Andrzej KŁOS[1]

DETERMINATION OF SORPTION PROPERTIES
OF HEAVY METALS IN VARIOUS BIOSORBENTS

WYZNACZANIE PARAMETRÓW SORPCJI METALI CIĘŻKICH
W RÓŻNYCH BIOSORBENTACH

Abstract: Various techniques of determination of properties of physicochemical processes of heavy metal sorption in biosorbents were analysed. The methods of preparing and storing samples, conditions of experiment performance, as well as the methods of data interpretation were discussed. Two procedures of study were analysed: (1) in the static system of biosorbent-solution contact and (2) in the system of dynamic flow of solution. Copper cation sorption was studied. The effect of consecutive stages of the study on the quality of final results was shown. A high degree of uncertainty of the sorption capacity assessment was reported, which was dependent on the manner of conducting the study. The application of the pseudo-second order reaction model was substantiated to describe kinetics of cation-exchange sorption and the model of Langmuir isotherm to describe equilibria. The study conducted reveals that in order to perform comparative analyses, it is necessary to establish a joint concept of conducting studies and the interpretation of results.

Keywords: biosorption, heavy metal, kinetics, equilibria, analytical procedures, results interpretation

Introduction

In recent years, studies results on heavy metal sorption in biomass have been frequently published. The kinetics and process equilibrium have been studied, e.g. [1], the sorption capacity was determined, e.g. [2], as well as the conditions for optimal sorption of heavy metals in solutions, e.g. mercury sorption in marine algae [3]. It has been found that one of the mechanisms of heavy metal cation sorption in biomass is ion-exchange: in lichen [4] and moss [5], aquatic moss [6], algae [7] and microorganisms [8]. The authors also point to the possibility of metal cations complexing as well as physical adsorption [9].

An important aim of this study is to evaluate the possibilities of biomass application in the process of remediation, e.g. [10]. Such studies use the waste biological material, which is often physically and chemically modified, e.g. [11] and modified natural mineral sorbents [12, 13]. These results are also helpful in primary studies regarding the sorption properties of organisms used in biomonitoring of environmental pollution [14].

The literature reveals the lack of a homogeneous concept regarding the experimental methodology. The studies of sorption processes on variously prepared biological materials

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[1] Chair of Biotechnology and Molecular Biology, University of Opole, ul. kard. B. Kominka 6, 45-032 Opole, Poland, phone +48 77 401 60 42, email: aklos@uni.opole.pl

are carried out under static conditions e.g. [15], with various proportions of biosorbent mass and volume of solution in which it was immersed, but also under dynamic conditions, e.g. [16], in which the sorbent is rinsed with the solution of specified parameters of flow rate and contact time. The results obtained from different study methods are difficult to compare since various interpretation standards are frequently applied.

Equilibrium parameters are most frequently described by the Langmuir isotherm model, e.g. in moss [17], algae [18] and other biological materials which are waste from the food production process; e.g. in husks of *Cicer arientinum* [19], and are described by the Freudlich model, e.g. in lichen [20], and less frequently in the Dubinin and Raduszkiewicz model [21] and Temkin model [22]. A study regarding the adjustment of 10 different isotherm models to describe the equilibrium of Cu, Cd and Pb sorption in cyanobacteria was presented by Dhananjay Kumar et al. [23]. Most authors show that the best adjustment was revealed in the Langmuir isotherm model; however, the Freudlich model, e.g. [20] and the Toth model [23] are also mentioned. The problem is that the authors rarely provide information on the uncertainty of sorption capacity measurements results. For instance, the sorption capacity of the alga *Spirogyra* sp. for copper cations is 133 mg/g [24], and the alga *Spirogyra insignis* only 19.1 mg/g [25]. Frequently, the only given statistical parameter is the R^2 determination coefficient [21, 22, 26], which does not unequivocally suggest the uncertainty of determinations.

The kinetics of sorption taking place due to ion-exchange is described by the pseudo-first order rate equation and more frequently by the pseudo-second order rate equation [21, 26-28]. These models are used to determine the constants of the reaction rate. This parameter, similar to the sorption capacity, is required to assess the possibility of the practical application of biosorbents [29]. Frequently, the effect of temperature on the biosorption processes is also studied. By means of the Arrhenius equation, thermodynamic parameters are assessed, e.g. the biosorption activation energy, e.g. [30]. Also here, the only statistical parameter given is the R^2 determination coefficient.

This paper is a companion of empirical knowledge obtained in the long process of conducting and publishing our own studies, e.g. [31], supplemented by the results of experiments carried out for this particular purpose. The aim of the analyses is assessment of the effect of sample preparation and storage on the changes in sorption properties, the effect of hydrogen cations on heavy metals sorption as well as the effect of experiment conditions on the properties to be determined. The assessment of the uncertainty of equilibrium and kinetics parameters determination of the ion-exchange process will also be commented on. The presented results concern the sorption properties of copper cations. Copper was chosen due to its good affinity with the active centres of the studied biosorbents and slight uncertainty of measurements.

