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ALGAE - HEAVY METALS BIOSORBENT

GLONY - BIOSORBENT METALI CIĘŻKICH

Abstract: The publication is a synthetic collection of information on the sorption properties of marine and freshwater algae. Kinetics and sorption equilibrium of heavy metals in algae-solution system, influence of abiotic factors on the process of sorption and desorption of analytes from biomass are discussed. In paper the results of laboratory tests conducted using different species and types of algae, which purpose was to assess their usefulness as natural sorbents, are described. The conclusions drawn from current research confirm the results from literature.

Keywords: algae, heavy metals, kinetics and sorption equilibria, desorption

Introduction

The dawn of algology (phycology - a subdiscipline of botany studying, *inter alia* the taxonomy, biology and ecology of algae) as a field of science dates back to the first half of the 19th century, together with the publication of works by Carl Adolph Agardh (1785-1859) - the father, entitled *Systema algarum* (1824) and Jacob Georg Agardh (1813-1901) - the son, entitled *Algae maris Mediterranei et Adriatici, observationes in diagnosin specierum et dispositionem generum* (1842). In Poland, algology developed under the influence of the studies conducted, among others, by Jadwiga Woloszynska (1882-1951) - a disciple of Marian Raciborski, and Roman Gutwiński (1860-1932) - a disciple of Józef Rostafiński [1-5].

The term *algae* (Gr. *Phykos,* Lat. *Algae*) is used to refer to a group of thallus plants, *ie* paraoza (morphological groups: *Protophyta* and *Thallophyta*). Among them, apart from eukaryotes (inter alia *Spirogyra* sp.), there are also organisms with prokaryotic cell structure, such as blue-green algae (*eg Nostoc commune*), also known as *Cyanobacteria* [4, 5].

Algae are encountered in every place where water is present, at least periodically. They inhabit both the aqueous environment and land. They live both in saltwater (saline, salty lakes, seas and oceans) and in freshwater (springs, rivers, ponds, lakes and swamps). Some

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species are able to live on snow and ice, while others in hot springs (the highest temperature at which algae were found was 358.2 K) [4-6].

Algae display varied morphological structure of the thallus (single-celled species (*Ochromonas ludibunda*), species forming colonies (*Hydrurus foetidus*), and multi-celled organisms (*Ulva lactuca*), species with thread-like thallus (*Cladophora*) and ramified thallus (*Caulerpa prolifera*). They also vary in shape and size, from species as small as 1 μm to large, leaf-like species that fix to surfaces using rhizoids (thread-like processes). In the trophic chain, algae are mostly autotrophic, although heterotrophic algae and algae that enter symbiotic relations with other organisms are also encountered. For instance, the symbiotic relations between algae and fungi take the form of lichens [4-7].

Studies carried out on algae concentrate on, among others, their chemical composition, biology, taxonomy, physiography and also their application for the assessment of water contamination with heavy metals, pesticides and radionuclides.

The aim of this study was to collect and systematize information on the sorption of heavy metals in different species and types of algae. Practical application of these studies, including phytoremediation of water and wastewater treatment, were indicated.

Sorption properties of algae thalli

Laboratory tests carried out with different species of algae are aimed, among others, at assessing the sorption properties (kinetics and sorption equilibrium), as well as the potential desorption of the accumulated heavy metals by algae for the purpose of their multiple application as biosorbents in water treatment.

The main mechanism of heavy-metal cation sorption in algae biomass is the ion-exchange between the solution and the thallus [8-10]. On the basis of the conducted studies, it was found that the algae cell wall is built not only of organic compounds, but it also consists of, *eg*, Na^+, K^+, Ca^{2+} and Mg^{2+} ions [11]. During cobalt biosorption by the alga *Ascophyllum nodosum*, the release of Na^+, K^+, Ca^{2+} and Mg^{2+} ions from the alga cells to the solution was observed [12, 13]. During sorption of Cr^{3+} and Pb^{2+} by the alga, an increase of calcium contamination in the solution, in which they were immersed, was observed. The process of ion exchange of heavy metals with Ca^{2+} (CaX_2) ions was described by the authors, by means of corresponding stoichiometric equations [14]:

$$2Cr^{3+} + 3(CaX_2) \leftrightarrows 3Ca^{2+} + 2(CrX_3) \tag{1}$$

$$Pb^{2+} + (CaX_2) \leftrightarrows Ca^{2+} + (PbX_2) \tag{2}$$

The authors concluded that the process of ion exchange is a basic mechanism during heavy-metal sorption in the algae-solution system [14].

Kinetics and equilibria in the algae-solution system

Some differences in the sorption properties of different types and species of algae have been observed, which are connected, among others, with the physiological and morphological structure of thalli, with the location from which the biomass is collected and with the manner of algae preparation for the analysis [15]. Most frequently, the kinetics of the process is described and parameters of equilibrium and algae sorption capacity are determined [16].

