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X-ray photoelectron spectroscopy investigations of lignocellulosic materials

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Hydrolyzed plant biomass from willow, paulownia and straw was studied by using XPS and IR spectroscopy method in order to understand in depth their chemical composition and the nature of the functional groups on their surfaces. The surface concentration and the presence or absence of some functional groups and their amount on the surface of these materials were studied by the XPS method. The calculated O/C ratio shows that the surface of lignin, paulownia and willow samples was lignin rich, while the surface of straw sample was cellulose rich.

Key words: Hydrolyzed lignocellulosic materials, X-ray photoelectron spectroscopy

INTRODUCTION

In recent years there is increased interest toward the use of waste lignocellulosic materials as adsorbents for water purification from heavy metals [1-6].

The lignocellulosic biomass could be straw, grass, corn-stover, reed, wood, agricultural waste, forestry residues, paper and household waste. The low cost and absence of competition with food industry is the main advantage of using such type of materials. Lignocellulosic biomass contains mainly cellulose, hemicelluloses, lignin, proteins; lipids and ash, which together form a complex solid structure. The ratios of these components in various lignocellulosic materials depend on the source of the biomass (softwood or hardwood, grass and annual plants, energy crops, agricultural waste-straw, husks, bagasse).

One of the questions that arise when studying the adsorption properties of such materials concerns the mechanism of adsorption and the existing adsorption sites.

In ref. [7] through examination of the EPR and EXAFS the conclusion is made that Cr(III) ions are in octahedral position. In ref. [8] it is stated that in relation to its adsorption ability, the lignin isolated from the black fluid has affinity toward metal ions in the following order: Pb(II) > Cu(II) > Cd(II) > Zn(II) > Ni(II). According to the authors, the adsorption sites are phenol and carboxyl OH-groups, the phenol ones having higher affinity towards metal ions.

In our former study we showed that hydrolyzed waste lignocellulosic materials are effective adsorbents of heavy metal ions from aqueous solutions [9].

Agricultural by-products are mostly composed of lignin and cellulose, as well as of other polar functional group-containing compounds, which include alcohols, aldehydes, ketones, carboxylates, phenols and ethers.

These groups are able to bind heavy metals through replacement of hydrogen ions with metal ions in solution or by donation of an electron pair from these groups to form complexes with metal ions in solution [10]. The use of these materials as adsorbents requires detailed investigation of their surface chemical composition.

The biosorption mechanism is difficult to be determined, due to many mechanisms that can contribute to the overall process according to the material used as a biosorbent, environmental factors, presence or absence of metabolic processes in case of presence of living organisms. Biosorbents include various components with a highly complex structure, whose various building elements comprise a plurality of different molecules, which in turn show several binding sites.

One widely used method for this purpose is IR spectroscopy. Nevertheless, infrared analysis of wood surfaces is not considered to be sufficiently surface-sensitive because the depth of infrared radiation into the sample is of the order of 100 μm. Consequently, the changes in infrared features as a result of changes of surface chemistry are often masked by spectral features coming from the bulk [11]. In X-ray photoelectron spectroscopy (XPS) analysis the electrons are ejected from the core levels of atoms in the surface and their binding energies are determined from their kinetic energy and the energy of the incidence beam. Simultaneously, the binding energy of a given atom

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is influenced by its chemical environment and the sample depth of the XPS is around 5-10 nm.

Therefore, the aim of this work is to demonstrate the ability of this method in studying waste lignocellulosic material in case of their further application as adsorbents or carriers of catalysts. As a result, the hydrolysis of woody chips (willow and paulownia) and wheat straw, that are the subject of this investigation, were studied by X-ray photoelectron spectroscopy.

EXPERIMENTAL

Sample preparation Procedures

In the present study we used hydrolyzed plant biomass from willow, paulownia and wheat straw (denoted as w; p; and s; respectively) as raw materials.

The sample named LC was produced after high-temperature hydrolysis with dilute sulphuric acid of softwood and hardwood chips to sugars under factory conditions, which were further subjected to yeast fodder production. The LC was washed and milled. The 0.1 - 0.3 mm fraction was used.

The samples pLC(w) and pLC(p) were obtained by steam explosion treatment for hydrolysis facilitation, followed by enzymatic hydrolysis with cellulose enzyme complex combined with β-glycosidase of willow and paulownia, respectively. The steam explosion was performed in a 2 L stainless steel laboratory installation at hydromodul ratio of 1:10; initial temperature 100°C; maximal temperature 190°C; pressure 12.8 bar; heating time 60 min and time at maximal temperature 10 min. The cellulosic hydrolysis was carried out in polyethylene bags in a water bath previously heated to the desired temperature. Enzymatic treatment conditions were as follows: temperature 50°C, reaction time 24 h, lignocellulosic content 10 wt.%, $pH_{initial}$ 5.5 - 6.0, pH_{final} 4.2 - 4.6 and 5 wt.% charge of the cellulose enzyme complex NS 22086 in combination with 0.5 wt.% of β-glycosidase NS 22118.

