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STUDY OF CHEMICAL SURFACE STRUCTURE OF NATURAL SORBENTS USED FOR REMOVING OF Pb²⁺ IONS FROM MODEL AQUEOUS SOLUTIONS (PART II)**BADANIE CHEMICZNEJ STRUKTURY POWIERZCHNI SORBENTÓW NATURALNYCH WYKORZYSTANYCH DO USUWANIA JONÓW Pb²⁺ Z MODELOWYCH ROZTWORÓW WODNYCH (CZĘŚĆ II)**

This article presents the results of the chemical structure research of organic sorbent surface such as walnut shells, plums stones and sunflower hulls with using such methods as infrared spectrometry (FTIR) and elemental analysis. Based on the IR spectra identification of functional groups present on the surface of studied materials has been done as well as determination of their effect on the sorption mechanism of Pb²⁺ ions from aqueous model solutions.

Keywords: Sorption, ion exchange, lead ions, walnut shells, plums stones, sunflower hulls, FTIR method

W artykule przedstawiono wyniki badań chemicznej struktury powierzchni sorbentów organicznych takich jak: łupiny orzecha włoskiego, pestki śliwek oraz łuski słonecznika z wykorzystaniem metody spektrometrii w podczerwieni (FTIR) oraz analizy elementarnej. W oparciu o uzyskane widma IR dokonano identyfikacji grup funkcyjnych obecnych na powierzchni tych materiałów i określono ich wpływ na mechanizm sorpcji jonów Pb²⁺ z modelowych roztworów wodnych.

Analiza elementarna wykazała, że spośród badanych sorbentów, największą zawartość węgla (49,91%) i wodoru (5,93%) mają pestki śliwek. Najwięcej azotu (1,59%) zawierają łuszczyzny słonecznika (tabela 1). Zawartość siarki we wszystkich badanych materiałach jest znikoma, dlatego nie udało się jej oznaczyć tą metodą. Obecność pozostałych pierwiastków może świadczyć o istnieniu zarówno alifatycznych jak i aromatycznych połączeń organicznych. Potwierdzeniem tego są również zarejestrowane widma IR (rysunki 1-3).

W oparciu o uzyskane wyniki można przypuszczać także, iż udział procesu wymiany jonowej w sorpcji ołowiu z roztworów wodnych jest znaczący. Świadczą o tym m.in. intensywności pasm na widmach IR dla próbek badanych materiałów po ich kontakcie z roztworami jonów Pb²⁺ (rysunki 4-6).

Słowa kluczowe: sorpcja, wymiana jonowa, jony ołowiu, łuski słonecznika, łupiny orzecha, pestki śliwek, metoda FTIR

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1. Introduction

Biosorption is the process of binding substances (such as metal ions or chemical compounds) from the solutions to the surface of organic sorbents (Chojnacka, 2010; Farooq et al., 2010). The exact mechanism of this process is not fully known, but it is supposed that biosorption can be based on several different mechanisms.

Organic sorbents cell wall is mainly composed of proteins and polysaccharides. Due to this, functional groups which are able to binding metals may be present on the surface of cell wall. Among of them may be such as a carboxyl, phenyl, hydroxyl, sulfonate and amino groups. Apart from chemisorption, physical adsorption, redox reactions and microprecipitation can also occur on biomass surface. The biosorption process can also be a combination of all described mechanisms (Świdarska-Bróz, 1980; Chojnacka, 2010).

However, the papers research shows, that the most likely mechanism for the metals removing by using organic sorbents is ion exchange process (Pino et al., 2006; Meena et al., 2008). The biomass cell wall might have functional groups bound with metals ions such as K^+ , Na^+ , Ca^{2+} , Mg^{2+} , and the exchange process these ions for other metal ions from the solution can occur. The functional groups are not bonded with other metals may also be present on the sorbents surface. Then the process is based on the hydrogen ions exchange (Meena et al., 2008).

