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Effect of alkaline treatment of wooden sawdust for the removal of heavy metals from aquatic environments

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ABSTRACT

This paper reports a study of the removal of heavy metals from water by unconventional waste products including the wooden sawdust of poplar, cherry, spruce and hornbeam. The efficiency of Cu(II), Zn(II), and Fe(II) ion sorption under various initial concentrations from model solutions by raw and alkaline-modified sawdust was investigated. Data obtained by neutron activation analysis revealed that ion exchange is one of the mechanisms underlying metal removal by the selected sawdust from the model solutions. Analysis of the structure and morphology of natural and alkali-modified wooden sawdust by SEM/EDX did not reveal significant changes. The FT-IR spectra showed changes in functional groups due to the alkaline modification of sawdust where the intensity of hydroxyl peaks was considerably increased. It was found that the sorption capacity of the modified sawdust for the model solutions of 50 mg.L^{-1} of Cu(II) and Zn(II) was approximately 4.5 times higher in comparison to the untreated sawdust; however, the alkaline-modified sawdust had a negative influence on Fe(II) ion removal because of organic-metallic dye formations. The adsorption capacity of the alkaline modified wooden sawdust for the removal of heavy metals from wastewater was improved.

Keywords: Heavy metals; Sorption; Wooden sawdust; Alkaline treatment; Neutron activation analysis; FT-IR spectroscopy

1. Introduction

Increased concentrations of heavy metals are often detected in industrial wastewaters, primarily from metallurgical plants, tanneries, petroleum refining, agriculture, and mining [1]. Such heavy metals are non-biodegradable, accumulate in living organisms and can cause various serious diseases and disorders, even at low concentrations [2,3]. Various physical-chemical methods and techniques are used for the removal of metals from wastewater, such as chemical precipitation, ion-exchange, electroflotation, membrane separation, reverse osmosis, electrodialysis, and solvent extraction. However, these techniques are often accompanied by high operating costs and the formation of large amount of sludge [4].

The biosorption technique fulfils the requirements for more effective and economical methods for treating wastewater contaminated by metals due to the inherent

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property exhibited by inactive, non-living substances of biological origin to remove metal ions from an aqueous solution [5,6]. According to the literature [6–8], the binding of metal ions is a physical-chemical process, independent of metabolism, with the basic mechanism being sorption. The biosorption of heavy metals can also be accompanied with ion exchange, surface complexation, and precipitation.

The wooden sawdust of various tree species has been used as efficient biosorbents by Shukla et al. [9]. Other studies [10–12] demonstrated the use of materials based on chitosan, polysaccharide and lignin as economical biosorbents.

Among agricultural waste materials, sawdust is one of the most appealing materials for removing pollutants such as dyes, salts, and heavy metals from water and wastewater. The material consists of lignin, cellulose, and hemicellulose, with polyphenolic groups playing an important role in binding the dyes through various mechanisms [9,13].

It is known that wooden sawdust has the potential to interact with heavy metal ions through the mechanisms of ion exchange and adsorption. The process of ion exchange occurs through intensive changes in the pH of the solution. The adsorption mechanism involves the potential presence of hydroxyl, methyl, carboxyl, and amide functional groups in the structures that bind heavy metal ions. Elements such as K, Na, and Ca present in the structure of wooden sawdust may play important roles in the ion-exchange mechanisms. Other mechanisms underlying heavy metal biosorption by wooden sawdust may include complexation and microprecipitation [14].

A previous analysis of the surface properties of the wooden sawdust [9] showed that the binding of the heavy metals is primarily connected with the presence of phenolic and alcohol hydroxyl functional groups. Various natural biosorbents, such as spirogyra, pine bark, rubber leaves, walnut shells, rose petals, and wooden sawdust exhibited an enhanced biosorption capacity after alkaline modification [15]. Additionally, a higher biosorption capacity for positively charged Cu(II) and Ni(II) was obtained following the modification of date pits (*Phoenix dactylifera*) by calcium oxide [16] due to formation of strong basic sites on the surface. Moreover, potassium hydroxide (KOH) proved to be an effective alkaline activating agent in the modification of biosorbents for Ni(II) and Zn(II) removal in wastewater treatment [17]. Despite the fact that alkaline treatment has a positive effect on the improving of the adsorption properties of wooden materials there very few references about the alkaline modification of wooden sawdust [18,19]. From this reason, it is necessary to deal in more detail investigate the influence of alkaline treatment of wooden sawdust on their adsorption abilities.