Materials and methods

The study used various biosorbents: lichens *Hypogymnia physodes*, moss *Pleurozium schreberi*, freshwater alga *Spirogyra* sp. and saltwater alga *Palmaria palmate*. Collected moss and lichen samples were cleaned from mechanical impurities and, after drying at the temperature of 323 K, were stored in airtight polyethylene containers. Also, the saltwater alga *Palmaria palmate*, purchased as merchandise goods from the company Bogutyn Mlyn from Radzyn Podlaski (Poland), were stored in polyethylene containers. Further preparation of moss, lichen and saltwater alga samples, similarly to the freshly collected alga *Spirogyra*

sp., depended on the detailed aims of the study to be conducted. A short description of the final sample preparation can be found in each subchapter concerning the presented results. The applied analyte proportions were also defined together with the manner of conducting the study: in conditions of a static biosorbent-solution contact, or in conditions of dynamic solution flow.

Static and dynamic conditions of study

In the static system, the biosorbents samples (the mass dependent on the purpose of the study) were immersed in the copper sulphate solution of 200 cm^3. The solution was stirred intensely with a magnetic stirrer. The process was carried out for 30-50 min, depending on the sorbent applied. The changes of copper concentrations were determined in the solution.

In the dynamic system, the biosorbents samples were placed in a container through which the copper sulphate solution was permeated at app. 200 cm^3/min, providing constant concentration of copper cations in the solution in which the biosorbent was immersed. The process took place for 40 min. Copper was determined in the initial solution and in biosorbents prior to and after the sorption.

Equipment and reagents

To determine copper, the SOLAAR 969 atomic absorption spectrometer from UNICAM manufactured by Thermo Electron Corporation, USA was used. Calibration of the spectrometer was performed with standard solutions from ANALYTIKA Ltd. (Czech Republic). The value of the highest standard copper solution used for calibration equalling 5 mg/dm was assumed as the threshold of linear dependence between the signal and concentration. To examine the pH of solutions in which biosorbents were immersed, the pH meter CP551 manufactured by Elmetron Sp.j. from Zabrze (Poland) was used, which had an absolute error of readings of: $\Delta pH = 0.02$. Biosorbents (0.4 g of dry mass) were mineralised in the mixture of nitric acid and hydrogen peroxide in the MARS-X microwave oven manufactured by CEM. The solutions were prepared with the MERCK reagents.

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 summarised in Table 1.

Table 1

Measured and certified values of Cu concentration in the BCR 414 plankton and BCR 482 lichen reference material; q_v - certified value, U - uncertainty; SD - standard deviation, D - deviation: the relative difference between measured by AAS and certified concentrations in [%]

BCR 414 plankton					BCR 482 lichen				
q_v	$\pm U$	AAS		D	q_v	$\pm U$	AAS		D
		Mean	$\pm SD$				Mean	$\pm SD$	
[µg/g]				[%]	[µg/g]				[%]
29.5	1.3	27.8	1.9	−5.8	7.03	0.19	6.54	0.18	−7.0

Results and discussion

The presented results have been systematised in accordance with successive stages of the study: the sample collection stage, the analyses stage preceded by the assessment of hydrogen cations effect on sorption processes and the stage of interpretation and assessment of results uncertainty.

Effect of samples preparation and storage on their sorption properties

The preparation of biological material usually consisted of separating it from mechanical impurities, sometimes rinsing with water and drying into a solid mass in the process of thermal vaporisation of water from, e.g. algae [27], or in the process of lyophilisation [32]. Cleaned and dried samples were stored in paper containers or tightly closed plastic containers [3].

Frequently, in order to average the system, the samples were homogenised in mortar grinders [3]. Sometimes, the homogenised biological material immobilised on various carriers, e.g. polisilicates [5].

Our own studies show that averaging the content of mobile cations bound in biosorbent may be achieved by bathing it in demineralised water. Physical substances bound on the surface dissolve in water, provoking the ion-exchange process, which, as a consequence, causes averaging of the content of mobile cations bound with the active centres in the whole biosorbent mass. While stirring intensely, satisfying results were obtained after 30 min of bathing. This did not cause mechanical damage of cellular structures. It may also be used to saturate the active centres with required cations, e.g.: H^+, Na^+, K^+, Mg^{2+} and Ca^{2+} [33].
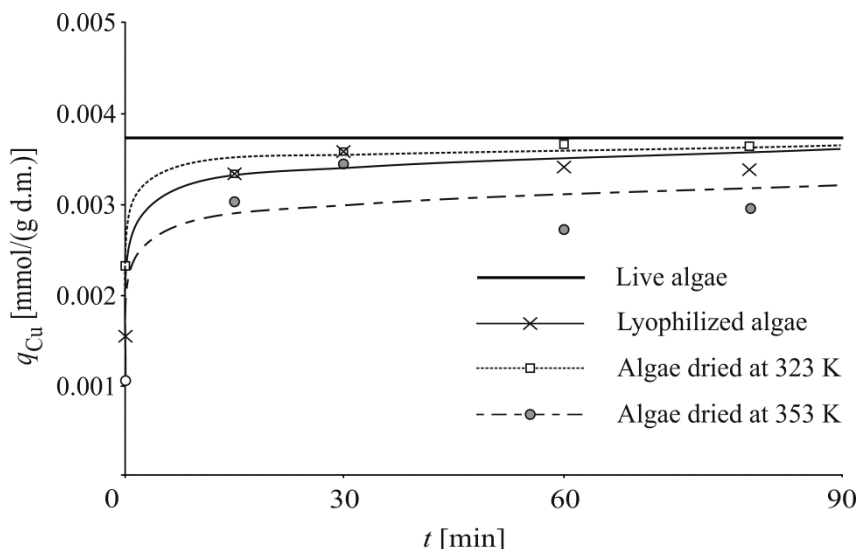

Fig. 1. Influence of time of alga conditioning in demineralised water on the sorption properties (for $t = 0$ the algae were not conditioned) [34]

Improvement of sorption properties, especially in the case of algae, was achieved in the process of sample conditioning in demineralised water directly prior to the experiment [34]. Examples of changes in the sorption properties of algae *Spirogyra* sp. in relation to conditioning time in water, before the actual experiment, are shown in Figure 1. Alga samples with the mass of 0.4 g d.m. (dry mass) were immersed in 200 cm^3 of copper sulphate with the initial concentration of 0.017 mmol/dm^3. For the purpose of comparison, the Figure presents the average concentration value of copper absorbed in the same conditions on living algae.