The sample hLC(s) was obtained by hydrothermal treatment for hydrolysis facilitation, followed by enzymatic hydrolysis with cellulose enzyme complex combined with β-glycosidase of wheat straw. The hydrothermal hydrolysis of the agricultural lignocellulosic raw materials was performed in 1000 mL stainless steel laboratory autoclaves rotated at constant rate under the following conditions: biomass/water ratio of 1:10; initial temperature 100°C; max. temperature 190°C; heating time 60 min, time at maximum temperature 30 min.; Enzymatic treatment conditions were as follows: temperature 50°C, reaction time 72 h, lignocellulosic content 10 wt.%, $pH_{initial}$ 5.5 - 6.0 and 5 wt.% charge of the cellulose enzyme complex NS 22086 in combination with 0.5 wt.% of β-glycosidase NS 22118 of Novozymes AS. All amounts and experimental conditions were used according to the Novozymes Application Sheet.

Sample characterization

The cellulose content in the studied lignocellulosic materials was determined according to [12]; the lignin content (acid-insoluble lignin in wood and pulp, TAPPI standard test method T 222 om-11) and ash (ash in wood, pulp, paper and paperboard: combustion at 525°C, TAPPI standard T 211 om-02).

An elemental analyzer Eurovector EA 3000 was used for analysis of C, N, S and H. The oxygen content of the samples was calculated by the difference between 100% and the sum of carbon, hydrogen, nitrogen, sulphur and ash.

Infrared spectra were measured on a Varian 660 IR spectrometer. The spectra were collected in the mid-infrared region (4000-400 cm^{-1}). The samples were prepared by the standard KBr pellet method.

XPS investigations were carried out by means of ESCALAB MKII spectrometer with Al Kα (unmonochromatized) source at 1486.6 eV with a total instrumental resolution of ~1 eV, under a base pressure of 10^{-8} mbar. The C1s, O1s, N1s, photoelectron lines were recorded and calibrated to the C1s line at 285.0 eV. XPSPEAK 4.0 fitting program was used for deconvolution of the photoelectron peaks. All data were recorded at 45° take-off angle.

RESULTS AND DISCUSSION

The used waste hydrolyzed lignocellulosic materials were obtained after different pre-treatment methods for hydrolysis facilitation and enzymatic hydrolysis with cellulose enzyme complexes with different activity. For these reason, part of the hardly hydrolyzable polysaccharides was not hydrolyzed. In Table 1 the data for the chemical and the elemental composition of the investigated materials are presented. The data show that the samples substantially differ as regards the lignin and cellulose contents. The highest lignin content is observed in sample LC - 78 %, in the other samples it is lower and slightly changes from 37.4 (pLC(p)) to 44.1 % (pLC(w)). Concerning the cellulose content, the lowest amount is observed in LC - 12.8 %, while in the other samples it is higher and slightly changes from 50.4 in hLC(s) to 58.6 in pLC(p).

Table 1. Chemical and elemental composition data of the investigated hydrolyzed materials

Samples	Elemental Composition					Chemical Composition		
	H, %	C, %	O, %	N, %	S, %	Cellulose, %	Lignin ,%	Mineral substances, %
LC	6.3	58.6	25.3	-	0.7	12.8	78.0	9.1
pLC(p)	6.6	58.7	30.5	0.9	-	58.6	37.4	3.4
pLC(w)	6.3	54.9	35.5	0.6	-	52.3	44.1	2.7
hLC(s)	6.2	48.3	38.4	0.6	-	50.4	42.9	6.5

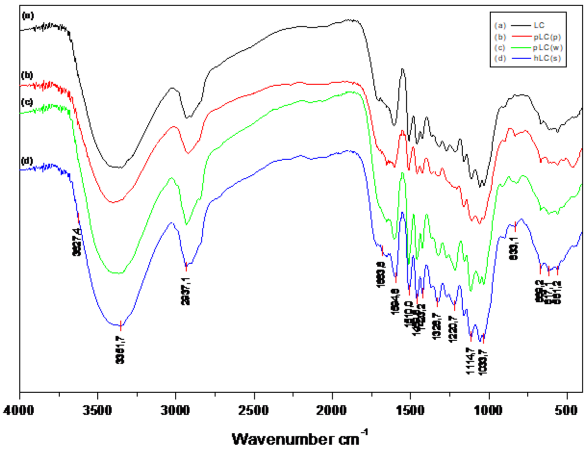

Figure 1. IR spectra of CL, pCL(p), pCL(w) and hCL(s) samples.