The present study involves the biosorptive properties of selected types of natural wooden sawdust (poplar, spruce, cherry, and hornbeam) for Cu(II), Zn(II), and Fe(II) removal. The selected wooden sawdust was modified by 1 M sodium hydroxide or potassium hydroxide, and their sorptive properties were compared with those of untreated wooden sawdust. Neutron activation analysis was used to determine the elemental composition of wooden sawdust (raw and Cu-loaded), and SEM/EDX analysis was used to study the structure and morphology of natural and modified poplar wooden sawdust. Also, the influence of changes of specific surface area of poplar wood sawdust and its modification on adsorption capacity was studied. The IR spectroscopy was applied to identify the functional groups responsible for metal binding. Additionally, changes in the structure of the sawdust influenced by the alkaline modification were identified.

2. Materials and methods

2.1. Preparation and characterisation of adsorbents materials

The wooden sawdust of poplar, spruce, cherry, and hornbeam species of locally available wood was sieved, and only the fractions with a particle size maximum of 2.0 mm were used for the subsequent experiments. Modifications of the wooden sawdust were realised using a 1 M solution of NaOH or KOH, where 200 mL of the appropriate hydroxide was mixed with 20 g of each kind of wooden sawdust for 24 h. After 1 d, the modified wooden sawdust was filtrated, washed with deionised water and dried. A total of 1 g of dried wooden sawdust (natural and modified) was weighed and used for the adsorption experiments. A specific surface area as a significant sorption parameter was estimated by low-temperature gas adsorption using nitrogen gas (Quantachrome NOVA 1000e, USA).

2.2. Adsorbate solutions

The adsorbate solutions of Cu(II), Zn(II) and Fe(II) (with initial concentrations of C_0 = 10 mg.L^{-1} and C_0 = 50 mg.L^{-1}) were prepared by dissolving $CuSO_5.5H_2O$, $ZnSO_4.7H_2O$, and $FeSO_4.7H_2O$ in deionised water. The input pH values of all model solutions were not additionally adjusted. Concentrations of the appropriate ions were determined using the colorimetric method with a Colorimeter DR890, (HACH LANGE, Germany) and the appropriate reagents. The copper concentration was determined from the reaction with bicinchoninic acid, which forms a purple coloured complex proportional to the copper concentration at the wavelength 560 nm. Zinc reacts with the 2-carboxy-2′-hydrox y-5′-sulfoforamazyl benzene (“zincon”), forming a blue colour that is proportional to the zinc concentration at the wavelength 540 nm. The iron concentration was determined from the reaction with 1,10-phenanthroline, which forms an orange colour at the wavelength 510 nm.

2.3. Adsorption studies

Batch adsorption experiments were performed under static conditions, where in 1 g of dried adsorbent material was mixed with 100 mL of the model solution containing 10 or 50 mg.L^{-1} of copper, zinc, or iron. After 24 h sorbent-sorbate interaction under static conditions, the wooden sawdust was removed by filtration through laboratory filter paper. The residual concentrations of the appropriate ions in the various solutions were determined by the colorimetric method. The changes of pH values were determined by inoLab pH 730 pH metre (WTW, Germany) which was standardised using buffer solutions of different pH values (4.01, 7.00). The % efficiency of ion removal η was calculated using the following equation:

$$\eta = \frac{(c_0 - c_e)}{c_0} \times 100\% \quad (1)$$

where C_0 is the initial concentration of the appropriate ion (mg.L^{-1}), and C_e is the equilibrium concentration of the ion (mg.L^{-1}).

The amount of equilibrium adsorption was calculated using the equation [20]:

$$q_e = \frac{(c_0 - c_e).V}{m} \quad (2)$$

where q_e is the adsorption capacity per unit mass of adsorbent (mg.g^{-1}), V is the volume of the aqueous phase (L), and m is the mass of the adsorbent (g). All adsorption experiments were performed in triplicate under batch conditions, and the results are expressed as arithmetic mean values.

2.4. Infrared spectrometry of wooden sawdust

The FT-IR spectra of natural and modified wooden sawdust were obtained for the characterisation of functional groups responsible for metal binding. The IR measurements of the adsorbent materials were performed on a Bruker Alpha Platinum-ATR spectrometer (BRUKER OPTICS, Ettingen, Germany). A total of 24 scans were performed on each sample and the spectra were recorded in the range from 4,000 to 400 cm^{-1}. SEM (Tescan-VEGA3 LMU) was also performed with EDX analysis (Bruker, Germany).

2.5. Neutron activation analysis of adsorbents

To determine the elemental composition a neutron activation analysis (NAA) of untreated and the Cu(II) loaded sawdust (poplar, spruce, cherry and hornbeam) was performed at the pulsed fast reactor IBR-2 of the Frank Laboratory of Neutron Physics, JINR, Dubna, Russia. As a representative study of the change of chemical composition before and after adsorption experiments were chosen Cu-loaded sawdust due to the stable nature of the copper ions. The concentration of Cu(II) in the model solution before the adsorption experiment was 10 mg.L^{-1}. For the analysis, the adsorbent materials were dried at 40°C to a constant weight. Samples of approximately 0.3 g were packed in polyethylene foil bags for short-term irradiation or in aluminium cups for long-term irradiation. A total of four elements (Na, Mg, K, and Ca) were analysed. More details concerning the irradiation time and gamma spectra processing can be found in [21]. The difference between the certified and measured content of elements of the certified material varied between 1% and 10%.