The results indicate that the lyophilised algae and the algae dried at 323 K should be immersed in demineralised water for at least 15 min to reach the proper sorption properties. The algae dried at 353 K generally had slightly worse sorption properties. The need to condition the alga samples in demineralised water prior to sorption has also been suggested by other authors [2, 35].

An easy way to assess the irreversible changes taking place in biosorbents, which are stored for too long, is to perform conductometry of the demineralised water in which a sample is immersed. This was used e.g. to assess the destruction of lichen cell membranes, which takes place under the influence of contamination of the atmospheric aerosol [36]. On the basis of the alga *Spirogyra* spp., it was reported that water conductivity after a 180-minute contact with the samples of prepared algae compared to living algae increased in the series: living algae < lyophilised algae ≈ algae dried at 323 K < algae dried at 353 K < algae dried at 323 K and stored for 30 days [34]. The sorption properties of algae change in the reversed series. Some studies report better sorption properties of dead biomass, e.g. of alga *Chlorella vulgaris* [37].

To conclude, even at the stage of sample preparation and storage, changes in sorption properties may appear, which can be assessed by changing the conductivity of demineralised water in which the biosorbent is immersed. Prior to the performance of appropriate analyses, the conditioning of dried biosorbents in demineralised water may have an effect on the course of the sorption process.

Effect of hydrogen cations on sorption processes

The effect of pH on the sorption properties of heavy metals in biomass in lichen, e.g. [38], moss, e.g. [39] and algae, e.g. [40] is widely recognised. Most study results show that the maximum sorption of heavy metals is achieved for pH ranging from 4 to 6, depending on the type of absorbed metal, its initial concentration and the applied sorbent. Usually, a decrease of heavy metal sorption in acidic solutions is explained by a competitive sorption of hydrogen cations, while in alkaline solutions, this is due to the creation of hydrocomplexes, insoluble metal compounds, mainly hydroxides, as well as the blockade of active centres or the change in the ion form of metals [3, 21, 38, 41, 42]. It should be pointed out that this is in accordance with the formula: $pH_{prec.} = z^{-1} \cdot (14 \cdot z - \log c_{Me} + z - pK_{sp})$, where: $pH_{prec.}$ is the pH value above which hydroxides precipitate, z is the cation valence, $c_{Me} + z$ is the cation concentration in solution [mol/dm^3], K_{sp} is the solubility product constants ($pK_{sp} = -\log(K_{sp})$), and hydroxides precipitate at pH = 5.7 from the copper salt solution with the concentration of 1 mmol/dm^3.

Another approach in this area is the assessment of hydrogen cation participation in the process of ion-exchange. Our own studies reveal that depending on the biosorbent properties as well as the initial concentration of metal cations and pH of the solution, the hydrogen cations may be sorbed or desorbed in the solution. Figure 2 presents the changes

of hydrogen cations, c_H, in $CuSO_4$ solutions of 200 cm^3, the initial copper concentration of mmol/dm^3 and initial pH = 4.6, in which lichen *Hypogymnia physodes*, moss *Pleurozium schreberi*, and marine alga *Palmaria palmate* were immersed. For the purpose of this study, 1 g d.m. of each biosorbent was used.
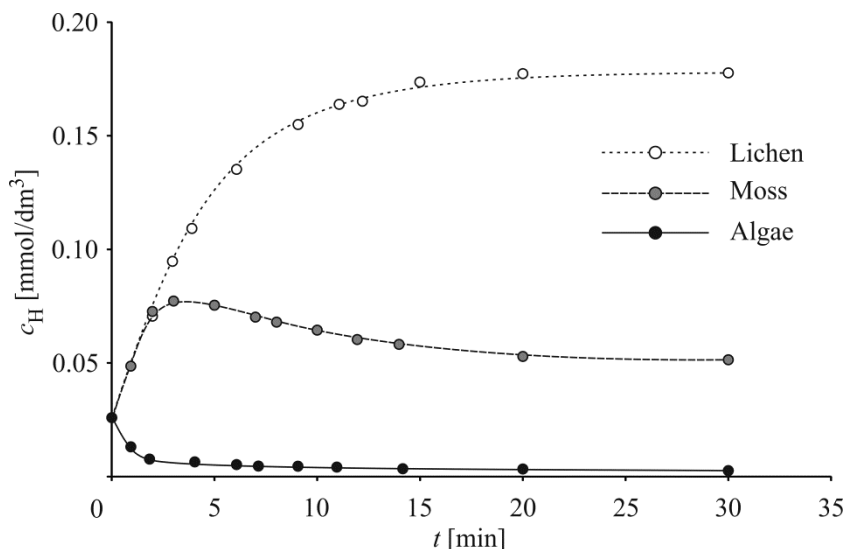

