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COMPARATIVE ^{13}C NMR SPECTROSCOPY
OF LIGNOCELLULOSE SORBENTS

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The composition and structure of initial and modified lignocellulose materials have been investigated by ^{13}C NMR spectroscopy. Changes in functional structure and composition of the samples have been found to arise due to modifying as a result of chemical transformations and hemicelluloses removing. Sorption properties of lignocellulose composites have been studied in relation to heavy metals. They have been found to depend on changes in the composition and functional structure of the materials.

INTRODUCTION

When separating or purifying vegetative raw materials it is impossible to produce without intensive chemical treatment the samples of cellulose containing no lignin, or cellulose free lignin preparations [1]. Meanwhile, dividing vegetative fabrics into separate high-molecular components is not necessary for manufacture of useful related materials. The products obtained from the waste of vegetative biomass, even without preliminary dividing into components, can have new properties essentially distinctive from components. Besides, use of the whole biomass in a uniform production is undoubtedly technologically rational and economic.

EXPERIMENTAL

The objects under research were different kind lignocelluloses complexes of vegetative raw materials (hazelnut shell, corncob, and cacao husks) and the materials obtained due to their acid-alkaline modifying by the method described in the patent [2]; for comparison the lignin-containing medical preparation *"Polyphepan"* [3] has been selected as the closest analogue of investigated materials.

To determine the composition of lignocelluloses complexes ^{13}C solid-state spectra of Cross-Polarization Magic-Angle Spinning Nuclear Magnetic Resonance (CP MAS NMR) of initial and modified powdered samples of investigated materials have been recorded and analyzed. The spectra were registered by a Bruker AVANCE 400 radio-spectrometer in a pulse mode of accumulation with working frequency of 100.3 MHz and cross-

polarization on frequency of 400.13 MHz (H^1); the interval between pulses was 4 s. The rotation speed of the samples under the magic corner was of 12 kHz. The values of chemical shifts (δ) of the signals from carbon atoms in ^{13}C nuclear magnetic resonance spectra were defined concerning standard TMS ($\delta = 0$ ppm).

The study on selectivity and sorption capacities of the chosen materials was carried out under static conditions with use of salt solutions of heavy metals (lead, cadmium, nickel, copper, strontium) containing different concentrations (5–100 mg/l) of metal ions. Initial and equilibrium concentrations of metals in solutions were defined by a Selma KASS-120.1 atomic-absorption spectrophotometer.

RESULTS AND DISCUSSION

It is known [4] that signals of various carbon atoms in both natural and biosynthetic polymers, with few exceptions, are not overlapped and consequently are characteristic, so allowing to identify separate types of structural units in such materials. In the ^{13}C NMR spectra of natural and biosynthetic lignins in a lignocellulose complex, four basic ranges of δ are allocated [4, 5]:
  - 5–45 ppm – signals of aliphatic carbon atoms, non-bonded with oxygen atoms (>CH–, –CH$_2$–, and –CH$_3$ groups);
  - 55–90 ppm – signals of aliphatic carbon atoms bonded with oxygen atoms;
  - 100–160 ppm – signals of carbon atoms in sp^2-hybridization [6] as a part of aromatic and olefine structures;

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– 160–180 ppm – intensive signals of γ-carbon atoms entering ester or di-γ-lactone groupings, and also carboxyl groups.

The analysis of the spectra obtained shows that the initial and modified samples of wood nut shell, corn cabbage stumps and cacao vela contain signals with the following δ value: 20–40 ppm from –CH$_3$ and –CH$_2$- groups of hemicelluloses; 60 ppm from methoxy groups of lignin; 65 ppm from carbon atoms C-6; 70–75 ppm from atoms C-2,3,5 of cellulose; 80–90 ppm from atoms C-4 of cellulose; 120–160 ppm from aromatic carbon atoms of lignin; 175 ppm from carboxyl carbon atoms of hemicelluloses.

^{13}C CP MAS NMR spectra of the modified samples differ from those of predecessors by essential reduction signal intensity of –CH$_3$ and =CH$_2$ groups of hemicelluloses (20–40 ppm), and also alkyl (30–33 ppm) and carboxyl (170–175 ppm) groups of hemicelluloses.

It is also seen from Fig. 1*a-c* that signals of hemicelluloses groups disappear, and intensity of other lines (groups of cellulose and lignin) increases. This testifies to structural changes in lignocellulose skeleton due to its modifying.

The investigated samples differ from that of *Polyphepan* (Fig. 1*d*) intensity of signals in areas of 60 and 120–160 ppm that specifies a higher content of lignin in the preparation than those in investigated ones. It is natural, as *Polyphepan* is produced from wood which is richer by lignin vegetative raw material.