3. Results and discussion

3.1. Neutron activation analysis of wooden sawdust

The NAA data obtained for natural wooden sawdust and Cu(II)-loaded wooden sawdust are presented in Table 1, from which it is clear that the biosorption of Cu(II) influenced the content of other elements in the sorbents. The amount of potassium in the Cu-loaded wooden sawdust after the 24-h adsorption experiments decreased to under the detection limit. A significant decrease in the calcium content of Cu-loaded wooden sawdust was also observed by a factor of 10 for spruce sawdust. Based on the obtained NAA results, it can be concluded that ion exchange is one of the mechanisms underlying copper biosorption. Beside calcium, the significant decrease of sodium, magnesium content was notices. Release of earlier-mentioned elements indicates on their active involvement in the ion exchange process that occurs during the copper biosorption. For example, Bozic et al. [22] showed that sodium and potassium release from sorbent can be associated mainly with their washing out by water from the treated solution.

3.2. Characterisation of natural and modified wooden sawdust by SEM/EDX

Based on the data previously obtained by NAA showing a significant decrease in the potassium content after the adsorption experiments, the wooden sawdust was modified with 1 M potassium hydroxide and sodium hydroxide to increase the adsorption efficiency. Characterisation of the structure and morphology of natural and alkali-modified wooden sawdust was performed using SEM/EDX. Natural

Table 1
Chemical composition of natural wooden sawdust and wooden sawdust after Cu(II) adsorption experiments

Element	Average content of elements in adsorbents (mg.kg^{-1})			
	Na	Mg	K	Ca
Poplar	12.5 ± 0.9	264 ± 18.5	1790.0 ± 286	1810.0 ± 181
Poplar_Cu(II)	12.3 ± 0.9	174 ± 12.2	**<151.0**[a]	**1520.0 ± 152**
Spruce	5.8 ± 0.4	497 ± 34.8	287.0 ± 45.9	5210.0 ± 521
Spruce_Cu(II)	1.8 ± 0.1	37.4 ± 2.62	**<63.0**[a]	**495.0 ± 49.5**
Cherry	21.2 ± 1.5	175 ± 12.3	606.0 ± 97	1040.0 ± 104
Cherry_Cu(II)	15 ± 1.1	8.7 ± 0.61	**<232.0**[a]	**697.0 ± 69.7**
Hornbeam	48.6 ± 3.4	376 ± 26.3	1570.0 ± 267	4350.0 ± 435
Hornbeam_Cu(II)	11.3 ± 0.8	220 ± 15.4	**<214.0**[a]	**2660.0 ± 266**

[a]Values under detection limits. Note: The bold values are represents the significant decrease of calcium content ("Ca") in wooden sawdust after adsorption.

and modified poplar sawdust was chosen as representative materials for this study due to the natural similarity of all types of adsorbent materials. Fig. 1 represents the morphology of dried natural and modified poplar sawdust. As shown in this Fig. 1(a), the distribution and size of the particles in the sawdust are inhomogeneous. In the case of both alkali modifications, something similar to a "pulping effect" can be seen (Figs. 1(b) and (c)).

The chemical composition of natural and alkali-modified poplar sawdust is shown in Table 2. The adsorbate materials are composed primarily of carbon, oxygen and nitrogen. As shown in Table 2, the modification with NaOH had a positive influence on the sodium (Na) concentration in the adsorbent material that was not detected in the natural poplar wooden sawdust. The modification with KOH led to an increase in the potassium (K) concentration in studied adsorbent material.

