

Removal of Zinc Ions from Aqueous Solutions with the Use of Lignin and Biomass

Part II

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Abstract

In response to the trend toward sustainable management of by-products from the pulp and paper industry as well as plant waste, practical and economical methods are being developed to use them in a way that does not pose a threat to the environment. The main aim of the research was to study the possibility of using lignin and plant biomass as biosorbents for the removal of zinc ions from aqueous solutions. The secondary aim was to build an optimal multilayer system made of biosorbents selected during the research in order to obtain the highest sorption efficiency and to determine the best conditions of the sorption process. The effectiveness of zinc ion sorption was assessed using an appropriate combination of sorbents such as lignin, oat bran, rice husk, chitosan, pectin, sodium alginate, pine bark, coconut fiber and activated carbon, selected on the basis of literature data and the preliminary results of tests carried out using FTIR and AAS. The main component of the sorption system was lignin separated from black liquor. Results indicate that the best Zn sorption system was based on coconut fiber, lignin, and pine bark, for which the maximum sorption efficiency was 95%. The research also showed that the increase in the process temperature, the mass of biosorbents used and the alkaline pH are the factors that increase the efficiency of the sorption. It can be concluded that lignin and plant biomass can be used as ecological sorbents of zinc ions from water solutions. They are safe for the environment, produced from renewable sources, and are by-products or waste materials, which is part of the sustainable development and circular economy currently promoted in the EU.

Keywords

lignin, sorption, biomass, zinc ions, water treatment.

1. Introduction

In times of sustainable economic development, the constant search for innovative solutions for the use of waste materials derived from biomass is an important issue. Lignin, occurring in large quantities as a by-product in pulp production, and so far used mainly for energy purposes, enjoys unflagging interest. The structure of lignin creates great opportunities for scientific and applicative activities [1–8], while its recovery from black liquors can provide significant environmental benefits. For example, the extensive structure of the lignin molecule and the presence of characteristic functional groups on its surface allows to use it as a sorbent to capture metal ions and effectively remove them from the environment. [9–11]. Most of the adsorbents used so far are produced by processing crude oil (a non-renewable energy source). Nowadays, with the sharp increase in oil prices, the production process is becoming less and less economically profitable.

The essence of the problem is to replace expensive traditional sorbents with cheaper alternatives, which are often produced from waste materials and by-products e.g. wood pulping. A newly emerging alternative technology for the purification of solutions (including wastewater) from heavy metals is biosorption, i.e., sorption of raw materials and plant-derived materials [12,13]. It is an environmentally friendly technique of purifying aqueous diluted solutions with certain types of biomass. The reason behind taking up the research problem in this publication stems from the need to solve three important issues in the field of environmental protection: I - removal of heavy metal ions present in surface waters, II - management of by-products (black liquors) from the pulp and paper industry, III - replacement of the existing sorbents of petrochemical origin with a natural, fully ecological sorbent. Zn (II) ions were selected for the study due to their highest share in exceeding the permissible level of metal ions in surface waters. The principle of the method is based on

passing water solutions containing zinc ions through various fractions of natural sorbents placed in a sorption column in order to eliminate metal ions. Selected samples of waste products of natural origin and by-products of the cellulose and paper industries (lignin) presented in the article meet the requirements of advanced technologies that fit in with the assumptions of sustainable development and the circular economy [14]. The lignin obtained in this way is a cheap biopolymer due to its low or zero economic value [15]. A description of the samples used in the research is provided part I of the article [16].

The main aim of the research was to check the possibility of using lignin and plant biomass as biosorbents for the removal of zinc ions from aqueous solutions. In addition, the aim was to determine an optimal multilayer system made of biosorbents selected during the research to obtain the most effective sorption efficiency of zinc ions.

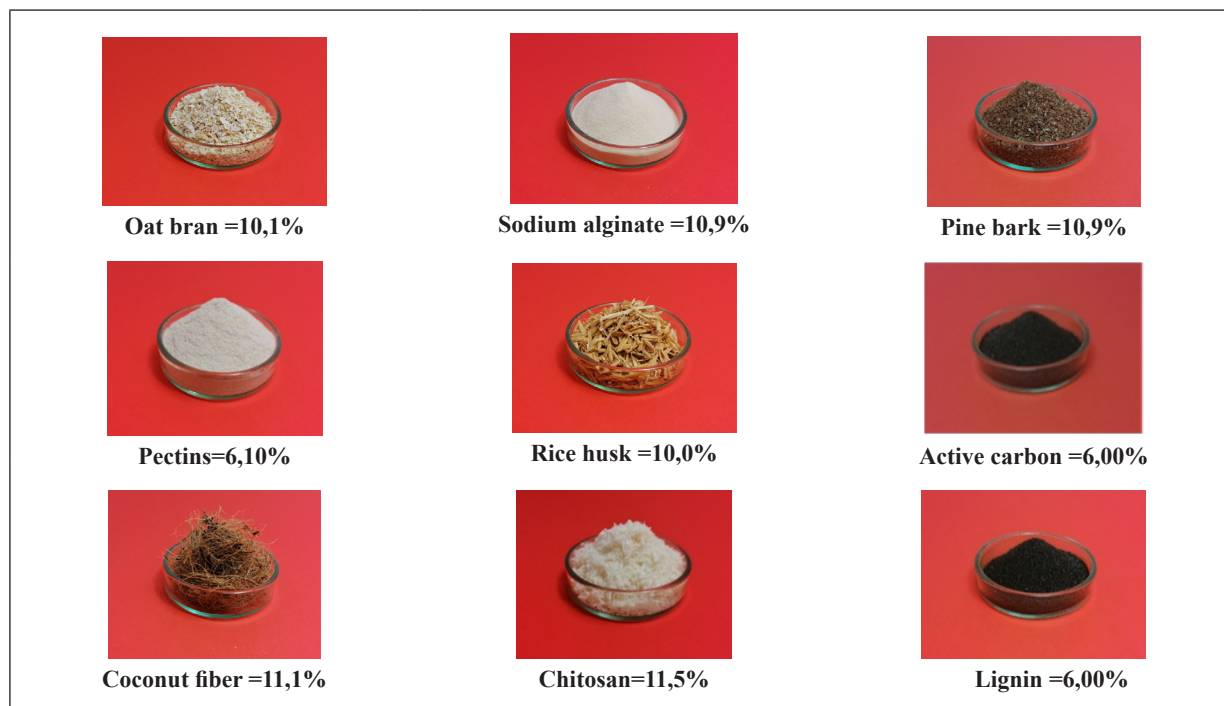


Fig. 1. Materials used for sorption tests and their relative humidity

2. Research Materials and Methods

The sorption process was tested for samples that were examples of raw natural waste without chemical treatment. These were commercially available research materials:

- Rice husk (DEPTANA.PL), used for beer filtration
- Oat bran (SANTE), used in breakfast cereals
- Coconut fiber (HORTICENTER.PL), mainly used as a substrate for orchids or fertilizer in gardening
- Pectin (VITAFARM), used in gelling fruit preserves
- Active carbon- Norit p.a. (Chempur, PL)
- Pine bark (KOR-PAK.PL), mainly used in horticulture as a soil acidifying ingredient.
- Chitosan (Vanson Halo Source, USA) with the following physicochemical parameters: average molecular weight (\overline{M}_v) = 319.7 kD, degree of deacetylation (SD) = 77.5%, ash content = 40 ppm
- Sodium alginate- Ceroga NA5030
- Black liquor- after softwood cooking process

In the case of pine bark trials, the material was ground in a Waring laboratory mill before the sorption tests began. The grinding time was 45 sec. The average relative humidity of the samples was $9 \pm 3\%$. Fig. 1. presents the raw materials used for sorption studies.

2.1. Isolation of lignin fractions

Lignin fractions were separated from black liquor, which was received as a by-product of the chemical treatment of wood. The lignin from the black liquor was precipitated with sulfuric acid. 1 M H_2SO_4 was added to the black liquor until a pH of 2.0. The resulting sediment was then centrifuged using a MPW-351 laboratory centrifuge (4200 rpm for 30 minutes). The lignin precipitate was redissolved in 0.1 M NaOH solution, and then the lignin was precipitated with 1 M H_2SO_4 solution. The precipitate was filtered off, centrifuged, and washed with 0.1 M H_2SO_4 and water. The washed and filtered lignin was dried by stirring at $50^\circ C$ [17].

2.2. GPC analyses of the isolated lignin

GPC/SEC analysis was performed in a solution of 0.5% LiCl in *N,N*-dimethylacetamide (DMAc) at a flow rate of 0.5 ml/min. A GPC/SEC system (Agilent Technologies, USA) with a three-column configuration of PLgel Mixed-A, 300mm, 1260 Iso Pump, and 1260 ALS autosampler equipped with an Optilab T-rEX refractometric detector (Wyatt Technology, USA) was used at $80^\circ C$. The volume of the injected test sample was 100 μl . Column calibration was performed using polystyrene standards. Results of the GPC/SEC analysis, such as the molar mass distribution function (MMD), mean values of the molar mass ($\overline{M}_n, \overline{M}_w$) and polydispersity ($\overline{M}_w/\overline{M}_n$) were calculated using the conventional calibration method, presenting the results in units of calibration standards.

