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## Carbonization products in D-glucose - p-toluidin system as sorbents of carbohydrate caramels from aqueous solutions

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## Carbonization products in D-glucose - p-toluidin system as sorbents of carbohydrate caramels from aqueous solutions

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**Abstract.** The results of studies of the sorption of carbohydrate caramels from aqueous solutions by highly dispersed adsorbents - carbonization products synthesized in the D-glucose - p-toluidine system are presented. Based on the analysis of the structural features of the adsorbent and the adsorbate with the use of infrared Fourier spectroscopy data, the physical nature of the interaction of the caramel components with the surface is mainly shown. Meanwhile binding probably occurs due to polar groups of carbonyl nature. An analysis of the difference spectra in the region of 1500-1740  $\text{cm}^{-1}$  allows detailing the examination and confirming the nature of the sorption interaction. The research results are promising in the development of methods for the synthesis of carbon-saturated products, sorption-active with respect to substances of carbohydrate nature, which is of interest for food and pharmaceutical industries.

The products of non-enzymatic staining reactions in carbohydrate-based systems have important practical applications in food and pharmaceutical industries, and the problem of their sorption binding is still urgent. Having an intense colour, melanoidins and caramel, falling into rivers, create obstacles to the passage of sunlight, which leads to the degradation of aquatic ecosystems [1]. The nature of the binding of melanoidins and caramels due to the heterofunctionality of their structure by adsorbents can be different, the parameters of adsorption for a number of model systems are determined by the authors [1]. The processes of extracting substances from solutions with solid adsorbents have recently been intensively studied [2-4]. Various methodological approaches to the study of the adsorption of sugary substances on carbon-saturated (carbonized) materials have been proposed. The study of the processes of adsorption of a large number of carbohydrates on activated carbons allowed the authors of [2] to obtain analytical expressions relating the chemical composition of the surface with the parameters of sorption. For the experimental study of sorption processes, volumetric methods [2], visible spectroscopy [3] and IR spectroscopy [4] are widely used.

Previously, we synthesized carbonization products in monosaccharide – p-toluidine systems, which are characterized by a higher carbon content in comparison with the initial carbohydrates and functionalization close to that of natural carbon-saturated materials [5], which makes them promising as adsorbents, especially in relation to close to the nature of adsorbates. In this work, we studied the possibility of using carbonization products based on D-glucose as available reagents for the sorption of components of carbohydrate caramel solutions synthesized in water-ethanol media [6].

Carbonization products were obtained by heating equimolar (0.002 mol) mixtures of monosaccharide with p-toluidine in 20 ml of solvent (dried ethanol) in a weakly acidic medium while



incubating for 1 hour at 70 ° C in flasks with reflux condenser. The dynamics of the reactions was monitored spectrophotometrically (SF-2000 spectrophotometer, OKB "SPEKTR", St. Petersburg, Russia) for which samples (1 ml) were taken, which were diluted with ethanol at a ratio of 1:10, then they were photometric in quartz cuvettes. The solvent was removed from the main reaction mass, and the solids were washed twice with absolute ether to remove the residual p-toluidine, then they were washed with distilled water on glass filters until a colorless solution was obtained over the insoluble precipitate. For all dried solid products in several intervals of the frequency range with a resolution of 1-4 cm<sup>-1</sup> and the number of scans from 16 to 30, FT-IR spectra were taken (FSM-2201 FT-IR spectrometer, Infracpek St. Petersburg, Russia). Mathematical processing of the spectra was carried out in FSpec programme. To enable a comparative analysis of the absorption spectra, a baseline was carried out, which was approximated by a polynomial of the 4th degree in the regions with no intense absorption bands ( $\delta_{OH, CH}$  and  $\nu_{OH}$  short-wave boundaries).

Caramel was synthesized by thermostating (90° C) of water-ethanol solutions (90% EtOH) containing 0.002 mol of carbohydrate in 25 ml of solvent in the presence of  $3 \cdot 10^{-4}$  mol of NaOH in flasks with reflux condenser for a specified time. The selection of viscous colour products was carried out by removing the solvent under reduced pressure; the vibrational spectra of the dried substances were taken in potassium bromide tablets. The dialysis of the solutions at the end of the temperature control was carried out for 48 hours in a solvent free of reagents.

Experiments on the adsorptive binding of caramel dyes were performed by shaking 0.04 g of the adsorbent in an aqueous solution of 0.2 g/l caramel for 2 hours. The filtered and dried adsorbent was studied by FTIR spectroscopy, the spectra were taken on FSM 2201 FT-IR spectrometer with a spectral resolution of 2-4 cm<sup>-1</sup> at 40 scans, the difference spectra were obtained and investigated using FSpec and PeakFit software packages.