Different models are applied to describe the sorption kinetics, *eg* the pseudo-first-order kinetic model, defined as the Lagergren's equation [17-19], the pseudo-second-order model [17, 19], as well as the Weber and Morris' model [17, 20]. The sorption kinetics, while expressing the concentrations translated into an ion unit charge: $c* = z \cdot c$ [mol/dm³]; (z - ion valence; a non-dimensional value); can be described in a detailed way by means of a second-order equation [21]; however, it is necessary to trace concentration changes, both in the sorbed and desorbed ions by the thalli. In the case of algae such as *Palmaria palmate*, this model is difficult to apply due to lack of data regarding the quality of ions desorbed by algae in the process of ion exchange and the effect of a competitive sorption of H^+ ions [22].

The studies of heavy-metal sorption kinetics by algae show that the time needed to attain the dynamic equilibrium depends, among others, on the type of algae and the degree of biomass fragmentation. The biomass of the marine alga *Ecklonia maxima*, with the thalli of 1.2 mm, attained the equilibrium during sorption of Cu, Pb and Cd after roughly 60 min, while for thalli of the size of 0.075 mm after grinding, the equilibrium stabilised after approximately 10 min [23]. It was found that the cosmopolitan alga *Chlorella vullgaris* and the freshwater alga *Scenedesmus quadricauda* sorb 90-95% of Cu within the first 15 min of the experiment (equilibrium is stabilised after approx. 2 h) [24], and the sea alga *Caulerpa lentillifera* within 10-20 min (equilibrium was reached after 20 min) [20]. Biosorbents (DP95Ca and ER95Ca) developed on the basis of the marine algae *Durvillaea potatorum* and *Ecklonia radiate* sorb 90% of Cu and Pb ions within 30 min (equilibrium stabilised after approx. 60 min) [25], the alga *Chlorella vulgaris* within 45 min of the process sorbs 53% and 60% of Ni and Cu ions, respectively (the immobilised algae sorb 70% of Ni and 90% of Cu) [26], and the marine alga *Ulva lactuca* sorbs 80% of Cr^{6+} ions within the first 20 min of the process (equilibrium stabilised after approx. 40 min) [27]. The data from the cited literature confirm the results of our own laboratory tests carried out on the sea alga *Palmaria palmate* and the freshwater alga *Spirogyra* sp. [22, 28]. The dynamic equilibrium during heavy-metal sorption by alga *Palmaria palmata* stabilised after approx. 50 min. At this time, in the algae sample, approx. 87% of Mn^{2+} ions, 95% of Cu^{2+}, 96% of Zn^{2+} and 97% of Cd^{2+} ions which were in the initial solution are accumulated (initial solution concentrations were, respectively: Mn - 1.16, Cu - 1.47, Zn - 1.55 and Cd - 2.13 mg/dm³). In the first 10 min of the process, approx. 60-70% of ions of the determined heavy metals is sorbed from the solution to the biomass, as compared with their concentration accumulated in algae in the equilibrium state (for Cu - 0.56 mg/g dry mass (d.m.)). It is interesting to notice that the dynamic equilibrium during sorption of, *eg* Mn, Cu, Zn and Cd by the alga *Spirogyra* sp. is attained after approx. 30 min. At this time, on the freshwater algae approx. 80% of Mn^{2+} ions, 94% of Cu^{2+} ions, 92% of Zn^{2+} ions and 94% of Cd^{2+} ions, which were in the initial solution, are accumulated (initial solution concentrations were, respectively: Mn - 0.97, Cu - 1.47, Zn - 1.19 and Cd - 2.01 mg/dm³). The chart in Figure 1 shows the course of changes in mercury concentrations in the solution with the initial concentration of 53.6 μg/dm³, in which the alga *Spirogyra* sp. was immersed [29].

The conducted studies show that the dynamic equilibrium stabilises after roughly 30 min. At this time, in the sample of *Spirogyra* sp., almost 51% of Hg^{2+} ions present in the initial solution was accumulated. Within the first 10 min of the process, approx. 90-95% of mercury ions is sorbed from the solution to the biomass, as compared with the concentration of mercury accumulated in algae in the equilibrium state (9.62 μg Hg/g d.m.) [29].
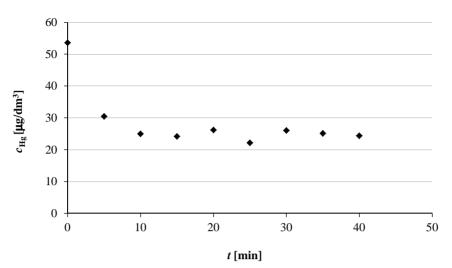
Fig. 1. Mercury concentration changes in the solution-algae system

On the basis of literature data analysis regarding the kinetic studies of heavy metal sorption by algae, it can be stated that the concentration of the absorbed analytes as well as the time needed for equilibrium to stabilise depends, among others, on the alga species, methodology of its preparation and on the initial concentration of analyte in the solution. It was observed that algae accumulate approx. 90-95% of the absorbed metals within the first 10 min of the experiment. Results of laboratory analyses regarding the kinetics of heavy metal sorption by algae are used while planning the biomonitoring tests *in situ*. When the species of algae is known, it is possible to determine the time of their exposure in a given ecosystem, after which the dynamic equilibrium of algae-water system will stabilise.