2.3. Functional group analysis using the FTIR method

FTIR spectra of the adsorbents analysed enabled to define characteristic functional groups on the surface of the samples analysed. A Nicolet iS50 spectrometer

(Thermo Scientific, USA) equipped with a DTGS ATR detector was used with the following parameters: range 4000-400 cm^{-1} , resolution 4.0 cm^{-1} , number of scans with background collection [7,18].

2.4. Analysis of chemical composition

Chemical composition analysis of the selected biosorbents: rice husk, oat bran, pine bark and coconut fiber was carried out in accordance with the PN-92/P-50092 standard [19].

2.5. Tests of zinc ion adsorption from model water solutions

Zinc nitrate hexahydrate $\text{Zn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ p.a. (Chempur, PL) was used as a precursor of zinc ions. In a series of tests, the sorption capacity of all the sorbent materials was examined at a constant temperature of 25°C, for 120 minutes, at a pH of 4 and 7, which was obtained by adding an appropriate amount of HNO_3 (2M) or NaOH (2M).

In the sorption tests about 1 g of sorbent was placed in 250 cm^3 conical flasks and 100 cm^3 of an aqueous zinc solution with an ion concentration of 10 mg/cm^3 and appropriate pH (4 and 7) was added. The glass-stoppered flasks were incubated on a shaker for 120 minutes at a constant temperature of 25°C and rotation speed of 155 rpm. After the set time had elapsed, the mixture obtained was filtered under reduced pressure. Blank tests containing the initial concentration of zinc ions at pH 4 and 7 were also subjected to filtration. The concentration of zinc ions in the filtrate acquired was determined by atomic absorption spectrometry (AAS).

2.6. Atomic Absorption Spectroscopy (AAS) test

The zinc content in the filtrate was determined by flame atomic absorption spectrometry using a ContraAA 700 (Jena Analytik) high resolution atomic absorption spectrometer.

Certified IONEX (Chem-Lab) of Zn^{2+} concentration $1000 \pm 2 \mu\text{g}/\text{dm}^3$ was used as the standard. Before the determination, the filtrates and standards were acidified with 1% hydrochloric acid.

Basic parameters of the analysis were as follows: wavelength - 213.857 nm, flame - acetylene/air, spectral buffer - 0.1% KCl, characteristic concentration corresponding to absorption of 1% of lamp radiation (absorbance 0.0044) - 0.005 $\text{mg Zn}/\text{dm}^3$.

Sorption efficiency was calculated from the following formula:

$$\text{Yield} = (C_0 - C)/C_0 \times 100\% \quad (1)$$

Where: C_0 – initial concentration of Zn ions [mg/dm^3], C – concentration of Zn ions after the set time of the adsorption process [mg/dm^3]

2.7. Zinc ion adsorption tests with the use of a filter column

The adsorption test was performed using a glass column, inside which selected biomass and lignin raw materials were placed in layers and model aqueous solution of zinc ions was passed through the column. The aim was to determine the influence of the process parameters: the contact time of the ion with the adsorbent, the pH of the aqueous solution, the mass of the sorbent, the concentration of the ion, and the process temperature, on the efficiency of Zn ion removal from the aqueous solutions.

The effect of the processing time was studied at a concentration of 10 mg/dm^3 and 40 mg/dm^3 of zinc at pH 4 & 7 and temperature of 25°C. The aqueous zinc solution was passed through a suitably prepared column (Fig. 13). The ratio of the sorbent mass to the adsorbate volume was 0.5 g per 50 cm^3 of the zinc solution. The time of one passage through the column was about 4 minutes. The process was carried out in a circulation system for 4 hours. After 30 min, 60 min, 120 min and 240 min, about 10 cm^3 of the adsorbate was collected, filtered through a filter set, and the amount of

zinc ion that was not adsorbed on the bed was determined. The blank test zinc ion aqueous solution was filtered in the same way.

The effect of the sorbent mass was studied at a concentration of 10 mg/dm^3 of zinc at pH 4 & pH 7 and temperature of 25°C. The ratio of the sorbent mass to the adsorbate volume was 1 g per 50 cm^3 of zinc solution and 2 $\text{g}/50 \text{ cm}^3$ of zinc solution. The aqueous zinc solution was passed through the prepared column. The process was carried out in a circulation system for 1 hour. After this time, 10 cm^3 of the filtrate was withdrawn and the metal content was determined by the AAS technique.

The influence of temperature on the sorption process at a concentration of 10 mg/dm^3 of zinc at pH 4 and 7 was tested. The ratio of the sorbent mass to the adsorbate volume was 0.5 g per 50 cm^3 of the zinc solution. The prepared column with the receiving flask was placed in a water bath at 40°C. The duration of one full flow through the column was 1.5 minutes. The process was carried out in a circulation system for 1 hour. After this time, 10 cm^3 of the filtrate was withdrawn and the metal content was determined by the AAS technique. Similar tests were performed at a temperature of 25°C.

3. Results of the Research

3.1. Isolation of lignin from black liquor

A two-stage process of lignin separation from black liquor aimed at cleaning it of non-lignin deposits. Lignin fractions were obtained with an average yield of 45 g/dm^3 .

3.2. GPC/SEC analysis

Using the GPC/SEC technique, the structure of the separated lignin was investigated. The average molecular weight determined was 5.900 g/mol according to PS standards, and polydispersion (Mw/Mn) was 2.20. Based on literature data, the molecular

weight of lignin is within the range of 4600-8000 g/mol, which is close to the values obtained in the analysis of molar masses of lignin in softwood [20,21]. The peak of the sample tested overlaps with that of the eluent used (0.5% LiCl/DMAc), as evidenced by the asymmetric MMD plot. Results of the GPC analysis are presented in Tab. 1. and Fig. 2.

3.3. FTIR-ATR analysis of sorbent materials

A study of the structure of the surface groups: oat bran, rice husk, coconut fiber, sodium alginate, chitosan, pine bark, and pectin was performed with FTIR-ATR. The sorbents analyzed contain such substances as lignin, cellulose, hemicellulose, and other polysaccharides, as well as many different aliphatic and aromatic substances [22].

It was found that the spectra for lignin fractions are characteristic of lignin structures. In the samples tested, there are characteristic absorption bands at wavelengths (3400 cm^{-1}) corresponding to hydroxyl groups (-OH) and bonds C-H corresponding to the lignin in the aliphatic chain - 3372 cm^{-1} (Fig. 3). The bands around 2930 cm^{-1} correspond to the methyl, methylene, and methoxy groups in the guaiacylsringil units of lignin. The characteristic stretching bands for lignin occur at wavelengths around 1600 cm^{-1} and 1500 cm^{-1} . They correspond to the -C-C- bonds in the aromatic ring. The 1701 cm^{-1} band corresponds to the carboxyl group (-C=O), while the 1460 and 1420 cm^{-1} bands are related to the presence of asymmetric bending deformations of the C-H groups in guaiacyl propane and guaiacyl syringil units in the samples tested. The 1208 cm^{-1} wavelength corresponds to the aromatic guaiacyl rings that are characteristic of lignin. On the other hand, the 1122 and 1029 cm^{-1} bands confirm the presence of syringyl groups [23,24].

In all spectra analyzed, Fig. 3-11, there is a system of bands in the region of 3250 - 3400 cm^{-1} corresponding to the vibrations of $\nu(\text{O-H})$ bonds that may come from alcohols, phenols, and carboxylic acids,

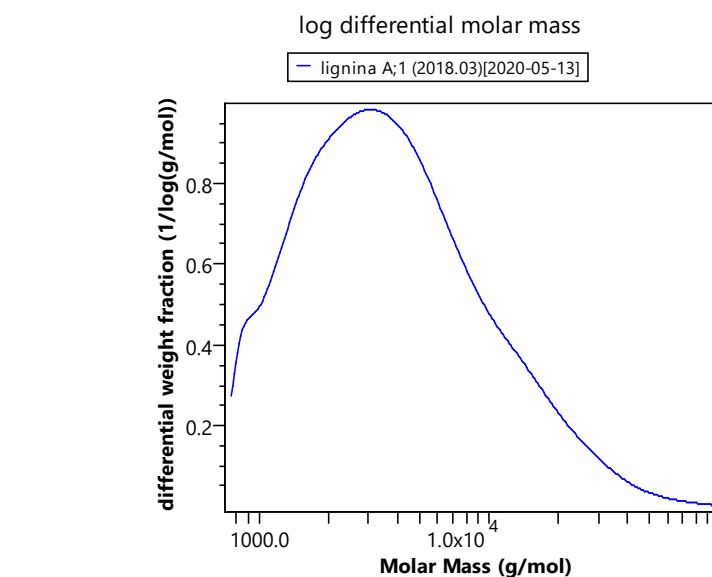


Fig. 2. MMD of lignin separated from black liquor

Mn (PS standard) [g/mol]	Mw (PSstandard) [g/mol]	Mw/Mn
2 710	5 970	2.20

Table 1. Results of GPC analysis of the lignin sample expressed in standard units

as well as intramolecular hydrogen bonds of cellulose [22]. The width of these bands is characteristic for carbohydrates due to the presence of many hydroxyl groups in their structure [25]. The bands in the wavenumber range of 2950 - 2850 cm^{-1} can be attributed to the vibrations $\nu(\text{C-H})$, 2950 - 2962 cm^{-1} , coming from asymmetric stretching vibrations, and 2850 cm^{-1} , from symmetrical stretching vibrations.