Fig. 2. Changes of hydrogen cations, c_H, in $CuSO_4$ solution during sorption by lichen *Hypogymnia physodes*, moss *Pleurozium schreberi*, and marine alga *Palmaria palmate* [31]

The results presented on the chart point to clear differences in changes of hydrogen cations concentrations in solutions in which the studied biosorbents were immersed. According to the chart, during the ion-exchange process lichens desorb the hydrogen cations, and moss initially desorbs and later sorbs, while in algae, there is a simultaneous sorption of copper cations and hydrogen cations. This is influenced by the cation-exchanging properties of biosorbents and the conditions of their vegetation. A characteristic feature of lichen is its ability to produce lichen acids [43]. Their amount, depending on the species, ranges from 0.5 to 10 % of lichen dry mass. A natural lichen mechanism is acidification of its surroundings; therefore, in solutions, the sorption of heavy metals takes place with a simultaneous desorption of hydrogen cations [44]. The moss natural environment in terms of pH is similar to the conditions of the experiment. The registered non-monotonic changes of hydrogen cations concentration during the sorption process probably result from stabilisation of equilibrium between the H$^+$ and Cu^{2+} cations and the mobile cations desorbed from moss, e.g.: Na$^+$, K$^+$, Ca^{2+} and Mg^{2+}. Also, other authors report the limited heavy metal sorption by cations which are naturally present in the environment [15, 27].

Algae behave in a dissimilar manner. Salt water, which is their natural environment, is slightly alkaline (pH = 7.5 to 8.4); therefore, from the acid and slightly acid solutions (the initial pH of copper solution used in the experiment was 4.6), the sorption of hydrogen cations takes place simultaneously with the sorption of heavy metal cations.

The examples presented substantiate the need to investigate the changes in pH of solutions during sorption. This enables the detection of possible changes of cation concentrations produced by the creation of insoluble chemical forms of metals during the experiment; also, it suggests a possible competitive sorption of hydrogen cations, especially at low metal concentrations in solution, which, as a consequence, has an effect on the measurement results.

Effect of experiment conditions on the kinetics and sorption equilibrium parameters

As mentioned in the introduction, to describe the kinetics of heavy metals sorption, the Lagergren model, pseudo-first order model (Eq. (1)) and pseudo-first order models (Eq. (2)) are frequently used. To describe parameters of the equilibrium state, the Langmuir isotherm model e.g. [45] is most frequently applied (Eq. (3)).

$$\ln\left(q_{M(1)} - q_{M(t)}\right) = \ln q_{M(1)} - k' \cdot t \tag{1}$$

$$\frac{t}{q_{M(t)}} = \frac{1}{k'' \cdot \left(q_{M(1)}\right)^2} + \frac{1}{q_{M(1)}} \cdot t \tag{2}$$

$$\frac{1}{q_{M(1)}} = \frac{1}{q_{M(\max)}} + \frac{1}{q_{M(\max)} \cdot K_L} \cdot \frac{1}{c_{M(1)}} \tag{3}$$

where: k' and k'' are constants of the pseudo-first and pseudo-second order reaction rates, respectively, $q_{M(t)}$ is the metal concentration in sorbent after time t, $q_{M(1)}$ is the metal concentration in the sorbent, which is in equilibrium with the concentration of this metal in solution: $c_{M(1)}$, $q_{M(\max)}$ is the sorbent sorption capacity, and K_L is the Langmuir equilibrium constant.

The pseudo-second order reaction model used in this article was proposed and interpreted by Yuh-Shan Ho [46-48]. It should be noticed that this model can be used in determination of the analyte concentration in biosorbent in equilibrium state: $q_{M(1)}$.

Sorption in the static system

In the static system, the sorption kinetics parameters depend on the ratio of mass, volume and initial concentration of solution. It was found that the constant reaction rate is influenced by the initial solution concentration [30], but also, at the same initial concentrations, the ratio of sorbent mass to solution volume [49]. The reaction rate constant increases together with the increase of biosorbent mass [37]. Equilibrium parameters also undergo some changes. This was confirmed by the study of sorption processes of Cu^{2+} and Ni^{2+} cations depending on the mass of the applied alga *Chlorella vulgaris* [37], as well as the sorption of copper cations by the alga *Spirogyra* sp. [21].

Figure 3 presents temporal changes of copper concentration in *Pleurozium schreberi* during sorption. In the solution volume of 200 cm³ and at initial concentration of 0.08 mmol/dm³ the moss samples were immersed with their respective mass: 0.2, 0.3, 0.4, 0.6, 0.8 and 1.0 g d.m. In the system of the static contact of biosorbent-solution, the kinetic and equilibrium parameters are most easily determined by the measurements of initial and final concentrations of solutions on which sorption was performed:

