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## TRANSLOCATION OF CATIONS DURING SORPTION OF COPPER IN THE SYSTEM SOLUTION - ALGAE (*Spirogyra* sp.)

### TRANSLOKACJA KATIONÓW PODCZAS PROCESU SORPCJI MIEDZI W UKŁADZIE ROZTWÓR - GLONY (*Spirogyra* sp.)

**Abstract:** Kinetics of the sorption of copper cations in *Spirogyra* sp. algae was analysed, together with the accompanying processes of hydrogen cations sorption and releasing to the solution the cations bonded in the algae: Na<sup>+</sup>, Mg<sup>2+</sup>, K<sup>+</sup> and Ca<sup>2+</sup>. It was established that, in a static system, at the fixed proportion of algae mass to the solution volume, these processes occur simultaneously, however presumably the quantity of the released salts influences the parameters of heterophase equilibrium of ion exchange. In the experiment conditions, the quantity of the released cations was nearly 10 times larger than the quantity of the sorbed cations. The equilibrium parameters, determined from the model of pseudo second order reaction, were compared with the parameters obtained after 30 min of the process duration, *ie* at relatively stable indications of measuring equipment. On the example of the sorbed copper, the difference is approximately 8%. It was confirmed that the solution conductivity is a good parameter for the estimation of the state close to equilibrium.

**Keywords:** algae, copper cations, biosorption, ion exchange equilibrium

## Introduction

Algae are thallophytes, *ie* they have undifferentiated bodies with varied morphological structure, among others there are single-cell and multicellular organisms, species with thread-like (*Spirogyra* sp.) or furcate (*Palmaria palmata*) thallus. There are species with dimensions of a few  $\mu\text{m}$ , as well as larger forms, anchored to the bottom by rhizoids - thread-like protuberances [1, 2].

Fresh water algae *Spirogyra* sp. belong to *Chlorophyta* division and have thread-like cells of the size 20-60  $\mu\text{m}$ , which create colonies on water surface, resembling green mats [3, 4].

Numerous laboratory tests with the use of various algae types have been carried out, in order to assess their sorption properties and the possibility to use them in biomonitoring and phytoremediation of waters and effluent [5-10].

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The main mechanism of heavy metals cations sorption in algae biomass is the ions exchange between the solution and thallus [11, 12]. The carried out research confirmed that the cellular wall of algae contains, among others, ions  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  [13]. During biosorption of, eg cobalt in algae *Ascophyllum nodosum* the release of ions  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  from algae cells to the solution was determined [14, 15].

On the basis of an analysis of the data from literature, regarding the research of kinetic sorption of heavy metals in algae, it can be stated that algae accumulate approximately 90% of the sorbed metal during the first 10-20 min of an experiment. Whereas the time required to achieve the status of dynamic equilibrium, depending among others on the type of algae, is reached after approximately 20 minutes (*Caulerpa lentillifera*) or 40 minutes (*Ulva lactuca*) [16, 17]. Declaring the equilibrium parameters, the authors actually provide the parameters of the status, during which they do not observe changes of the measuring equipment readings.

Various models are applied to describe the sorption kinetics, among others pseudo-first order reaction model expressed with Lagergren equation [17-19], pseudo-second order model [16, 18, 20, 21], used in this article for interpretation of the results, and Weber and Morris model [16, 18, 22].

The objective of the carried out research was to demonstrate, on the example of copper cations, that simultaneously with the process of heavy metal cations sorption, taking place in consequence of ions exchange, there is hydrogen cations sorption as well as the processes of dissolving of the salts of cations naturally bonded in algae thallus; another objective was to prepare the balance of the mass of cations sorbed in algae and cations passed to the solution, in consequence of various processes. In the system of a static contact of biosorbent - solution, these processes influence the status of heterophase equilibrium.

## Materials and methods

Algae *Spirogyra* sp. were used in the research, sampled from little polluted waters from the reservoir formed in a closed gravel pit, within the limits of Opole town (PL). The algae samples were cleaned from plant and water organisms impurities, and rinsed in demineralised water (conductivity  $\kappa = 0.5 \mu\text{S}/\text{cm}$ ) then dried for 24 hours at the temperature of 323 K. The research was carried out in static conditions, ie at a defined proportion of algae mass to the solution volume.

