

IR SPECTRA OF THE HYDROLYSIS LIGNIN OF COTTONSEED HUSKS AND ITS DERIVATIVES BEFORE AND AFTER THE SORPTION OF LEAD IONS

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The characteristic frequencies of the hydrolysis lignin of cottonseed husks and its derivatives before and after the sorption of lead ions have been studied. The possibility of the intermolecular coordination of the lignin macromolecules by lead ions with both the ionic and the coordination types of bonds has been shown by the IR spectral method.

We have previously presented the characteristics of the hydrolysis lignin of cottonseed husks (HLCSH) and its derivatives [1]; on the basis of the results of functional analysis and of the calculation and comparison of semiempirical formulae, and also of an IR-spectral investigation, we revealed the main reaction centers (OH, C=O, and COOH groups) of the initial HLCSH and its derivatives.

In the present work we have used IR spectroscopy to study the sorption of lead ions by HLCSH and its derivatives. The results obtained for the frequencies of the stretching vibrations of the OH, C=O, and COOH groups of the lignins under investigation before and after the sorption of lead acetate are given in Table 1.

In the IR spectrum of lead acetate, the carboxylate ion CH_3COO^- is characterized by absorption bands at 1543 and 1486 cm^{-1} , relating to asymmetrical and symmetrical vibrations, respectively (Fig. 1).

A comparison of the IR spectra of HLCSH before (1) and after (1a) the sorption of Pb^{2+} ions showed the disappearance of the bands at 1752 and 1700 cm^{-1} due to C=O stretching vibrations (carboxylic, ketonic, and ester groups) and the appearance of two broad absorption bands at 1559 and 1374 cm^{-1} , which, as is known, may be assigned to the asymmetrical and symmetrical vibrations of the carboxylate ion, respectively (Fig. 2). Analogous changes in the stretching vibrations of C=O groups were observed in the IR spectra of the nitro- and sulfolignins (2a and 3a) (Figs. 3 and 4).

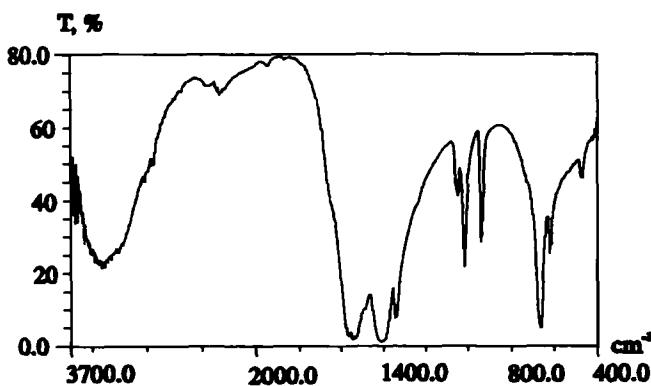


Fig. 1.

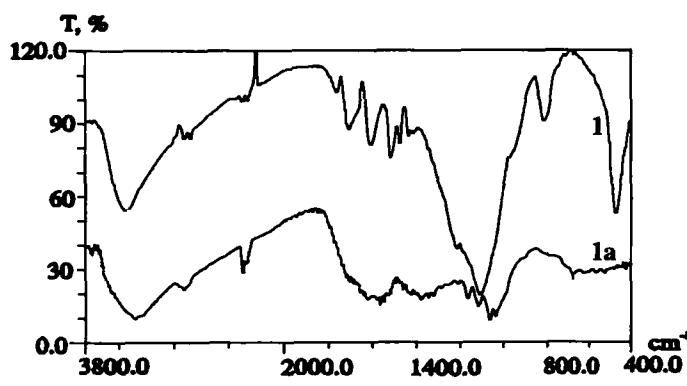


Fig. 2.

Fig. 1. IR spectrum of lead acetate.

Fig. 2. IR spectrum of HLCSH before (1) and after (1a) the sorption of lead ions.

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TABLE 1. Frequencies of the Stretching Vibration of OH, C=O and COO⁻ Groups of the Hydrolysis Lignin of Cottonseed Husks and its Derivatives

Lignin specimen		OH	C=O	COO ⁻
before sorption	after sorption	cm ⁻¹		
1. HLCSH		3421	1752, 1700	-
1a.	HLCSH	3337	-	1559, 1375
2. SL		3397	1752*, 1702	-
2a.	SL	3400	-	1559, 1374
3. NL		3406	1751, 1700	-
3a.	NL	3343	-	1559, 1374
4. CL		3357	1750*, 1701	-
4a.	CL	3340	1700**	1600, 1374
5. DML		3404	1751*, 1703	-
5a.	DML	3421	1700**	1600, 1374
6. PML		3353	1750*, 1700, 1663	-
6a.	PML	3348	1700**	1600
7. PPML		3400	1752, 1701	-
7a.	PPML	3394	1700**	1600
8. OL		3351	1751, 1701	-
8a.	OL	3342	1700**	1600
9. PL		3406	1751, 1701	-
9a.	PL	3421	1700**	1600, 1437

*The absorption band at 1750 cm⁻¹ appeared in the form of an inflection on a wing of the 1700 cm⁻¹ absorption band.