Comparing ^{13}C NMR spectra of investigated samples with literary data [5], it is possible to assign the signals observed in the field of 5–45 ppm to carbon atoms in groups > CH–, –CH$_2$–, –CH$_3$, non-bonded with atoms of oxygen, in lateral aliphatic chains between aromatic rings of lignin. The total number and position of signals in spectra of all the samples coincide. In the spectra of investigated lignocellulose complexes, there are signals with δ = 53.5 and 53.8 ppm testified to presence of coumaran and pinoresinol fragments in macromolecules. In investigated lignocellulose materials, there are also two accurate resonant signals of OCH$_3$-groups: δ = 55.7 and 55.9 ppm. It is known [4] that a signal with δ =55.6 ppm is caused by methoxyl group in ortho-position, and a signal of 56.0 ppm presents carbon atoms in methoxyl groups of syringyl rings.
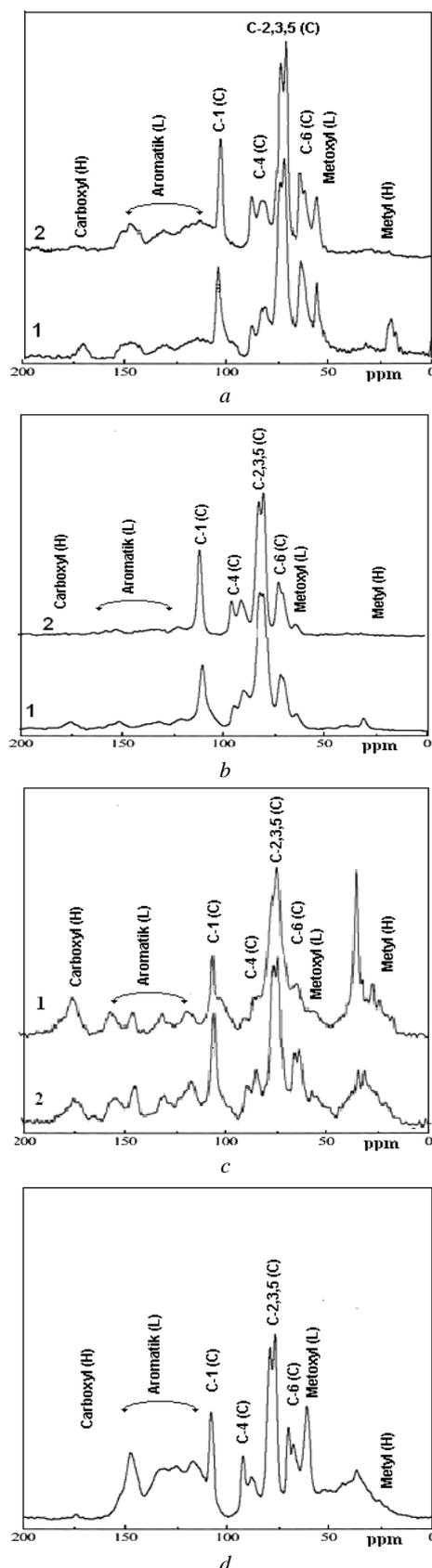

Fig. 1. ^{13}C NMR spectra of samples: hazelnut shell (*a*), corncob (*b*), cacao husks (*c*), and preparation *Polyphepan* (*d*); *1* – initial, *2* – modified

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As it was already mentioned, the area of 100–160 ppm of a spectrum contains resonant signals of carbon atoms with sp^2-hybridizations of valent electrons [6] involved in aromatic and olefine structures. In this area, four intervals are conditionally allocated [1]:

– 100–117 ppm, where signals of tertiary carbon atoms including those of C-atoms in ortho-position with oxygen function (C-2 and C-5 in not condensed fragments) are registered;

– 117–125 ppm, where signals of C-H$_{ar}$ (C-2/C-5 - structures replaced in position C-1 of aromatic ring) are observed;

– 125–142 ppm, where the signals belong to aromatic quaternary carbon atoms, mainly C-1 and C-5;

– 142–160 ppm, where the signals caused by presence of esterified carbon atoms of aromatic ring are registered.

In our case, in spectra of ^{13}C CP MAS NMR, signals of carbon atoms of (C-2/C-6) in the range $\delta = 103$–107 ppm are observed caused by presence of syringyl aromatic rings, and this is the main difference of spectra for lignin of investigated samples (guaiacyl-syringyl type) from those of lignin of coniferous species [1].

