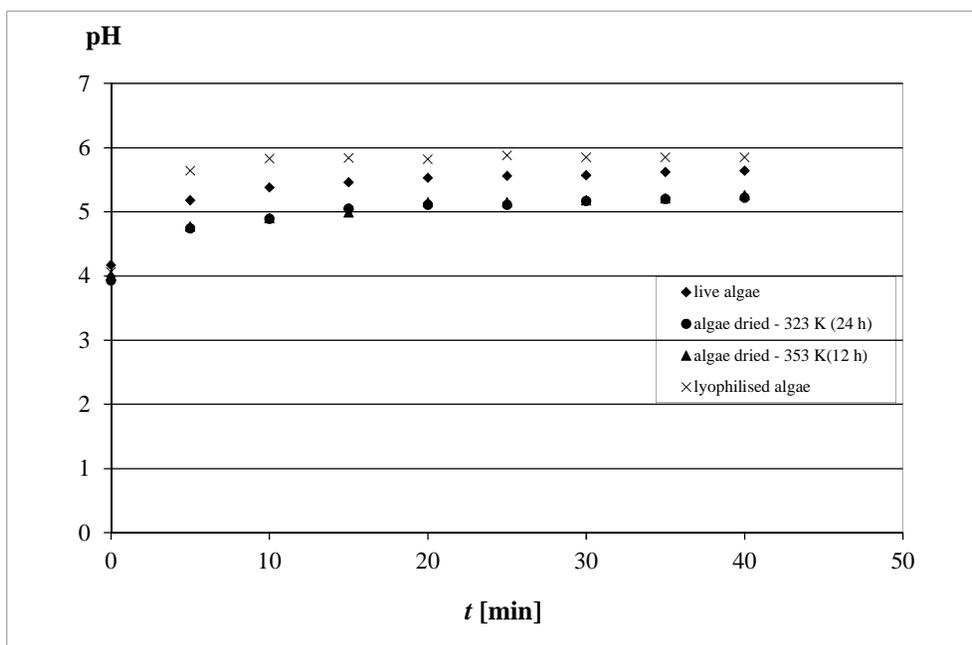


Fig. 5. Changes of  $H^+$  ions concentration in zinc solution, in which live and prepared algae were immersed, activated in demineralised water

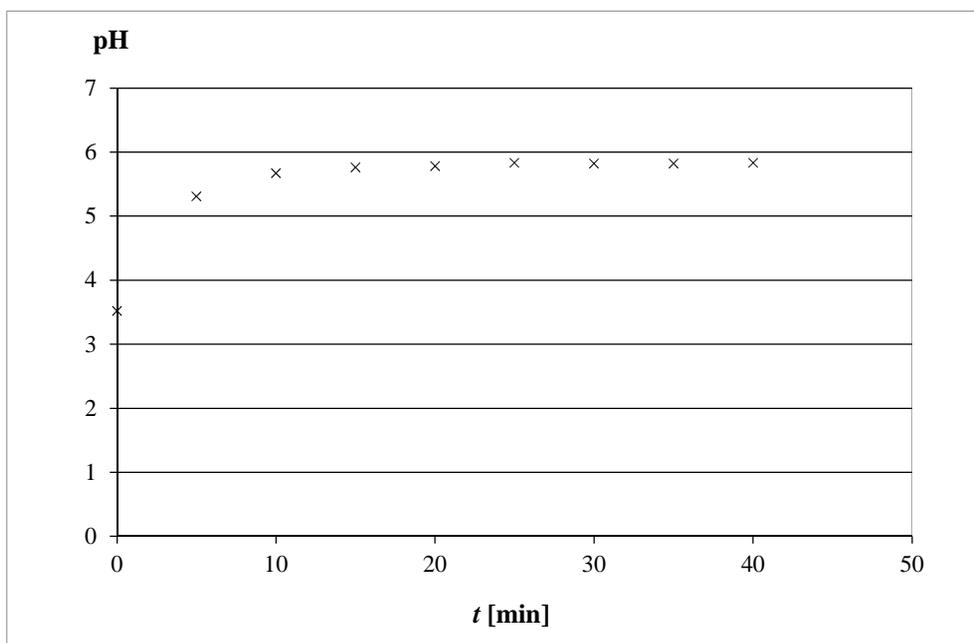


Fig. 6. Changes of  $H^+$  ions concentration in zinc solution with  $pH = 3.5$ , in which the freeze dried *Spirogyra* sp. algae were immersed