$$q_{M(1)} = \frac{\left(c_{M(0)} - c_{M(1)}\right) \cdot V}{m} \tag{4}$$

where: V is the volume of solution on which sorption was performed, m is the sorbent mass, and the indices (0) and (1) refer to the initial and final solution concentrations, respectively.
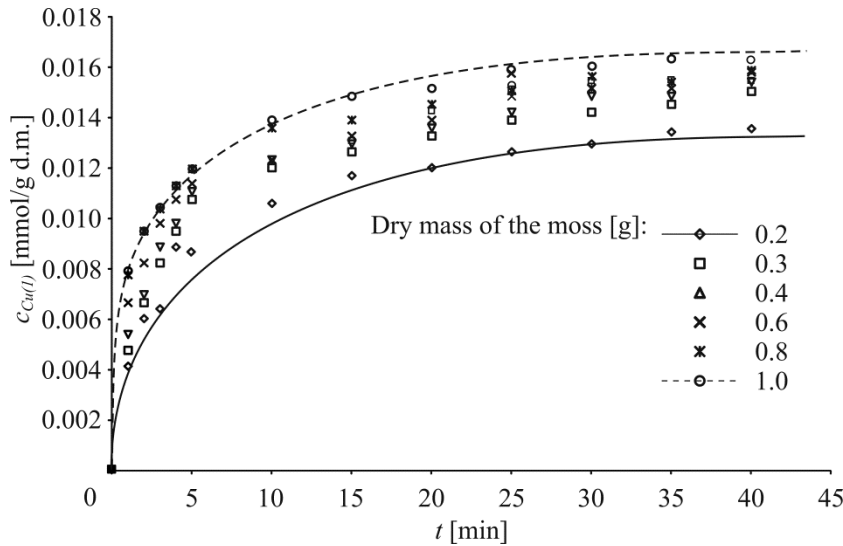

Fig. 3. Effect of the mass of moss *Pleurozium schreberi* on the changes of copper concentrations in solution during the sorption process

In Figure 4 lines with parameters calculated from pseudo-first and pseudo-second order (Eq. (1) and (2)) models are shown.
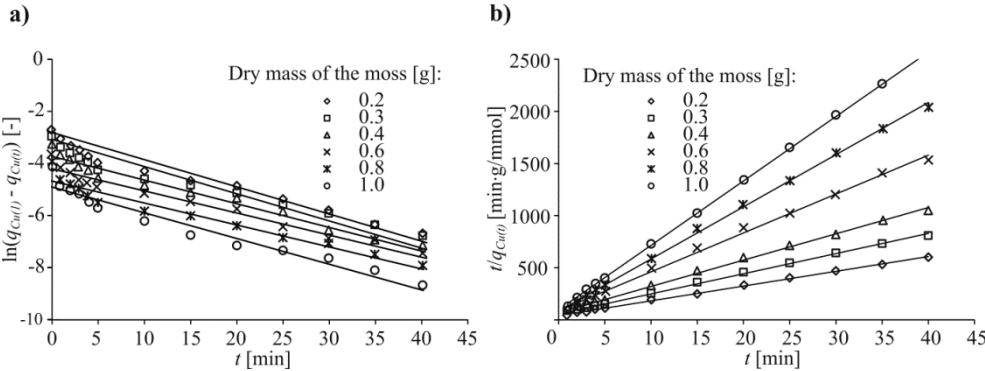

Fig. 4. Kinetics of copper sorption in moss *Pleurozium schreberi* described by: a) pseudo-first and b) pseudo-second order reaction model

Table 2 contains data collected regarding kinetic properties described by the reaction model of the pseudo-first and pseudo-second order, established on the basis of the results presented in Figure 4. The results, in compliance with dependence (4), were calculated at 1 g d.m. of moss.

Table 2

Kinetic parameters of the process described by the reaction model of the pseudo-first (dependence (1))
and pseudo-second (dependence (2)) order

Dry mass of the moss	Pseudo-first order		Pseudo-second order	
	$q_{Cu(1)}$	k'	$q_{Cu(1)}$	k''
[g]	[mmol/g]	[1/min]	[mmol/g]	[g/(mmol·min)]
0.2	0.0464	0.105	0.0707	4.83
0.3	0.0309	0.084	0.0517	6.73
0.4	0.0234	0.086	0.0397	9.26
0.6	0.0148	0.082	0.0268	15.9
0.8	0.0093	0.085	0.0200	29.8
1.0	0.0074	0.099	0.0162	39.9

Data collected in Table 2 show that there are changes in sorption kinetics parameters depending on sorbent mass, which has been confirmed by other studies [30]. These data also point to a better adjustment of the pseudo-second order reaction model as well as to discrepancies in $c_{Cu(m,1)}$ values, i.e. different concentration values of copper accumulated in a mass unit of moss in equilibrium, determined on the basis of the applied models. It is interesting, however, that they are in a linear correlation: $q_{Cu(1),k''} = 1.4 \cdot q_{Cu(1),k'}$.
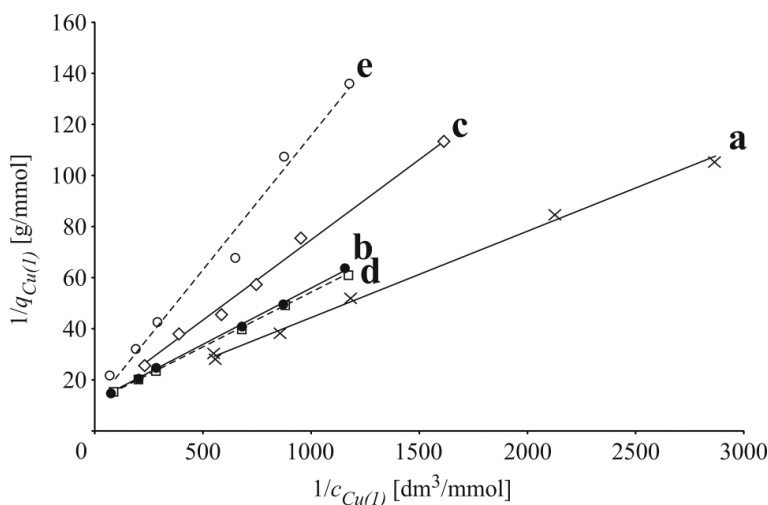