The signals shown in investigated samples with $\delta = 102$–104 ppm correspond to non-replaced carbon atoms C-2 and C-6 in syringyl fragments of preparations, δ in a range of 150–160 ppm – with C-3/C-5 atoms bound with methoxy groups. A signal at $\delta = 119$ ppm specifies in presence of guaiacyl fragments (C-6). Peaks with values $\delta = 131.4$-131.5 ppm (C-2–C-6 atoms in N-units) are characteristic of *n*-cumarone structures [1, 5].

In the range of 160–180 ppm there are peaks of γ-carbon atoms entering ester and di-γ-lactone groups and those of carboxyl groups. As in this range there are no signals of other carbon atoms, there is a basic possibility of reliable definition of various type structural fragments carboxyl carbon, and signals with $\delta > 170$ ppm confirm presence such groups in preparations. A group of three close located signals in the field of $\delta = 171.0$–173.2 ppm is caused, probably, by the presence of carboxyl carbon atoms in 3-alkyl-arilether structural elements [4].

So, the results of the analysis of nuclear magnetic resonance ^{13}C CP MAS spectra on chemical shifts of resonant signals (Table) testify that lignin macromolecules, which are a part of lignocelluloses complexes of investigated samples, are built by structural units of guaiacyl, syringyl, and *n*-cumarone types.

Table. Chemical shifts of resonant signals of ^{13}C NMR spectra of lignocelluloses complexes of modified vegetative raw materials (ppm)

Groups	Cacao husks	Hazelnut shell	Corncob	*Poly-phepan*
–CH$_3$	14.6; 19; 24	29	24.5	18; 23
–CH$_2$-	30; 33; 36	33	33	33; 37; 45
C$_\beta$ in β5 and (β-β)	54	53.8	53.5	53.8
Ar-OCH$_3$ G and S rings	56	56	55.9	55.7
C$_\gamma$(β-5) and (β-O-4) G ring	62; 64	63; 65	66; 68	62; 65
C$_\alpha$(β-O-4) G and S rings	72; 74	72; 74	76; 78	72; 74
C$_\beta$	–	83; 88	87	84; 88
C$_{alif}$-3	–	–	92	–
C-2 and C-6 in S and S'	100.9; 104.9	104	108	105
C-2 G ring	119	118	119	114
C-1 in H	–	122	–	123
C$_\alpha$ and C$_\beta$ in coniferil-aldehyde structures and (or) C-2 and C-6 H	–	–	–	130.9
C-2 and C-6 H, H'	131	132.9	131	–
C-4 S S'	–	–	–	–
C-4 G' non-esterified	144.4	144	–	146
C-3 G non-esterified	–	–	–	–
C-3 G' esterified	–	–	–	–
C-3 and C-5 S' esterified	154.5	152	151	151
C=O COOR in β-O-4	–	171	–	–
C=O COOH in β-O-4	172	–	–	–
C=O COOH in β-5	174	–	–	–

Dependences of sorption properties on the composition and structure of multi-component vegetative materials were found. It is revealed that cellulose and lignin joint into biopolymer complexes in non-treated (initial) materials show weak sorption capability in relation to heavy metal ions whereas modified lignocellulose materials possess quite high absorption characteristics.
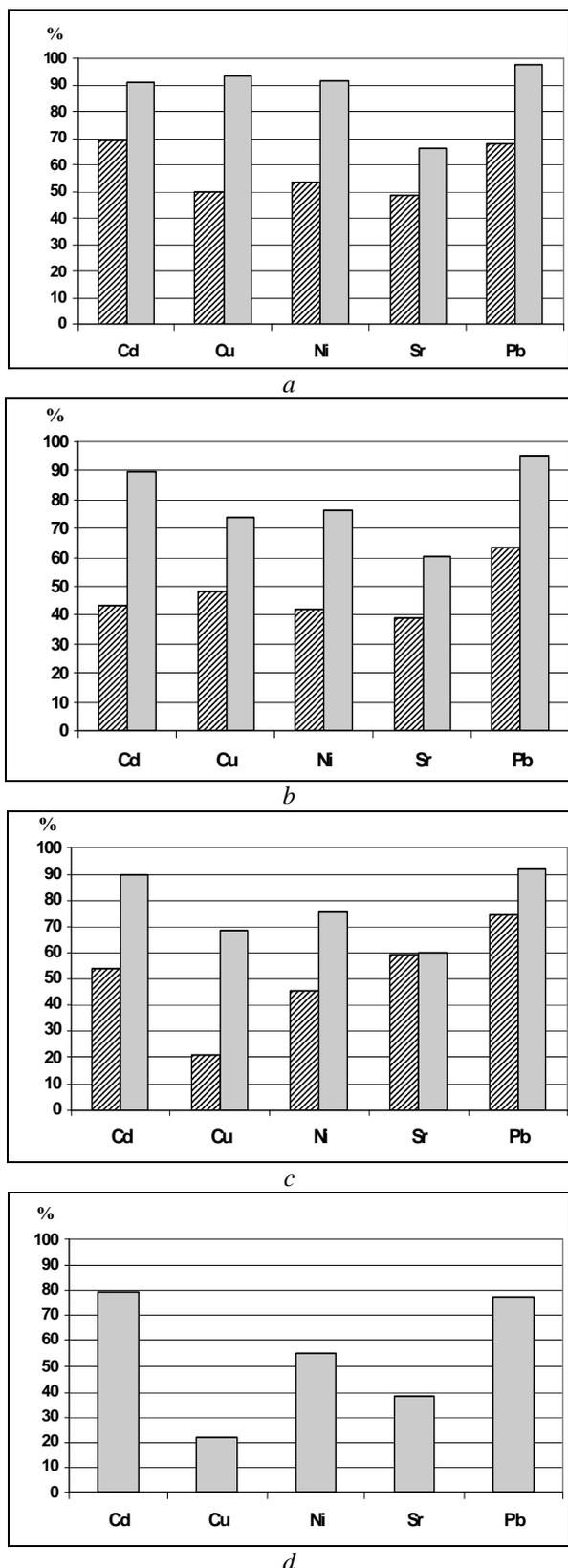
Fig. 2. Diagrams of adsorption of heavy metals from solutions by vegetative biosorbents: (*a*) cacao husks, (*b*) hazelnut shell, (*c*) corncob, (*d*) *Polyphepan*