To describe the equilibrium, the following models are applied: the Freundlich isotherm model [30, 31], the Langmuir model [30, 32], the Redlich-Peterson model [27] and the Koble-Corrigan model [27]. Frequently, the best correlations between the experimental and computed data are obtained with the Langmuir isotherm model, on the basis of which the sorption capacity of algae is determined [27, 33-36].

Laboratory tests indicate that the maximum sorption capacity of, *eg* the alga *Cladophora glomerata* is 15.0 mg/g d.m. for Cu and 22.5 mg/g d.m. for Pb, respectively [37], while that of the marine algae, such as *Ecklonia radiata*, *Ecklonia maxima*, *Laminaria japonica* and *Laminaria hyperbola* is 207 to 332 mg/g d.m. for Pb, 63.5 to 76.2 mg/g d.m. for Cu, and 89.9 to 135 mg/g d.m. for Cd [38]. The maximal sorption capacity for Cu of the algal-bacterial biomass was 8.5 ± 0.4 mg/g d.m. [39]. A two-year investigation confirmed that the biosorbents (DP95Ca and ER95Ca), based on the marine algae *Durvillaea potatorum* and *Ecklonia radiate*, had the sorption capacity comparable to that of synthetic ion-exchange resins, and much higher than natural zeolites or pulverised active carbon (the capacity of DP95Ca was 82.6 mg/g for Cu and 332 mg/g for Pb, while the capacity of ER95Ca was 69.9 mg/g for Cu and 269 mg/g for Pb) [40]. It is interesting to compare the

sorption capacity of such natural sorbents as diatomaceous earth, bentonite, kaolinite and compost for Cu, which is: 5.54, 7.59, 4.47 and 12.77 mg/g, respectively [41].

Literature data review regarding the sorption capacity of different species of algae is presented in Table 1.

Table 1

Sorption capacity values of algae and physicochemical parameters of their preparation for the analyses:
T - drying temperature, t_s - drying time, t_k - conditioning time

Algae type/species	Metal; sorption capacity [mg/g d.m.]	Physicochemical parameters			References
		T [K]	t_s [h]	t_k [h]	
Cladophora glomerata	Cu; 15.0	323	24	-	[37]
Cladophora glomerata	Pb; 22.5	323	24	-	[37]
Oedogonium	Pb; 145	343	24	-	[33]
Nostoc sp.	Pb; 93.5	343	24	-	[33]
Oedogonium	Cd; 31.0	343	24	-	[42]
Spirogyra sp.	Cr; 14.7	-	6	-	[43]
Spirogyra sp.	Pb; 140	343	24	-	[34]
Spirogyra sp.	Cu; 133.3	-	6-8	-	[16]
Ecklonia maxima	Cu; 85-94	373	24	3	[23]
Ecklonia maxima	Pb; 227-243	373	24	3	[23]
Ecklonia maxima	Cd; 83.5	373	24	3	[23]

The results presented in the table indicate significant differences in sorption capacity of algae depending on their species. Unfortunately, the authors do not provide information on the uncertainty of the measurement results.

On the basis of our own laboratory tests, it was possible to conclude that, while leaving out the algae specific diversity, an important role is played by the manner of algae preparation and the methodology of the tests. In the static system (Fig. 2a) - with a decreasing concentration of metal ions in the solution during the process, the parameters of metal-ions sorption by the alga *Spirogyra* sp. depend on, among others, the proportion of algae mass and the solution volume. In the dynamic system (Fig. 2b) - with a constant concentration of metal ions in the solution, this problem does not appear.

The time of storing the algae that are later used for the experiments is also important [44]. The studies conducted on the alga *Spirogyra* sp. showed that the uncertainty of determination of sorption capacity for copper may be as high as 10^4%, depending on the manner of conducting the experiment, especially on the manner of algae preparation [44].

The results of our own experiments indicate also a significant effect of hydrogen cations on the heavy metal sorption by algae. The competitive sorption of hydrogen cations has an impact on the kinetics and equilibrium of ion-exchange with heavy metals. It also influences the uncertainty of the results, for instance, as far as the sorption capacity of algae is concerned. While determining the sorption capacity on the basis of the Langmuir isotherms, a clear impact of hydrogen cations on the copper concentration in algae and in the solution in equilibrium was observed. The sorption capacity of the alga *Palmaria palmata* for copper is $c^* = 0.99$ mmol/g (31.5 mg/g d.m.), and for the total of H^+ and Cu^{2+} $c^* = 0.39$ mmol/g (12.4 mg/g d.m.). These illogical values indicate that the assessment of sorption capacity may be significantly faulty. It was found that the uncertainty of sorption capacity determination for copper cations exceeds 300%, while for H^+ and Cu^{2+} cations it is

less than 32%. Such high uncertainty of assessments, especially for copper itself, explains the discrepancies in determination of algae sorption capacity. However, it seems that in order to determine their sorption capacity, the total amount of sorbed hydrogen and copper cations should be taken into consideration [10]. With a constant initial pH of the solution, together with an increase of the value of the copper gram-equivalent fraction in the initial solution, the competitive sorption of hydrogen cations is decreasing.
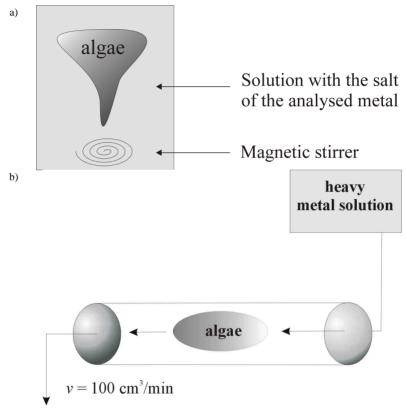

