Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2020.25626

186 (2020) 258–266
May

Optimization of the sorption process of copper cations from aqueous solution by pine bark (*Pinus sylvestris*)

Sławomir Wierzba[a,*], Agnieszka Dołhańczuk-Śródka[a], Jan Kříž[b]

[a]*Institute of Biotechnology, University of Opole, ul. Kardynała Kominka 6a, 40-035 Opole, Poland, Tel. +48 77 401 60 55; emails: slawomir.wierzba@uni.opole.pl (S. Wierzba), agna@uni.opole.pl (A. Dołhańczuk-Śródka)*
[b]*Department of Physics, University of Hradec Králové, Jana Koziny 1237, Hradec Králové, Czech Republic, email: jan.kriz@uhk.cz (J. Kříž)*

Received 17 October 2019; Accepted 4 February 2020

ABSTRACT

This study examined the effect of the chemical modification of pine bark (*Pinus sylvestris*) on the sorption efficiency of copper cations. The results were interpreted using pseudo-first order and pseudo-second order reaction models as well as Langmuir and Freundlich isothermal models. The sorption experiments were carried out using the batch technique. The study indicated the effect of the competitive sorption of copper cations and hydrogen cations as well as the adverse effect on the sorption efficiency of copper hydroxides formed under alkaline conditions. The need to assess the measurement uncertainty in determining the basic parameters of the sorption process was indicated. It was also shown that the modification of the pine bark with a solution of hydrochloric acid and sodium hydroxide, when compared to the raw bark, reduced the sorption capacity by more than 29%. It was confirmed that the main mechanism of the sorption of heavy metals in natural sorbents is ion exchange.

Keywords: Biosorption; Copper; Pine bark; Ion exchange; Kinetics

---

1. Introduction

Heavy metals pose a significant threat to the aquatic environment, especially in highly industrialized areas. The main anthropogenic sources of heavy metals are: mining, metallurgy, metal processing, galvanization, tanning, dye production, battery production, and fertilizer production [1,2]. In many European countries, uncontrolled low emissions, especially during the heating season, are also an important source of contamination [3]. The high bioavailability of heavy metals to lower trophic levels may cause their accumulation in the tissues of higher consumers, which may be particularly dangerous for the human body [4].

Copper is one of the trace elements commonly found in plant and animal organisms. Thanks to the ease of electron collection and donation during oxidation changes, it is a part of the active centre of many enzymes. Excess copper in the body can increase the formation of reactive oxygen species, and consequently lead to liver damage. Oxidative stress can also cause damage to DNA structures and chromosomes, which can lead to epigenetic changes that can result in pathological conditions and diseases such as cancer and Alzheimer's disease [5]. Cu(II) can penetrate surface water and groundwater from installations made of copper, brass, or bronze. Larger amounts of copper compounds are usually present in the waste water from the metallurgical, engineering, or chemical industries [6].

Conventional methods of removing heavy metals from waste water and effluents include: chemical precipitation and filtration, electrochemical methods, adsorption, flotation, and reverse osmosis [4]. These methods are mainly used to remove contaminants present in concentrations above

---

[*] Corresponding author.

Presented at the 14th Conference on Microcontaminants in Human Environment, 4–6 September 2019, Czestochowa, Poland

100 mg L^{-1}. Therefore, despite advanced technologies, they become ineffective for low concentrations of heavy metals in waste water and sewage [7]. In addition, their use is energy-intensive, costly, and environmentally unfriendly due to the large amount of secondary pollutants that are difficult to remove [2]. An example is the use of active carbon-based materials as adsorbents, which on the one hand is advantageous due to its ability to adsorb large quantities of a wide range of pollutants, and on the other hand is strongly limited by high costs and problems in the regeneration process [8].

An alternative to conventional techniques is biosorption, which uses the natural ability of biomass to bind heavy metals to aqueous solutions. The biological material used is usually a waste product, which is why these methods are cheap, efficient, and can be combined with other separation processes. Other advantages of biosorption are: high efficiency of metal removal from diluted solutions, minimization of chemical and/or biological deposits, and the possibility of biosorbent regeneration and metal recovery. The biosorption process involves several mechanisms including: transport through cell membranes, complexing, chelation, ion exchange, precipitation, and physical adsorption [4,9]. Metals can be bonded by biomass with different functional groups. Most of them occur on the surface of biosorbents, mainly in the following groups: carboxylic, thiol, amino, phosphate, sulfate, phenolic, carbonyl, amide, and hydroxyl groups [10]. In addition, the sorption properties of organic materials can be increased by modifying the functional groups on the surface of the biosorbents, most often using physical (temperature) or chemical (acid, base) methods. Such modifications increase the active surface of the biosorbent by loosening the structure or increasing the availability of functional groups for metal ions by depriving the surface of the biosorbent of masking components (minerals, proteins, and lipids) [11–13].

Biosorbents can be divided into two categories: living or dead microorganisms such as bacteria, fungi, algae, and by-products from the food, agricultural, and forestry industries such as: agave fibres [14], true hemp fibres [15], coconut [16], coffee husks [17], sorghum and oat straw [18], barley straw [19], soya meal [20], brewer's spent grain [21], oak sawdust [22], pine bark [23], sugar cane and maize pomaces [24], orange peel [25], bone composite [26]. An interesting solution is also activated carbons made of waste materials, which combine the advantages of conventional adsorbents and biosorbents [25–27]. The advantage of food, agricultural and forestry industry by-products over microorganisms is that they do not need to be specifically produced for biosorption as they are already available in large quantities as by-products or waste. They are rich in lignin, cellulose, and hemicellulose and are characterized by the presence of numerous functional groups, for example, hydroxyl and carboxylic, capable of binding metal cations in a heterophase ion exchange process [28,29].

The aim of the study was to evaluate the effect of the chemical modification of pine bark on the yield of sorption of copper cations. The evaluation was made by comparing the kinetics of the process of sorption of copper cations and the kinetics of changes in the concentration of hydrogen cations sorbed or desorbed from pine bark to the solution, depending on the modification method. Copper was selected due to the small error of determination by atomic absorption spectrometry and the high sensitivity to chemical form changes depending on the pH of the solution in which the sorption was carried out.

2. Materials and methods

Pine bark (PB) (*Pinus sylvestris*) collected from forest areas around Opole (Poland) was used in the research. PB was first washed with demineralized water of $\kappa = 0.5$ μS cm^{-1} conductivity to remove dirt, lichen, and resin, and then dried for 24 h at 323°K. The dried PB was ground using a fraction of 1.25–1.50 mm grain size for experiments. The PB part was chemically modified by intensive mixing for 1 h in NaOH or HCl solutions of various initial concentrations (0.03–0.1 mol L^{-1}). After the process, the PB was rinsed with demineralized water and dried.