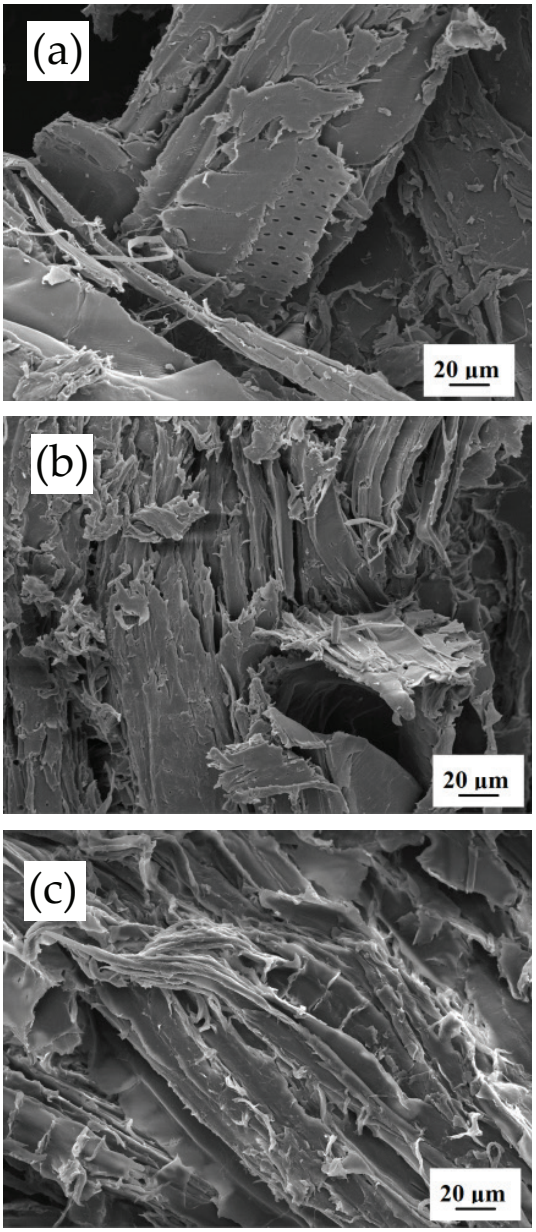

Fig. 1. Structure and morphology of poplar sawdust: (a) natural; (b) modified by NaOH; (c) modified by KOH.

3.3. Specific surface area of wooden sawdust

The specific surface area (SSA) plays an important role in the adsorption process. However, there are also other mechanisms influencing the progress of adsorption (e.g., complexation, ion-exchange abilities, chelation, etc.). The "pulping effect" observed by SEM on alkaline modified polar wooden sawdust could be connected with increasing of specific surface area. In order to evaluate the differences among the samples, the SSA determination of by the physisorption of nitrogen gas at 77 K according to the BET method was carried out. Degassing of the samples was carried out with respect to their thermal stability determined by a thermal analyzer (Netzsch STA 449 F3, Germany). The results are presented in Table 3. As one can see, differences among the samples of poplar and poplar_NaOH are minimal, and the SSA is not corresponding with the results of the sorption experiments discussed below. Šćiban et al. [23] reported that in the case of unmodified poplar wood, and especially for modified one, specific surface is less than surface area of common activated carbons. It indicates that adsorption mechanism may be accompanied about some other mechanisms of ions removal. These facts show indicate a different background of the adsorption process. Even pottasium hydroxide treatment of poplar sawdust was decrease of poplar specific surface area. It could be caused by partially pore clogging during pulping.

3.4. Infrared spectrometry characterisation of natural and modified wooden sawdust

The metal adsorption capacity of wooden sawdust is influenced by various factors but is closely linked with the surface structures of –OH, –COOH, –NH, $–NH_2$, and $–NH_3$ functional groups that are present in organic materials [24]. The functional groups of poplar, cherry, spruce, and hornbeam wood sawdust were determined using FTIR spectroscopy. The IR spectra of natural and alkali-modified wooden sawdust are shown in Fig. 2 (poplar) and Fig. 3 (cherry). The Table 3 summarises the detailed bands assignments according to the poplar, cherry, spruce, and hornbeam wooden sawdust functional groups. According to the literature [25], it can be supposed that the structure of wooden sawdust is primarily formed by cellulose, hemicellulose, and lignin. The FTIR spectra of natural and modified wooden sawdust reveal several major intense bands that can be divided into the following three significant areas of wavenumbers: 3,650 to 3,000 cm^{-1}, 3,000 to 2,800 cm^{-1}, and 1,750 to 800 cm^{-1}.

In the Fig. 2 the strong broad of –OH stretching (3,650 to 3,000 cm^{-1}) and C–H stretching of methyl and methylene groups (3,000 to 2,800 cm^{-1}) can be seen. The strong broad of –OH stretching at this area is caused by the presence of hydroxyl functional groups or from the adsorbed atmospheric moisture too. The ending of a strong boarded peak centred at a wavenumber approximately 3,337 cm^{-1} could also be attributed to amine (–NH) functional groups. The presence of hemicelluloses is demonstrated by the typical

Table 2
Chemical composition of natural and modified poplar wooden sawdust

Element	Average ratio of elements in adsorbents [%]				
	C	O	K	N	Na
Poplar	58.86 ± 1.60	29.80 ± 1.40	0.22 ± 0.17	11.12 ± 1.63	<0.05
Poplar_NaOH	56.74 ± 3.64	29.50 ± 3.45	0.07 ± 0.06	12.65 ± 1.75	**1,05 ± 0.69**
Poplar_KOH	63.52 ± 4.70	19.59 ± 1.71	**1.99 ± 0.07**	14.92 ± 0.40	<0.05

Note: The bold values are represents the confirmation of increasing content "Na" , "K" respectively after sawdust alkaline treatment.