Fig. 2. Heavy metal sorption by the algae biomass - experiment conditions: a) static system, b) dynamic system

     The cation affinity depends mainly on the value of ion electric charge, ion beam and the degree of hydratation. The higher the cation charge, the higher the force of its attraction by inversely charged functional groups, *eg* lipids, polysaccharides and proteins which build the algae cell walls [37]. In the case of the equal-value cations, their size determines the exchange potential. The higher the cation volume, the weaker the electric field generated by this cation in the solution, which, in turn, decreases the degree of hydratation. With an increase of the atomic mass, there is a decrease in the so-called cation hydrodynamic beams, and by this their exchange energy is increasing [45]. On the basis of the conducted studies, the affinity columns of metals by sorption structures were determined, *eg* the alga *Cyanidium caldarium*: Zn > Mn > Ni > Cu [46], *Caulerpa lentillifera*: Pb > Cu > Cd > Zn

[17], *Fucus vesiculosus*: Pb > Cu > Cd [47] and *Chaetophora elegans*: Ni > Zn > Pb > Cd [48]. The algae of the phyla: green algae (*Chlorophyta*: *Caulerpa lentillifera, Chaetophora elegans*) and brown algae (*Phaeophyta*: *Fucus vesiculosus*) are characterised by convergent affinity columns of heavy metals to their thalli.

Moreover, cation affinity to the cellular structures of algae thalli is conditioned by *eg* molecular composition of these structures, and mainly the type and quantity of functional groups.

The studies on kinetics and sorption equilibrium of heavy metals by algae show that in the first minutes of the experiment they sorb 90% of the heavy-metal ions accumulated in their thalli. The efficiency of the process depends on the algae species, methodology of their preparation, metal concentration in the solution and the presence of other ions, *eg* H^+. The competitive sorption of hydrogen cations has impact on kinetics and ion-exchange equilibria with heavy metals. It also influences the uncertainty of results, among others in relation to the algae sorption capacity.

The results of kinetics and equilibria studies conducted in laboratory conditions are later used in the biomonitoring studies or phytoremediation of ecosystems polluted with heavy metals. The kinetic studies allow to define the time needed for equilibrium to stabilise in the algae-water system of a chosen ecosystem, while the equilibrium studies, *eg* in the biomass-sewage system, help to predict the analyte concentration that will be removed from water, by sorbing on a given algae mass.

The effect of physicochemical factors on the sorption properties of algae

The efficiency of heavy-metal sorption by algae used for the purposes of the *in situ* studies depends on the abiotic factors, *eg* the temperature, pH, the intensity of the photosynthetically active light as well as the presence of other ions and anions which cause, *eg* complexing of the metal ions (chlorides and humus substances) or development of difficult to dissolve metal compounds (phosphates). The biotic factors, for instance organic matter suspended in water through the surface sorption processes, decrease the equilibrium concentration of metals in water [15]. Due to the complexity of the aqueous environment as well as the interactions among various factors and elements of the ecosystem it is difficult to estimate, under natural conditions, the effect of the bioaccessible forms of heavy metals on the algae cells.

On the basis of laboratory tests conducted with algae, the assessment of the effect of physiochemical factors on the sorption properties of different algae species was carried out. It was observed that changes in pH of Cu^{2+} and Pb^{2+} salt solutions (analyte concentration in solution was 100 mg/dm^3) in the range $5.8 < pH < 8.5$ did not have any effect on the concentration of the ions accumulated in the alga *Ecklonia maxima*. Lack of increase in copper and lead concentrations in algae may have been caused by precipitation of the insoluble hydroxides from the solution and at the same time a limitation of their sorption by the thalli [23]. A decrease of solution pHs (pH < 4) reduced the sorption of the analysed heavy metals. This outcome was induced by, *eg* competitiveness of H^+ ions in relation to Cu^{2+} and Pb^{2+} ions and a decrease in the number of negative charges on the surface of cell walls, which depends on the dissociation degree of functional groups, *eg* the carboxyl and amine groups. Together with the decrease in pH, the dissociation of carboxyl group of amino acids decreases (at pH = 2 it is totally receded). Under such conditions, a strong protonation of the amine group to NH_3^+ takes place, which allows for a conclusion that in

a strongly acid environment the amino acid particles are present in the form of a positive ion [16, 23].