2.1. Equipment and reagents

The absorption atomic spectrometer iCE 3500 from Thermo Electron Corporation, USA, was used for the detection of copper. For copper, the limits of detection and quantification of the apparatus are 0.0045 and 0.033 mg L^{-1}, respectively. The highest concentration of the standard (production: ANALYTIKA Ltd., Czech Republic) used for calibration (5 mg L^{-1}) was taken as the limit for linear concentration dependence of the signal. The conductivity test was carried out with the CC-551 conductivity meter from Elmetron in Zabrze (PL), whose absolute error of indication was $\Delta\kappa = 0.1$ μScm^{-1}. The pH of solutions was tested with the CP551 pehameter from Elmetron Sp.j. in Zabrze (Poland), whose absolute error of indication was $\Delta pH = 0.02$.

2.2. Testing methodology

Experiments on copper sorption in PB were carried out using the batch technique under conditions of constant mass of biosorbent and constant volume of solution for different initial concentrations of copper. For the tests, 0.5 ± 0.02 g of dried PB sample was used. The sample was placed in perforated PE (polyethylene) containers (about 15 mL) and immersed in 200 mL copper sulfate solutions. The initial concentration of copper in the solution ranged from 1.0 to 12.0 ± 0.05 mg L^{-1} depending on the type of experiment carried out. During the process the solutions were intensively stirred using a magnetic stirrer. The process was run for 60 min. Both kinetics and sorption balance parameters were determined by measuring the initial, temporary, and final concentrations of copper in the solution in which the experiment was conducted. Three repetitions of the experiment were performed. During the sorption process, the pH and conductivity of the solution were also determined.

2.3. Quality control

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

Table 1
Measured and certified values of Cu concentration in the BCR 414 plankton and BCR 482 lichen reference material; C_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				
C_v (µg g^{-1})	±*U*	AAS		*D* (%)	C_v (µg g^{-1})	±*U*	AAS		*D* (%)
		Mean	±SD				Mean	±SD	
29.5	1.3	27.8	1.9	–5.8	7.03	0.19	6.54	0.18	–7.0

The results presented in the table confirm the legitimacy of the choice of copper as the element with which the research was conducted.

2.4. Interpretation of results

The concentration of copper ions in KS after the sorption process [$q_{M(1)}$] was determined using Eq. (1):

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

where $c_{M(0)}$, initial concentration of copper ions in the solution (mmol L^{-1}); $c_{M(1)}$, final concentration of copper ions in the solution (mmol L^{-1}); *V*, volume of solution from which sorption was carried out; *m*, sorbent mass.

The initial and final state of the process were marked in the lower index by 0 and 1, respectively.

To describe the kinetics of the process the pseudo-first order reaction model was used [30] [Eq. (2)]:

$$\ln\left(c^{*}_{\mathrm{Ct}(i),1} - c^{*}_{\mathrm{Ct}(i),t}\right) = \ln c^{*}_{\mathrm{Ct}(\mathrm{i}),1} - k' \times t \tag{2}$$

and the pseudo-second order [31], Eq. (3):

$$\frac{t}{c^{*}_{\mathrm{Ct}(i),t}} = \frac{1}{k'' \times \left(c^{*}_{\mathrm{Ct}(i),1}\right)^{2}} + \frac{1}{c^{*}_{\mathrm{Ct}(i),1}} \times t \tag{3}$$

where: *k*′, a pseudo-first order reaction rate constant (min^{-1}); *k*″, pseudo-second order rate constant (g mmol^{-1} min^{-1}); $c^{*}_{\mathrm{Ct}(i),t}$, concentration of cations in PB after time *t* expressed in gram equivalents (mmol g^{-1}); $c^{*}_{\mathrm{Ct}(i),1}$, concentration of cations in pine bark in equilibrium expressed in gram equivalents (mmol g^{-1}).

Such an expression of concentrations makes it possible to compare the process of ion exchange of cations of different values [32].

To describe the balance parameters, the Langmuir [33] and Freundlich [34] isothermal models were used, the linear forms of which are represented by Eqs. (4) and (5):

$$\frac{1}{q_{M(1)}} = \frac{1}{q_{M(\max)}} + \frac{1}{q_{M(\max)\times K_L}} \times \frac{1}{c_{M(1)}} \tag{4}$$

$$\log q_{\mathrm{M}(1)} = \frac{1}{n} \log c_{\mathrm{M}(1)} + \log K_F \tag{5}$$

where K_L, Langmuir constant (L mmol^{-1}); K_F, Freundlich constant (L mmol^{-1}); 1/*n*, sorption intensity constant; $q_{M(\max)}$, maximum sorption capacity of PB (mmol g^{-1}).

It should be noted that in periodic studies, in the case of a heterophase ion exchange reaction, the Langmuir constant describes the state of equilibrium of the reaction:

$$M^{+} + CtR \leftrightarrows \mathrm{MR} + \mathrm{Ct}^{+} \tag{6}$$

where Ct^{+}, cation desorbed from pine bark in the ion exchange process.

The Excel software package was used to assess the uncertainty of determining the parameters of linear equations.

3. Results and discussion

3.1. Sorption kinetics of copper cations

In order to interpret the processes occurring during the sorption of copper cations by pine bark (PB), the parameters describing the concentration of copper cations and hydrogen cations in a solution and biosorbent were compared. Measurements were carried out from 5 to 60 min. It was assumed that after 60 min a state near balance between cations in the solution and the biosorbent had been reached. After this time, the recorded changes in concentrations and pH of the solution had reached the limit of determination and resolution of the analytical methods used. On the other hand, the registration of measurements from the fifth minute of the process was justified by the fact that the phenomena occurring in the first minute of contact between the biosorbent and the solution had not yet been explained. In our sorption studies conducted using the example of brewers' grains, we have attempted to interpret these phenomena [35]. We have shown that in the first minute of sorption we can observe non-standard changes in the proportion of metal cations in relation to hydrogen cations in the solution and biosorbent, which can indicate dynamic changes in the solution's composition caused by factors other than ion exchange. Only from the fifth minute of the process do these changes become monotonic. Therefore, in the study of sorption kinetics, changes in parameters occurring from the fifth minute of the process were taken into account.