### The research method

For the research, homogenised, 1.000 ( $\pm 0.001$ ) g samples of dried algae were used; they were placed in perforated PE containers (approximately 15 cm<sup>3</sup>) and immersed for 15 min in demineralised water, in order to activate the sorption centres [23]. The samples prepared in this manner were placed in solutions of copper sulfate with 400 cm<sup>3</sup> volume. The sulfate solutions used in the research were acidified with nitric acid to approximately pH = 5 value, in order to avoid creation of not dissociated hydroxides [24]. During the process duration, the solutions were stirred vigorously, using a magnetic agitator. The solution was regularly sampled directly from the container, in order to determine cations concentration. The experiment was repeated several times, three times for each of the determined metals:  $\text{Cu}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$  and  $\text{Ca}^{2+}$  (AAS). The process was carried out for

30 min. During the sorption process, the solution pH and the conductivity values were measured.

### Equipment and reagents

For the purpose of determining concentrations of  $\text{Cu}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$  and  $\text{Ca}^{2+}$  in the solutions, the absorption atomic spectrometer iCE 3000 made by Thermo Electron Corporation, USA was used. The solutions conductivity was measured by a conductometer CC551 manufactured by Elmetron Sp. j. from Zabrze (PL), which absolute reading error was  $\Delta\kappa = 0.1 \mu\text{S}/\text{cm}$ . The pH of solutions in which alga samples were immersed was measured with a CP551 pH-meter from Elmetron Sp. j. in Zabrze (PL). The absolute error of readings was  $\Delta\text{pH} = 0.02$ .

MERCK reagents were used to prepare the solutions.

### Quality control

Calibration of spectrometer was performed with a standard solution from ANALYTIKA Ltd. (Czech Republic). The values of the highest concentrations of the models used for calibration (5  $\text{mg}/\text{dm}^3$  for Cu, 10  $\text{mg}/\text{dm}^3$  for Na, Mg, K and 30  $\text{mg}/\text{dm}^3$  for Ca) were approved as linear limits of the signal dependence on the concentration.

Table 1 shows the concentrations of metal elements determined in the reference material BCR 414 (plankton) and BCR 482 (lichen), using the AAS spectrometer.

Table 1

Comparison of measured and certified data in BCR 414 (plankton) and BCR 482 (lichen)

Element	AAS		BCR 414 plankton		Dev.*	AAS		BCR 482 lichen		Dev.*
	Mean	$\pm SD$	Certified value	$\pm$ Uncertainty		Mean	$\pm SD$	Certified value	$\pm$ Uncertainty	
	[ $\mu\text{g}/\text{g d.m.}$ ]				[%]	[ $\mu\text{g}/\text{g d.m.}$ ]				[%]
Cu	27.8	1.9	29.5	1.3	-5.8	6.54	0.18	7.03	0.19	-7.0
Na	-	-	-	-	-	108	3	119	2	-9.2
Mg	-	-	-	-	-	527	6	578	4	-8.8
K	7.12	0.23	7.55	0.17	-5.7	3665	235	3900	224	-6.0
Ca	-	-	-	-	-	2463	189	2624	180	-6.1

\*Deviation: the relative difference between measured by AAS and certified concentrations in [%]

### Results interpretation method

In order to determine changes in concentrations of sorbed or desorbed cations from the unit dry mass of algae:  $c_a$  [ $\text{g d.m.}$ ], the results of concentrations determined in the solutions:  $c_s$  [ $\text{mg}/\text{dm}^3$ ] were calculated, according to the relation:

$$c_a \cdot [\text{mmol} \cdot (\text{g d.m.})^{-1}] = \frac{c_s \cdot V \cdot z}{M \cdot m_a} \quad (1)$$

where:  $M$  - molar mass [ $\text{mg} \cdot \text{mmol}^{-1}$ ],  $V$  - volume of solution [ $\text{dm}^{-3}$ ],  $m_a$  - algae mass [ $\text{g d.m.}$ ],  $z$  - cation valence (non-dimensional value).

Thus expressed molar concentrations, converted to an ion unit charge (the former val unit), enable comparison of cations with different values.