Table 3
Specific surface area of natural and modified poplar wooden sawdust

Sorbent	S_{BET} [$m^2.g^{-1}$]	R^2 [–]
Poplar	1.52	0.998
Poplar_NaOH	1.70	0.992
Poplar_KOH	0.59	0.998

S_{BET} – specific surface area.
R^2 – correlation coefficient.

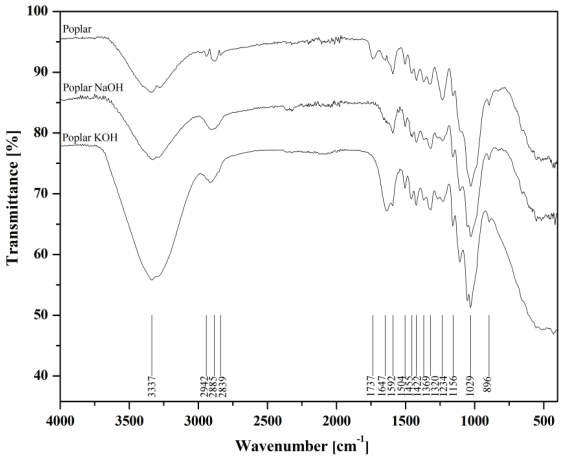

Fig. 2. Infrared spectra of poplar wooden sawdust: (a) natural; (b) modified by NaOH; (c) modified by KOH

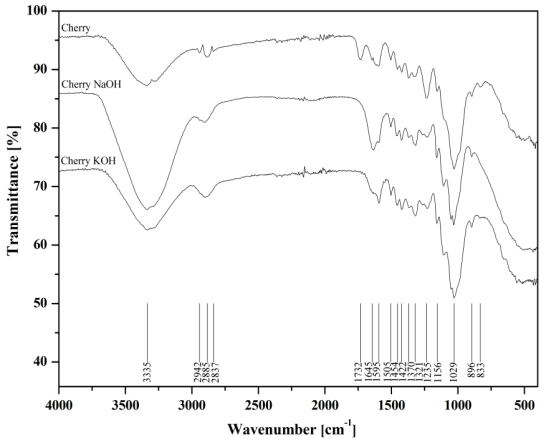

Fig. 3. Infrared spectra of cherry wooden sawdust: (a) natural; (b) modified by NaOH; (c) modified by KOH.

stretching band around at 1,736 cm^{-1}, caused by the presence of C=O from the acetyl groups [26]. The infrared spectra of lignin in wooden sorbent materials [27] revealed characteristic bands at 1,503 and 1,454 cm^{-1} (corresponding to aromatic skeletal vibrations of lignin) and at 1,320 cm^{-1} (syringyl and guaiacyl condensed lignin). Wavenumbers at 1,422, 1,367, 1,315, 1,153, 1,024 and 894 cm^{-1} correspond to cellulose, which occurs in two forms: crystalline (at 1,315 cm^{-1}) and amorphous (at 894 cm^{-1}). Functional groups of aromatics, carboxylic acids and alkyl halides were observed at 829 cm^{-1} [28].

The alkaline modification had the significant influence on the intensification of strong broad –OH stretching that was reflected in the spectra as a wide peak –OH deformation functional group at wavenumber 3,337 cm^{-1}. The modification with sodium hydroxide led to a significant increase in the number of hydroxyl functional groups, especially in the case of cherry (Fig. 3), spruce and hornbeam wooden sawdust. On the other hand, potassium hydroxide considerably increased the intensity of hydroxyl functional groups in poplar sawdust (Fig. 2). Differences were also observed at wavenumbers of 3,000 to 2,800 cm^{-1} where the asymmetric C–H stretching was rearranged to symmetric, resulting in the alignment of the triple peak at the wavenumber 2,885 cm^{-1}.

For a better understanding of the FT-IR spectra, the band assignments according to the literature and band shifts are listed in Table 4 [24–29].

3.5. Adsorption study

The results of the absorption experiments for solutions with cation concentrations of 10 $mg.L^{-1}$ are shown in Table 5. The selected wooden sawdust used in the absorption experiments was able to remove copper, zinc and iron ions from the solution. The natural poplar wooden sawdust exhibited a metal ion removal efficiency of approximately 80%. These results correspond with the study Holub et al. [30] dealing with adsorption of Cu(II) and Zn(II) from single-component aqueous solutions onto non-modified poplar sawdust (concentrations range from 1 to 150 $mg.L^{-1}$). The authors [9,10,30] also report that low-cost waste materials like wooden sawdust could be used as economically viable for the removal of heavy metal ions in acidic conditions. Due to the low removal capacity of natural non-modified wooden sawdust, it is recommended that this treatment be used for the purification of wastewater with low metal concentrations or post-treatment wastewater. A previous study [9] investigated metal removal by various sawdust sorbents that appeared to be promising for metal removal from wastewater and potentially more economical than the current removal processes.