2. Aim of the study

The aim of this study was to determine the chemical structure of the surface of natural sorbents such as walnut shells, plum stones and sunflower husk by using infrared spectrometry (FTIR) and elemental analysis. Based on the recorded IR spectra, functional groups present on the surface of these materials were identified and their effect on the mechanism of the sorption process was determined. The results of Pb^{2+} ions removing from aqueous solutions by using walnut shells, plum stones and sunflower hulls studies were published in Part I of the article and in the papers (Gala & Rydlewska, 2010, 2011a, 2011b; Bożęcka & Rydlewska, 2013).

3. Methods of the study

Walnut shells (*Juglans regia* L.), plum stones (*Prunus domestica* L.) without the kernels and sunflower hulls (*Helianthus* L.) were used for the study as natural sorbents. All studies were performed for the fraction with a particle size less than 0.5 mm.

In order to identify the surface functional groups, absorption spectra of studied sorbents were recorded on spectrometer BIO–RAD FTIR–165 in the range of the wave number from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} . Test samples in the form of tablets were made from the mixture of 0.5 mg dried sorbent and 200 mg of spectrally pure potassium bromide (KBr). Tablets were obtained as a result of pressing the above-mentioned mixture in a vacuum at a pressure of 10 MPa. The spectra were recorded for the materials before and after the sorption process of Pb^{2+} ions from solutions with initial concentration equal 109.4 mg/L.

Elemental analyses of walnut shells, plums stones and sunflower hulls samples were performed on the analyser CHNS Elementar Vario EL III 2. The weight percent of nitrogen, carbon,

hydrogen and sulphur in the studied material was determined. Given values are the averages of two determinations.

The Pb^{2+} ions content in the solutions after adsorption was determined by flow-through coulometry using EcaFlow 150 GLP apparatus manufactured by POL-EKO. Before measurements, the solutions were filtered to remove solid particles. Three measurements were performed for each sample.

4. Discussion of the results

4.1. Identification of functional groups present on the surface of tested sorbents

The IR spectra of the “raw” samples of walnut shells, plums stones and sunflower hulls are shown in Figures 1-3.

A comparison of the IR spectra shows that characteristic absorption band at 3427 cm^{-1} (sunflower hulls), 3416 cm^{-1} (walnut shells) and 3420 cm^{-1} (plum stones) are occurring for all the tested sorbents. These peaks can be assigned to stretching vibration of OH groups from alcohols and phenols. The highest intensity of these peaks are observed for sunflower hulls. Thus, it can be assumed that this material in its composition has the most of hydroxyl functional groups. In the region of the OH group vibrations, there are also characteristic bands of the other compounds (such as amines, carboxylic compounds, aromatic compounds). However, the broad and strong band assigned to OH groups vibration could overlap them, so they are not visible in the spectrum. Additionally, the bands occurring in range from 2930 cm^{-1} to 2840 cm^{-1} for all the tested materials, were derived from CH stretching vibrations of alkyl groups of the compounds forming its composition. Peaks at a wavenumber equal, about 1740 cm^{-1} can be derived from the C=O group of carbonyl compounds (ketones, aldehydes, carboxylic compounds, esters, etc.). The