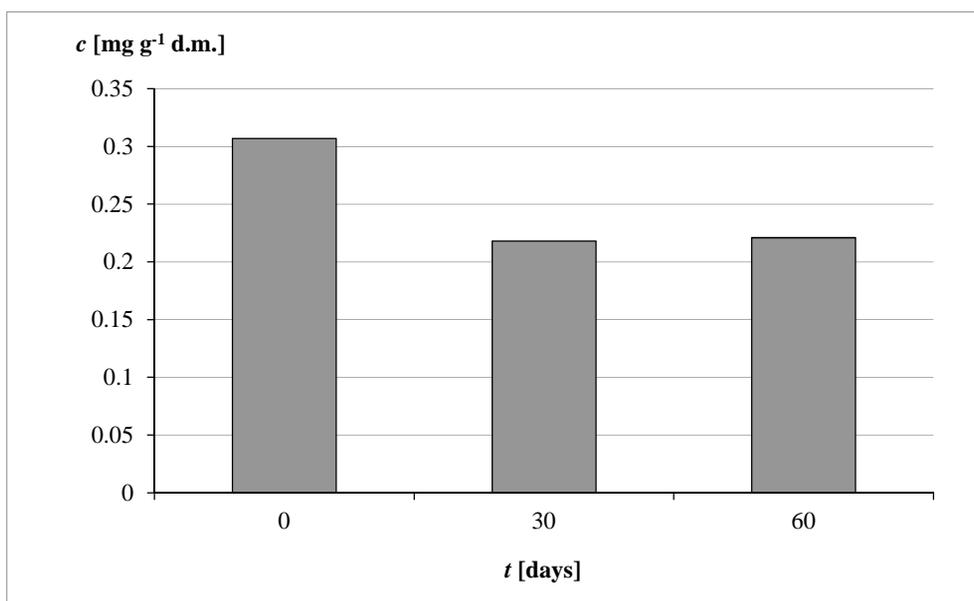


Fig. 7. Zinc concentration in freeze dried algae samples, depending on the storage period

The influence of algae samples storage period on zinc sorption was also analysed. The biomass samples for analyses were stored in a tightly closed polyethylene container. The graph in Figure 7 shows the values of zinc concentration accumulated in algae, which were prepared for analysis, after 30 and 60 days from the collection.

It was found out that the algae sorption qualities changed after 30 days of storage. Approximately 29% less zinc ions accumulated in biomass samples, in comparison to the samples used for analyses directly after freeze drying. Extension of algae storage period up to 60 days did not cause any further changes. It can be assumed that the observed changes in algae sorption capacity are the result of chemical decomposition of the algae structures, destroyed during the freeze drying process.

#### Assessment of sorption capacity of freeze dried *Spirogyra* sp.

The next stage included analyses of equilibria during  $Zn^{2+}$  ions sorption from its salt solutions and assessment of sorption capacity of freeze dried *Spirogyra* sp.

On the basis of measurements of heavy metals concentrations in the solution  $c_{(s)}$ , before (0) and after (1) sorption process, metals concentrations were determined  $c_{(a)}$ , converted to 1 g d.m. (dry mass of the algae). In order to maintain the experiment conditions (0.5 g d.m. of algae introduced to 200 cm<sup>3</sup> of metals salts solution), it should be assumed that sorption in 1 g d.m. of algae is carried out from 400 cm<sup>3</sup> of the solution. The change of the sorbent mass in comparison to the solution volume in static conditions influences the equilibrium status.

The results calculated according to correlation (2) are presented in Figure 8.