Table 4
Infrared assignments of bands for spectra of selected wooden sawdust

Band position	Poplar	Spruce	Cherry	Hornbeam	Proposed assignment
Wavenumber (cm^{-1})					
3,700–3,000	3,337	3,336	3,335	3,331	O–H str., H–bonded, N–H str. (H_2O)
3,050–2,950	2,942	2,942	2,942	–	C–H str.
2,915	2,885	2,883	2,885	2,892	Asym. C–H str. of CH_2 and CH_3 in CH_3–N
2,849	2,839	2,839	2,837	–	Sym. C–H str. of CH_2 and CH_3 in CH_3–N
1,731	1,737	–	1,732	1,731	C=O str.
1,700–1,600	1,647	1,648	1,645	–	OH deform. (H_2O)
1,600–1,550	1,592	1,602	1,595	1,593	N–H bend, C–C str. (in–ring)
1,503; 1,493	1,504	1,508	1,505	1,503	N–O asym. Str., C=C str. (in-ring), C–H asym. deform. vib. of CH_3
1,452	1,455	1,451	1,454	1,454	C–H deform. vib. of –CH_2 and –CH_3 and C=C str. vib., CH_2 scissor vib.
1,421	1,422	1,422	1,422	1,422	C–C str. (in–ring), C=C (in-plane)
1,370	1,369	1,367	1,370	1,369	C–H rock, C–H sym. deform. vib. of CH_3, C–H deform. vib. of aliphatic group
1,320	1,320	1,316	1,321	1,321	C–N stretch, C–O stretch
1,231	1,234	–	1,235	1,232	C–H wag (–CH_2X), CH_3 roc. vib. and asym. CCN stre. Vib. in –CH_2–$N_2(CH_3)_3$…OH–
1,181; 1,157	1,156	–	1,156	1,156	C–H wag (–CH_2X) and C–H deform., C–N str.
1,068; 1,028	1,029	1,026	1,029	1,031	C–N stretch, C–H deform., –SO_3H group
924; 890; 858	896	895	896	897	=C–H bend, N–H wag, C–H "oop", C–N str. vib. in N–CH_3
828; 803	–	806	833	830	C–H "oop", N–H wag, C–Cl str.

Table 5
Results of adsorption experiments with selected wooden sawdust and their modifications at C_0 = 10 $mg.L^{-1}$ of dissolved heavy metals ions in model solutions

Sorbent	Cu(II)				Zn(II)				Fe_{total}			
	Initial pH = 5.8				Initial pH = 5.4				Initial pH = 5.4			
	C_e ($mg.L^{-1}$)	η (%)	q_e ($mg.g^{-1}$)	pH	C_e ($mg.L^{-1}$)	η (%)	q_e ($mg.g^{-1}$)	pH	C_e ($mg.L^{-1}$)	η (%)	q_e ($mg.g^{-1}$)	pH
Poplar	1.42 ± 0.03	85.8	0.86	5.2	2.60 ± 0.09	74.0	0.74	5.8	2.2 ± 0.07	78.0	0.78	5.7
Poplar_NaOH	0.49 ± 0.03	**95.1**	0.95	7.5	0.82 ± 0.06	**91.8**	0.92	7.7	7.4 ± 0.18	26.0	0.26	7.0
Poplar_KOH	0.68 ± 0.06	**93.2**	0.93	7.3	0.51 ± 0.04	**94.9**	0.95	7.8	7.3 ± 0.15	27.0	0.27	7.1
Spruce	1.90 ± 0.05	81.0	0.81	4.9	3.00 ± 0.11	70.0	0.70	5.3	3.0 ± 0.09	70.0	0.70	5.0
Spruce_NaOH	1.27 ± 0.08	87.3	0.87	7.7	1.20 ± 0.04	88.0	0.88	7.9	10.0 ± 0.22	<0.05	<0.05	7.5
Spruce_KOH	2.78 ± 0.10	72.2	0.72	7.8	2.59 ± 0.07	74.1	0.74	8.3	10.0 ± 0.25	<0.05	<0.05	7.6
Cherry	2.30 ± 0.04	77.0	0.77	4.9	6.00 ± 0.13	40.0	0.40	5.2	4.0 ± 0.13	60.0	0.60	5.0
Cherry_NaOH	0.46 ± 0.03	**95.4**	0.95	6.8	0.38 ± 0.02	**96.2**	0.96	8.2	3.0 ± 0.11	**70.0**	0.70	6.9
Cherry_KOH	1.82 ± 0.02	81.8	0.82	7.1	1.37 ± 0.05	86.3	0.86	7.7	7.8 ± 0.16	22.0	0.22	6.9
Hornbeam	2.72 ± 0.07	72.8	0.73	5.2	3.20 ± 0.10	68.0	0.68	5.9	3.7 ± 0.06	63.0	0.63	5.5
Hornbeam_NaOH	1.38 ± 0.02	86.2	0.86	7.2	0.59 ± 0.02	**94.1**	0.94	7.7	6.3 ± 0.09	37.0	0.37	6.9
Hornbeam_KOH	1.94 ± 0.04	80.6	0.81	7.3	1.09 ± 0.04	89.1	0.89	7.5	9.6 ± 0.10	4.0	0.04	7.1

Note: The bold values are represents the most significant efficiencies for heavy metals ion removal.