As an example in Fig. 2 the diagrams of efficiency of heavy metal ions extraction from model aqueous solutions of Cu, Pb, Sr, Ni, Cd salts (at initial concentration of metals in a solution 1×10^{-3} mol/l) are resulted. They demonstrate that the modified adsorbents based on vegetative waste have high indices of extraction of heavy metal ions from aqueous solutions. Sorption properties of initial vegetative raw materials in relation to heavy metals ions are rather close to those of preparation *Polyphepan*; the modified materials show, as a whole higher sorption capabilities. A comparison of the modified and initial samples shows that the extraction level of metals from solutions becomes more than 2 times greater. It is obvious also that the medical preparation *Polyphepan* considerably concedes to the materials obtained in extraction degrees of such metals as Cu, Ni, Sr.

From a content ratio of lignin, cellulose, and hemicelluloses (intensities of peaks of the corresponding groups) a dependence row of adsorption capability on the material composition is constructed. For example, for Cu^{2+}-ions adsorption the capability increases as follows:

Cacao husks > Hazelnut shell > Corncob.

CONCLUSIONS

Comparison of the results obtained on adsorption of heavy metals with data of ^{13}C NMR spectroscopy, taking into account structural-sorption characteristics of the materials obtained [7], shows that sorptive properties of the latter are defined not only by volume of sorption pores but also essentially depend on the structure of lignocelluloses complexes, chemical bonds between their components, and nature of metals.

The results obtained testify that acid-alkaline modifying natural raw materials allows us to remove hemicelluloses from vegetative raw materials of various origins and to prepare new sorption materials with higher availability of functional groups to heavy metal ions. As the materials obtained show a definite selectivity in relation to ions of some heavy metals, it is possible to recommend usage of such biosorbents for deep extraction of these elements from industrial solutions and sewage waters.

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Порівняльне дослідження лігноцелюлозних сорбентів методом ^{13}C ЯМР-спектроскопії

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Методом ^{13}C ЯМР-спектроскопії досліджено склад і структуру вихідних і модифікованих лігноцелюлозних матеріалів, а також їх сорбційні властивості. Встановлена залежність сорбційних властивостей лігноцелюлозних композитів по відношенню до важких металів від змін у функціональному складі й структурі лігноцелюлозних композитів внаслідок їхнього перетворення й видалення геміцелюлози в результаті кислотно-лужного модифікування.

Сравнительное исследование лигноцеллюлозных сорбентов методом ^{13}C ЯМР-спектроскопии

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Методом ^{13}C ЯМР-спектроскопии исследован состав и структура исходных и модифицированных лигноцеллюлозных материалов. Изучены сорбционные свойства лигноцеллюлозных материалов, и установлена зависимость сорбционных свойств их композитов по отношению к тяжелым металлам от изменений в функциональном составе и структуре лигноцеллюлозных композитов, вызванных их превращением и удалением гемицеллюлозы при кислотно-щелочном модифицировании.