Fig. 5. Isotherms of copper sorption in moss *Pleurozium schreberi*: a - m = const., V = const., b - $c_{Cu(0)}$ = const., V = const., c - $c_{Cu(0)}$ = const., m = const., d - $c_{Cu(0)}$ = const., V = const., $q_{Cu(1),k''}$, e - $c_{Cu(0)}$ = const., V = const., $q_{Cu(1),k'}$ [31]

Langmuir isotherms (dependence (3)) are most frequently determined by measuring the equilibrium properties in the system of different initial concentrations of solution and constant volume of solution and sorbent mass, e.g. [50]. Their main aim is to assess the sorption capacity. However, it should be stressed that isotherms may also be determined in the system of different volumes of solution or different sorbent mass, at a constant initial concentration of solution. Figure 5 presents the isotherms localisation determined for copper in the following systems: a) different initial concentrations with a constant sorbent mass and solution volume, b) constant volume, constant initial concentration and different

sorbent mass, c) constant sorbent mass, constant initial concentration and different solution volumes. Additionally, isotherms are presented, which are determined on the basis of $q_{Cu(1)}$ concentration values determined from simple parameters describing the kinetics of reaction: d) the pseudo-second and e) the pseudo-first order (Table 2).

Determined sorption capacities are contained between 0.0841 mmol/g (isotherm b) and 0.0920 mmol/g (isotherm a). A statistically significant assumption may be made that the isotherms (b) and (d) are the same. These isotherms were determined on the basis of data presented in Figure 3; however, as mentioned before, in order to draft isotherm (b), the values $q_{Cu(1)}$ were used which were determined in accordance with dependence 4, on the basis of measurements of copper concentration in the solution in the equilibrium state, while, in order to draft isotherm (d), the data from Table 2 were used, which were determined on the basis of directional coefficients of lines describing the reactions of pseudo-second order. This points to good correlations between the Langmuir model and the model describing the kinetics of the pseudo-second order reaction. It should be noted that the $q_{Cu(1)}$ values determined from the pseudo-second order reaction model are usually larger than the values determined experimentally.

The issue to consider is the reason for changes in directional coefficients of lines described by the Langmiur model, which can be observed at the change of V/m ratio, while maintaining the same initial concentrations of solutions on which sorption was performed. Many authors report this regularity, e.g. [37].

The Langmuir isotherm model, described by dependence (3), may be transformed into the following form:

$$K_L = \frac{q_{M(1)}}{c_{M(1)}} \cdot \frac{1}{q_{M(\max)} - q_{M(1)}} \tag{5}$$

and later, assuming that $q_{M(\max)} - q_{M(1)} = q_{R^-}$, where c_{R^-} is the concentration of the unfulfilled active spaces in the sorbent mass, $q_{M(1)} = q_{MR}$ is the concentration of metal bound in sorbent, and that $c_{M(1)} = c_{M^+}$ is the concentration of cations of the sorbed metal in solution, in equilibrium, it can be stated that:

$$K_L = \frac{q_{MR}}{c_{M^+} \cdot q_{R^-}} \tag{6}$$

i.e. that the Langmuir equilibrium constant describes the reaction equilibrium state:

$$M^+ + R^- \leftrightarrows MR \tag{7}$$
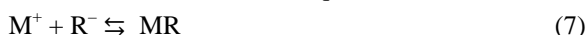
The kinetics of such a reaction is described by the pseudo-second order model, which, in turn, substantiates the fact that lines (b) and (d) overlap, which is presented in Figure 4.

It should be noted that the real process of ion-exchange of biosorbent-solution takes place until equilibrium is attained between the sorbed and desorbed cations in the biosorbent and in the solution. It is described by the equation of the heterophasic ion-exchange:

$$M^+ + CtR \leftrightarrows Ct^+ + MR \tag{8}$$

where Ct^+ is the cation desorbed due to ion-exchange.

As a consequence, while comparing equation (6) with the equilibrium constant of the heteropasic ion-exchange K_{IE}, which characterises the reaction described by equation (8) (R^- from equation (7) is equivalent with CtR from equation (8)), the following ratio can be determined:

$$K_{IE} = c_{Ct^+} \cdot K_L \qquad (9)$$

Equilibrium of the ion-exchange suggests that, with the constant initial concentration of the sorbed metal in the solution ($c_{M(0)}$ = const.), the concentration of cations released into the solution due to ion-exchange increases with the increase of sorbent mass and decreases with the increase of solution volume. Therefore, in different conditions of the process, assuming that K_{IE} = const., the value of K_L changes, which influences the inclination of Langmuir isotherm: tgα = $1/q_{M(\max)} \cdot K_L$, decreases together with the increase of V/m. Dependence (9) has a limited range since at $c_{Ct}^+ \to 0$ the equilibrium is described by equation (7).

Regardless of the manner of sorption procedure, the kinetics and equilibrium state parameters are influenced by the temperature of the process [15, 26, 30, 50-52]. The constant of reaction rate decreases together with the temperature increase.