The obtained results of measurements of copper cation concentration and the pH of solutions are summarized in Table 2. We analyzed the sorption process of copper cations in raw PB, the sorption of copper cations in PB modified in 0.1 mol NaOH solution, and the sorption of copper cations in PB modified in 0.1 mol HCl solution. As previously

Table 2
Changes in the concentration of copper cations and the pH of the solution during the sorption of raw PB, and modified PB in solutions of NaOH and HCl with concentrations of 0.1 mol L^{-1}

t (min)	PB		PB + NaOH		PB + HCl	
	$c^*_{\mathrm{Cu}(s),t}$ (mmol L^{-1})	pH	$c^*_{\mathrm{Cu}(s),t}$ (mmol L^{-1})	pH	$c^*_{\mathrm{Cu}(s),t}$ (mmol L^{-1})	pH
0	0.0321	4.52	0.0315	4.55	0.0305	4.53
5	0.0221	4.34	0.0195	5.67	0.0221	4.01
10	0.0165	4.28	0.0174	6.23	0.0185	3.99
15	0.0132	4.26	0.0161	6.55	0.0171	3.95
20	0.0112	4.25	0.0153	6.78	0.0157	3.94
25	0.0095	4.24	0.0146	7.08	0.0146	3.93
30	0.0081	4.24	0.0143	7.31	0.0139	3.92
35	0.0074	4.23	0.0142	7.61	0.0134	3.91
40	0.0064	4.23	0.0142	7.98	0.0131	3.91
45	0.0059	4.22	0.0141	8.21	0.0126	3.90
50	0.0049	4.22	0.0141	8.41	0.0122	3.91
55	0.0045	4.22	0.0140	8.68	0.0121	3.90
60	0.0042	4.21	0.0139	8.94	0.0119	3.89

mentioned, the concentrations of cations in solution (s) are expressed in gram equivalents ($c^* = z \cdot c$, where: z–valence of cation, c–concentration expressed in mmol L^{-1}).

Table 3 presents the values of copper concentrations in KS in the balanced state $c^*_{\mathrm{Cu}(i),1}$, and the values of reaction rate constants (k) determined on the basis of models of pseudo-first order and pseudo-second order reaction kinetics. Greater consistency of the determined values of $c^*_{\mathrm{Cu}(i),1}$ with experimental data of $c^*_{\mathrm{Cu}(i),1,\mathrm{exp}}$ and high values of determination coefficients R^2 (0.999) indicate the better fit of the pseudo-second order model of the reaction. These conclusions are consistent with our earlier studies [21,35,36] and are also confirmed by other authors' studies [37,38]. Therefore, in further stages of the study, the pseudo-second order reaction model was used to interpret the phenomena occurring during the process of copper ion sorption in PB.

The visualization of the results contained in Table 2 is shown in Figs. 1 and 2 using the pseudo-second order model (dependence 3). An example of the simultaneous sorption of copper cations and hydrogen cations in PB modified with sodium hydroxide is shown in Fig. 1. In this case, however, it should be emphasized that the modification of the biosorbent with the NaOH solution alkalizes the environment, causing a reduction in the concentration of hydrogen cations in the solution read by the pH measurement as sorption of hydrogen cations in PB. The directional coefficient a of the straight line determined on the basis of the pseudo-second order model (dependence 3) makes it possible to determine the concentration of sorbed cations in equilibrium: $a = 1/c^*_{\mathrm{Ct}(i),1}$.

For the directional coefficients presented in Fig. 1, the concentrations of the sorbed cations are: $c^*_{\mathrm{Cu}(i),1} = 0.0075$ mmol g^{-1}, $c^*_{\mathrm{H}(i),1} = 0.0113$ mmol g^{-1}, and $c^*_{\mathrm{Cu+H}(i),1} = 0.0186$ mmol g^{-1}. This data indicates a significant reduction in the sorption of copper cations in an alkaline environment. Most authors' research indicates that the maximum sorption of copper is achieved in the pH range from 5.0 to 5.5 [10,21,39]. Above pH 5.5, insoluble copper (II) hydroxide begins to precipitate and settle on the walls and bottom of the vessel [40]. The specificity of AAS measurements means that with intensive mixing of the solution, both copper cations active in the ion exchange and their insoluble hydroxides are introduced into the apparatus. As a result, the amount of copper cations involved in the ion exchange process is even smaller than the results from the obtained measurement data. A more comprehensive explanation of this phenomenon is presented in one of our other articles [35].

A different course of the process was observed in raw PB and PB modified in 0.1 mol HCl. The examples shown

Table 3
Kinetic parameters of the process of sorption of copper cations in raw and modified PB in 0.1 mol HCl and 0.1 mol NaOH; $c^*_{\mathrm{Cu}(i),1}$, concentration of copper in PB in the balanced state (mmol g^{-1}); $c^*_{\mathrm{Cu}(i),1,\mathrm{exp}}$, concentration of copper in PB determined experimentally; k', pseudo-first order reaction rate constant (min^{-1}); k'', pseudo-second order reaction rate constant (g mmol^{-1} min^{-1}); and R^2, correlation coefficient

Biosorbent	$c^*_{\mathrm{Cu}(i),1,\mathrm{exp.}}$	Pseudo-first order model			Pseudo-second order model		
		$c^*_{\mathrm{Cu}(i),1}$	k'	R^2	$c^*_{\mathrm{Cu}(i),1}$	k''	R^2
PB	0.0112	0.0145	0.185	0.913	0.0134	6.428	0.999
PB + NaOH	0.0071	0.0022	0.135	0.918	0.0073	51.12	0.999
PB + HCl	0.0075	0.0056	0.143	0.989	0.0084	15.72	0.999

in Fig. 2 are characterized by the simultaneous sorption of copper cations in PB, and desorption from PB to the solution of hydrogen cations.

For the process carried out with the use of raw PB, the concentration of copper cations in the biosorbent in equilibrium was $c^{*}_{\mathrm{Cu}(i),1}$ = 0.0133 mmol g^{-1}. This caused a decrease in the copper concentration in the solution (V = 0.2 L) by 0.0667 mmol. In turn, the concentration of hydrogen cations released into the solution from PB increased by 0.0676 mmol. In the analyzed variant, the number of sorbed copper cations was very close to the number of desorbed hydrogen cations, which indicates ion exchange as the main sorption mechanism. Such conclusions are confirmed in studies by many authors [36,37,41,42].