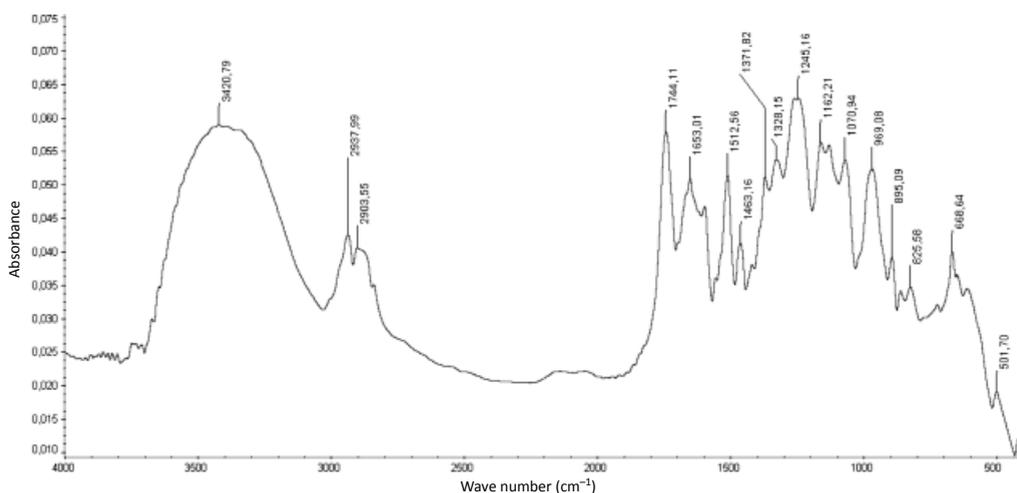


Fig. 1. The IR spectrum obtained for the sample of “raw” plum stones

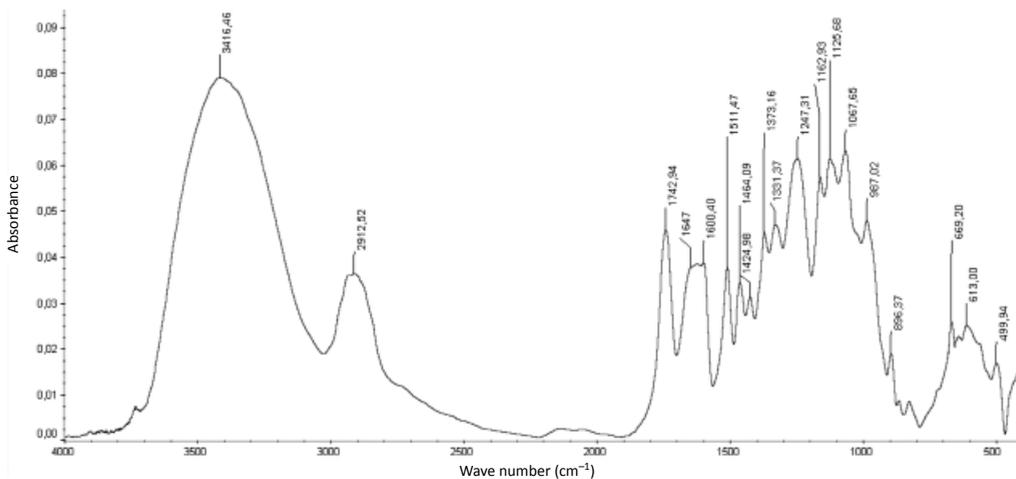


Fig. 2. The IR spectrum obtained for the sample of “raw” walnut shells

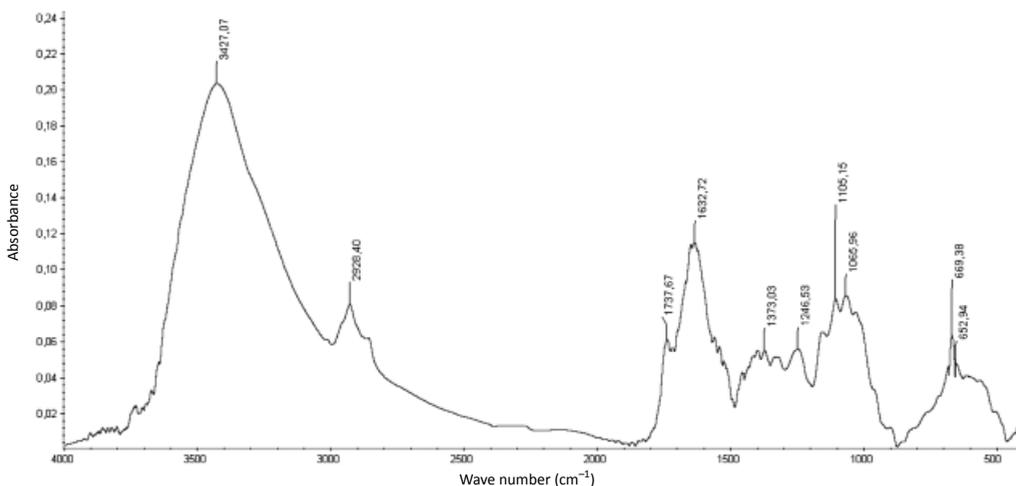


Fig. 3. The IR spectrum obtained for the sample of “raw” sunflower hulls

absorption bands in the region about 1630 cm^{-1} can be assigned to stretching vibrations of $\text{C}=\text{O}$ groups or bending vibrations of NH groups from amides (so called first and second amide band). In the range of frequency about $1650\text{--}1580\text{ cm}^{-1}$ may also occur bending vibrations band of NH groups from amines. For sunflower hulls, these bands are stronger than for the other materials. This is probably related to the higher content of nitrogen in this material (Table 1). The absorption in the wave number range from about 1600 to 1400 cm^{-1} probably indicates the presence of aromatic compounds. Bands occurring between 900 and 675 cm^{-1} may also be aromatic bands which are probably assigned to the out of plane bending vibrations of CH groups (Uluozlu et al., 2008; Azouaou et al., 2010; Silverstein et al., 2012).

Elemental analysis of tested materials has also confirmed the presence of the above-mentioned functional groups (Table 1).