To sum up, the number of active centres in a mass unit of sorbent should have a defined value which, in a constant temperature, remains unchanged in relation to a given cation. The chemical character of active centres may prefer the sorption of defined cations of heavy metals. Neither the Langmuir model nor the pseudo-second order reaction model provide for the interaction between the sorbed and desorbed cations, which, in turn, at the change of V/m parameter, influences the value of directional coefficients of lines describing equilibria and kinetics of ion-exchange.

Sorption in the dynamic system

In the case of a dynamic flow of solution, it may be assumed that $c_{M(0)}$ = $c_{M(1)}$ and that c_{Ct}^+ = 0. In this case, the equilibrium is described by equation (7). This enables repeatable parameters required to determine the Langmiur isotherm to be obtained, which in a limited scope are independent from the mass of the applied sorbent. The disadvantages of this method are large volumes of solution used and a complicated measurement of kinetics parameters of the process. This method also requires determination of analytes in sorbent samples, as opposed to the static method, in which equation (4) may be applied.
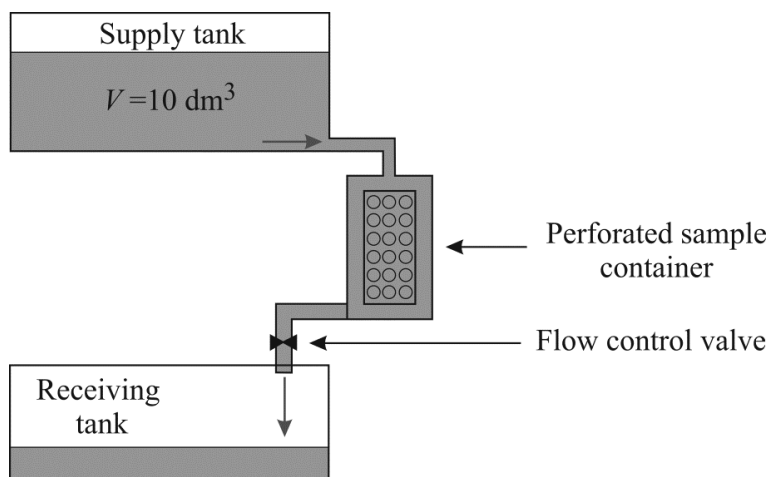

Fig. 6. Diagram of the set for determination of equilibrium parameters in the system of a dynamic solution flow

Figure 6 presents the diagram of the set for determination of equilibrium parameters in the system of a dynamic solution flow.

Figure 7 presents Langmuir isotherms determined in the dynamic method for moss *Pleurozium schreberi*, lichen *Hypogymnia physodes* and alga *Spirogyra* sp. In order to determine the isotherm parameters, solutions of copper sulphate with the concentrations ranging from 0.015 to 0.080 mmol/dm^3 were let through the samples of arbitrary mass ranging from 0.5-1.0 g d.m. Copper was determined in the solution and in biosorbent samples prior to and after sorption.
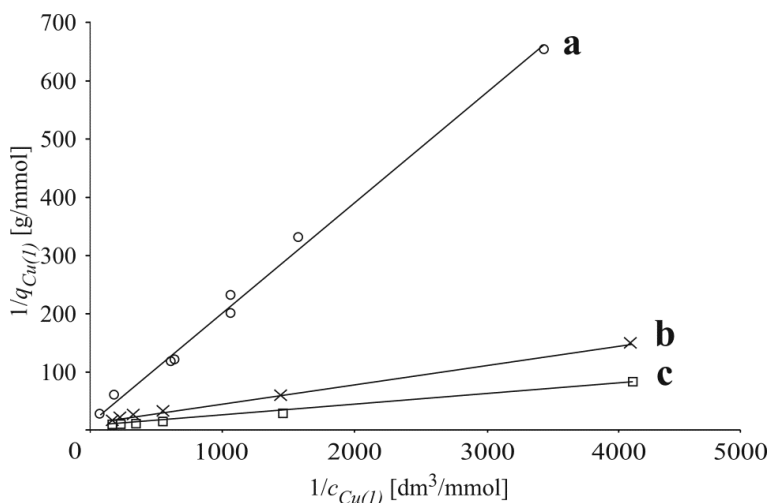

Fig. 7. Langmuir isotherms determined by the dynamic method for: a - *Spirogyra* sp., b - *Hypogymnia physodes*, c - *Pleurozium schreberi*

Detailed results together with the assessment of measurement uncertainty were presented in Table 4. It is important that, as opposed to the static method, this manner of conducting the study enables to compare equilibrium parameters regardless of the type of the studied biosorbents and applied proportions of biosorbent-solution, and, moreover, in relation to the processes of remediation or active biomonitoring of waters, it is comparable with real conditions. An advantage of this method is also the possibility of an arbitrary enrichment of solutions with chemical ingredients at their constant concentration during the experiment.

Uncertainty of determination of parameters of equilibrium and kinetics of the ion-exchange processes

As mentioned before, frequently the only given statistical parameter of lines determined from the dependences (1)-(3) is the determination coefficient R^2. Some authors additionally provide standard deviation determined from the series of experiment repetitions, e.g. [7, 15].

Our own studies reveal that significant statistical parameters are the standard error of the absolute term *a* and the standard error of directional coefficient *b* of the lines: $y = b \cdot x + a$, determined from the dependences (1)-(3). To determine standard errors of *a* and

b coefficients, various statistical software packages and calculation sheets may be used, e.g. Excel or LibreOffice Calc. On the basis of these parameters, the uncertainty of determination of reactions rate constants as well as sorption capacities may be calculated. Tables 3 and 4 present collected statistical data regarding the *a* and *b* coefficients of lines describing kinetics of sorption process with the pseudo-first and pseudo-second order model (Fig. 4) and statistical data regarding the isotherms presented in Figures 5 and 7.