**An appreciable lowering of the intensity of the 1700 cm⁻¹ absorption band was observed.

SL — sulfolignin; NL — nitrolignin; CL — chlorolignin; DML — demethylated lignin; PML — piperidinomethylated lignin; PPML — phosphorylated piperidinomethylated lignin; OL — oxidized lignin; PL — phosphorylated lignin.

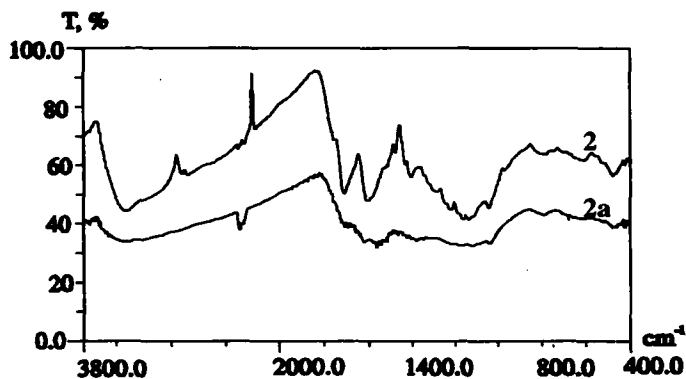


Fig. 3.

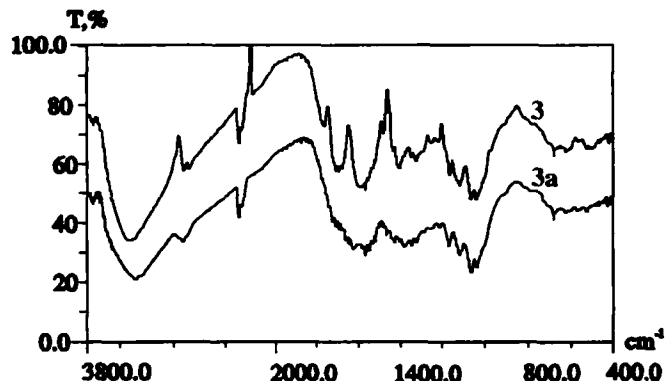


Fig. 4.

Fig. 3. IR spectrum of SL before (2) and after (2a) the sorption of lead ions.

Fig. 4. IR spectrum of NL before (3) and after (3a) the sorption of lead ions.

The observed frequencies of the stretching vibrations of a carboxylate ion in spectra (1a—3a) presuppose the formation of complexes with an ionic nature of the metal—ligand bond [2—4]. The presence in the spectra of lignins (6a—8a) of only the 1600 cm⁻¹ bond, characterizing the absorption of the carboxylate ion, also presupposes an ionic mechanism of the sorption of lead cations Pb²⁺ by lignins (6—8).

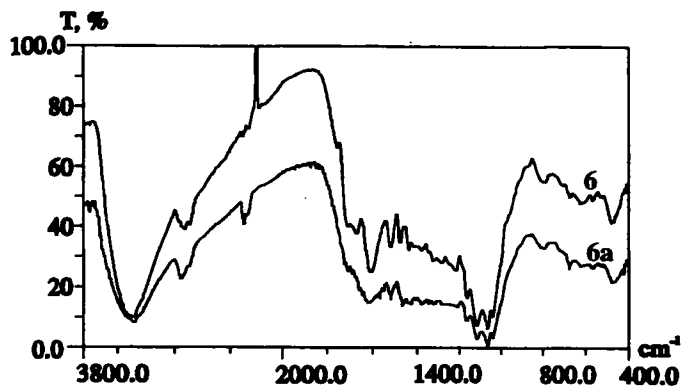


Fig. 5.

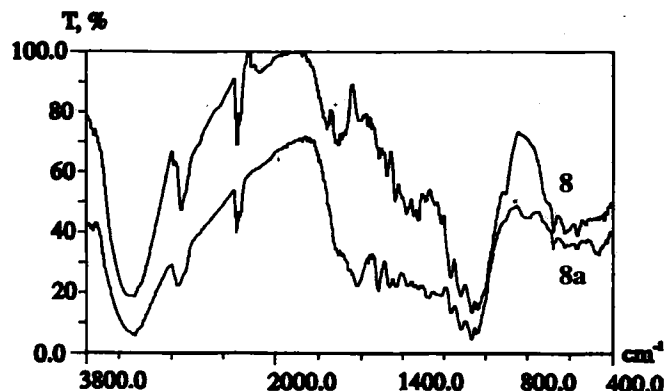


Fig. 6.