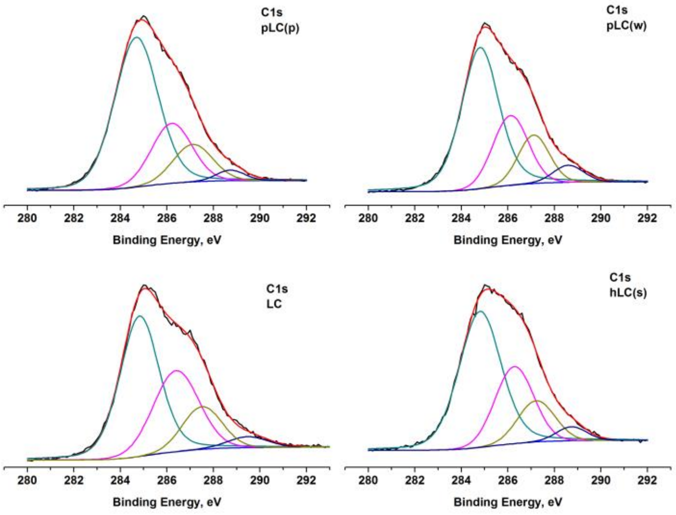

Figure 2. C1s photoelectron lines for the studied lignocellulosic samples.

The carbon, hydrogen and oxygen contents in all samples do not substantially differ from each other. The samples, obtained after hydrolysis of wheat straw (hLC(s)) contained the highest quantity of oxygen and the lowest quantity of carbon. Based on these observations, the structure of hLC(s) is probably condensed to a lower scale and has contained a larger number of free groups. Only LC contains sulphur because of the use of sulphuric acid as a catalyst of the hydrolysis process, and does not contain nitrogen. The information concerning the nature of the functional groups and ions playing the role of adsorption sites in the hydrolyzed biomass is obtained by using IR spectroscopy. The data of the studied materials are presented on fig. 1.

It is seen that the FTIR spectra of the hydrolyzed lignocellulosic materials are identical. The broad bands in the range of 3500-3100 cm^{-1} are due to stretching vibrations of the hydrogen bonding alcohol and phenol hydroxyl groups. The range 1663-1720 cm^{-1} is characteristic for the carbonyl absorption, which is related with ketones and acids. The bands at 3000-2850 cm^{-1} are referred to symmetrical and asymmetrical stretching vibrations of the C-H bonds in methyl and methylene groups. The IR bands that appear at 1600 and 1510 cm^{-1} for skeleton vibrations of the aromatic rings were characteristic for all materials which contained lignin. It is thought that the bands at 1460 cm^{-1} and at 1424 cm^{-1} are related to CH deformation vibrations in the methyl and methylene groups. The presence of different functional groups such as -OH, -COOH, -C-O-C-, etc., as well as the shapes of the spectral bands are complex and broad due to the hydrogen bonds and conformational structure of the materials. It is obvious that the IR spectroscopy method provides information about the presence of functional groups in these materials, but their quantity on the surface is difficult for evaluation.

A surface-sensitive technique such as XPS is useful to examine the carbon and oxygen content of various organic materials in order to determine the type and relative amount of chemical groups at their surfaces. In most XPS spectra of organics materials, we would expect to find four functional groups and the presence of more than one relative to another would be evidence of a chemical change at the surface.

The recorded C1s photoelectron spectra of wasted wood samples were further subjected to a fitting procedure for better evaluation of the amount of different functional groups on their surface (see figure 2).

Obviously, there are four peaks as a result of the above mentioned procedure applied. The first one named C1 and situated at around 285 eV we associated with C–C and C-H bonds. The second C2 peak at ~286.5 eV was related to C-OH or C-O-C bonds. The next C3 peak situated at ~288.0 eV corresponds to a C=O bond and the last C4 to a O-C=O bond at 289.5 eV. Shake-up peaks (π-π* at 290-292 eV) were not detected. The quantitative results from the fitting are summarized in Table 2. The change in the relative amount of those components as a function of oxygen ratio shows the change in the surface composition of the studied lignin and waste wood samples. As a result, only the change in the presence of C-O/C-OH functional groups on the surface is remarkable.

Table 2. Evaluated functional groups on the surface of the studied products by X-ray photoelectron spectroscopy.