Biosorbents (DP95Ca and ER95Ca) developed on the basis of the marine alga *Durvillaea potatorum* and *Ecklonia radiate* sorbed 90% of the determined metal ions at pH = 4.5. A decrease in pH (down to pH = 1) caused a decrease of the concentration of the absorbed metal ions [25]. It was observed that the alga *Ulothrix zonata* sorbs the most Cu^{2+} ions at pH = 4.5 [49] and the algae *Spirogyra* sp., *Chlorella vulgaris*, *Scenedesmus obliquus* and *Synechocystis* sp. at pH = 5.0 [16, 50].

The example of the effect of solution pH on the metal sorption by algae is presented on the chart in Figure 3.
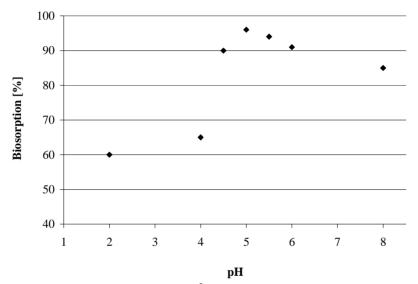

Fig. 3. Effect of pH of the solution on the Cd^{2+} sorption by the alga *Ceramium virgatum* [18]

The authors concluded that the maximal sorption of cadmium ions (96% biosorption capacity) by the alga *Ceramium virgatum* can be attained at pH = 5.0. At pH = 4.5, 90% of Cd^{2+} ions was sorbed, which was caused by the competitive sorption of hydrogen ions from the solution. The increase of pH (pH > 5) caused the decrease in process efficiency, which, according to the authors, was connected with the development of complexes with hydroxide anions [18]. The effect of pH increase on the development of metal hydroxides in the solution was also observed by other authors [51]. The equation (3) helps to determine pH which should be attained for precipitation of hydroxide at a given concentration of metal ions [52]:

$$pH = 1 \, n^{-1} \, (14n - \log [Me^{n+}] - pK_{so})$$

(3)

where: n - metal valence, pK_{so} - solubility product.

Review of literature regarding the effect of pH on the sorption capacity of different species of algae is presented in Table 2.

Table 2

pH values at which algae sorbed the maximal concentrations of the studied heavy metals

Algae type/species	pH value	Metal; sorption capacity [mg/g d.m.]	References
Padina sp.	5.0	Cu; 50.8	[53]
Padina sp.	5.0	Cd; 59.6	[54]
Ecklonia radiata	5.5	Pb; 259	[55]
Durvillaea potatorum	5.5	Cd; 123	[40]
Ulva fasciata	5.5	Cu; 73.5	[56]
Sargassum sp.	5.5	Cu; 72.5	[56]
Oedogonium hatei	5.0	Ni; 40.9	[35]
Chlorella vulgaris	3.5	Cu; 5.3	[26]
Chlorella vulgaris	5.5	Ni; 14.1	[26]
Chlorella vulgaris	5.0	Ni; 42.3	[50]
Chlorella vulgaris	2.0	Cr; 23.0	[50]
Scenedesmus obliquus	5.0	Ni; 18.7	[50]
Scenedesmus obliquus	2.0	Cr; 15.6	[50]
Synechocystis sp.	5.0	Ni; 15.8	[50]

Numerical data presented in Table 2 show the differences in the assessment of sorption capacity. Not only do these differences result from the sorption properties of different algae, but also from the degree of uncertainty of these results. Unfortunately, the authors of the literature sources quoted in Table 2 do not provide the calculus of errors.
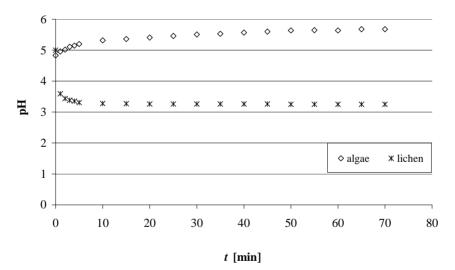

Fig. 4. pH changes in the solutions during Cu^{2+} ions sorption by algae and lichen

The effect of the competitive hydrogen ions sorption in relations to heavy-metal ions is confirmed by the own studies of the author of this paper [10]. In the case of algae, the hydrogen ions are sorbed in a competitive or parallel manner in relation to heavy-metal cations. A dissimilar effect is observed for lichen (the alga-fungus symbiotic system)

immersed in the heavy-metal saline solution, where distinctive changes in pH during the sorption process can be observed. The chart in Figure 4 shows pH changes during copper sorption by the algae *Palmaria palmata* and the lichen *Hypogymnia physodes*.

The experimental studies and literature data confirm that during the ion exchange, the cations of metals natural in the environment are released: Na^+, K^+, Mg^{2+} and Ca^{2+}, and not the hydrogen ions, which takes place in the case of lichen. These differences result from the specificity of the environments in which these biosorbents exist. Under natural conditions, algae exist in waters of high pH (*eg* pH of the Large Turawa Lake, Poland, is approximately 9). Laboratory tests of the equilibrium and kinetics of heavy-metal sorption by algae in static conditions are usually carried out at pH lower than that of water in which algae naturally exist. As a result, during the experiment, there is a parallel sorption of hydrogen cations and the cations of the analysed metals, and desorption of the ions naturally present in the environment. Under *in situ* conditions, lichen exists on the ground base whose pH depends on the pH of atmospheric waste on a given area and may be *eg*: pH = 4-5. It should be assumed that the hydrogen ions present in atmospheric water during the vaporisation are bound through the ion exchange in the cation-active layer of lichen and are desorbed to the solution, when its pH is higher than natural. Too high concentration of hydrogen ions in the solution phase (pH < 3.9) leads to the destruction of lichen thalli and the ions naturally present in the cells leak to the solution [21, 45].