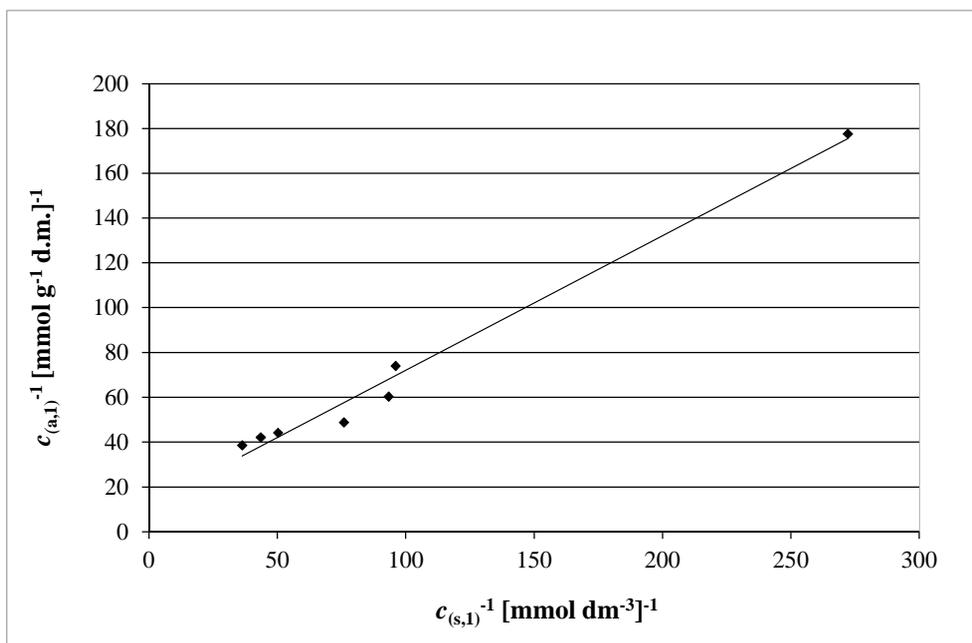


Fig. 8. The Langmuir isotherm describing sorption equilibrium Zn ( $t_{sorption} = 30$  min)

The Langmuir isotherms parameters are presented in Table 2.

Table 2

Function  $y = a \cdot x + b$  parameters presented in Figure 8; linear regression parameters:  $\pm SD_a$  - standard deviation of the parameter  $a$ ,  $\pm SD_b$  - standard deviation of the parameter  $b$ ,  $R^2$  - correlation coefficient and  $c_{(a,max)}$  - sorption capacity

The Langmuir isotherm model					
$a$	$b$	$\pm SD_a$	$\pm SD_b$	$R^2$	$c_{(a,max)}$ [mmol g <sup>-1</sup> d.m.]
0.600	12.1	0.032	3.88	0.986	0.083

On the basis of the carried out research, it was determined that the analysed algae absorb zinc in proportion to its content in the solution. The Langmuir isotherm model is well adjusted ( $R^2 = 0.986$ ) to the experiment data. Little value  $\pm SD_a = 0.032$  of the  $a$  parameter of the Langmuir isotherm shows the linear correlation of zinc concentration in algae and its content in a solution. The defined by Langmuir isotherm sorption capacities  $c_{(a,max)} = 0.083$  mmol/g d.m. is a reference value only, because it is highly unreliable, expressed by  $\pm SD_b$ . One may assume that one of the causes of wide distribution of measuring points, versus the theoretical straight line defined by the Langmuir isotherm (Fig. 8), is the competitive sorption of hydrogen cations [34]. Therefore, in order to determine sorption capacity of algae, one should consider the sum of absorbed hydrogen and zinc cations.

In order to perform detailed comparison of equilibria parameters of two valence zinc cations and one valence hydrogen cations, their concentrations were expressed as:  $c^* = z \cdot c$ , where  $z$  - cation valence (nondimensional number),  $c$  - concentration expressed in mmol dm<sup>-3</sup> or mmol g<sup>-1</sup>. Table 3 contains a summary of concentrations  $c^*$  of zinc cations in solutions ( $s$ ) and in algae ( $a$ ) before ( $0$ ) and after ( $I$ ) sorption process, and concentrations  $c^*$  of hydrogen ions in solutions ( $s$ ) and in algae ( $a$ ) after ( $I$ ) sorption process. The initial concentrations of H<sup>+</sup> and Zn<sup>2+</sup> in algae were assumed as equal to zero.