Fig. 5. IR spectrum of PML before (6) and after (6a) the sorption of lead ions.

Fig. 6. IR spectrum of OL before (8) and after (8a) the sorption of lead ions.

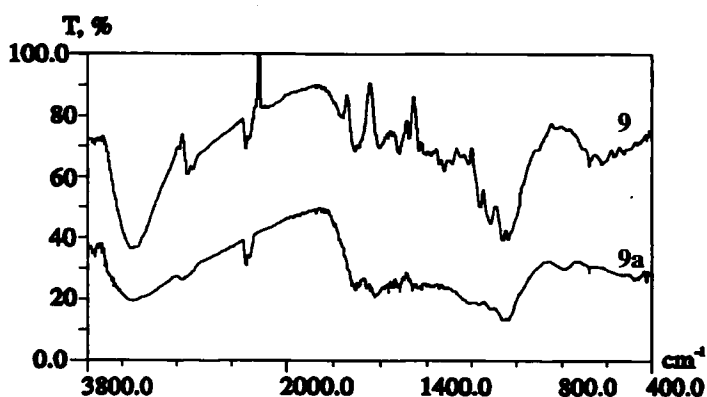


Fig. 7. IR spectrum of PL before (9) and after (9a) the sorption of lead ions.

We must mention the presence of bands at 1700 cm^{-1} in the spectra of lignins (4a—9a) having considerably lower intensities than those observed in the spectra of lignins (4—9) (Figs. 5—7), and also the absence of the 1752 cm^{-1} band from the spectra of all the lignins investigated after the sorption of Pb^{2+} (1a—9a). This experimental fact may indicate a possible formation of a coordination bond between the stereochemically free electron pair of Pb^{2+} and the oxygen atom of a carbonyl group [5—7].

Additional information on the structure of the lead-containing lignins (1a—9a) was given by an analysis of the frequencies of the stretching vibrations of hydroxy groups. As can be seen from Table 1, in the spectra of the lignin derivatives (1a) and (3a) there was a shift on 84 and 53 cm^{-1} in the low-frequency direction of the maximum of the absorption band due to the stretching vibrations of the OH substituent relative to the frequencies of the stretching vibrations of the OH groups in the spectra of compounds (1) and (3) (Figs. 2 and 3).

The observed shift in the maxima of the bands characterizing OH stretching vibrations in the spectra of lignin derivatives (1a) and (3a) presupposes the formation of stronger hydrogen bonds in the lead-containing hydrolysis lignin of cottonseed husks (1a) and in nitrolignin (3a) than in the initial lignins (1) and (3), respectively. In the other lignins, after the sorption of lead acetate (2a, 4a—9a) the frequency of the OH group variations had scarcely changed.

Thus, on the basis of the results of an IR-spectral investigation of the characteristic frequencies of technical lignins and their derivatives before and after the sorption of lead ions, the possibility has been shown of the appearance of intermolecular coordination of the lignin macromolecules with lead ions both with the ionic and with the coordination type of metal-ligand bond, the main reaction centers in the lignins investigated being hydroxy and carbonyl groups.

EXPERIMENTAL

The IR spectra of the specimens were taken on a Perkin-Elmer Fourier IR system 2000 spectrometer (Sweden) with a resolution of 4 cm^{-1} , rate of scanning 0.2 cm/s , number of scans 500. The samples were prepared by molding with KBr.

Sorption of Lead Acetate Solution by the Lignins. The lignin sample (100 mg) was brought into contact with 5 ml of a 1% solution of lead acetate for 0.5 h. After this time, the lignin was separated off by filtration and was dried at room temperature.

REFERENCES

1. G. N. Dalimova and É. L. Kristallovich, *Khim. Prir. Soedin.*, 392 (1998).
2. I. V. Karpunskii, N. N. Chalilova, O. L. Leonova, and O. N. Evstaf'eva, *Zh. Neorg. Khim.*, **35**, 583 (1990).
3. N. V. Gaivoronskaya, G. M. Vasil'eva, and G. P. Grigor'ev. *Zh. Prikl. Khim.*, **43**, No. 10, 2364 (1970).
4. N. V. Gaivoronskaya, G. M. Vasil'eva, and G. P. Grigor'ev. *Zh. Prikl. Khim.*, **47**, No. 3, 667 (1974).
5. Yu. M. Chernoberezhskii and A. B. Dyagileva, *Kolloidn. Zh.*, **52**, No. 6, 1213 (1990).
6. D. E. Fenton, D. H. Cook, and I. W. Nowell, *J. Chem. Soc., Chem. Commun.*, No. 8, 274 (1977).
7. D. A. Armitage, *Organomet. Chem.*, **8**, 110 (1980).
8. S. N. Bhattacharya and M. Khurrawa, *Indian J. Chem.*, **A16**, No. 11, 988 (1978).