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TÍTULO: Estudio de la actividad de sorción por cáscaras de frutas nativas y modificadas de trigo, avena y cebada en relación con el tinte aniónico verde brillante.

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RESUMEN. En el estudio se obtuvieron materiales de sorción que contienen celulosa a base de cáscaras de fruta de trigo, avena y cebada, y granos modificados con soluciones débilmente concentradas de ácidos sulfúrico, nítrico y clorhídrico, estudiándose la modificación de la estructura de los biopolímeros de los reactivos iniciales y modificados así como la estructura de la superficie del material de sorción. Se reveló que el proceso de sorción de tinte verde brillante aniónico con materiales modificados avanza más completamente en comparación con los materiales nativos, así como que los procesos de absorción del colorante aniónico de color verde brillante con cáscaras de trigo nativas y modificadas, avena y cebada son procesos de adsorción física.

PALABRAS CLAVES: sorción, isotermas de adsorción, modificación, materiales de sorción que contienen celulosa, valores termodinámicos.

TITLE: The study of sorption activity by native and modified fruit shells of Wheat, Oats and Barley in relation to Bright Green Anionic Dye.

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ABSTRACT: In the study, sorption materials containing cellulose based on fruit husks of wheat, oats and barley, and grains modified with weakly concentrated solutions of sulfuric, nitric and hydrochloric acids were obtained, studying the modification of the structure of the biopolymers of the initial and modified reagents as well as the structure of the surface of the sorption material. It was revealed that the process of sorption of bright anionic green dye with modified materials advances more completely compared to the native materials, as well as that the absorption processes of the bright green anion dye with native and modified wheat hulls, oats and barley they are physical adsorption processes.

KEY WORDS: sorption, adsorption isotherms, modification, cellulose-containing sorption materials, thermodynamic values.

INTRODUCTION.

The trend of highly efficient, affordable and cheap sorption material creation is the most priority area in the study and the application of sorption wastewater treatment from various pollutants. In world practice, industrial and agricultural waste as a basis for the manufacture of sorption materials has been widely used for a long time. The most large-tonnage from the list of the last are the agricultural waste generated during the processing of grain crops (straw, flour, grain husk, etc.).

The fruit shells of grain crops, which are formed in large quantities on elevators, create a fire hazardous environment. Currently, there are three ways to neutralize these wastes: their use in the manufacture of animal feed, burying in the ground and burning. However, according to the results of numerous studies, grain husks can be used as sorption materials to remove heavy metal ions [T.G. Chuah, A.Jumasiah, I.Azni, S.Katayon, S.Y.Thomas Choong, 2005], phenol [M. Ahmaruzzaman, Vinod K. Gupta, 2011; A. Bhatnagar, M. Sillanpaa, 2010], oil and the products of its processing [D. AngelovaaI, UzunovbS.Uzunovaa, A.Gigovac, L. Minchevol, 2011; L.Vlaev, P. Petkov, A. Dimitrov, S. Genieva, 2011] from waste and natural waters. In order to increase the sorption capacity, the materials based on waste processing of grain crops are subjected to various types of modification.

DEVELOPMENT.

One of the hardly decomposed liquid wastes are the dyed drains from textile enterprises. They, in its turn, have high toxicity (the maximum permissible concentration of bright green anionic dye in reservoirs for fisheries makes 0.0001 mg/dm3), and are the toxicants for humans and many hydrobionts, which complicates wastewater treatment by biocenosis, microorganisms, active sludge and biological treatment plants. As world practice shows, the sorption purification of colored water with agricultural waste is widely applicable [Y.S. Ho, G. Mckay, 1998; Y.S. Ho, C.C. Chiang, 2011; M.A. Mohd Sallehab, D. K. Mahmoud, W.A., 2011].

In connection with the foregoing, the sorption properties of native and modified fruit membranes of barley, wheat and oat grains were studied in relation to a bright green anionic dye.