The pseudo-second order reaction model [25] was used to determine the kinetics and equilibrium parameters:

$$\frac{t}{c^*_{C(a,t)}} = \frac{1}{c^*_{C(a,1)}} \cdot t + \frac{1}{k'' \cdot (c^*_{C(a,1)})^2} \quad (2)$$

where:  $k''$  - constant reaction speed,  $t$  - time,  $c^*_{C(a,t)}$  - cation concentration in algae after time  $t$ ,  $c^*_{C(a,1)}$  - cation concentration in algae in equilibrium.

The linear form of the equation allows to determine the constant reaction speed graphically. This equation can also be applied to determine the sorbed cations concentration in sorbent in equilibrium:  $c^*_{C(a,1)}$  as well as, as in the present article, to determine the loss of cations released from algae in equilibrium:  $-c^*_{C(a,1)}$ . In the second case, the sign (-) will also be applied to the constant  $k''$ .

The mass exchange balance was verified by conductometric measurements. In diluted solutions of electrolytes, conductivity increases in a linear manner, together with the increase of electrolyte concentration. In conversion to the unit electrical charge of ion, for the simple metal salts type AB, A<sub>2</sub>B, AB<sub>2</sub>, the approximate value of the directional coefficient of the straight line is 113, whereas for acids - 401. This results from approximately seven times higher mobility of hydrogen cations, in comparison to metal cations [26]. On that basis, it is possible to determine the relation describing the changes of solution conductivity, caused by dissolution of the salts released from algae and the sorption of hydrogen cations, resulting in consequence of the ions exchange with metal cations:

$$\Delta\kappa = 113 \cdot (c^*_{Me(s,1)} - c^*_{Me(s,0)}) + 401 \cdot (c^*_{H(s,1)} - c^*_{H(s,0)}) \quad (3)$$

where:  $c^*_{Me(s,1)}$  and  $c^*_{H(s,1)}$  - concentration of metal and hydrogen cations, respectively. Indices (s,0) and (s,1) mean initial and final cations concentrations in the solution, respectively.

## Results and discussion

Table 2 contains the results of the solution conductivity and pH changes and the results of changes in time of metals concentrations in the solution, from which sorption was carried out. The presented results are the mean value from 3 repeated processes. The standard measurement deviation from the mean value was not greater than 5% for conductivity, 8% for pH and concentration of copper in the solution and smaller than 15%, for determination of light metals.

Table 2  
Changes of conductivity, pH and concentration of cations in a copper salt solution during sorption

$t$ [min]	$\kappa$	pH	Cu	Na	K	Mg	Ca
	[ $\mu$ S/cm]						
0	5.1	4.98	1.03	0.00	0.00	0.00	0.00
5	23.1	5.49	0.68	0.26	2.44	0.28	2.68
10	32.3	5.82	0.58	0.31	3.53	0.34	3.05
15	37.8	5.99	0.56	0.32	4.08	0.39	3.54
20	41.9	6.11	0.56	0.32	4.27	0.43	3.86
25	44.2	6.19	0.56	0.31	4.43	0.50	4.21
30	46.4	6.25	0.55	0.31	4.53	0.56	4.48

The graph in Figure 1 presents kinetics of changes of cation concentrations in algae *Spirogyra* sp. The results from Table 2 were converted according to the relation (1), and

substituted to the equation, which describes kinetics of a pseudo-second order reaction (relation (2)).