Sample	Carbon functional groups,%				Oxygen functional groups, %		Surface concentration of elements, at.%			
	C1	C2	C3	C4	O1	O2	C	O	N	O/C
LC	51.3	31.2	13.9	3.6	27.5	72.5	79.7	27.3	-	0.37
pLC(p)	62.2	22.0	13.2	2.6	41.2	58.8	76.0	21.9	2.1	0.35
pLC(w)00)	57.3	23.3	14.4	5.0	33.6	66.4	78.1	20.3	1.6	0.26
hLC(s)*	56.6	26.3	13.4	3.7	26.9	73.1	60.9	32.0	1.7	0.53

* On the surface a small quantity of silicon (5.7 at.%) was detected

A higher amount was evaluated for the lignin sample. The oxygen photoelectron lines were subjected to a fitting procedure too (see figure 3). Two peaks are necessary to fit the O1s photoelectron spectra. The O1 component situated at 532 eV is due to the presence of C=O bond, while the O2 component at 533.5 eV was associated to C-O/C-OH groups. The evaluation of the presence of different oxygen groups on the wood surfaces s also shown in Table 2.

The calculated O/C ratio is also shown in the table. The latter clearly indicates if the surface is lignin- or cellulose-rich [13].

Simultaneously, the calculated surface concentration of the studied wood waste materials permits to classify them as lignin or cellulose. The lignin, paulownia and willow samples have O/C ratios equal or slightly lower than the theoretically calculated one (between 0.33-0.36) typical for lignin. Higher is only the O/C ratio for the sample from straw, equal to 0.53. This shows that the surface is lignin-rich for lignin, paulownia and willow samples, while the surface of the straw sample is cellulose-rich. The observed difference between the bulk phase composition and that on the surface of the studied woods could be due to the migration of lignin to the surface for paulownia and willow, while opposite migration of lignin to the bulk of wood was observed for the straw sample. The reason for that could be the specific way of wood treatment. Similar observation was already reported [14]. On the surface of paulownia, willow and straw samples small amount of nitrogen was detected. These observations coincide with the bulk chemical analysis results.

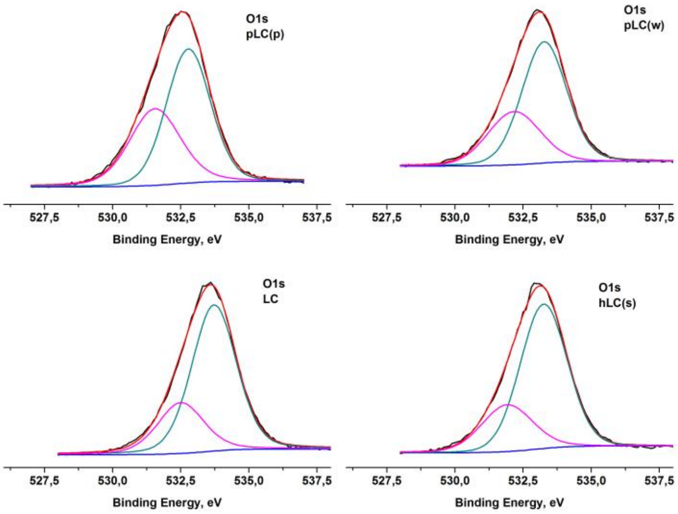

Figure 3. O1s photoelectron lines for the studied lignocellulosic samples.

CONCLUSIONS

The results demonstrate the capability of the XPS method for evaluation of surface characteristics such as chemical composition and existing functional groups in lignocellulosic products. Moreover, obtaining of such data may help clarify issues of the mechanism of adsorption, such as adsorption sites and oxidation state and evaluate the coordination of adsorbed ions. Also, the way to increase the absorption capacity should be held in mind, considering that these lignocellulosic waste materials may be used as carriers for catalytically active components.

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ИЗСЛЕДВАНЕ НА ЛИГНО-ЦЕЛУЛОЗНИ МАТЕРИАЛИ ПОСРЕДСТВОМ РЕНТГЕНОВА ФОТОЕЛЕКТРОННА СПЕКТРОСКОПИЯ

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(Резюме)

Изследвана е хидролизирана растителна биомаса, получена от върба, пауловния и пшенична слама с помощта на РФС и ИЧ спектроскопски методи с цел изясняване както на техния химичен състав, така и на природата на повърхностните функционални групи в тях. Повърхностната концентрация, присъствието или отсъствието на някои функционални групи и тяхното количество на повърхността на тези материали са определени чрез РФС метода. Отношението О/С показва, че повърхността на пробите от лигнин, пауловния и върба се обогатява на лигнин, докато повърхността на пробата от слама е богата на целулоза.