The bands characteristic for $\delta(\text{O-H})$ and $\delta(\text{C-H})$ vibrations occur in the range of 1200 - 1500 cm^{-1} , with the O-H bands coming from bending vibrations occurring in first and second order alcohols. For the C-H bond band, bending vibrations occur in this range, symmetrically at approx. 1375 cm^{-1} and asymmetrically at approx. 1450 cm^{-1} . There are many bands in the 900 - 1200 cm^{-1} region, which can be mainly attributed to the stretching vibration of bonds $\nu(\text{C-O})$ and $\nu(\text{C-C})$ [26]. For all compounds tested, the bands in the range 1000 - 1035 cm^{-1} represent vibrations of the glycosidic bond originating from the polysaccharide backbone, including vibrations $\nu(\text{C-O})$

and C-O-C [27]. Moreover, the band at 1158 cm^{-1} corresponds to vibrations of the C-O-C groups in the anomeric regions of hemicelluloses. Additionally, the intense band at 1030 cm^{-1} may be related to the vibrations bending in the plane of the C-H groups in the aromatic syringyl and guaiacyl units of lignin [22]. In the spectrum of chitosan (Fig. 6), there are also two characteristic bands for this polysaccharide, the first one at a wavenumber equal to 1588 cm^{-1} , resulting from vibrations of the N-H bond (amide II) [27], and the band in the region of 1645 cm^{-1} , corresponding to vibrations of the carbonyl group C=O of the amide group CONHR (amide I). The 1320 cm^{-1} range characteristic of the C-N bond (amide III) is also noticeable [28]. The spectrum of alginate (Fig. 11) shows an intense band from asymmetric vibrations at 1593 cm^{-1} and symmetrical vibrations of 1405 cm^{-1} , as well as stretching of the -CO bonds in the -COO- group at 1021 cm^{-1} , related to asymmetric vibrations of -COC, and at 814 cm^{-1} , related to mannuronic acid residues [28,29]. In the case of pectins (Fig. 10), the most

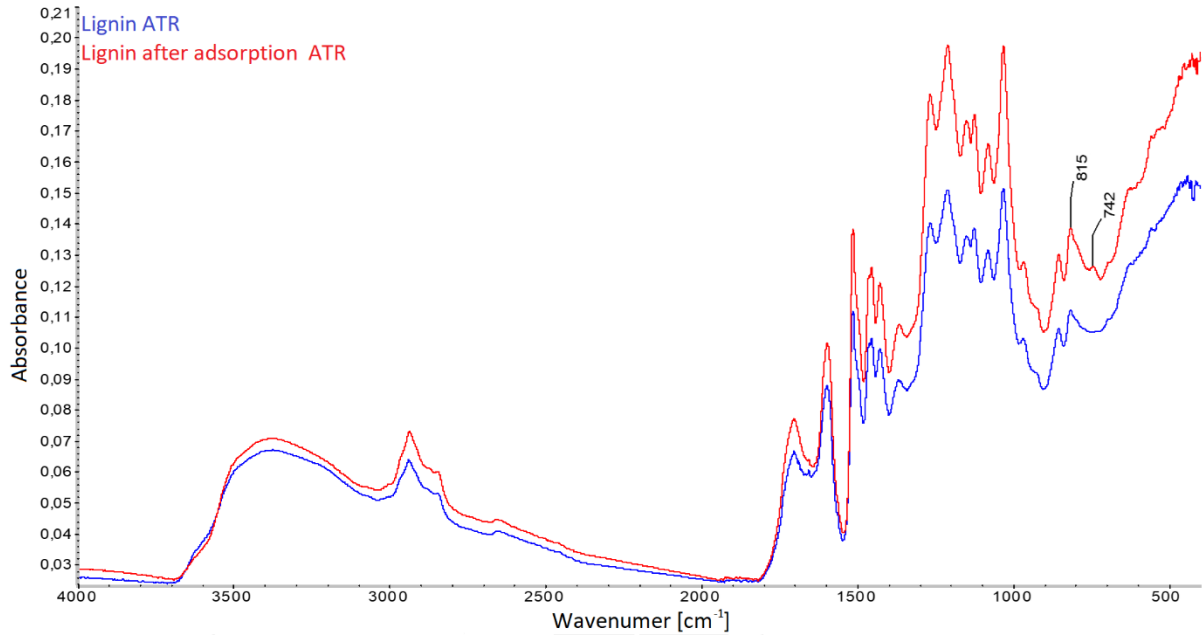


Fig. 3. FTIR-ATR spectrum of lignin in the range 400-4000 cm^{-1} before and after adsorption of zinc ions

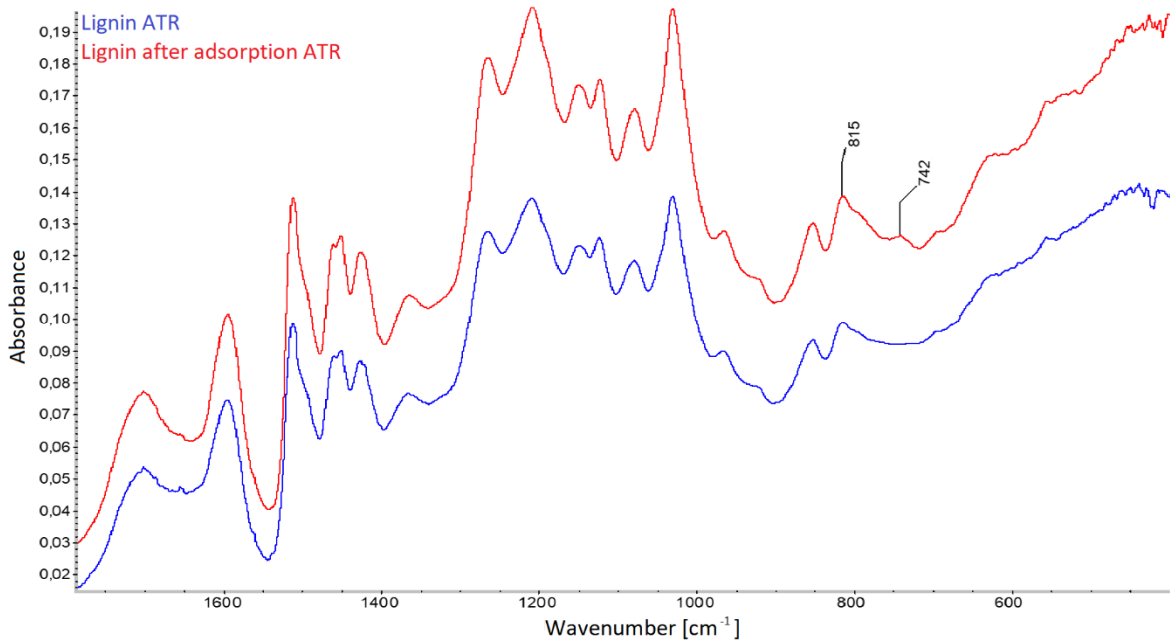


Fig. 4. FTIR-ATR spectrum of lignin in the range 400-1500 cm^{-1} before and after adsorption of zinc ions

characteristic bands which distinguish them from other polysaccharides are 1323 cm^{-1} and 831 cm^{-1} , resulting from vibrations of the pyranose ring, as well as 944 cm^{-1} , representing bending vibrations of the C-O bond. Moreover, in the pectin spectrum at a wavenumber of 1737 cm^{-1} , there is a characteristic band for vibration $\nu(\text{C}=\text{O})$ for carbonyl esters and at 1592 cm^{-1} for the stretching vibration of COO-carboxyl ions [30–33].

FTIR examination confirmed that the structures of the sorbents analysed are a mixture of various polysaccharides dominated by hydroxyl, carboxyl, and carbonyl groups, and they can act as active centers involved in the binding of various harmful compounds, e.g., zinc ions. Therefore, on the basis of the FTIR analysis, it was confirmed that the selected natural wastes are suitable for the development of an ecological biosorption system [22].