Table 3

Zinc concentrations in dry mass of algae and solutions before and after sorption process and hydrogen ions concentration in solutions and algae after sorption process

Measurement series	$c^*_{Zn(s,0)}$	$c^*_{Zn(s,I)}$	$c^*_{Zn(a,I)}$	$c^*_{H(s,I)}$	$c^*_{H(a,I)}$
	[mmol dm <sup>-3</sup> ]	[mmol dm <sup>-3</sup> ]	[mmol g <sup>-1</sup> ]	[mmol dm <sup>-3</sup> ]	[mmol g <sup>-1</sup> ]
1	0.0318	0.0037	0.0056	0.0014	0.0047
2	0.0781	0.0104	0.0135	0.0019	0.0059
3	0.0937	0.0107	0.0166	0.0009	0.0048
4	0.1157	0.0132	0.0205	0.0015	0.0045
5	0.1332	0.0199	0.0226	0.0019	0.0053
6	0.1417	0.0229	0.0238	0.0013	0.0061
7	0.1573	0.0275	0.0259	0.0011	0.0054

Figure 9 presents the Langmuir isotherm determined pursuant to correlation (2), for the sum of cations H<sup>+</sup> and Zn<sup>2+</sup>.

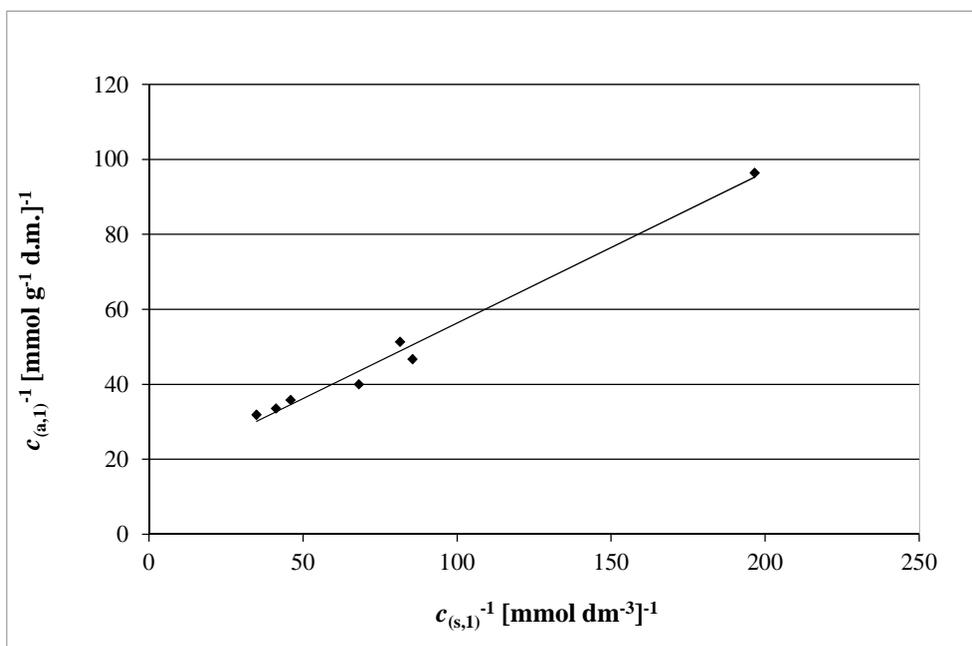


Fig. 9. The Langmuir isotherm determined for the sum of cations  $H^+$  and  $Zn^{2+}$

The parameters for the Langmuir isotherm determined for the sum of cations  $H^+$  and  $Zn^{2+}$  are presented in Table 4.