The adsorption by unmodified wood materials is often accompanied with the leaching of organic components with less adsorption capacity into the purified water. The adsorption experiments showed that alkaline-modified wooden sawdust greatly reduced the release of organic compounds into the model solution. As can be seen from Table 5, the alkali modification enhanced the absorption efficiency of biomass for copper and zinc ion removal from the model solution. Based on the FTIR results, the alkaline modification considerably increased the intensity of hydroxyl functional groups, resulting in an increase in absorption properties of wooden sawdust. The most pronounced increase occurred with the of biosorption capacity of NaOH-modified cherry biomass, which increased from 77% (Cu(II) and 40% (Zn(II)) (untreated biomass) to above 95% (modified biomass). A slight decrease of adsorption efficiency was observed only for KOH-modified spruce compared with original sawdust.

While the alkaline modification had a positive effect on the removal of Cu(II) and Zn(II) ions from the model solutions, in the case of Fe(II) ion removal, the influence of hydroxides had significant effect on the decreased removal efficiency. This finding can be explained by the formation of organic-metallic dyes dissolved in the solution without the possibility of sorption. The biosorption of iron ions on modified spruce sawdust led to the oxidation of ferrous ions to ferric ions. These Fe(III) ions reacted with organic matter from the wooden sawdust and caused a colouring of the solution. This similar effect was also described by Ahalya et al. [31] in study based on bio-sorption of heavy metals. The mechanism of organic-metallic dyes formation was explained as probably effect of the complexation of Fe(III) ions and carboxyl groups in the wooden sawdust. An exception was observed only for adsorption by NaOH-modified cherry, where the model solution remained uncoloured even after the Fe(II) adsorption, and there was also an increase of the adsorption efficiency from 60% (unmodified cherry sawdust) to 70%.

Due to the different input pH values of the model solutions and the different kinds of wooden sawdust material, the adsorption took place in slightly different pH ranges for the various metals. In a study by Wan Ngah et al. [32], it was identified that the pH of a solution is the most important variable affecting the biosorption process. Shukla et al. [9] observed that at decreasing of pH values, the positively charged metal ion species can compete with H^+ and be absorbed at the surface of the sawdust through the ion exchange mechanism. On the other hand, some heavy metals may cause the releasing of OH^- instead of H^+ when they are adsorbed by sawdust materials, and therefore result in an increase in pH. The adsorption process may be accompanied with the ion exchange mechanism. According to a previous study [33], the removal of Cu(II), Zn(II), and Fe(II) is a two-stage process. At the beginning of the sorbent-sorbate interaction, the intensive increase in pH is accompanied with ion-exchange. In the second stage, the adsorption of metals ions takes place at stabilised pH values. In this study, the alkaline modification significantly influenced the increasing pH values in comparison with natural raw sawdust. It can be assumed that in addition to adsorption and ion-exchange processes, the increase in pH results in the precipitation of metal ions.

Based on results obtained from the adsorption experiments, the efficiency of metal ion removal was then compared using concentrations of metals five times higher in the model solutions. Table 6 presents the efficiency of metal ion removal from solutions with initial metal concentrations of 50 mg L^{-1}. The increase in metal ion concentration resulted in a lower efficiency of unmodified sawdust for copper, zinc and iron removal from the solutions.

Table 6
Results of adsorption experiments with selected wooden sawdust and their modifications at C_0 = 50 mg.L^{-1} of dissolved heavy metals ions in model solutions