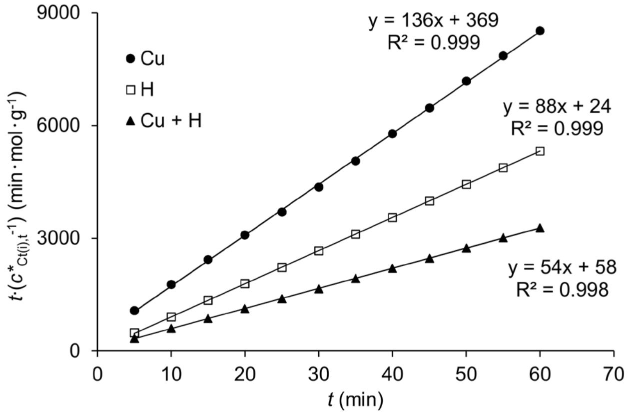

Fig. 1. Sorption kinetics of copper cations and hydrogen cations in PB modified in 0.1 mol NaOH solution.

In the case in which PB modified in hydrochloric acid was the biosorbent, the concentration of sorbed copper cations was $c^{*}_{\mathrm{Cu}(i),1}$ = 0.0084 mmol g^{-1}, as a result of which 0.0417 mmol of copper disappeared from the solution, whereas the concentration of hydrogen cations released into the solution from the biosorbent increased by 0.2083 mmol. Based on the presented data, it can be concluded that during the ion exchange process, the acid physically associated with PB in the process of its modification and drying was released into the solution [35].

The influence of the pH of solutions on the sorption processes of heavy metals has been repeatedly taken into account during studies assessing the possibilities of using various types of biosorbents for the treatment of waste water and sewage [38]. Most of the test results indicate that the best sorption performance is achieved in the pH range from 4 to 6, depending on the type of metal, its initial concentration, and the sorbent used. The reduction in sorption of heavy metals from acidic solutions is most often explained by the competitive sorption of hydrogen cations. The pH impact assessment is usually made on the basis of equilibrium data, not taking into account the description of the process kinetics.

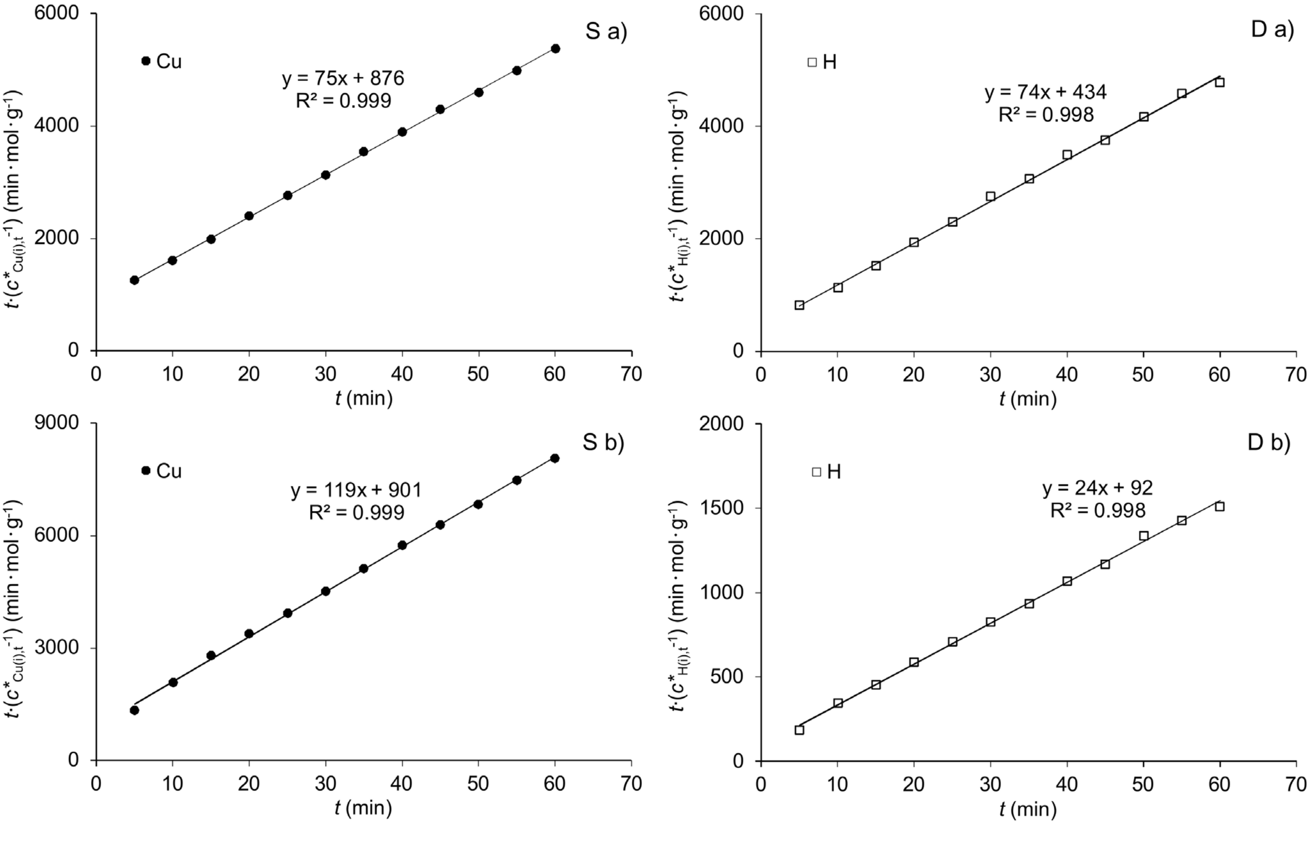

Fig. 2. Kinetics of the sorption (S) of copper cations and desorption (D) of hydrogen cations with raw PB (a) and PB modified in 0.1 mol HCl solution (b).

The examples of kinetics of the sorption process presented in Figs. 1 and 2 indicate possible factors limiting the sorption of copper cations. In the case of PB modified with the NaOH solution (Fig. 1), the concentration of ionic cations active in the ion exchange is reduced in the solution due to the formation of insoluble hydroxides, which consequently has a negative effect on the sorption efficiency. The modification of PB with the HCl solution saturates the functional groups on the surface of the biosorbent with hydrogen cations and gradually acidifies the solution, also due to the release of the acid physically bound to the PB during modification and drying (Fig. 2b). The acidification of the solution, taking into account the heterophasic double-replacement reaction (dependence 6), shifts the reaction direction to the left, that is, in the direction that limits the sorption of copper cations [35].