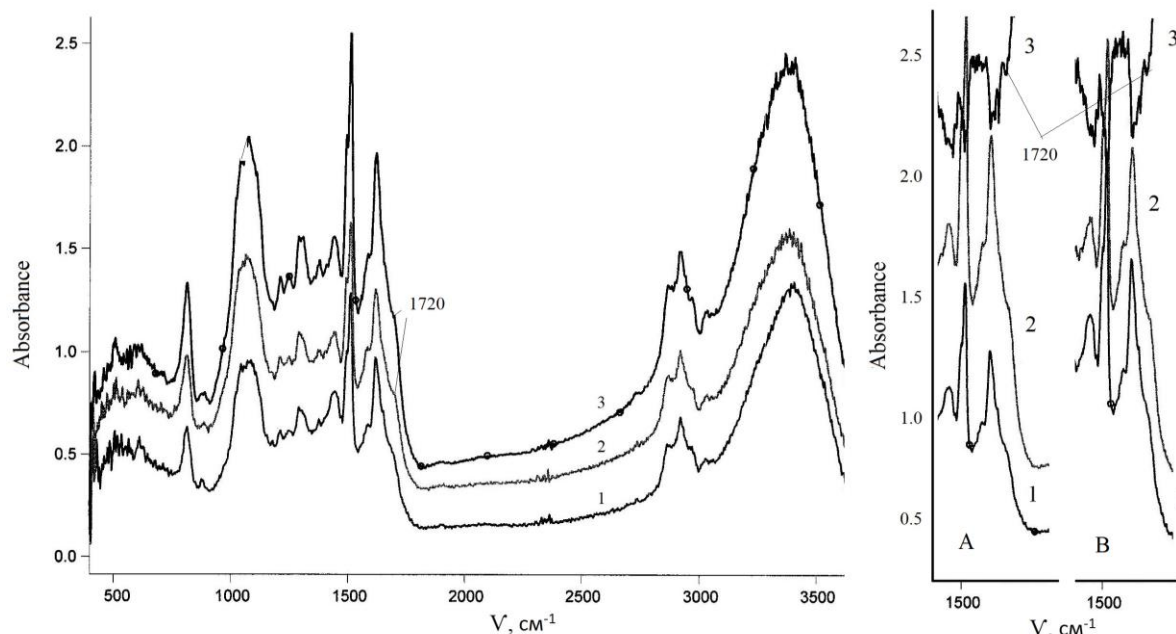
The study of the structure of the products of non-enzymatic staining reactions is a complex task, since the formation of their final structure occurs along several independent directions and largely depends on external factors. To study the laws of sorption and the nature of the interaction at a qualitative level, it is necessary to know the structural features of the adsorbent and adsorbate, which was studied earlier [5,6].

The functionalization of both types of products is similar, the main difference is that the cyclic component of carbonation products includes condensed aromatic rings, while caramels are represented by an irregular structure consisting of oligoglycoside and unsaturated chromophore fragments. The initial hard candies did not undergo preliminary dialysis, since it is necessary to study the sorption activity of carbonization products with respect to the caramel substances of the complete reaction system.

According to the elemental analysis data (Vario MICRO Cube elemental analyzer, Elemental Analyzer GmbH, Germany), adsorbent samples contain 65-68% of carbon, which makes it possible to study the structure and character of surface processes with a high degree of reliability using Fourier transform IR spectroscopy [7].

The FTIR spectra of the carbonization products before and after the adsorption experiments are presented in figure 2, the assignment of the main bands in the FTIR spectra, on the basis of the comparison of which the formulation of the conclusions is supposed, is presented in table 1.

The aromatic properties of the adsorbents synthesized using the methods described above show intense bands of 1580 cm<sup>-1</sup> with signals at 3030 cm<sup>-1</sup>, indicating a combination of condensed and isolated aromatic rings in the product structure [7]. The aromaticity parameter  $f_a$  was estimated according to the method [5] in the range of wave numbers 2750-3150 cm<sup>-1</sup>. The spectral portion was approximated after reduction to the baseline by the method of selecting the optimal curve. Calculated  $f_a$  values were  $0.60 \pm 0.02$ .



**Figure 1.** FTIR spectra of carbonization products prior to adsorption experiments (1); after keeping in solution caramel based on D-glucose (2); after keeping in solution caramel based on D-lactose (3) (on the left); Fragments of the FTIR spectra of carbonation products prior to adsorption experiments (1A, 1B); after keeping in solution caramels based on D-lactose (2A), D-glucose (2B); Difference FTIR spectra (3A, 3B) (on the right).

**Table 1.** Assignment of the main bands in the IR Fourier spectra to the elements of the structure of carbonation products.