The effect of pH on heavy-metal sorption in the solution-algae system was also proved by other authors [57-62].

The cations naturally present in the algae environment, *eg* Na^+, K^+, Mg^{2+} and Ca^{2+} also influence heavy-metal cation sorption by their thallii. The laboratory tests revealed a competitive sorption of Na^+ ions (introduced to the solution in the form of NaCl of the concentration = 1M) in relation to Hg^{2+} ions (reduction of Hg^{2+} sorption by 80%) by the alga *Cystoseira baccata*. Mercury concentration in the initial solutions was 500 and 1000 mg/dm^3. Sodium and potassium ions introduced to the solution in the form of $NaNO_3$ and KNO_3 led to the increase of concentration of the absorbed mercury ions. The authors did not observe any effect of Ca^{2+}, Mg^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+} and Cu^{2+} ions on the sorption of Hg^{2+} by the alga *Cystoseira baccata* [63].

The presence of K^+, Mg^{2+} and Ca^{2+} ions in the saline solution of Cu^{2+} led to the decrease of concentration in the absorbed metal ions by the alga *Padina* sp. by 4, 11 and 13%, respectively. Sodium ions introduced to the copper saline solution in the form of NaOH did not have any effect on sorption of Cu^{2+} ions [53]. Na^+ and K^+ ions (concentrations 0-10 mM) did not have any effect on sorption of Pb^{2+} and Cu^{2+} by the alga *Ecklonia radiata*, while Ca^{2+} and Mg^{2+} ions lead to a 10-18 and 5-10% decrease of sorbed metal ions in thalli respectively, depending on the introduced concentration of Ca^{2+} and Mg^{2+} (0-10 mM) [55].

Experimental results of sorption of Cr^{3+} ions by the algae *Spirogyra condensata* and *Rhizoclonium hieroglyphicum* indicate a competitive sorption of other metal ions. It was observed that enriching the chromium-ion solution with additional ions of Cu^{2+} and Pb^{2+} led to the reduction of chromium ions sorption by 38 and 36%, respectively [58]. Reduction of copper sorption from solution by the alga *Spirogyra neglecta* due to lead ions was also observed. A reverse phenomenon was also observed: copper limited lead sorption, however, the competitiveness of sorption was changing in the column Pb > Cu [64].

Presented study results are only partially convergent with the results of analyses carried out by the author of this paper. It may result, for instance, from lack of estimation of measurements uncertainty by, *eg* Herrero et al, by which it is difficult to decide whether the indicated differences are statistically significant. On the basis of her own study, the author of this paper observed that sodium ions introduced in the form of NaCl ($\kappa = 1.05$ mS) to the $HgCl_2$ solution of the concentration equalling 1.76 µg Hg/dm^3 reduce mercury-ion sorption by the alga *Spirogyra* sp. by 86% (approx. 14% of Hg^{2+} was absorbed). When the solution was without sodium ions, approx. 51% of mercury ions accumulated in the thalli of algae [29]. During the experiments with $HgCl_2$ solutions with the Hg^{2+} concentrations comparable to the concentrations that are determined in surface waters (*eg* 0.07 µg/dm^3) the effect of Ca^{2+} ions on mercury sorption by thalli of *Spirogyra* sp. was observed. After the introduction of Ca^{2+} ($\kappa = 466$ µS) to the mercury solution with the concentration of 1.12 µg Hg/dm^3; approx. 4% of Hg^{2+} was absorbed by the algae thalli.

On the basis of own studies, the author also stated that the alga *Palamaria palamata*, first introduced to the $CdCl_2$ solution with cadmium concentration $c_{Cd} = 0.042$ mol/dm^3, and later to the Cu saline solution with copper concentration $c_{Cu} = c_{Cd}$, desorbed cadmium ions. The reverse experiment did not lead to copper-ion desorption. This may suggest for instance the effect of copper ions on cadmium sorption and metal affinity to thalli of *Palamaria palamata*, which changes along with the Cu > Cd column.

It can be unequivocally stated that the cations naturally present in the environment have an effect on heavy-metal sorption by algae: the lower the concentration of the analysed particle, the stronger the effect of other ions in the solution. In order to compare the results of laboratory experiments and environmental studies, the analyses should be carried out with solutions of heavy-metal salts with concentrations comparable to those of the natural environment.