The most efficient results of the copper cation sorption process occurring mainly through ion exchange were obtained for raw PB. In chemical terms, the bark is a very complex conglomerate characterized by the presence of numerous hydroxy acids and phenolic acids. This affects the saturation of active centres on the bark surface with various cations, including those active in the ion exchange process with hydrogen cations, which increases the sorption efficiency.

3.2. Equilibrium of copper cation sorption

The Langmuir and Freundlich isothermal models [Eqs. (4) and (5)] were used to describe the parameters of the balance of sorption of heavy metals in PB. The linear interpretation of isotherms is shown in Fig. 3, and their parameters describing the balance of sorption are presented in Table 4.

The results contained in Table 4 indicate a better match between experimental data and the Langmuir isothermal model (determination factors $0.983 < R^2 < 0.993$). This model assumes the existence of a certain number of active sites on the surface of the biosorbent where only one molecule can be sorbed. The results obtained suggest that the PB surface is covered with a monolayer of copper cations and there is a uniform distribution of active centres on the surface of the sorbent, which is justified in the event of ion exchange [11,20]. There are reports confirming good matching of balanced data of copper sorption in pine sawdust with both Langmuir and Freundlich isotherms [43].

Ligninocellulose materials are undoubtedly susceptible to chemical modification, which may change their structure, increase porosity, or generate more active sites on the biosorbent surface [12,31,44]. However, in our own research, chemical modification with acid and alkali caused a decrease in the efficiency of copper ion sorption in PB from 29.7% to 43.6%. There are literature reports [13,45], which confirm a decrease in the sorption capacity of PB modified with acids. Usually, a decrease in the sorption capacity would be observed, together with an increase in the time of contact of acid with PB and an increase in the concentration of acid used for modification. Similar results were obtained with NaOH or ammonia [46]. Moreover, the authors [13,46] stated that the chemical modifications did not significantly affect the porosity of the bark. Therefore, the size of the surface did not determine the sorption process. The efficiency

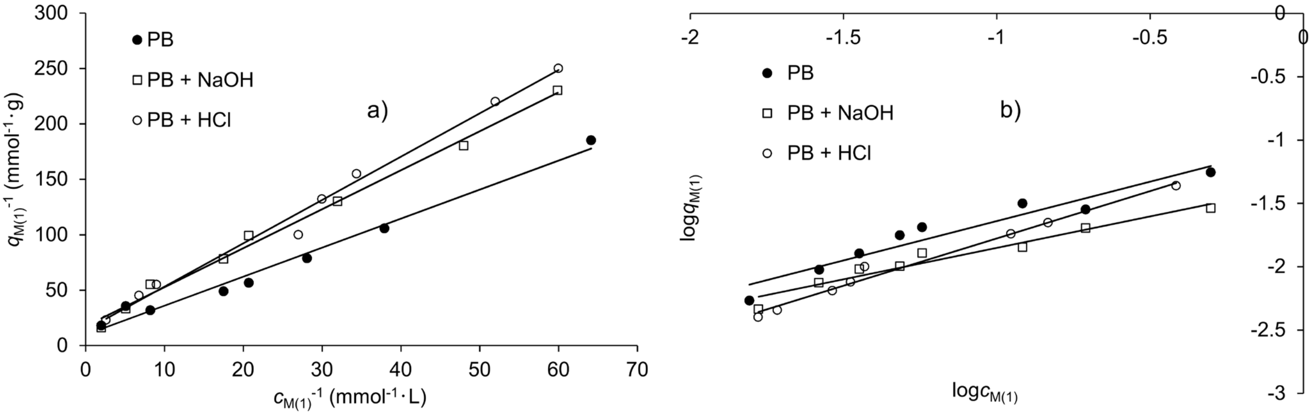

Fig. 3. Langmuir (a) and Freundlich (b) isotherms describing the parameters of balance of sorption of copper ions.

Table 4
Sorption balance parameters of copper ions in raw and modified PB 0.1 mol HCl and 0.1 mol NaOH determined using the Langmuir and Freundlich models; $q_{M(\max)}$, sorption capacity (mmol g^{-1}); K_L, Langmuir constant (L mmol^{-1}); K_F, Freundlich constant (L mmol^{-1}); $1/n$, sorption intensity constant; R^2, correlation coefficient; s, uncertainty standard; and u, combined uncertainty

Biosorbent	$q_{M(\max)} \pm s$ (%)	$K_L \pm u$ (%)	R^2	$K_F \pm s$ (%)	$1/n$	R^2
PB	0.101 ± 14	25.8 ± 16	0.990	0.096 ± 15	0.622	0.926
PB + NaOH	0.057 ± 16	61.2 ± 18	0.993	0.044 ± 17	0.496	0.986
PB + HCl	0.071 ± 18	55.2 ± 19	0.983	0.093 ± 17	0.747	0.949

of the process was determined mainly by the type of functional groups associated with lignin, which is most abundant in the chemical composition of bark (about 50%). Among the functional groups, lignin, phenolic, hydroxyl, carboxylic, benzyl alcohol, methoxyl, and aldehyde groups were identified [42].

Table 5 summarizes the values of sorption capacities of various biosorbents determined from the Langmuir isotherm model. Most authors present sorption parameters in: mg g^{-1}, mg L^{-1}. Such results require recalculations. Reactions occur in molar ratios and only the interpretation of concentrations expressed in moles enables the proper assessment of the affinity of cations to functional groups of biosorbents. In Table 5, for the purpose of this article, concentrations were converted to mmol g^{-1}. The efficiency of copper sorption in PB, in comparison with other biosorbents, was medium. Lower $q_{M(\max)}$ values (below 0.1 mmol g^{-1}) were found for coconut shell, rice straw, and barley straw, while much higher values (above 0.4 mmol g^{-1}) were found for beech sawdust, meranti sawdust, and peach pips. It is worth noting that in comparison to conventional adsorbents, such as activated carbon or fly ash, raw PB had a higher sorption capacity.

The sorption capacity of PB with respect to the compared biosorbents was on an average level. None of the quoted articles attempts to assess the uncertainty of sorption capacity measurements. And, as shown in other studies, even with relatively large correlation coefficients ($R^2 > 0.9$), the uncertainty of the sorption capacity determined from the Langmuir model may be close to or greater than the calculated value of $q_{M(\max)}$ [21]. In this article, the measurement uncertainty $q_{M(\max)}$ does not exceed 18% (Table 4).