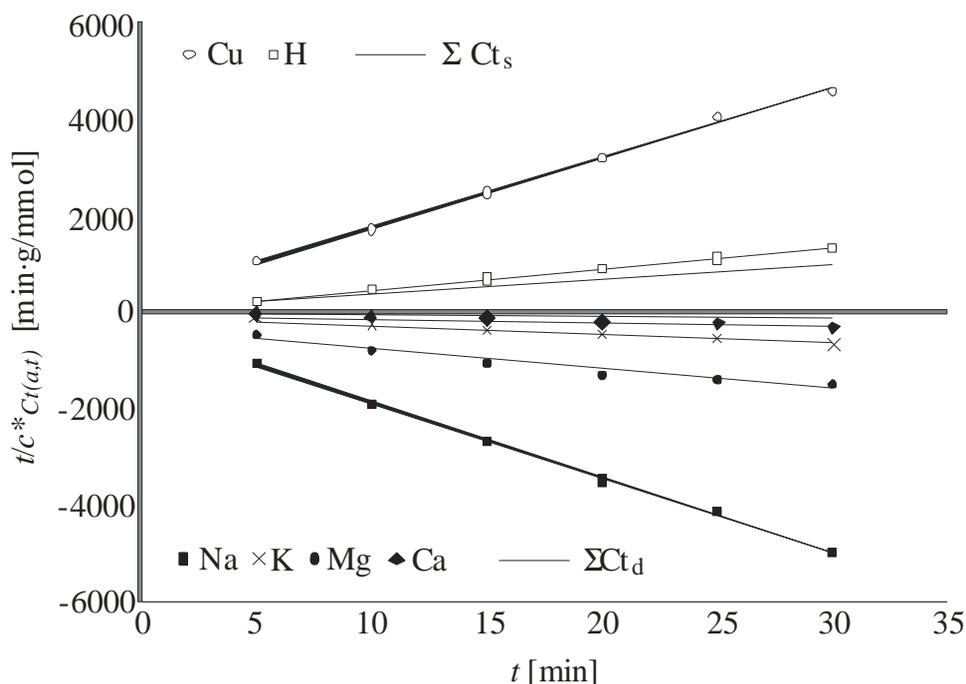


Fig. 1. Kinetics of the changes of cations in the prepared algae *Spirogyra* sp.

Table 3 contains the parameters of the functions presented in the graph in Figure 1 and the kinetic parameters, determined on the basis of the relation (2). The table also contains the sum of concentrations of the cations sorbed in algae:  $\Sigma Ct_{so}$  and the loss of the sum of concentrations of the cations from algae:  $\Sigma Ct_{de}$ .

Table 3

The parameters of the function  $y = ax + b$  and the determined on their basis constant speeds of reaction  $k''$  [ $\text{mmol}^{-1} \text{dm}^3 \text{min}^{-1}$ ] and the values of gain or loss of cations concentration in algae in equilibrium  $c^*_{Ct(a,l)}$  [ $\text{mmol g}^{-1}$ ]

Cation	Parameters of the function: $y = ax + b$					Kinetic parameters	
	$a$	$\pm SD_a$	$b$	$\pm SD_b$	$R^2$	$k''$	$c^*_{Ct(a,l)}$
H	43.21	0.031	1296	0.61	1	145	0.023
Cu	143.3	3.5	291	68	0.998	70.3	0.0070
$\Sigma Ct_{so}$	33.29	0.16	20.4	3.1	0.999	54.4	0.030
Na	-154.3	3.9	-345	77	0.997	-687	-0.0065
K	-18.52	0.43	-101.9	8.3	0.998	-3.35	-0.054
Mg	-39.3	5.2	-391	97	0.936	-395	-0.025
Ca	-7.67	0.42	-82.6	8.2	0.988	-0.72	-0.130
$\Sigma Ct_{de}$	-4.68	0.16	-39.5	3.2	0.995	-0.55	-0.214

The data presented in the table confirm the proper adjustment of the pseudo-second order reaction model to the description of the sorption of copper and hydrogen cations and changes of concentrations of light metals cations: Na, K, Mg and Ca. The standard deviations from parameters  $a$  and  $b$  are not higher, respectively, than: 15% and 25%, which confirms that the uncertainty of measurements in determining  $c_{C(a,1)}$  is not greater than 15%.

The main process of cations sorption in algae is ions exchange, which was confirmed in many publications, eg [27-30]. The data presented in the table confirm that, in the discussed case, expressing concentrations as  $c^*$ , only several percent of light metal cations released to the solution participate in the process of ions exchange ( $\text{Cu}^{2+}$ ,  $\text{H}^+$ ). It can be assumed that the remaining cations are released in the process of dissolution of the salts remaining on the surface of algae, or released from intracellular space, in consequence of destruction of cell membranes.

The correctness of the experiment is confirmed by the results of the changes in conductivity of the solution, during the process duration. Conductivity of the solution after 30 min of the experiment duration, calculated on the basis of relation 3, using the data from Table 2, increased by 39.5  $\mu\text{S}/\text{cm}$ , whereas the measured increase of conductivity after 30 min of the experiment duration was 41.3  $\mu\text{S}/\text{cm}$ . The difference between the measured and the calculated value is not more than 5%.

The pseudo-second order equation can also be applied to the description of the solution pH and conductivity changes. Parameters of the straight lines determined on the basis of the data presented in Table 2 are contained in Table 4.