Methods.

The preliminary preparation and modification of sorption materials.

At the first stage of the sorption material preparation, they performed a thorough washing of the initial sorption materials with distilled water in order to remove dust and other undesirable impurities from the sorbent surface. Then they dried the fruit shells of wheat, oats, and barley grains in a drying cabinet at the temperature of 110 °C to constant weight. After the preliminary preparation, 3 native sorption materials were obtained: the fruit shells of wheat, oats, and barley.

The study of native and modified cellulose-containing sorption material structure by the method of IR Fourier spectroscopy.

The structure of sorption materials before and after modification was studied using IR Fourier spectroscopy vis "Avatar-360" device in the frequency range of 400–4000 cm-1 with the "OMNIC" software and KBr glasses.

The study of surface morphology of native and modified cellulose-containing sorption materials by atomic force microscopy.

The surface morphology of cellulose-containing sorption materials was studied using "Innova" (Bruker) scanning probe microscope in the intermittent-contact mode. During scanning, they used RTESP (Veeco) rectangular cantilevers with silicone probes.

The resonant frequency of these cantilevers is in the range of 250–350 kHz, and the radius of the probe curvature is 10–13 nm. They obtained the microscopic images were with the resolution of 512x512 pixels per frame at the scanning speed of 1 Hz. In order to eliminate the distortions associated with the “shake” of the microscope under the influence of external noises, they used anti-vibration system SG0508 was used, which is able to smooth out the vibrations with the frequency of up to 0.5 Hz (lower limit).

The study of material sorption properties in static conditions.

The determination of material sorption properties was carried out under static conditions on model solutions of anionic bright green dye with the initial concentrations (C_s): 0 - 50 mg/dm^3 with the dosage of sorption materials 1 g/dm^3, the sorption time made 1 hour, temperature - 25 °C, the mixing of dye solutions with sorption materials was carried out using a magnetic stirrer.

The initial and the final concentration of the dye was determined according to pre-prepared calibration graphs, developed from the readings of optical density with the solution of various predetermined concentrations.

On the basis of the obtained dye sorption data by the modified barley fruit shells in the static adsorption mode, the sorption capacities of the materials (A) were calculated using the formula 1.

$$A = \frac{(C_s - C_e)}{m} \bullet V \qquad (1),$$

where A is the sorption capacity (mmol/g), C_s is the initial concentration of the adsorbate (mmol/dm^3), Ce is the concentration of the adsorbate after sorption (mmol/dm^3), V is the solution volume (dm3), m is the mass of the sorption material (g).

Results.

IR spectra of native and modified fruit shells of wheat, oats and barley grains are shown on Figures 1-3, respectively.

Fig. 1 FTIR spectra of raw (1) and modified (2) wheat husk.