3.3.1. FTIR-ATR analysis of sorbent materials after adsorption

FTIR analysis allows to determine chemical interactions. As a result of such interactions, characteristic bands for chemical groups may undergo a shift or deformation. The appearance of a new simple chemical compound in the structure of a large molecule, such

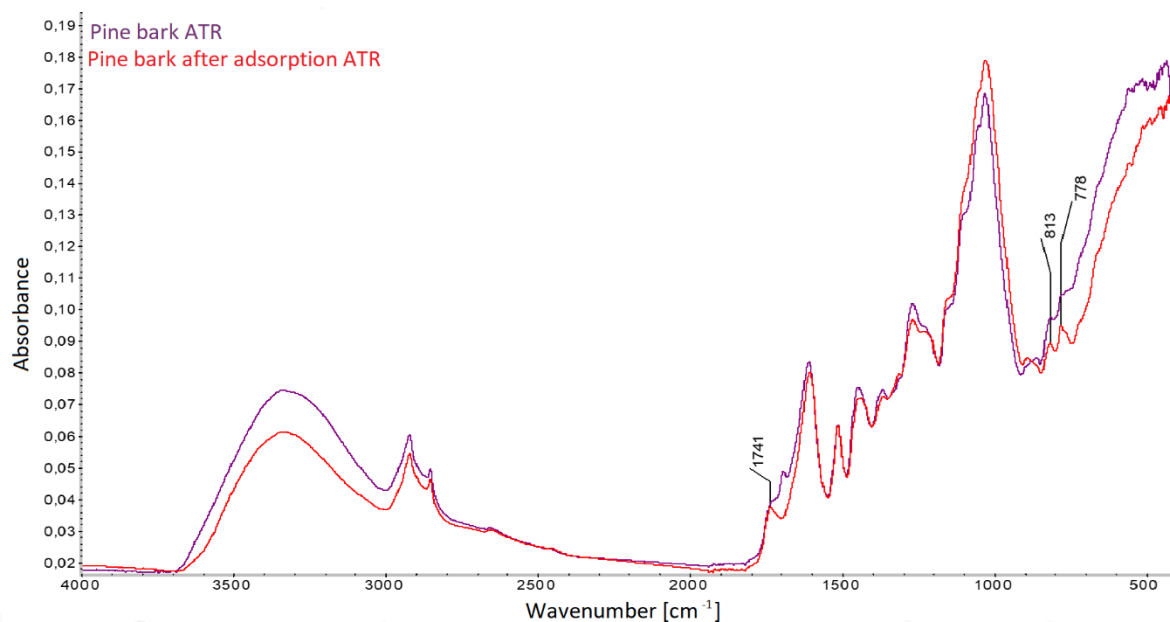


Fig. 5. FTIR-ATR spectrum of pine bark in the range 400-4000 cm^{-1} before and after adsorption of zinc ions

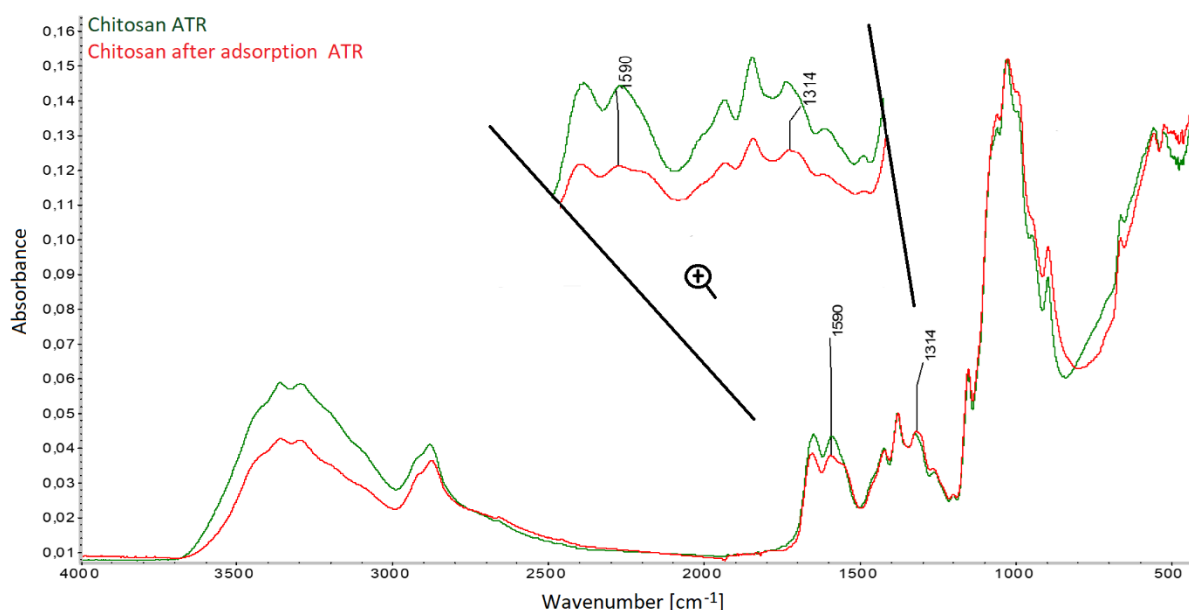


Fig. 6. FTIR-ATR spectrum of chitosan in the range 400-4000 cm^{-1} before and after adsorption of zinc ions

as a polymer, is often dominated by signals from large molecules. The bands overlap and are difficult to distinguish. Especially, such a phenomenon occurs only in the case of physical interactions. The individual sorbent materials after the sorption of zinc ions were subjected to FTIR-ATR analysis under the same measurement conditions. After the sorption process, the samples were dried at 30 $^{\circ}\text{C}$ in a vacuum dryer for 48h to remove water, which could cause an increase in the intensity of bands,

particularly the -OH group. The use of low temperature and a vacuum does not degrade biopolymers. For lignin (Fig 3-4) after zinc ion adsorption in the FTIR-ATR spectrum, a shift in the 815 cm^{-1} band and a new signal at 742 cm^{-1} were observed. Below 900 cm^{-1} there are bands for -OH groups. In general, the most characteristic region of the hydroxyl group is about 3300 cm^{-1} , where stretching vibrations are present. The band in this region is very intense, wide and difficult to interpret. In the range below 900 cm^{-1} , the band

of hydroxyl groups, due to out-of-plane bending vibrations, is more subtle and changes are more easily observed [34]. The shift in this band relative to lignin before the sorption process may indicate the interaction of hydroxyl groups, which are abundant in this polymer, with zinc ions. In addition, the 742 cm^{-1} band corresponds to the zinc signal [35]. A similar result was observed for pine bark (Fig 5). In addition, the deformation of a band around 1740 cm^{-1} was observed, which is characteristic for the carbonyl

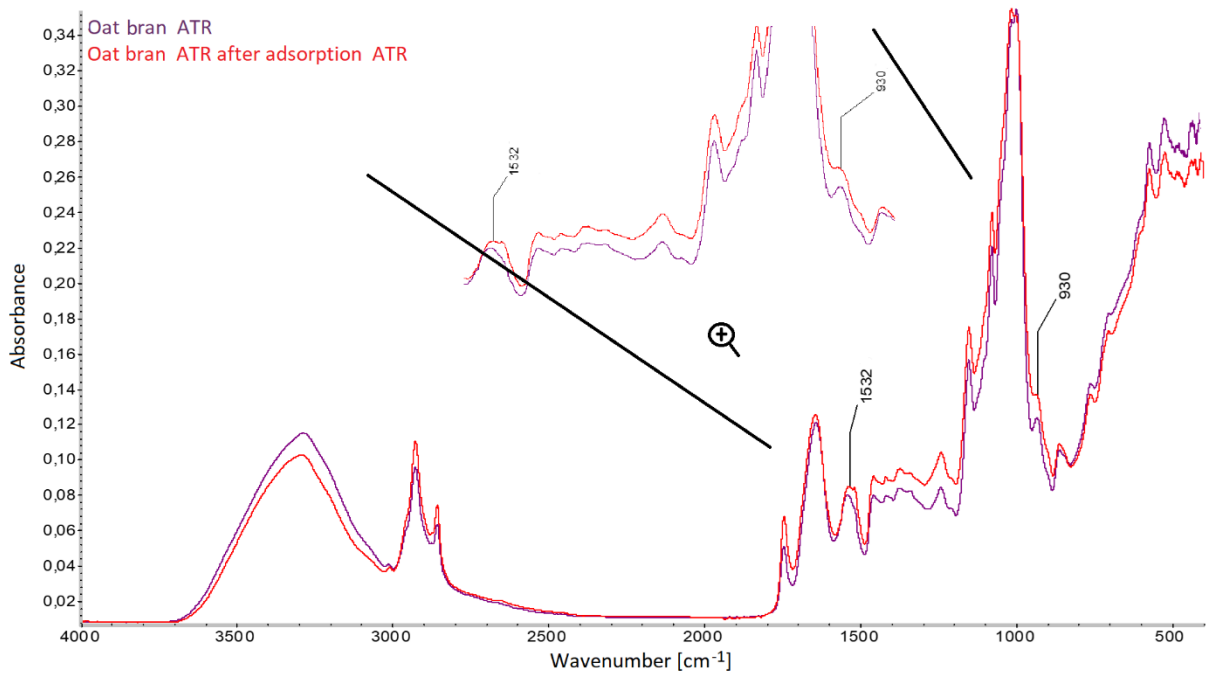


Fig. 7. FTIR-ATR spectrum of oat bran in the range 400-4000 cm^{-1} before and after adsorption of zinc ions