Table 4

Parameters of the function  $y = ax+b$  and, determined on their basis, constant speeds of solutions pH and conductivity changes, and parameters of the solution in equilibrium ( $PR$ )

Measured value	Parameters of the function: $y = ax+b$					Kinetic parameters	
	$a$	$\pm SD_a$	$b$	$\pm SD_b$	$R^2$	$k''$	( $PR$ )
pH	0.15530	0.00085	0.157	0.017	1	0.154	6.44
$\Delta\kappa$	0.01796	0.00011	0.1879	0.0022	0.999	00017	55.5

The determined pH and conductivity parameters in equilibrium are greater than the values measured after 30 min of the experiment duration (Table 2). In consequence it can be stated that the status achieved after 30 min of the sorption process duration is not equilibrium, which is pointed out in numerous works of Yuh-Shan Ho [25, 31-34], and which many times is not taken into consideration, during the experiment description. Declaring the equilibrium parameters, the authors actually provide the parameters of the status, during which they do not observe changes of the measuring equipment readings. The planned values of cation concentrations contained in table 2, converted into concentrations of sorbed and desorbed cations from 1 g of algae, are lower than the values determined on the basis of relation (2) (Table 3). For example, the concentration of copper sorbed in 1 g of algae after 30 min of the process duration is 0.0066 mmol/g, whereas the planned concentration of copper sorbed in algae in equilibrium (Table 3) is 0.0070 mmol/g. This difference, converted into the difference between concentrations of copper in the solution, determined by AAS method, is only 0.06  $\text{mg}/\text{dm}^3$  and is smaller than the determined 8% value of uncertainty of measurements. It seems that solution conductivity is a better parameter for the purpose of determining equilibrium. Uncertainty of measurements on the

level of 5% is approximately 3 times lower than the difference of conductivity values measured after 30 min and determined in equilibrium: 46.4 and 55.5  $\mu\text{S}/\text{cm}$ .

One should also take into account another aspect. The determined parameters of sorption equilibrium in static condition refer to a defined proportion of the sorbent mass and the solution volume. A change of the  $m/V$  parameter changes the status of heterophase equilibrium between sorbed and desorbed cations. The status of equilibrium is also influenced by the type and quantity of cations released to the solution, in consequence of other processes.

## Conclusions

The presented research results indicate that during the process of copper sorption in a static system algae - solution, heterophase equilibrium is established between the sorbed cations:  $\text{Cu}^{2+}$  and  $\text{H}^+$  and the cations released from algae:  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ . The pseudo-second order reaction model properly describes kinetics and equilibrium parameters. The model allows to define distribution of cation concentrations in algae and the solution in equilibrium, without the need to actually achieve that status. Measurement of the solution conductivity changes is a good parameter of the process control.

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## TRANSLOKACJA KATIONÓW PODCZAS PROCESU SORPCJI MIEDZI W UKŁADZIE ROZTWÓR - GLONY (*Spirogyra* sp.)

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**Abstrakt:** Zbadano kinetykę procesu sorpcji kationów miedzi w glonach *Spirogyra* sp. oraz towarzyszące mu procesy sorpcji kationów wodorowych i procesy uwalniania do roztworu kationów związanych w glonach: Na<sup>+</sup>, Mg<sup>2+</sup>, K<sup>+</sup> i Ca<sup>2+</sup>. Stwierdzono, że w układzie statycznym, przy stałym stosunku masy glonów do objętości roztworu, procesy te zachodzą równocześnie, przy czym należy przypuszczać, że ilość uwalnianych soli ma wpływ na parametry heterofazowej równowagi wymiany jonowej. W warunkach prowadzenia eksperymentu ilość uwolnionych kationów była blisko 10-krotnie większa niż ilość kationów sorbowanych. Porównano parametry równowagi wyznaczone z modelu reakcji pseudo-drugiego rzędu z parametrami uzyskanymi po 30 min trwania procesu, to jest przy względnie stałych wskazaniach przyrządów pomiarowych. Różnica na przykładzie sorbowanej miedzi wynosi ok. 8%. Stwierdzono, że dobrym parametrem do szacowania stanu bliskiemu stanowi równowagi jest konduktywność roztworu.

**Słowa kluczowe:** glony, kationy miedzi, biosorpcja, równowaga wymiany jonowej