TABLE 1

The elemental analysis results of tested materials samples

Sorbet	Content (%)			
	N	C	H	S
Plum stones	0.48	49.91	5.93	b.d.l.*
Walnut shells	0.26	48.75	5.82	b.d.l.*
Sunflower hulls	1.59	47.60	5.70	b.d.l.*

* b.d.l. – below detection limits

In order to confirm the role of the above-mentioned functional groups in the removing process of Pb^{2+} ions from aqueous solutions, IR spectra of tested materials samples after the sorption were also recorded.

Decrease of the intensity of all characteristic absorption bands, especially at about 3420 cm^{-1} is observed on the obtained IR spectra (Figures 4-6). This confirms that the hydroxyl groups OH (from alcohols, phenols, carboxylic acids), carbonyl groups $C=O$ (from carboxylic compounds, esters, ketones, aldehydes, etc.) and amino or amido groups may take part in the process of lead ions sorption. These results may indicate that blocking of these groups is a result of their binding with the Pb^{2+} ions present in solution. The obtained spectra can also confirm that the studied process takes place according to the mechanism of ion exchange.

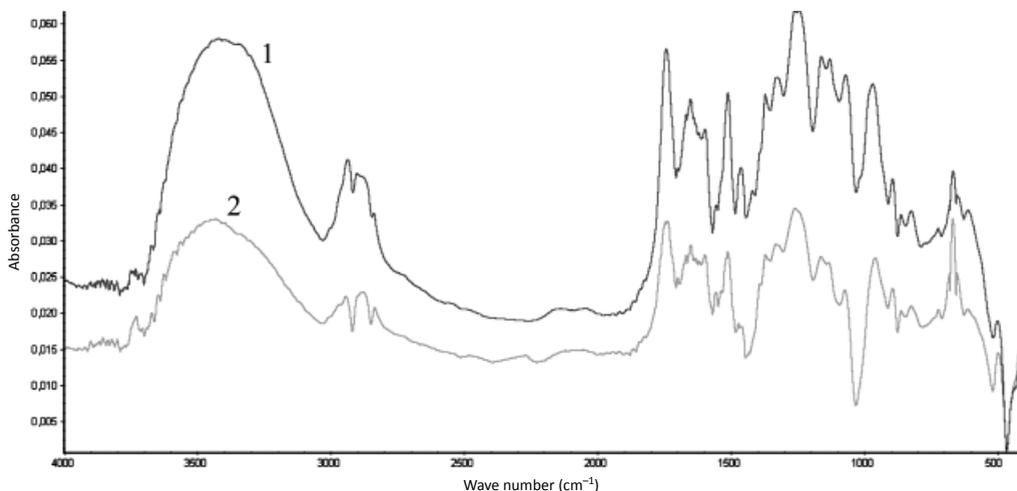


Fig. 4. The comparison of the IR spectra obtained for plum stones samples before (1) and after the process of Pb^{2+} sorption (2)