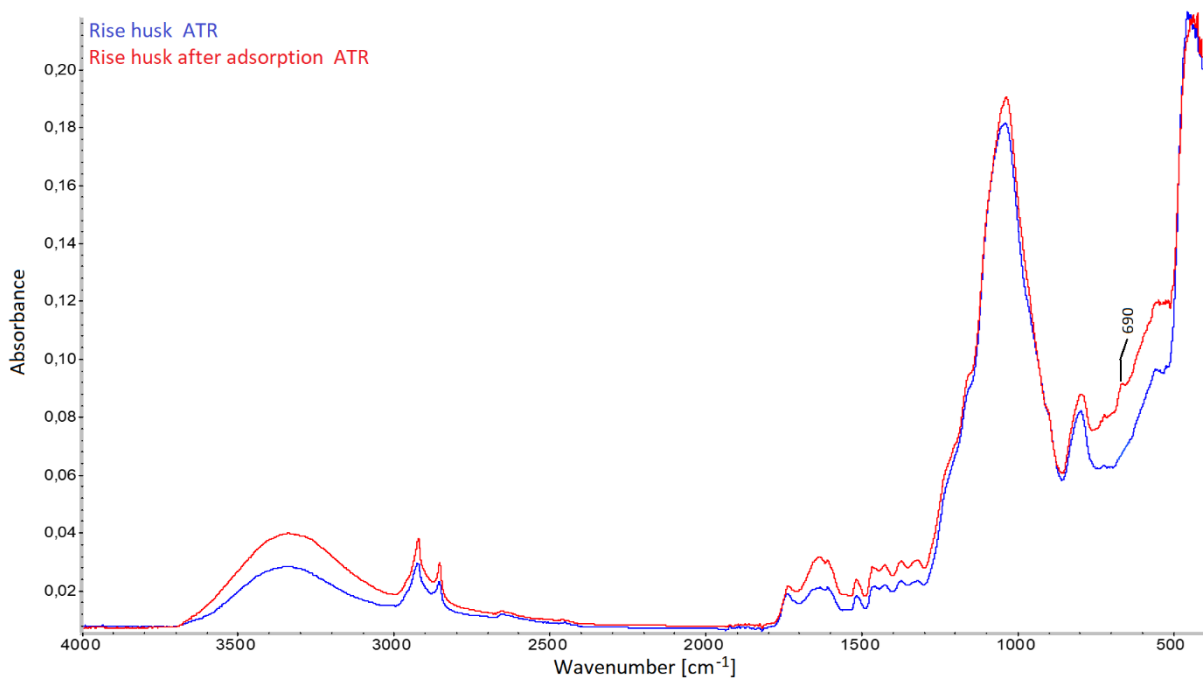


Fig. 8. FTIR-ATR spectrum of rice husk in the range 400-4000 cm^{-1} before and after adsorption of zinc ions

group. This indicates a chemical interaction of these structures with zinc ions. Oat bran is a mixture of various polysaccharides and has characteristic bands, one of which is around 1539 cm^{-1} for the stretching vibration of COO-carboxyl ions and the second around 940 cm^{-1} , representing vibrations of the C-O bending bond (Fig. 7) [30–33]. It was

observed that these particular regions in the FTIR-ATR spectrum were deformed after zinc ion adsorption, which demonstrates chemical interaction. On the other hand, no changes were observed in the FTIR-ATR spectrum for the rice husk (Fig 8). A band from zinc at 690 cm^{-1} was observed. Rice husk adsorbed zinc ions because of its structure; however, no

chemical interactions were observed in the spectrum. Coconut fibers, like other polysaccharides, showed the presence of zinc afterwards by a band at 699 cm^{-1} , but the intensity of the signal was very weak (Fig. 9). A very slight band at 1231 cm^{-1} and 2897 cm^{-1} deformation was also observed. The bands in the range of 2950-2850 cm^{-1} can be attributed to

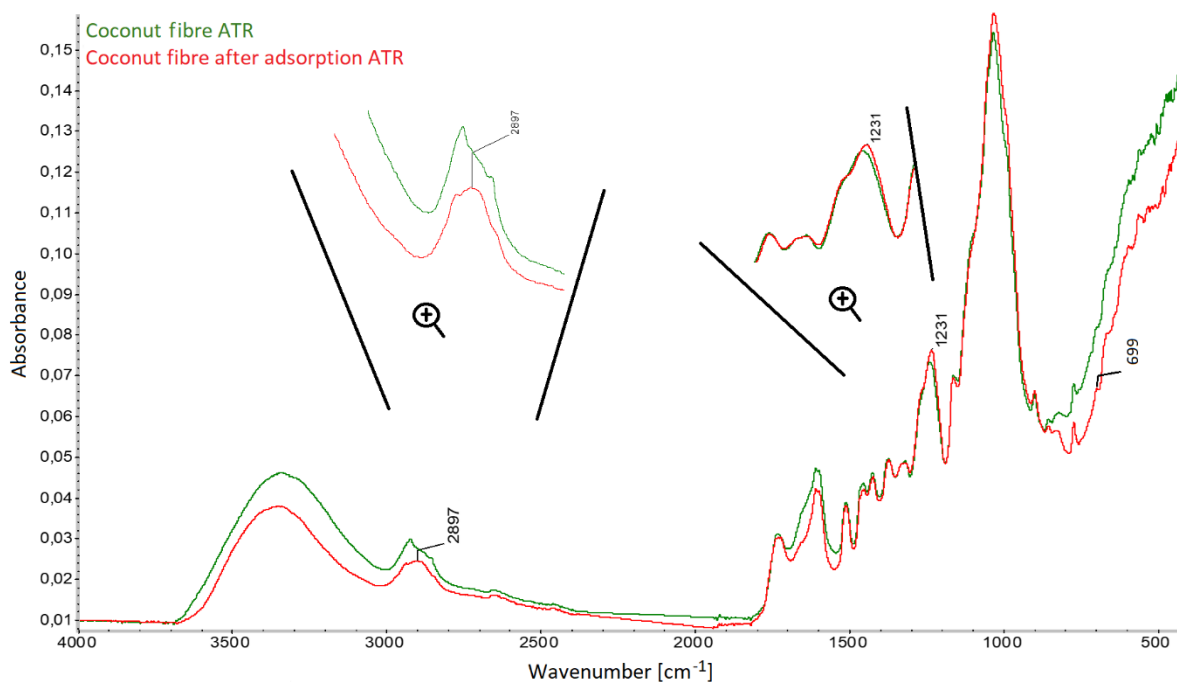


Fig. 9. FTIR-ATR spectrum of coconut fibre in the range 400-4000 cm^{-1} before and after adsorption of zinc ions

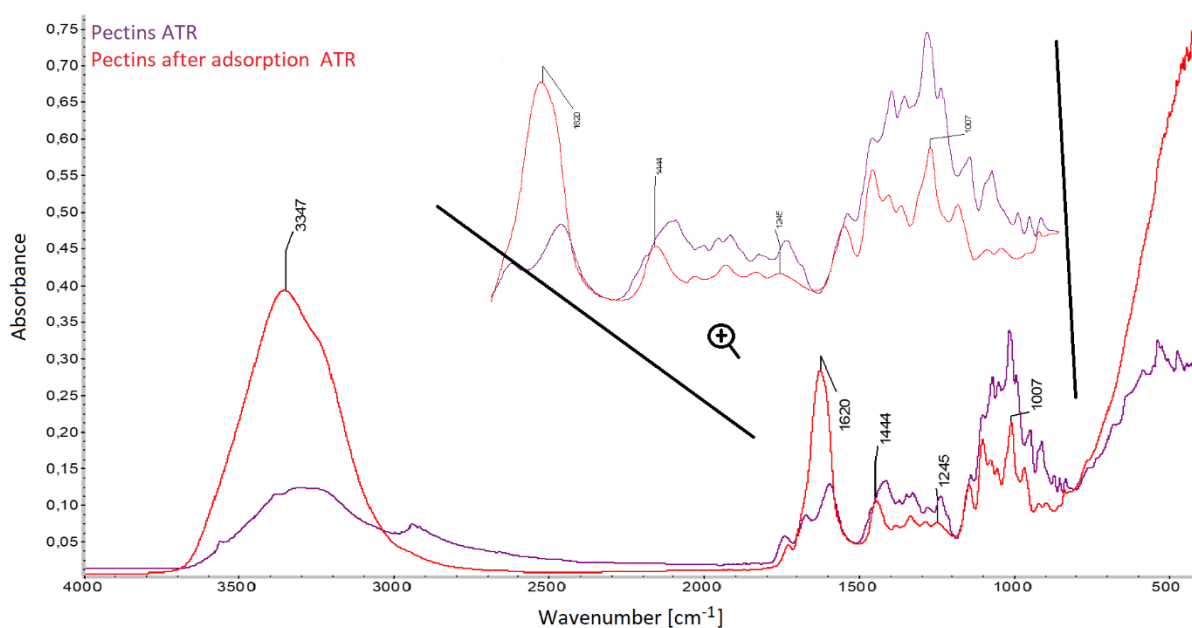


Fig. 10. FTIR-ATR spectrum of pectins in the range 400-4000 cm^{-1} before and after adsorption of zinc ions