Table 3

Parameters of lines $y = b \cdot x + a$ describing the pseudo-first order reactions: $a = \ln q_{Cu(1)}$, $b = -k'$ and pseudo-second order: $a = (k'' \cdot (q_{Cu(1)}^2))^{-1}$, $b = (q_{Cu(1)})^{-1}$ with a given standard error $\pm SE$ of directional coefficients and absolute terms

Dry mass of the moss [g]	Pseudo-first order					Pseudo-second order				
	a	$\pm SE_a$	*b*	$\pm SE_b$	R^2	*a*	$\pm SE_a$	*b*	$\pm SE_b$	R^2
0.2	–3.07	0.14	–0.1046	0.0081	0.943	41.4	3.5	14.14	0.17	0.999
0.3	–3.47	0.10	–0.0844	0.0056	0.958	55.5	5.1	19.33	0.25	0.998
0.4	–3.75	0.10	–0.0864	0.0060	0.954	68.6	7.2	25.20	0.35	0.998
0.6	–4.21	0.11	–0.0829	0.0062	0.947	87	13	37.30	0.61	0.997
0.8	–4.67	0.13	–0.0845	0.0078	0.922	94	11	50.04	0.54	0.999
1.0	–4.90	0.15	–0.0991	0.0086	0.930	95.8	7.1	61.81	0.34	0.999

Table 4

Parameters of lines determined from the Langmuir isotherm model, presented in Figures 5 and 7: $a = (q_{Cu(max)})^{-1}$, $b = (q_{Cu(max)} \cdot K_L)^{-1}$, $\pm SE$ - standard error, R^2 - determination coefficient, determined sorption capacity: $q_{Cu(max)}$ [mmol/g]

Isotherms	*a*	$\pm SE_a$	*b*	$\pm SE_b$	R^2	$q_{Cu(max)}$	$\pm SE_{qCu(max)}$ [%]
Fig. 5, a	10.9	2.3	0.0337	0.0011	0.996	0.092	16
Fig. 5, b	11.9	1.1	0.0439	0.0016	0.995	0.084	9.2
Fig. 5, c	11.8	2.3	0.0631	0.0026	0.993	0.085	20
Fig. 5, d	11.2	1.1	0.0433	0.0016	0.995	0.090	9.8
Fig. 5, e	11.3	4.9	0.1043	0.0073	0.981	0.087	43
Fig. 7, a	15.1	9.8	0.1854	0.0066	0.992	0.066	65
Fig. 7, b	12.9	1.5	0.0330	0.0084	0.997	0,077	12
Fig. 7, c	8.53	0.92	0.0182	0.0005	0.997	0.117	11

Statistical data presented in Table 3 show that the pseudo-second order model is better adjusted. On average, the standard error of *a* and *b* coefficients is approximately 1.5 %, while in the case of the pseudo-first order reaction model, this value is approximately 15 %. The determination coefficient also suggests a better adjustment.

The values of standard error determined for the biosorbent sorption capacities present themselves variously. Information in Table 4 suggests that the slightest error of sorption capacity determination in the static system is characteristic for the isotherm drafted in the conditions of $c_{Cu(0)}$ = const., V = const. (Fig. 5, b), determined from the lines describing kinetics of reaction of the pseudo-second order (Fig. 5, d), while in these two cases, the same conditions of process were maintained: different biosorbent mass, $c_{Cu(0)}$ = const., V = const. In the case of the alga *Spirogyra* spp., the uncertainty of determination of sorption capacity reaches 65 %. The studies revealed that depending on the experimental conditions, the uncertainty of determination of sorption capacity may exceed a determined value [34]. Data presented in Table 4 also suggest that the determination coefficient R^2 does not correlate with the values of standard errors; therefore, it should not be the only indicator of results reliability.

Compared with the isotherms presented in Figure 5, the isotherm determined for moss *Pleurozium schreberi* in the dynamic system is characterised by the lowest value of the directional coefficient ($(q_{Cu(max)} \cdot K_L)^{-1} = 0.0182$) and the absolute term ($(q_{Cu(max)})^{-1} = 8.53$, which, in accordance with the dependence (3), translates into the highest value of sorption capacity. As mentioned before, in the dynamic method, there are no interactions between the sorbed and desorbed cations. The results also suggest that sorption properties of the studied biosorbents, in relation to copper cations, change in the order: *Pleurozium schreberi* > *Hypogymnia physodes* > *Spirogyra* sp.

Conclusions

The presented study results suggest that various factors influence determination of sorption properties, mainly the manner of conducting the experiment, but also the manner of preparing and storing the samples, a competitive sorption, e.g. of hydrogen cations as well as interaction between cations of the sorbed heavy metals and the desorbed cations due to ion-exchange. An important element of the study is a statistical evaluation of the results showing the uncertainty of determined parameters, which, due to various factors, may reach significant values. It is possible that an optimal method which enables a comparison of equilibrium parameters of biosorbent-solution is the dynamic method, which in relation to the remediation processes or active biomonitoring of waters, is close to real conditions.

The conducted study shows that the assessment of sorption properties of various biosorbents requires the establishment of a joint concept for conducting studies and the interpretation of results.

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