Sorbent	Cu(II)				Zn(II)				Fe_{total}			
	Initial pH = 4.7				Initial pH = 5.1				Initial pH = 4.8			
	C_e (mg.L^{-1})	η (%)	q_e (mg.g^{-1})	pH	C_e (mg.L^{-1})	η (%)	q_e (mg.g^{-1})	pH	C_e (mg.L^{-1})	η (%)	q_e (mg.g^{-1})	pH
Poplar	28.5 ± 0.23	43.0	2.15	4.5	26.3 ± 0.29	47.4	2.37	5.0	26.6 ± 0.31	46.8	2.34	4.8
Poplar_NaOH	3.7 ± 0.08	**92.6**	4.63	7.0	2.34 ± 0.05	**95.3**	4.77	6.4	13.6 ± 0.20	72.8	3.64	5.8
Poplar_KOH	4.4 ± 0.09	**91.2**	4.56	6.8	2.19 ± 0.04	**95.6**	4.78	7.1	12.4 ± 0.17	75.2	3.76	5.3
Spruce	39.2 ± 0.31	21.6	1.08	4.4	31.3 ± 0.38	37.4	1.87	4.8	34 ± 0.35	32.0	1.60	4.7
Spruce_NaOH	1.0 ± 0.01	**98.0**	4.90	7.5	2.46 ± 0.03	**95.1**	4.75	7.3	5.8 ± 0.09	**88.4**	4.42	5.7
Spruce_KOH	1.4 ± 0.03	**97.2**	4.86	7.3	1.78 ± 0.02	**96.4**	4.82	7.5	8.4 ± 0.13	83.2	4.16	6.6
Cherry	37.6 ± 0.03	24.8	1.24	4.3	33.3 ± 0.27	33.4	1.67	4.9	34 ± 0.29	32.0	1.60	4.0
Cherry_NaOH	1.7 ± 0.03	**96.6**	4.83	6.2	2.43 ± 0.04	**95.1**	4.76	7.4	7.0 ± 0.14	**86.0**	4.30	5.6
Cherry_KOH	6.2 ± 0.12	87.6	4.38	7.0	2.49 ± 0.05	**95.0**	4.75	7.2	12.2 ± 0.17	75.6	3.78	5.6
Hornbeam	28.7 ± 0.21	42.6	2.13	4.5	25.6 ± 0.33	48.8	2.44	5.0	26.8 ± 0.29	46.4	2.32	4.5
Hornbeam_NaOH	8.0 ± 0.14	84.0	4.20	7.0	1.83 ± 0.04	**96.3**	4.82	7.3	24.2 ± 0.27	51.6	2.58	5.8
Hornbeam_KOH	8.7 ± 0.13	82.6	4.13	7.6	2.08 ± 0.06	**95.8**	4.79	7.2	25.2 ± 0.28	49.6	2.48	5.8

Note: The bold values are represents the most significant efficiencies for heavy metals ion removal.

In study of Bailey et al. [34] was reported the sorptive capacities of selected wooden sawdust (6–16 mg of the heavy metals ions on 1 g of wooden sawdust). The substantial impact of the alkaline modification of sawdust on the adsorption processes was comparable with results presented in Table 5 for Cu(II) and Zn(II). The modification with hydroxides resulted in an increase of sawdust absorption capacity, and the efficiency of copper and zinc removal increased from 82.6% to 96.4%.

An oxidation effect in the removal of Fe(II) by modified sawdust was also observed. The generated ferric ions reacted with organic compounds from the sawdust [31]. In comparison with previous results, it was observed that for iron ions, the removal was significantly more efficient. This phenomenon may be caused due to depletion of organic matter that reacted with ferric ions and the subsequent adsorption of dissolved Fe(III) ions.

As shown in Table 6, changes in pH were also observed during the static adsorption experiments. The unmodified sawdust did not affect the pH values in the model solutions. This phenomenon could be caused by the increase in metal ions concentrations in the model solutions. On the other hand, the modified sawdust increased the pH values of solutions after adsorption due to the influence of hydroxides. The improved adsorption properties can also be attributed to the pH changes during adsorption.

The study of changes adsorption capacity at equilibrium conditions are shown in Tables 5 and 6. These results correspond with previous study [30] that deals with adsorption of Cu(II) and Zn(II) by raw poplar sawdust. It was revealed that the poplar sawdust better correlated to the Langmuir´s model. The results indicate that the metal uptake capacity was increased almost in all causes after alkaline treatment that is in accordance with study of authors [35].

4. Conclusions

The application of low-cost adsorbents obtained from plant wastes or semi-products of various industries for the removal of heavy metals from wastewater has been intensively researched in recent decades. Organic materials with the high cellulose content can be obtained and employed as cheap adsorbents.

The neutron activation analysis revealed a decrease in the concentration of certain elements after the biosorption, indicating that ion-exchange is one of the mechanisms underlying the interaction of metal with the biosorbents. SEM/EDX was used for the characterisation of the structure and morphology of untreated and modified sawdust. On the surface of the modified sawdust, something like a "pulping effect" was observed, which may have been connected with the increase in specific surface area of the studied adsorbent materials. The FT-IR spectra indicated an increase in the number of hydroxyl functional groups on modified sawdust.

It was found that the sorption capacities of modified wooden sawdust for model solutions with concentrations 50 $mg.L^{-1}$ of dissolved Cu(II) and Zn(II) were approximately 4.5 times higher in comparison with untreated sawdust; however, alkaline-modified sawdust negatively influenced Fe(II) ion removal due to organic-metallic dye formations. Despite the supposition that the external addition of potassium compounds can enhance the ion-exchange process, this fact was not confirmed.

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