the vibrations $\nu(\text{C-H})$, while the band at 1231 cm^{-1} may have different origins, e.g. $\delta(\text{O-H})$ and $\delta(\text{C-H})$ vibrations occur in the range of 1200-1500 cm^{-1} . Deformation of these bands demonstrate chemical interaction with zinc ions. The FTIR-ATR spectrum of pectins after adsorption is very different from the initial material (Fig 10). The most significant is the change in position of the

stretching vibration of COO^- carboxyl ions from 1590 cm^{-1} to 1620 cm^{-1} . Other changes concerned band shifts from 1410 cm^{-1} to 1440 cm^{-1} , from 1234 cm^{-1} to 1245 cm^{-1} and from 1011 cm^{-1} to 1007 cm^{-1} . Carboxyl groups also show a weaker symmetric stretching band at around 1410 cm^{-1} , and the band at around 1234 cm^{-1} is attributed to side-chain vibrations, whereas the bands at around 1010 cm^{-1}

are assigned to conformations of the glycosidic bonds of pectin [36]. Analysis of FTIR-ATR spectra for pectins indicate the involvement of multiple structures in the chemical binding of zinc ions. Also, the structure of sodium alginate is engaged in chemical interactions with zinc ions (Fig 11). Shifts in the bands characteristic of stretching $-\text{CO}$ and $-\text{COO}^-$ (1593 \rightarrow 1601 cm^{-1} ; 1405 cm^{-1}

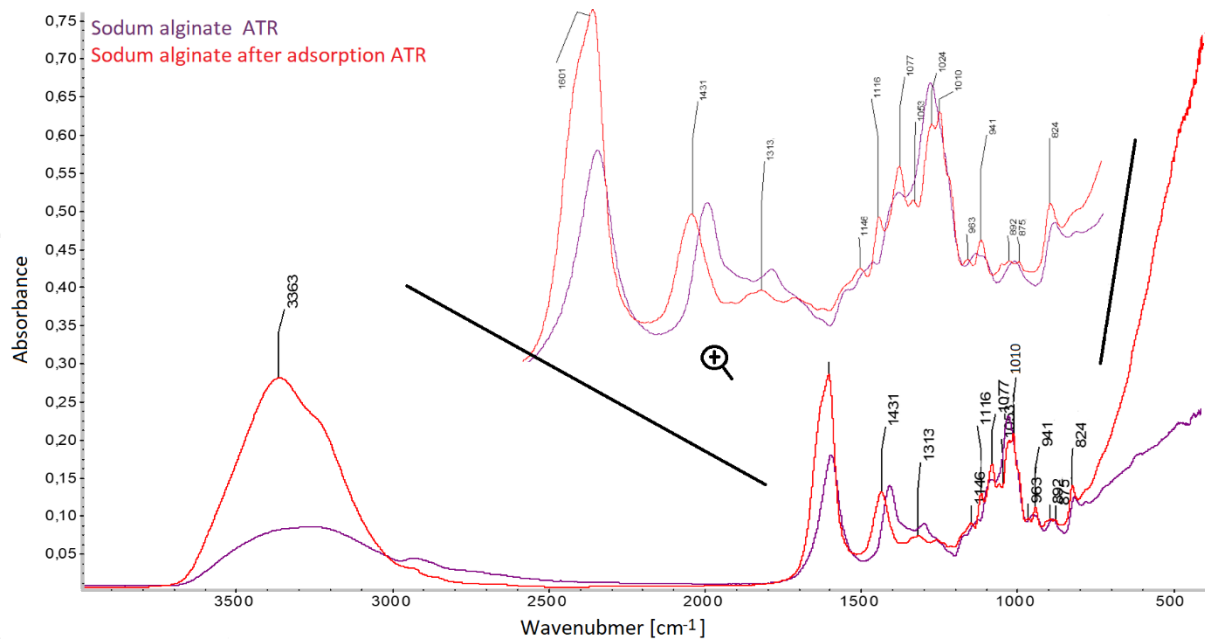


Fig. 11. FTIR-ATR spectrum of sodium alginate in the range 400-4000 cm^{-1} before and after adsorption of zinc ions.

	Content of analyzed fractions [%]			
	Rice husk	Pine bark	Coconut fiber	Oat bran
Ash	16.1	0.200	1.75	3.50
Compounds extractable in ethanol	1.97	7.85	1.24	3.09
Cellulose	44.3	25.6	40.7	5.61
Lignin	29.6	45.2	45.8	5.72

Table 2. Chemical composition of plant raw materials

$1 \rightarrow 1431 \text{ cm}^{-1}$) were observed. Also, in the range of 1010-1116 cm^{-1} and around 800 cm^{-1} , there were bands shifts. The band around 1021 cm^{-1} was related to asymmetric vibrations -COC, and at 814 cm^{-1} there was the presence of mannuronic acid residues [28,29].

3.4. Chemical composition analysis

Raw materials of plant origin used in the research: rice husk, pine bark, coconut fiber, and oat bran were analysed for their chemical composition. The tests were carried out according to the PN-92/P-50092 standard, the results of which are presented in Tab. 2.

The values for individual fractions present in the pine bark sample are similar to those given in the literature [37]. The highest cellulose content was obtained

in the samples of rice husk and coconut fibre. Lignin, on the other hand, is the fraction present in the largest percentage in pine bark and coconut fiber samples.

3.5. Tests of zinc ion adsorption from model water solutions

The sorption tests consisted in placing aliquots of about 1 g of sorbent in separate 250 cm^3 conical flasks and adding 100 cm^3 of an aqueous solution with a zinc ion concentration of 10 mg/dm^3 at pH 4 and 7. The flasks were covered with a glass stopper and incubated in a shaker for 120 minutes at a constant temperature of 25 $^\circ\text{C}$ and 155 rpm. After the set time the mixture was subjected to filtration under reduced pressure. The content of zinc ions in the filtrate was determined by AAS and the adsorption yield calculated. The results for 9 samples are presented in

Fig. 12. In the case of pectin and sodium alginate samples, in order to obtain a filtrate for the determination of Zn (II) by the AAS method, calcium pectinate, and calcium alginate were precipitated with the addition of about 12 g of calcium chloride to the solution and then filtered [38].

The results indicate that all the samples had the ability to absorb zinc ions. An important factor in sorption processes is the pH of the solution, which affects the efficiency of the process. In most cases, the sorption process performed better in an alkaline environment. The acidity of the solution can affect the metal ions and the surface charge of the adsorbent. At low pH, active surface groups (including hydroxyl and amine groups) are protonated, which can create a repulsive force between the positively charged metal ions and the positively charged sorbent surface. In addition,

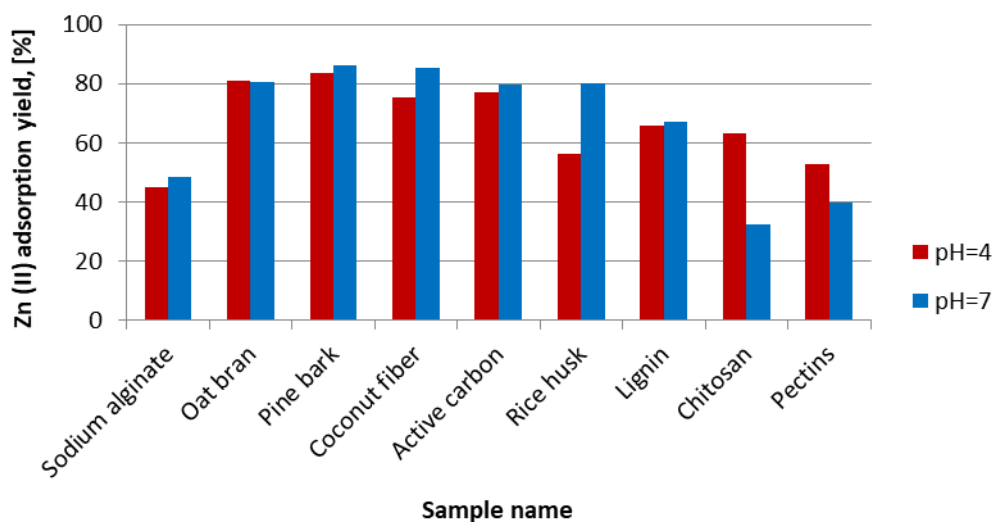


Fig. 12. Yield of Zn ion removal (10 mg/dm^3) from aqueous solutions for selected samples at pH 4 and 7

