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SORPTION OF POLAR COMPONENTS OF COTTONSEED OIL BY HYDROLYSIS LIGNINS AND MODIFIED LIGNINS

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The sorption activities of hydrolysis lignins from wood and from rice and cottonseed hulls and of modified lignins relative to the polar components of crude cottonseed oil in a nonpolar solvent have been studied.

The capacity of hydrolysis lignins (HLs) for sorbing many classes of compounds is widely known [1, 2]. Aqueous solutions are always used in these processes. In aqueous solutions and some polar solvents (ethanol) HLs swell greatly. The solvent molecules penetrate into the molecules of the lignin and change its sorption properties. In nonpolar solvents, lignins do not swell and their physicochemical properties scarcely change. Hexane is a suitable solvent, since it possesses a low coefficient of compressibility and a high degree of penetration into the pores of a sorbent [3].

We have studied the sorption properties of HLs relative to the highly polar components of crude cottonseed oil, using hexane as the solvent. The polar pigmentary components (PCs) were isolated from the cottonseed oil by a published procedure [4, 5].

It is known that the pigment composition of crude cottonseed oil includes tocopherols, gossypol and flavonoid components, products of their phytochemical reactions taking place during the processing of the cotton seeds, and other highly colored components. It has been shown [6] that gossypol is sorbed on natural and on acid-treated bentonites from chloroform solutions.

We have studied the HLs from cottonseed hulls, the HLs from sawdust and from rice hulls, and modified HLs obtained from the HLs of cottonseed hulls by demethylation [7], by piperidinomethylation [8], by oxidation with hydrogen peroxide [9], by chlorination [10], by sulfonation [11], by nitration [10], by piperidinomethylation followed by phosphorylation [12], and by nitration followed by sodium bisulfite reduction [11].

When woody material is subjected to acid hydrolysis, in the lignin molecule, in addition to degradation, cross-linking of the macromolecules takes place and this predominates and is, on the whole, responsible for the formation of a rigid three-dimensional structure with a large internal surface. With an increase in the severity of the regimes for acid hydrolysis the sorption capacity of the lignin with respect to phenolic compounds (for example, saligenin) rises [13].

The adsorption process was studied under static conditions at room temperature (20-21°C) using the procedure and formulas for determining the magnitude of adsorption given in [14]. To calculate the concentrations of PCs we used the optical densities before (from a calibra-

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tion curve) and after adsorption measured at 280 nm in a spectrophotometer, since the UV spectrum of the PCs of cottonseed oil taken in hexane have an absorption maximum at 270-285 nm.

The kinetics of the sorption process was studied for the unmodified HLs of cottonseed hulls, of wood, and of rice hulls. It was found that in the initial stage (up to 30 min) the levels of adsorption of all three HLs differed only slightly. The bulk of the substance was sorbed in 24 h. This time was used in the subsequent work.

Figures 1 and 2 show isotherms of the adsorption of cottonseed oil PCs on all the specimens of modified and unmodified lignins. From the isotherms given we found the maximum adsorption levels (a, mg/g):

HL of cottonseed hulls	115.3
Wood HL	65.0
HL oxidized with H_2O_2	58.4
Willstätter pine lignin	53.5
HL of rice hulls	51.2
Piperidinomethylated HL	47.5
Chlorinated HL	45.1
Demethylated HL	40.0
Piperidinomethylated and phosphorylated HL	39.5
Nitrolignin	34.5
Sulfolignin	25.0
Nitrosulfolignin	8.5

On the basis of the maximum levels of adsorption, the unmodified HLs can be placed in the following sequence: cottonseed hull HL > wood HL > rice hull HL. The technology of the hydrolysis of all these materials is the same but the maximum adsorption levels of the products obtained differ widely. The main role here is probably played by the structure of the cell walls of the initial plant material and its internal surface, which is freed on the hydrolytic destruction of the carbohydrates, so that the hydrolysis lignins observed have considerable differences in the structure of their active centers. With any modification of the cottonseed hull HL the maximum adsorption levels of the products obtained fell sharply (by a factor of 2-10).

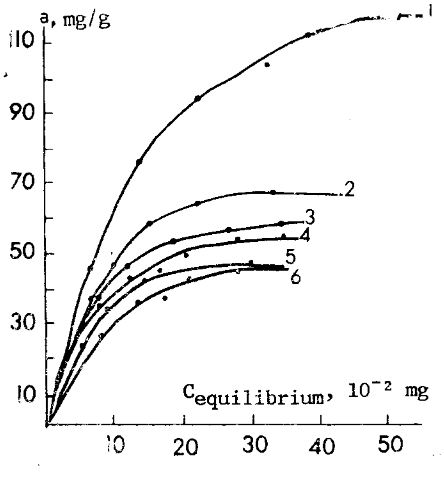

Fig. 1

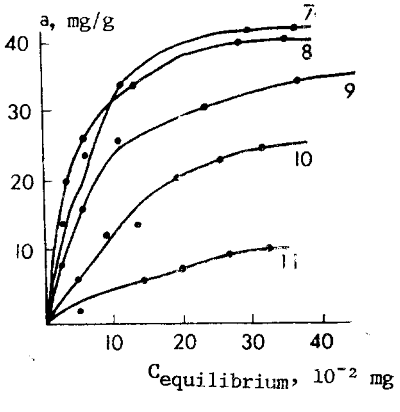

Fig. 2

Fig. 1. Isotherms of the adsorption of PCs on: 1) HL of cottonseed hulls; 2) wood HL; 3) HL oxidized by H_2O_2; 4) HL of rice hulls; 5) piperidinomethylated HL; 6) chlorinated HL.

Fig. 2. Isotherms of the adsorption of PCs on: 7) Demethylated HL; 8) piperidinomethylated and phosphorylated HL; 9) nitrolignin; 10) sulfolignin; 11) nitrosulfolignin.

Here it is difficult to correlate the severity of the treatment process with the sorption activity of the products. In the course of all the modifications, various functional groups (mainly polar ones) are introduced into the lignin molecule but the sorption activity of the lignins does not increasse. It is obvious that the main contribution to their adsorption capacity is made not by the polar functional groups but by the cell structure of the HL, which changes during the process of modification.

The maximum adsorption for Willstätter pine lignin is given above. If it is borne in mind that the Yangiyul' biochemical factory the wood HL is obtained from the wastes of furniture factories in which is mainly coniferous woods that are used, it may be considered that the wood lignin and the Willstätter lignin are obtained from similar materials but as the result of different reactions. The process of obtaining Willstätter lignin is considered milder [15] than industrial hydrolysis with sulfuric acid. The sorption capacity of HL is higher than that of Wilstätter lignin, which agrees well with the sorption capacities of lignins obtained under different conditions of acid hydrolysis.

EXPERIMENTAL

Preparation of the Sorbents. The HLs obtained in the Yangiyul' biochemical factory were washed with water 2-3 times to eliminate traces of sulfuric acid and were then extracted with a 1:1 mixture of alcohol and benzene. The modified lignins were obtained in accordance with the methods described above and were additionally extracted with ethanol. For the investigation fractions with a size of 0.1-0.2 mm were taken from each specimen.

The PCs from crude cottonseed oil were dissolved in hexane. Their adsorption on the HLs was also performed from hexane, by a standard procedure [14]. To calculate the concentrations of PCs a calibration graph was plotted beforehand by measuring the optical density of the PCs in hexane at 280 nm on a SF-16 spectrophotometer.

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