Table 4

Function  $y = ax + b$  parameters presented in Figure 9; linear regression parameters:  $\pm SD_a$  - standard deviation of the parameter  $a$ ,  $\pm SD_b$  - standard deviation of the parameter  $b$ ,  $R^2$  - correlation coefficient and  $c_{(a,max)}$  - sorption capacity

The Langmuir isotherm model					
$a$	$b$	$\pm SD_a$	$\pm SD_b$	$R^2$	$c_{(a,max)}$ [mmol g <sup>-1</sup> d.m.]
0.403	16.1	0.019	1.89	0.987	0.062

The *Spirogyra* sp. algae sorption capacity, determined from the Langmuir isotherm for zinc, amounts to:  $c^* = 0.083 \text{ mmol g}^{-1}$  ( $2.72 \text{ mg g}^{-1}$  of algae dry mass), and with reference to the sum of  $H^+$  and  $Zn^{2+}$  amounts to:  $c^* = 0.062 \text{ mmol g}^{-1}$  ( $2.03 \text{ mg g}^{-1}$  d.m.). The carried out research showed that, in reference to the sum of cations, unreliability of assessment of sorption capacity of freeze dried *Spirogyra* sp. algae is expressed by  $\pm SD_b = 1.89$ . These results show that the assessment of sorption capacity determined for zinc, carries a 50% greater error than the one determined for the sum of cations.

The carried out research results analysis shows that the differences in assessment of sorption capacity of different algae types may result from, among others, differences in sorption characteristics of different types of algae, the samples preparation methods as well as the selection of an appropriate model for the research results interpretation.

## Conclusions

On the basis of the carried out research, it was determined that the fresh water *Spirogyra* sp. algae accumulate  $Zn^{2+}$  ions from the solutions they come in contact with. Biomass sorption characteristics are influenced by the algae preparation method and storage period. The Langmuir isotherm model can be used to describe correlations between zinc concentrations in algae and the solution. This model is well adjusted to the experiment data. However, the determined sorption capacity value is characterised by high unreliability, expressed by  $\pm SD_b$ . The unreliability of results regarding algae sorption capacity is influenced by the competitive sorption of  $H^+$  ions. Therefore, in order to determine sorption capacity of algae, one should consider the sum of absorbed hydrogen and metal cations.

In order to validate the research procedures, the appropriate preparation and storage of algae samples methodology should be applied, as well as the relevant model of the research results interpretation. All the operations aim at obtaining the most reliable analyses results.

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## WPLYW SPOSOBU PREPAROWANIA PRÓBEK GLONÓW *Spirogyra* sp. NA ICH POJEMNOŚĆ SORPCYJNĄ

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**Abstrakt:** Zbadano wpływ sposobu preparowania próbek na parametry sorpcji jonów cynku na glonach *Spirogyra* sp. Proces sorpcji  $Zn^{2+}$  z roztworów soli tego analitu prowadzono w warunkach statycznych. Wyniki z przeprowadzonych badań wskazują, że sposób przygotowania próbek glonów do analiz (suszenie termiczne, liofilizacja, kondycjonowanie próbek w wodzie zdeminalizowanej) oraz czas przechowywania ma wpływ na ich pojemność sorpcyjną. Na podstawie przeprowadzonych badań kinetyki sorpcji tego metalu na żywych i preparowanych próbkach glonów stwierdzono, że stan równowagi zostaje osiągnięty po około 30 minutach. W warunkach prowadzenia eksperymentu 56% metali sorbowanych jest na glonach żywych w pierwszych 15 minutach. W próbkach glonów suszonych termicznie i liofilizowanych po 30 minutach trwania procesu zakumulowało się odpowiednio około 17 i 65% jonów cynku obecnych w roztworze. Stwierdzono, że kondycjonowanie próbek glonów przed procesem sorpcji w wodzie zdeminalizowanej podnosi jego wydajność. W celu wyznaczenia pojemności sorpcyjnej liofilizowanych glonów *Spirogyra* sp. zastosowano model izotermi Langmuira. Stwierdzono, że glony sorbują metale ciężkie proporcjonalnie do ich zawartości w roztworze, w którym zostały zanurzone. Wyznaczona z izotermi Langmuira pojemność sorpcyjna liofilizowanych glonów *Spirogyra* sp. względem cynku jest obarczona dużą niepewnością pomiarów. Stwierdzono wyraźny wpływ kationów wodorowych na stężenia miedzi w glonach i w roztworze w stanie równowagi.

**Słowa kluczowe:** cynk, glony *Spirogyra* sp., glony preparowane, kinetyka sorpcji, model izotermi Langmuira, pojemność sorpcyjna