3.3. Optimization of copper cation sorption

For specific initial conditions of the process, the use of the pseudo-second order model enables the assessment of instantaneous changes in cation concentrations in the solution and in the biosorbent, and enables the determination of kinetic and process equilibrium parameters. Table 6 summarizes the values of the parameters of straight lines $y = a\cdot x + b$ determined on the basis of the pseudo-second order model (dependence 3), for selected methods of the chemical modification of PB. Table 6 also presents the values of the standard deviation determined for: the directional coefficient s_a and the intercept s_b as well as the parameters characterizing the sorption process—the reaction constant k'' and the concentration of cations in the biosorbent in equilibrium $c^*_{\mathrm{Ct}(i),1}$. The determined correlation coefficients R^2 were not smaller than 0.994.

To describe the kinetics of the desorption process, as shown in Fig. 2, a pseudo-second order model can also be used. Then the function describing the model takes the form: $t/n^*_{\mathrm{Ct}(s),t} = f(t)$. In this case, the concentration of cations in the biosorbent, in equilibrium, is equal to the loss of the number of cations n^* that have been sorbed from the solution: $c^*_{\mathrm{Ct}(i),1} = n^*_{\mathrm{Ct}(s),0} - n^*_{\mathrm{Ct}(s),1}$. Under the conditions of the experiment (sorbent mass $m = 0.5$ g, volume of solution $V = 0.2$ L): $n^*_{\mathrm{Ct}(s),1}$ (mmol) = $c^*_{\mathrm{Ct}(s),1}$ (mmol L^{-1})·0.2 (L). Hence the number of cations released as a result of desorption in the solution, in equilibrium, is: $n^*_{\mathrm{Ct}(s),1} - n^*_{\mathrm{Ct}(s),0} = -c^*_{\mathrm{Ct}(i),1}$.

Table 5
Comparison of sorption capacities [$q_{M(\max)}$] of various biosorbents (mmol g^{-1})

Sorbent	Cu	Literature
Coconut shell	0.067	[37]
Coffee waste	0.183	[39]
Rice straw	0.043	[48]
Spent grain	0.164	[1]
Barley straw	0.073	[49]
Beech sawdust	0.476	[50]
Meranti sawdust	0.504	[51]
Lignin	0.360	[52]
Fly ash	0.074	[53]
Hazelnut shell powder	0.333	[44]
Pine sawdust	0.315	[43]
Peach pips	0.493	[43]
Activated carbon	0.096	[45]
Activated carbon modified with citric acid	0.235	[45]
PB	0.101	This work
PB + NaOH	0.057	This work
PB + HCl	0.071	This work

After converting the data set in Table 6, the average standard deviation of the directional coefficient was $s_a = 0.61\%$ (max 1.63%), and the intercept $s_b = 30.2\%$ (max 62%). The reaction rate constant is determined on the basis of intercept b and the directional coefficient a (dependence 3): $k'' = a^2/b$. However, the complex error of this expression often exceeds the designated value. Therefore, under the conditions of conducting this experiment, the sorption performance should be better determined on the basis of the directional coefficient a, which has a simple translation into the concentration of cations encapsulated in the biosorbent in equilibrium: $c^*_{\mathrm{Ct}(i),1} = 1/a$.

The determined values of $c^*_{\mathrm{Ct}(i),1}$ confirm that both the alkalization and acidification of PB cause the limitation of the sorption of copper cations. The best sorption parameters are obtained in the case of raw PB, in which the number of sorbed copper cations is close to the number of hydrogen cations desorbed from the PB to the solution. In comparison to chemically modified PB, the sorption capacity is nearly 30% higher. As mentioned earlier, the complex chemical structure of the bark and its natural saturation of active centres with hydrogen cations may have an impact on this.

A simple way to control the ion exchange process occurring according to: $M^+ + CtR \leftrightarrows MR + Ct^+$ (dependence 5) is the use of conductometric measurements and the comparison of changes in conductivity and hydrogen cations concentration in the solution during the process. The process of such exchange is simple $\kappa = a\cdot c^*_{\mathrm{H}(s)} + b$, where: κ, conductivity (μS cm^{-1}); $c^*_{\mathrm{H}(s)}$, concentration of hydrogen cations in the solution (mmol L^{-1}). The value of the directional coefficient a of the straight line between 260 and 290 indicates that the process was undisturbed [46]. Fig. 4 shows the course of changes in the conductivity and concentration of hydrogen cations in raw PB and PB modified in 0.1 mol HCl.

Table 6
Parameters of straight lines determined on the basis of the pseudo-second order model of the sorption (S) or desorption (D) of cations of copper, hydrogen, and the sum of these cations

Modification method	Cation	Process	a	s_a	b	s_b	k''	$c^*_{\mathrm{Ct}(i),1}$
NaOH (0.03 mol L^{-1})	Cu	S	115	1.51	613	52	21.6	0.0087
	H	S	88	0.23	32	21	242	0.0114
	Cu + H	S	51	0.37	85	15	30.6	0.0196
NaOH (0.1 mol L^{-1})	Cu	S	136	1.63	362	62	51.1	0.0073
	H	S	89	0.33	28	16	282	0.0112
	Cu + H	S	54	0.27	46	14	63.4	0.0185
PB raw	Cu	S	75	0.82	875	32	6.43	0.0133
	H	D	74	0.29	136	12	40.3	–0.0135
HCl (0.03 mol L^{-1})	Cu	S	105	0.56	750	38	14.7	0.0095
	H	D	34	0.64	172	28	6.72	–0.0294
HCl (0.08 mol L^{-1})	Cu	S	112	0.62	810	56	15.5	0.0089
	H	D	28	0.29	98	16	8.00	–0.0357
HCl (0.10 mol L^{-1})	Cu	S	120	0.78	890	49	16.2	0.0083
	H	D	24	0.28	63	12	9.14	–0.0417

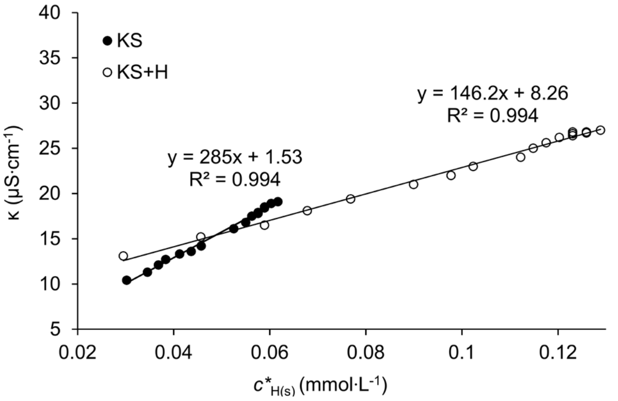

Fig. 4. Changes in the conductivity and concentration of hydrogen cations in the copper sulfate solution during sorption in raw PB and PB modified in 0.1 mol HCl.