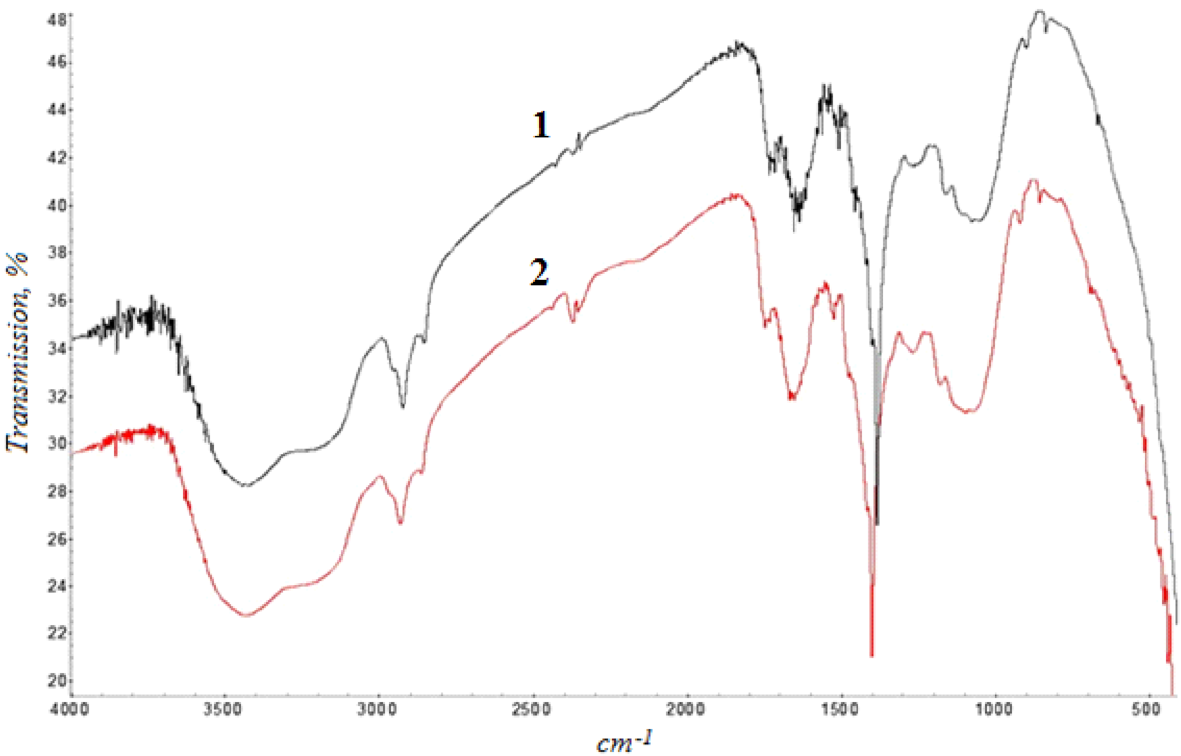


Fig. 2 FTIR spectra of raw (1) and modified (2) oat husk.