metal ions can compete with H^+ which leads to low removal efficiency. As the pH increases, the degree of deprotonation of functional groups gradually increases, which facilitates the adsorption of metal ions, as electrostatic attraction increases [27,39]. On the other hand, at high pH, metal ion hydrocomplexes may precipitate. These complexes have large sizes and are not dissociated in solution, hence they hardly interact with free carboxyl groups in the molecules, which leads to lower binding capacity [40]. In the water system, the surface of the sorbent takes a negative charge, which is important for the adsorption of positively charged metal ions harmful to the environment from model solutions [7]. The highest affinity to zinc ions after 120 minutes is shown by oat bran, pine bark, coconut fiber and activated carbon. According to literature data, oat bran adsorbs heavy metal ions due to the high content of β -glucans [41,42]. The lowest affinity can be attributed to chitosan, pectins and sodium alginate. Lignin absorbs approximately 66% of zinc ions. The sorption process is pH dependent for pectin, chitosan, and rice husk samples. The dependence of the process efficiency on the pH is mainly determined by the characteristic functional groups on the surface of the adsorbents. In the case of chitosan and pectin, higher adsorption values were obtained at an acidic pH, while rice husk sorbed better at a neutral than at an acidic pH.

3.6. Zinc ion adsorption tests from model aqueous solutions using a sorption column

After analysis of the results of Zn(II) sorption obtained and a preliminary study of the permeability of the sorption column, samples were selected for further testing. The samples met the following criteria: they should not dissolve in water (sodium alginate, pectin), nor swell and clog the sorption column (oat bran); they sorbed zinc ions best, were of plant origin: pine bark, coconut fiber or lignin, and the sorption process was zinc not pH-dependent (chitosan, rice husk). Sample weights used for further testing reflected the tests described in section 3.5.

The distribution of individual sorbents in the column (Fig. 13) assumed the use of coconut fiber as a component that prevents the movement of looser, smaller and lighter fractions (bark and lignin) when the aqueous solution was passed through the column. During sorption, the aqueous solution affects the sorbent mixture as it flows through successive layers. On each of them, impurities are successively reduced and the substance removed from the solution remains on the sorption bed.

The concept assumed the use of lignin in the sorption column as a valuable biopolymer of practical importance,

which has so far been mainly a by-product in the pulp and paper industry. The use of such a by-product, arising in the production of cellulose pulp, is a potential source for the production of ecological sorbent and the transformation of waste into raw material. In this way, the lignin would be fully utilized.

Tests of zinc ion adsorption from model water solutions with the use of a sorption column allowed to determine the influence of process parameters on the efficiency of the removal of Zn ions from water solutions. The parameters taken into account were: the contact time of the ion solution with the adsorbent, pH of the aqueous solution, sorbent mass, ion concentration, and process temperature.

3.6.1. Effect of ion-sorbent contact time, adsorbate concentration and pH on sorption yield of zinc ions

The effect of the processing time was investigated at a concentration of 10 mg/dm^3 zinc for pH 4 and 7. The columns contained stacked beds (each type of bed weighed 0.5 g) and an aqueous solution of zinc was circulated through a column. The time for 1 pass through the column was approximately 1.5 minutes. The ratio of the sorbent mass to the adsorbate volume was 0.5 g per 50 cm^3 of the zinc solution. The process was carried out for 4 hours.

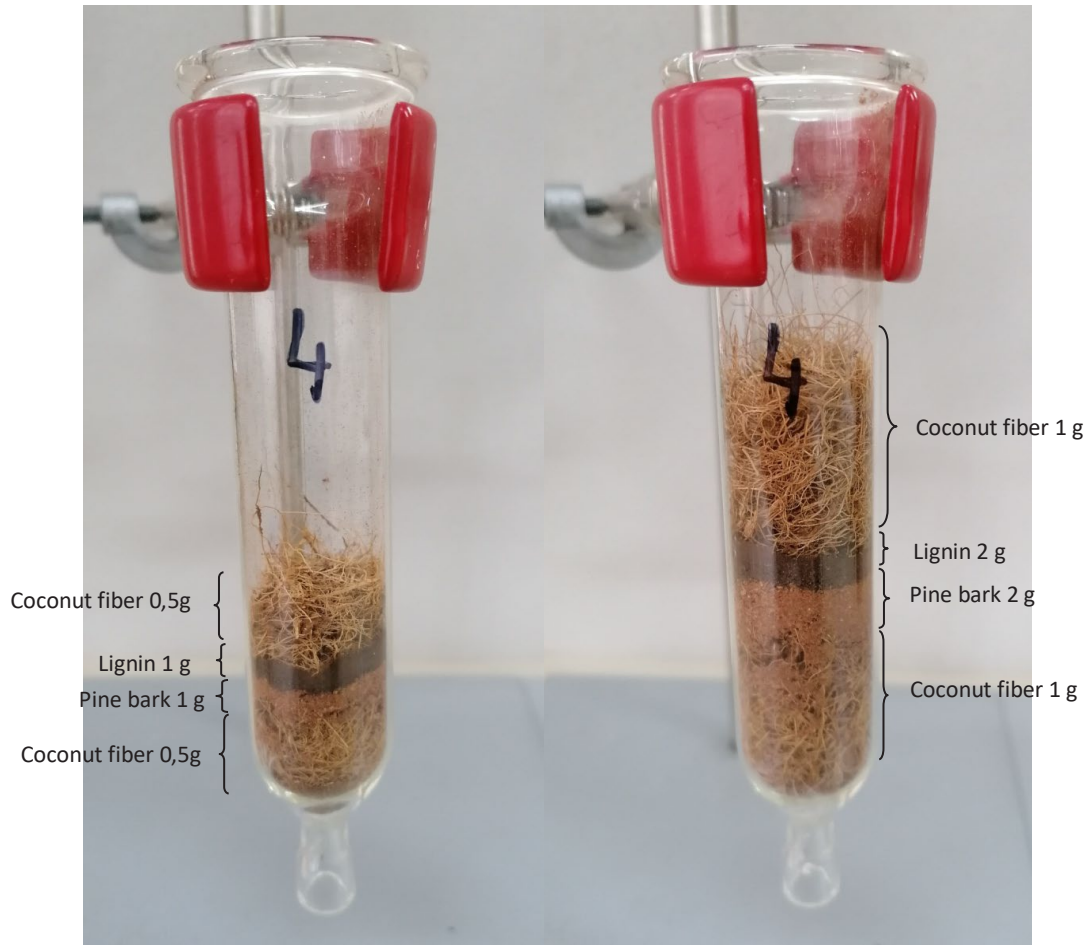


Fig. 13. Concept of a sorption column composed of 3 types of bed (coconut fiber, lignin, pine bark) : for 1 g and 2 g, respectively

After 30 min, 60 min, 120 min, and 240 min, approx. 10 cm³ of the adsorbate was collected and filtered through the filter assembly. The content of zinc ions in the filtrate was determined by AAS, and the adsorption yield was calculated.

Analyzing the results, presented in Fig. 14, it can be stated that, initially, the adsorption process is fast and then slows down. The adsorption equilibrium was established after about 120 minutes. It was also found that the effectiveness of the process was correlated with pH. In case of pH 7, after 240 minutes, the yield was at the level of approx. 83%, while at pH 4, it was slightly lower - approx. 76%. The test at a zinc concentration of 40 mg/dm³ (Fig. 15) shows similar tendency

The results obtained (Fig. 15) show that the adsorption yield decreases with the increasing concentration of zinc ions. This is due to the partial saturation of active sites on the sorbent surface, which

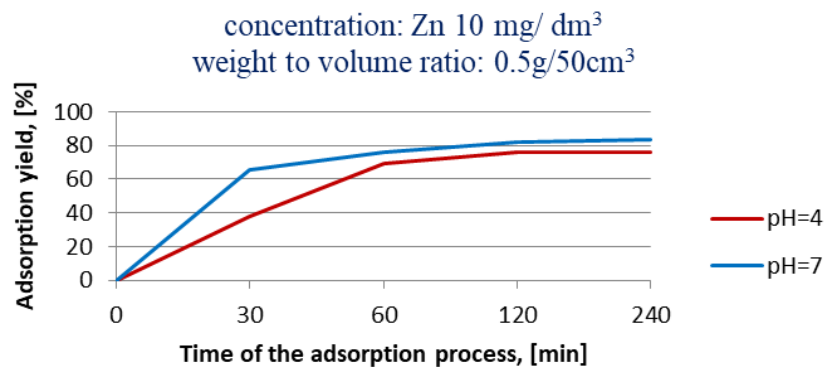


Fig. 14. Effect of time and system pH on the sorption yield of zinc ions (10 mg/dm³)

are capable of capturing metal ions. The increase in the number of metal ions in the solution increased competition for active centers, which makes the adsorption process less effective [7]. In the case of pH 4 and pH 7, after 240 minutes, a similar efficiency of approx. 40% was recorded.