4. Conclusions

Lignin-cellulose materials are susceptible to chemical modifications that can change their structure or generate more active areas on the sorbent surface [12]. However, surface modifications, through alkalization or esterification [29] often incur higher costs and, as a result, they may be unprofitable. The conducted research has shown that chemical modification with acid and base of lignin cellulose material such as PB does not always produce the desired effects. The presented research results indicate a significant effect of hydrogen cations on copper sorption (and probably also other heavy metals) in PB. Competitive sorption of hydrogen cations affects the kinetics of ion exchange and the sorption efficiency of copper cations. The best sorption efficiency was obtained for raw PB, in which active centres are naturally saturated with hydrogen cations. The results of the research also indicate the correct adjustment of the pseudo-second order model to the description of the kinetics of the ion exchange between the solution and PB. It has been confirmed that the main mechanism of sorption is ion exchange.

References

[1] S. Lu, S.W. Gibb, Copper removal from wastewater using spent-grain as biosorbent, Bioresour. Technol., 99 (2008) 1509–1517.

[2] A. Ronda, M.A. Martin-Lara, G. Blázquez, N.M. Bachs, M. Calero, Copper biosorption in the presence of lead onto olive stone and pine bark in batch and continuous systems, Am. Inst. Chem. Eng., 33 (2014) 192–204.

[3] T. Olszowski, M. Bożym, Pilot study on using an alternative method of estimating emission of heavy metals from wood combustion, Atmos. Environ., 94 (2014) 22–27.

[4] V. Javanbakht, S.A. Alavi, H. Zilouei, Mechanisms of heavy metal removal using microorganisms as biosorbent, Water Sci. Technol., 69 (2014) 1775–1787.

[5] M.C. Linder, The relationship of copper to DNA damage and damage prevention in humans., Mutat. Res., 733 (2012) 83–91.

[6] S. Yildiz, Kinetic and isotherm analysis of Cu(II) adsorption onto almond shell (*Prunus dulcis*), Ecol. Chem. Eng. S, 24 (2017) 87–106.

[7] S. Wierzba, Biosorption of nickel(II) and zinc(II) from aqueous solutions by the biomass of yeast Yarrowia lipolytica, Pol. J. Chem. Technol., 19 (2017) 1–10.

[8] S. Hajati, M. Ghaedi, S. Yaghoubi, Local, cheep and nontoxic activated carbon as efficient adsorbent for the simultaneous removal of cadmium ions and malachite green: optimization by surface response methodology, J. Ind. Eng. Chem., 21 (2015) 760–767.

[9] M. Rajfur, A. Kłos, M. Wacławek, Sorption of copper(II) ions in the biomass of alga *Spirogyra* sp., Bioelectrochemistry, 87 (2012) 65–70.

[10] P. King, P. Srinivas, Y.P. Kumar, V.S.R.K. Prasad, Sorption of copper(II) ion from aqueous solution by *Tectona grandis* l.f. (teak leaves powder), J. Hazard. Mater., 136 (2006) 560–566.

[11] N. Feng, X. Guo, S. Liang, Adsorption study of copper (II) by chemically modified orange peel, J. Hazard. Mater., 164 (2009) 1286–1292.

[12] M.E. Argun, S. Dursun, M. Karatas, Removal of Cd(II), Pb(II), Cu(II) and Ni(II) from water using modified pine bark, Desalination, 249 (2009) 519–527.

[13] L.A. Teles de Vasconcelos, C.G. González Beça, Chemical activation of pine bark to improve its adsorption capacity of heavy metal ions. Part 1: by acid treatment, Eur. Water Pollut. Control, 7 (1997) 41–46.

[14] A.M.B. Hamissa, A. Lodi, M. Seffen, E. Finocchio, R. Botter, A. Converti, Sorption of Cd(II) and Pb(II) from aqueous solutions onto *Agave americana* fibers, Chem. Eng. J., 159 (2010) 67–74.

[15] B. Pejic, M. Vukcevic, M. Kostic, P. Skundric, Biosorption of heavy metal ions from aqueous solutions by short hemp fibers: effect of chemical composition, J. Hazard. Mater., 164 (2009) 146–153.

[16] A.E. Ofomaja, Y.S. Ho, Kinetic biosorption study of cadmium onto coconut copra meal as biosorbent, Int. J. Environ. Pollut., 34 (2008) 466.

[17] E.A. Oliveira, A.S. Franca, L.S. Oliveira, S.D. Rocha, Untreated coffee husks as biosorbents for the removal of heavy metals from aqueous solutions, J. Hazard. Mater., 152 (2008) 1073–1081.

[18] G.R. Bernardo, R.M. Rene, A.D. Ma Catalina, Chromium (III) uptake by agro-waste biosorbents: Chemical characterization, sorption-desorption studies, and mechanism, J. Hazard. Mater., 170 (2009) 845–854.

[19] E. Pehlivan, T. Altun, S. Cetin, M. Iqbal Bhanger, Lead sorption by waste biomass of hazelnut and almond shell, J. Hazard. Mater., 167 (2009) 1203–1208.

[20] A. Witek-Krowiak, D. Harikishore Kumar Reddy, Removal of microelemental Cr(III) and Cu(II) by using soybean meal waste - unusual isotherms and insights of binding mechanism, Bioresour. Technol., 127 (2013) 350–357.

[21] S. Wierzba, A. Kłos, Heavy metal sorption in biosorbents – using spent grain from the brewing industry, J. Cleaner Prod., 225 (2019) 112–120.

[22] M.E. Argun, S. Dursun, C. Ozdemir, M. Karatas, Heavy metal adsorption by modified oak sawdust: thermodynamics and kinetics, J. Hazard. Mater., 141 (2007) 77–85.

[23] L. Semerjian, Removal of heavy metals (Cu, Pb) from aqueous solutions using pine (*Pinus halepensis*) sawdust: equilibrium, kinetic, and thermodynamic studies, Environ. Technol. Innov., 12 (2018) 91–103.

[24] U. Garg, M.P. Kaur, G.K. Jawa, D. Sud, V.K. Garg, Removal of cadmium (II) from aqueous solutions by adsorption on agricultural waste biomass, J. Hazard. Mater., 154 (2008) 1149–1157.