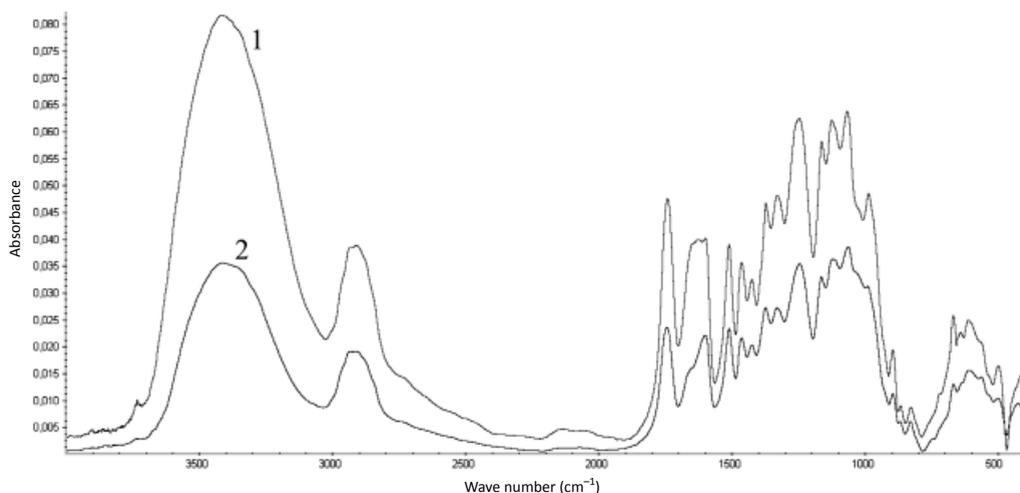


Fig. 5. The comparison of the IR spectra obtained for walnut shells samples before (1) and after the process of Pb^{2+} sorption (2)

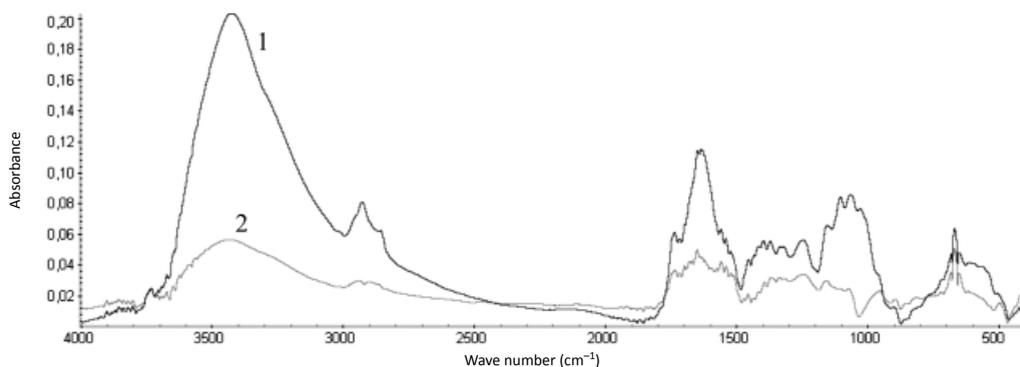


Fig. 6. The comparison of the IR spectra obtained for sunflower hulls samples before (1) and after the process of Pb^{2+} sorption (2)

5. Summary

IR spectra recorded for the tested sorbents (Figures 1-3) confirmed that functional groups may be present on their surface, such as hydroxyl groups, phenolic, carbonyl, etc.

Elemental analysis of tested materials (Table 1) also confirms the presence of organic compounds, both aliphatic and aromatic.

Based on the obtained results it can be assumed that the presence of ion exchange processes in the biosorption of lead from aqueous solutions is significant (observed decrease in the intensity of all the characteristic absorption bands in the IR spectra – Figures 4-6).

The mechanism of heavy metals ions removal on natural sorbents is extremely complex. This issue requires further research.

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