3.6.2. Effect of sorbent mass and pH on the adsorption process

The effect of the sorbent mass at a zinc concentration of 10 mg/dm³ and pH 4 & 7 on the adsorption yield was studied. The ratio of the sorbent mass to the adsorbate volume was 1 g/50 cm³ and 2 g/50 cm³.

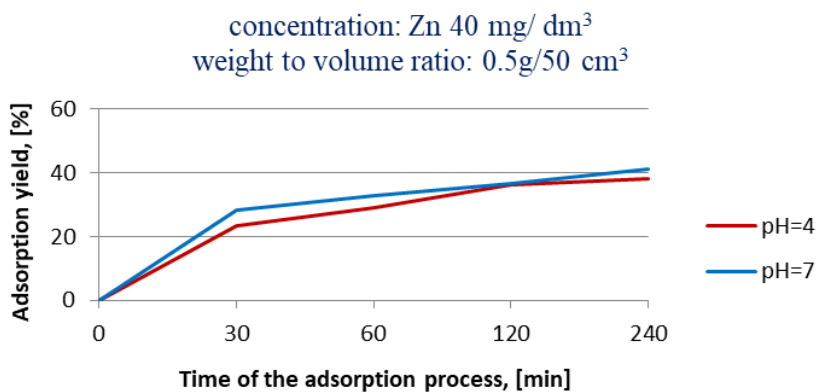


Fig. 15. Effect of time and system pH on the sorption yield of zinc ions (40 mg/dm³)

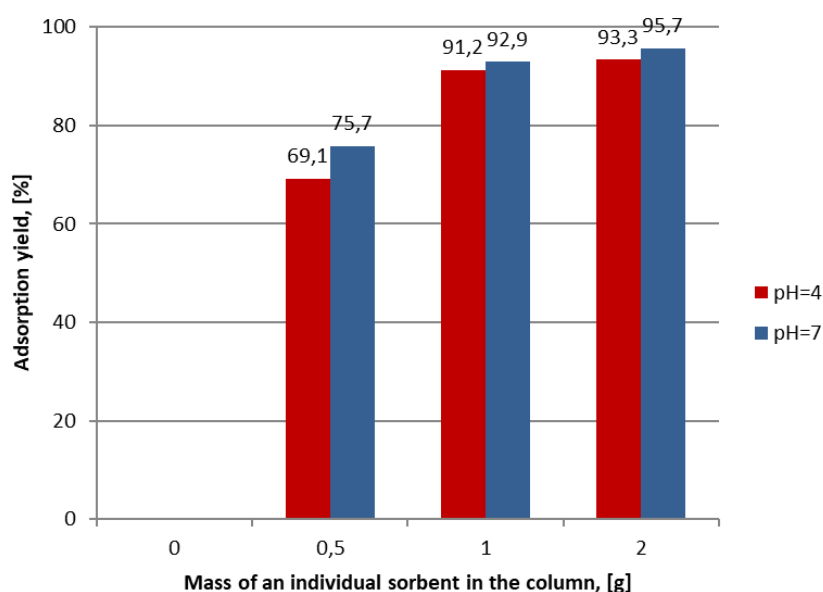


Fig. 16. Effect of sorbent mass and system pH on the sorption yield of zinc ions

The Zn solution circulated through the column, for which the time of a single passage was 2.5 minutes and 5 minutes, respectively. The process was run for 1 hour. After this time, approx. 10 cm³ of the adsorbate was collected and filtered. The zinc ion concentration was determined by the AAS method and then the adsorption yield calculated.

The results presented in Fig. 16 show that as the mass of the sorbents used increased, so did the yield of the process. It was caused by an increase in the area of the contact surface of the adsorbent and an increase in the number of characteristic functional groups present on its surface, which determine the sorption capacity. In this case the pH parameter was not

significant. For the column containing 1 and 2 g of each sorbent bed, similar yield values above 90% were obtained for pH 4 and 7, respectively.

3.6.3. Influence of temperature and pH on the adsorption process

Temperature is considered to be one of the most important parameters influencing the efficiency of the zinc ion adsorption process [43]. A study of the influence of temperature on the sorption process at a zinc concentration of 10 mg/dm³ at pH 4 and 7 was carried out. The ratio of the weight of the sorbent to the volume of the adsorbate was 0.5 g /50 cm³ of the zinc solution.

The column was filled with sorbents and the test solution circulated through it. A flask with zinc solution and another collecting the adsorbate were placed in a 40 °C water bath. The duration of one full flow through the column was 1.5 minutes. The process was carried out for 1 hour. After this time, approx. 10 cm³ of the adsorbate was collected, filtered through a filter set, and subjected to an AAS examination. The results are presented in Fig. 17.

The increase in temperature had a positive effect on the sorption yield in the sorbents tested. According to the literature data, an increase in the temperature of the reaction system causes a decrease in the viscosity of the solution, which results in an increase in the diffusion rate of ions to the adsorbent surface, as well as in an expansion of pores and activation of the adsorbent [44]. The maximum capacity yield of the process was achieved for a concentration of 10 mg/dm³ at 40 °C, which was approx. 90% at pH 7.

4. Summary and Conclusions

- Lignin was successfully separated from black liquor, yielding 45 g/dm³. The molecular weight of the lignin fraction obtained falls within the range of 4600-8000 g/mol, as confirmed by GPC tests and supported by literature data.
- Chemical analysis of the plant-based raw materials revealed that cellulose and lignin fractions possess the ability to adsorb zinc ions. The highest cellulose content was found in rice husk and coconut fiber samples, while the largest percentage of lignin was present in pine bark and coconut fiber samples.
- Zinc ion adsorption was observed in all materials tested and was found to be pH dependent. Chitosan and pectin exhibited higher adsorption efficiency at a slightly acidic pH, while rice husk was more effective at a neutral pH.
- The selected sorbents demonstrated an affinity for zinc ions based on their chemical structure and functional groups. Polysaccharides with reactive

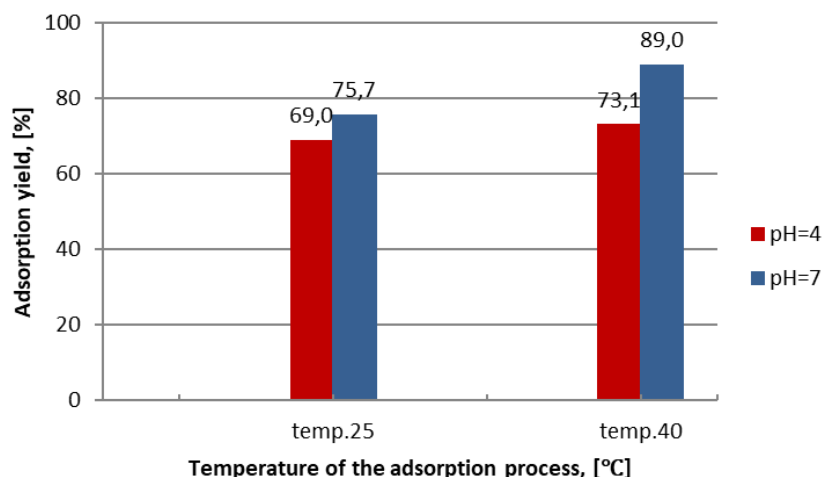


Fig. 17. Effect of temperature and pH of the system on the yield of zinc ion sorption

regions showed changes in FTIR-ATR spectra, indicating chemical interactions. FTIR-ATR spectral analysis before and after the sorption process revealed changes in the band system within the 3250-3400 cm^{-1} region, corresponding to $\nu(\text{O-H})$ bond vibrations. For lignin, a shift in the 815 cm^{-1} band and a new signal at 742 cm^{-1} were observed after zinc ion adsorption.

- The samples selected for the construction of the deposit adsorb zinc ions at the level of 70 %, which indicates a strong affinity of the sorbent to the ion tested.
- Increasing the adsorption process temperature resulted in enhanced zinc ion removal efficiency.
- Optimal adsorption conditions were determined to be 25°C and pH 7, which yielded the best results.

- A sorption efficiency of 95% was achieved using 2 g each of coconut fiber, lignin, and pine bark at 25°C and pH 7.
- The research conducted supports the conclusion that plant-based materials can be used as eco-friendly zinc ion sorbents in aqueous solutions. This highlights the potential for using lignin and plant biomass as sustainable and environmentally friendly sorbents for zinc ion removal, in line with the principles of sustainable development and circular economy currently promoted in the EU.

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