[25] D. Mohan, C.U. Pittman, Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water, J. Hazard. Mater., 137 (2006) 762–811.

[26] A.A. Oyekanmi, A.A.A. Latiff, Z. Daud, R.M.S.R. Mohamed, N.A.A. Aziz, N. Ismail, M. Rafatullah, A. Ahmad, K. Hossain, Adsorption of pollutants from palm oil mill effluent using natural adsorbents: optimization and isotherm studies, Desal. Water Treat., 169 (2019) 181–190.

[27] M.A. Rosli, Z. Daud, A.A.A. Latiff, S.E.A. Rahman, A.A. Oyekanmi, A. Zainorabidin, H. Awang, A.A. Halim, The effectiveness of peat-AC composite adsorbent in removing colour and Fe from landfill leachate, Int. J. Integr. Eng., 9 (2017) 35–38.

[28] S. Wierzba, M. Rajfur, M. Nabrdalik, A. Kłos, The application of electroanalytical methods to determine affinity series of metal cations for functional biosorbent groups, J. Electroanal. Chem., 809 (2018) 8–13.

[29] Y. Zhang, X. Luo, X. Lin, S. Huang, A sorbent based on liquor distillers' grains for the removal of Pb(II) and Cr(III) from aqueous solution, Proc. Environ. Sci., 31 (2016) 785–794.

[30] S. Lagergren, Zur theorie der sogenannten adsorption gelöster stoffe, K. Sven. Vetenskapsakademiens. Handl., 24 (1898) 1–39.

[31] Y.S. Ho, Review of second-order models for adsorption systems, J. Hazard. Mater., 136 (2006) 681–689.

[32] A. Kłos, S. Wierzba, Application of conductometric and pH metric measurements in determining the kinetics and equilibrium parameters of the heterophasic ion exchange: metal cation-proton, Electrochem. Commun., 102 (2019) 5–12.

[33] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc., 40 (1918) 1361–1403. doi:10.1021/ja02242a004.

[34] H.M.F. Freundlich, Uber Die Adsorption in Losungen, Z. Phys. Chem., 57A (1906) 385–470.

[35] S. Wierzba, M. Rajfur, M. Nabrdalik, A. Kłos, Assessment of the influence of counter ions on biosorption of copper cations in brewer's spent grain - waste product generated during beer brewing process, Microchem. J., 145 (2019) 196–203.

[36] A. Kłos, M. Rajfur, M. Wacławek, W. Wacławek, Ion exchange kinetics in lichen environment, Ecol. Chem. Eng., 12 (2005) 1353–1365.

[37] M.A. Acheampong, J.P.C. Pereira, R.J.W. Meulepas, P.N.L. Lens, Biosorption of Cu(II) onto agricultural materials from tropical regions, J. Chem. Technol. Biotechnol., 86 (2011) 1184–1194.

[38] K. Conrad, H.C. Bruun Hansen, Sorption of zinc and lead on coir, Bioresour. Technol., 98 (2007) 89–97.

[39] C. Escudero, C. Gabaldón, P. Marzal, I. Villaescusa, Effect of EDTA on divalent metal adsorption onto grape stalk and exhausted coffee wastes, J. Hazard. Mater., 152 (2008) 476–485.

[40] R. Herrero, P. Lodeiro, C. Rey-Castro, T. Vilarino, M.E. Sastre de Vicente, Removal of inorganic mercury from aqueous solutions by biomass of the marine macroalga *Cystoseira baccata*, Water Res., 39 (2005) 3199–3210.

[41] E.I. El-Shafey, Removal of Zn(II) and Hg(II) from aqueous solution on a carbonaceous sorbent chemically prepared from rice husk, J. Hazard. Mater., 175 (2010) 319–327.

[42] A. Witek-Krowiak, Analysis of temperature-dependent biosorption of Cu^{2+} ions on sunflower hulls: Kinetics, equilibrium and mechanism of the process, Chem. Eng. J., 192 (2012) 13–20.

[43] H.K. Hansen, F. Arancibia, C. Gutiérrez, Adsorption of copper onto agriculture waste materials, J. Hazard. Mater., 180 (2010) 442–448.

[44] L. Lü, X. Jiang, L. Jia, T. Ai, H. Wu, Kinetic and thermodynamic studies on adsorption of Cu^{2+}, Pb^{2+}, methylene blue and malachite green from aqueous solution using AMPS-modified hazelnut shell powder, Chem. Res. Chin. Univ., 33 (2017) 112–118.

[45] J.P. Chen, S. Wu, K.-H. Chong, Surface modification of a granular activated carbon by citric acid for enhancement of copper adsorption, Carbon, 41 (2003) 1979–1986.

[46] A. Kłos, M. Rajfur, M. Wacławek, W. Wacławek, Ion equilibrium in lichen surrounding, Bioelectrochemistry, 66 (2005) 95–103.

[47] A.L. Arim, D.F.M. Cecílio, M.J. Quina, L.M. Gando-Ferreira, Development and characterization of pine bark with enhanced capacity for uptaking Cr(III) from aqueous solutions, Can. J. Chem. Eng., 96 (2018) 855–864.

[48] C.G. Rocha, D.A.M. Zaia, R.V.S. Alfaya, A.A.S. Alfaya, Use of rice straw as biosorbent for removal of Cu(II), Zn(II), Cd(II) and Hg(II) ions in industrial effluents, J. Hazard. Mater., 166 (2009) 383–388.

[49] E. Pehlivan, T. Altun, S. Parlayici, Utilization of barley straws as biosorbents for Cu^{2+} and Pb^{2+} ions, J. Hazard. Mater., 164 (2008) 982–986.

[50] A. Witek-Krowiak, Application of beech sawdust for removal of heavy metals from water: biosorption and desorption studies, Eur. J. Wood Wood Prod., 71 (2013) 227–236.

[51] M. Rafatullah, O. Sulaiman, R. Hashim, A. Ahmad, Adsorption of copper (II), chromium (III), nickel (II) and lead (II) ions from aqueous solutions by meranti sawdust, J. Hazard. Mater., 170 (2009) 969–977.

[52] X. Guo, S. Zhang, X. Shan, Adsorption of metal ions on lignin, J. Hazard. Mater., 151 (2008) 134–142.

[53] L. Tofan, C. Paduraru, D. Bilba, M. Rotariu, Thermal power plants ash as sorbent for the removal of Cu(II) and Zn(II) ions from wastewaters, J. Hazard. Mater., 156 (2008) 1–8.