Sorption properties of algae are also influenced by anions, such as the chloride, sulphuric(IV) and (VI), phosphatic(V) and nitrate anions. The effect of chlorides, sulphates and nitrates on the Cr^{6+} ions sorption was studied (initial solution concentrations were 0.4-2.9 mmol/dm^3). It was observed that anions (concentrations: NO_3^-, Cl^- and SO_4^{2-} were 10 mmol/dm^3) decrease the concentration of the chromium ions absorbed by the thalli of *Cladophora albida* by 1.96% nitrates, by 6.63% chlorides and by 4.25% sulphates, respectively. The authors suggest that anions demonstrated a competitive sorption in relation to Cr^{6+} cation [65]. This conclusion seems to be incorrect since the effect of anion on the degree of chromium oxidation should be taken into consideration. Cr^{6+} is easily reduced to Cr^{3+}, a form of a lower affinity degree to the algae cellular membrane structures, and hence less toxic for these structures [66]. Reduction from Cr^{6+} to Cr^{3+} under the influence of anions helped the authors to observe a lower sorption of Cr^{6+}. However, the observed changes may be statistically insignificant while taking into account the uncertainty of measurements, which was not determined by the authors.

Temperature has a significant impact on various physical, biological and chemical processes that take place in an organism. For instance, it influences the viscosity, diffusion, osmosis, transport of mass and electrical charges, metabolic processes, as well as the stability of macromolecule structures of living organisms [52]. Various species of blue-green algae prosper in the temperatures between 303-308 K, and golden, red and green algae in the moderate temperatures of 288-298 K. The maximum temperature for algae to

survive has not been determined precisely. For many plants the critical temperature equals 323 K, because at this temperature some permanent changes in the protoplast take place, which leads to the organism death. The bottom range of temperatures for algae also has not been determined. In the case of the blue-green alga *Nostoc* sp., the process of photosynthesis takes place at 268 K [6]. Laboratory studies confirmed the effect of temperature on the sorption properties of algae. Together with the temperature increase within the range of 298-328 K, a statistically significant decrease of concentration of the sorbed cadmium ions was observed (with the initial cadmium concentration exceeding 390 μg/cm^3) by the alga *Sargassum* sp. [67]. However, the authors did not observe any effect of temperature on the lead sorption by this species of algae [68]. Temperature increase within the range of 298-318 K led to the increase of concentration in the absorbed Pb^{2+} ions by the algae *Oedogonium* sp., *Nostoc* sp. and *Spirogyra* sp. At the temperature equalling 298 K, in the analysed algae 144.92, 93.46 and 96.4 mg of Pb/g d.m. were found, respectively. Temperature increase to 318 K caused the increase of concentration of the absorbed Pb^{2+} ions up to169.49, 106.38 and 104 mg/g d.m., respectively. The increase of metal-ion biosorption along with the temperature increase suggests that the process is of an endothermic character. Temperature increase may lead to, among others, the increase of dissociation degree of functional groups of the algae cell walls [33, 34]. On the other hand, the Ni^{2+}-ion sorption by the alga *Oedogonium hatei* reveals an exothermic character. Temperature increase in the range between 289-318 K led to the decrease of metal-ion concentration by algae (298 K - 42 mg Ni/g d.m., 318 K - 37.3 mg Ni/g d.m.). In this case, temperature increase may have damaged the active centres responsible for nickel sorption. The optimal temperature chosen by the authors for the purpose of conducting the processes of heavy-metal sorption by the algae *Oedogonium* sp., *Nostoc* sp. and *Spirogyra* sp. was 298 K [35]. Table 3 presents data regarding the effect of temperature on the nickel sorption by the algae *Cystoseria indica, Nizmuddinia zanardini* and *Sargassum glaucescens* [69].

Table 3

Effect of temperature on Ni^{2+} sorption by algae [69]

T [K]	$c_{s,0}$ [mg/dm^3]	$c_{a,1}$ [mg/g d.m.]		
		Cystoseria indica	*Nizmuddinia zanardini*	*Sargassum glaucescens*
293	6.80	3.9	3.5	3.5
	14.9	8.1	7.3	7.0
	22	11.8	10.4	10.8
303	7.2	4.3	4.1	4.1
	14.9	8.8	8.4	8.6
	21.8	11.8	11.3	11.6
313	6.9	4.4	4.2	4.2
	14.7	8.8	8.7	8.7
	21	12.3	12	12

On the basis of the conducted studies, the authors concluded that along with the temperature increase within the range of 293-313 K, the concentration of the absorbed nickel ions by the chosen algae increases. For *Cystoseria indica, Nizmuddinia zanardini* and *Sargassum glaucescens*, the optimal sorption temperature is 313 K. The alga *Schizomeris leibleinii* reveals the best sorption properties at the temperature of 303 K [70].

Also in this case, lack of data regarding measurements uncertainty does not allow for the assessment of reliability of the obtained results.