Structure elements	Functions	Aromatic component	Aliphatic component
The position of the spectral bands and their assignment	1720 cm <sup>-1</sup> (ν <sub>C=O</sub> )	1510, 1580, 1620 cm <sup>-1</sup>	1000-1100 cm <sup>-1</sup>
	1190, 1210, 1260 cm <sup>-1</sup> (ν <sub>C-O, Car-O</sub> )	(ν <sub>C=C, C=O</sub> )	(ν <sub>CO</sub> + δ <sub>CO</sub> + ν <sub>CC</sub> + ν <sup>as</sup> <sub>ring</sub> )
	3400 cm <sup>-1</sup> (ν <sub>O-H, N-H</sub> )	750, 815, 870 cm <sup>-1</sup> (γ <sub>C-H</sub> )	2855, 2922, 2950 cm <sup>-1</sup> (ν <sub>C-H</sub> )

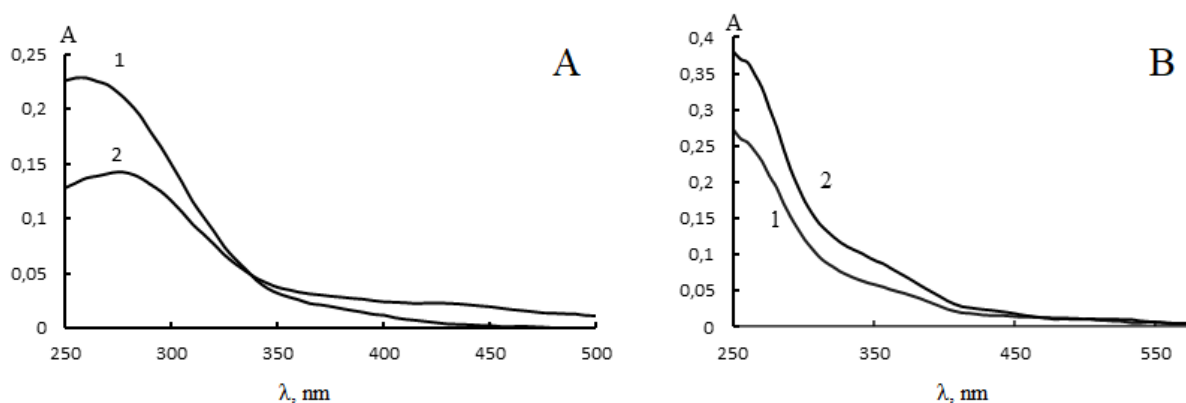
However, the structure of the synthesized adsorbent probably does not allow identifying the prevailing structures exclusively with aromatic ones. In particular, the low value of the ortho-substitution index ( $A_{750}/A_{815}+A_{870}$ ), indicating a low degree of condensation of aromatic fragments [8], while the increased intensity of the band at 1620 cm<sup>-1</sup> may be due to the contribution of quinoid carbonyl groups [5, 9].

Caramel, being products of thermal decomposition of carbohydrates, as it was established earlier [6], includes substances of non-dialyzed and dialyzed fractions, the former being relatively high-molecular oligomers constructed from carbohydrate residues and their transformation products, the latter are low-molecular compounds.

The main problem of studying the concentration of substances from a solution on the surface of solid adsorbents by the methods of vibrational spectroscopy is the imposition of the absorption of the adsorbent on the adsorbate bands. Comparison of the data in table 1 with the spectra of carbohydrate caramels [6] shows the overlap of most of the absorption bands of both types of systems, and therefore a more detailed study of the spectral profiles was carried out by the method of difference spectra [7,10], which allows to separate selectively the bands caused by the additional absorption of surface substances. The initial spectra show the presence of a weak shoulder in the 1720 cm<sup>-1</sup> region (figure 1, left position), corresponding to the stretching vibrations of the carbonyl groups and slightly differing

in integral intensity during the transition from the initial products to the products after adsorption. Difference spectra 3A and 3B (figure 1, right position, presented for convenience as transmission spectra) in the corresponding pairs 2A-1A and 2B-1B show a difference peak at  $1720\text{ cm}^{-1}$ , which indicates a higher absorption of the samples after adsorption, indicating on the concentration sorption of carbonyl derivatives from a solution on the surface [3]. Since no displacement of peaks in the spectra of materials after adsorption is observed in comparison with the signals of the starting material, it can be assumed that the sorption processes are predominantly physical in nature [4], which is confirmed by the data of [1]. In this connection, it can be assumed that the adsorption of mainly low-molecular components of caramels occurs [6].

Quantitative processing of difference FTIR spectra with curve approximation with the corresponding sum of Gaussians shows a greater value of the integral intensity of the difference peaks for systems with lactose caramels. The UV spectra of dialysates obtained from the caramels of the complete reaction systems are shown in figure 2, from the data of which it is clear that the low molecular weight colored products are formed during caramelization to a greater extent in systems based on lactose.



**Figure 2.** Electronic spectra of dialyzate caramel solutions based on D-glucose (A), D-lactose (B); 1 - dialysis for 24 hours; 2 - dialysis for 48 hours.

Thus, based on the data obtained, it can be argued that the carbonization products synthesized in the D-glucose-p-toluidine systems are capable of surface absorption of the carbonyl components of carbohydrate caramels from aqueous solutions. The research results are promising for the development of methods for the synthesis of carbon-saturated products, sorption-active with respect to substances of carbohydrate nature, which is of interest for the food and pharmaceutical industries.

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