Desorption of heavy-metal ions by algae

Cation-exchange properties of algae are connected, among others, with their cellular structures created by, *eg* alginic acid salts (alginates) [11, 40, 71, 72]. Laboratory tests revealed that cation desorption by algae cellular structures may be performed with, *eg* mineral acids: HCl and HNO_3 [64, 68, 73, 74], salt - NaCl, $Ca(NO_3)_2$ [16, 73], as well as the chelating complexes: sodium salt of ethylenediaminetetraacetic acid Na_2EDTA (often referred to as EDTA) [16, 68, 75]. Applying the hydrochloric acid of 0.1 M concentration, 80-85% of copper ions and approx. 90% of lead ions were desorbed by the thalli of *Spirogyra neglecta* [76]. During desorption (0.1 M HCl) of heavy metals (Hg^{2+}, Cd^{2+} and Pb^{2+}) by the alga *Chlamydomonas reinhardtii*, the authors obtained approx. 98% of process capacity [77]. Using mineral acids (HNO_3 and HCl) with concentrations of 0.05 M, during the first 2 min of the process approx. $92 \pm 5\%$ of copper ions were extracted by the algae *Ulva fasciata* and *Sargassum* sp. [56]. Figure 5 shows the results regarding copper desorption by the alga *Spirogyra* sp. [16].
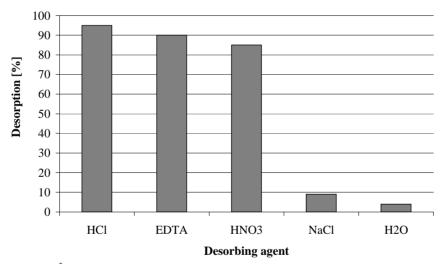

Fig. 5. Cu^{2+} desorption by the alga *Spirogyra* sp. [16]

Application of 0.1 M of HCl solution (process time - 15 min) induced 95.3% of metal desorption (Cu^{2+} concentration in algae - 133.3 mg/g d.m.) by the algae. NaCl solution and water desorbed Cu^{2+} from the biosorbent in 8.6 and 4.4%, respectively [16]. The presence of copper ions in H_2O was likely to be caused by the presence of this analyte on the surface of the biomass samples. After sorption, the algae should be rinsed in distilled water and only then should they undergo desorption. On the basis of author's own studies it was observed that distilled water does not cause desorption of heavy metals by algae.

In the process of Pb^{2+} ions desorption by the thalli of *Sargassum* sp., a 95% capacity was attained with 0.1 M solution of Na_2EDTA. This fact may be explained by a high value

of stability constant of the Pb(II)-EDTA complex ($K_f^{'} = 3.85 \cdot 10^{11}$ at pH = 5.0), which facilitates desorption of lead ions by the biomass [68]. Using 0.1 M of HCl for Pb^{2+} ions desorption by the thalli of *Oedogonium* sp. and *Nostoc* sp. led to the removal of metal from the biosorbent in approx. 90%. It was observed that carrying out the sorption-desorption process five times causes a 5% decrease in sorption capacity by the studied algae [33].

On the basis of the analysed results it can be concluded that algae may be repeatedly used as biosorbent in, *eg* sewage treatment [33].

On the basis of the author's own studies it was observed that applying hydrochloric acid with pH = 3.0 to algae in the symbiotic system with fungi (lichen) leads to the damage of their cells.

Carrying out desorption process of heavy metals by algae with low-pH acids (*eg* pH < 3.9 for algae living in lichen) leads to the damage of their cellular structures, and at the same time to the impairment of their biological functions. After desorption conducted in this manner, the algae, reused as sorbent, are likely to accumulate heavy metals only in the form of physical adsorption.

The presented study results indicate a significant effect of the abiotic factors on the concentration of analytes accumulated in thalli. However, there arises some controversy due to, for instance, lack of reliable methodology of preparation of algae samples for the analyses. The authors do not determine the uncertainty of measurements, and at the same time it is difficult to define whether the observed differences in the studied sorption parameters are statistically significant.

Proper recognition of the impact of the abiotic factors on heavy-metal sorption plays an important role in the processes of phytoremediation, sewage treatment with algae biomass as well as in the biomonitoring studies.

Conclusions

The analysis of concentrations of trace elements bound in thalli provides information regarding the pollutants introduced to the aqueous ecosystems.

The sorption mechanisms and dynamic equilibria in the system algae-solution, including contamination bioaccumulation time have not yet been recognised sufficiently. Determining correlations between analyte concentrations in algae and in solution (or *in situ*) in which they are immersed, as well as identification of the abiotic factors influencing sorption may in the future be used for the purpose of a simple measurement of heavy-metal concentrations in surface waters, which may be helpful in the development of a classification method of surface waters in which the algae will play the role of water quality biosensors.

Acknowledgements

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GLONY - BIOSORBENT METALI CIĘŻKICH

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Abstrakt: Publikacja jest syntetycznym zbiorem informacji dotyczących właściwości sorpcyjnych glonów morskich i słodkowodnych. Omówiono kinetykę i równowagi sorpcji metali ciężkich w układzie glony - roztwór, wpływ czynników abiotycznych na proces sorpcji i desorpcji analitów z biomasy. Przedstawiono wyniki badań laboratoryjnych prowadzonych z wykorzystaniem różnych gatunków i rodzajów glonów, których celem była ocena ich przydatności jako naturalnych sorbentów. Analizę wyników badań omówionych w cytowanej literaturze poparto wnioskami z badań własnych.

Słowa kluczowe: glony, metale ciężkie, kinetyka i równowagi sorpcji, desorpcja