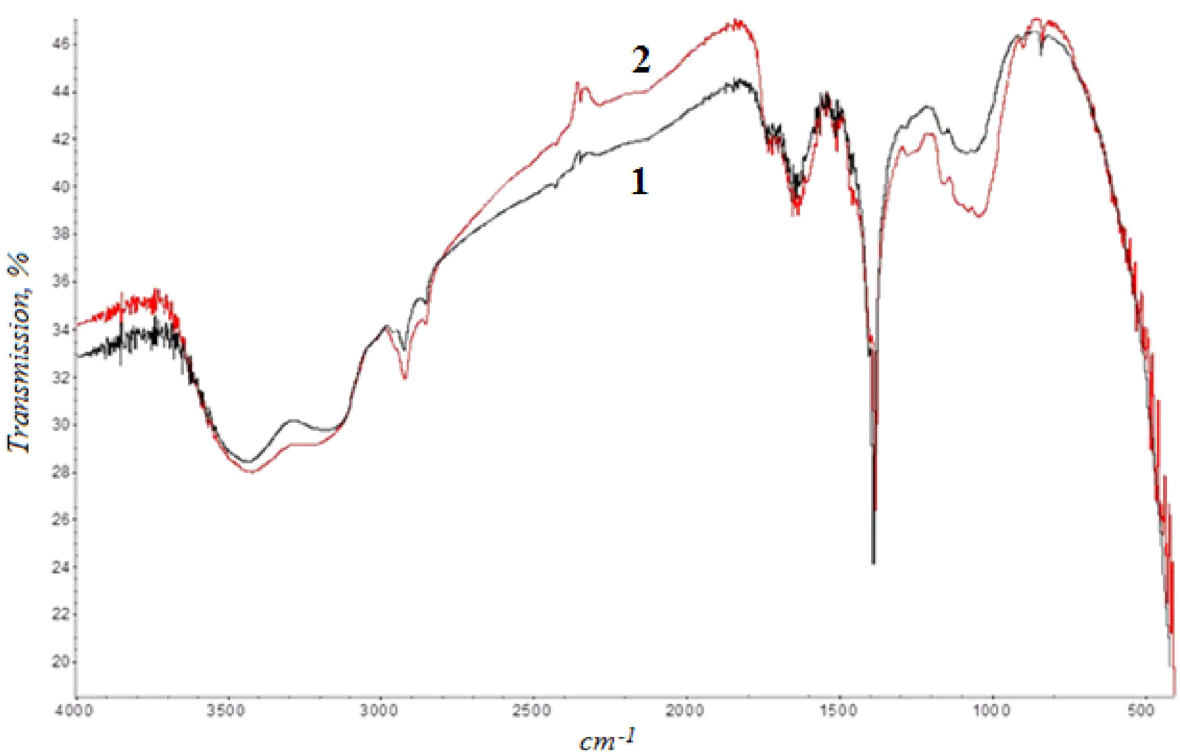
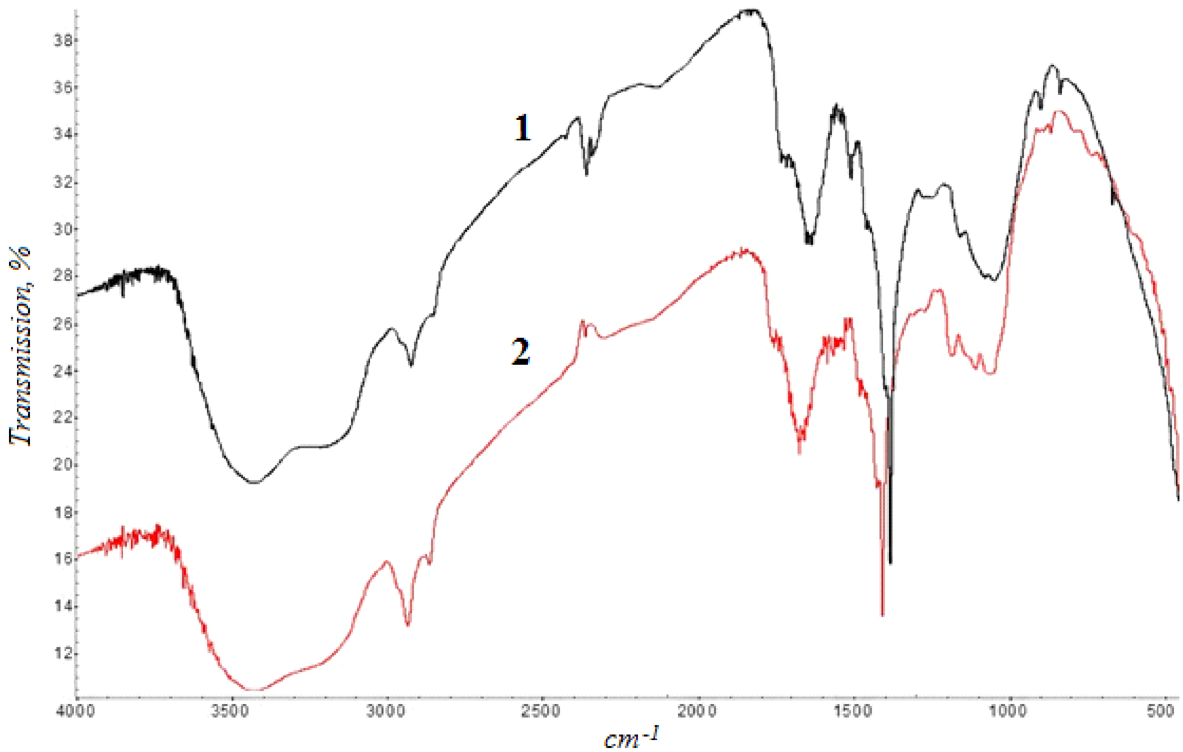
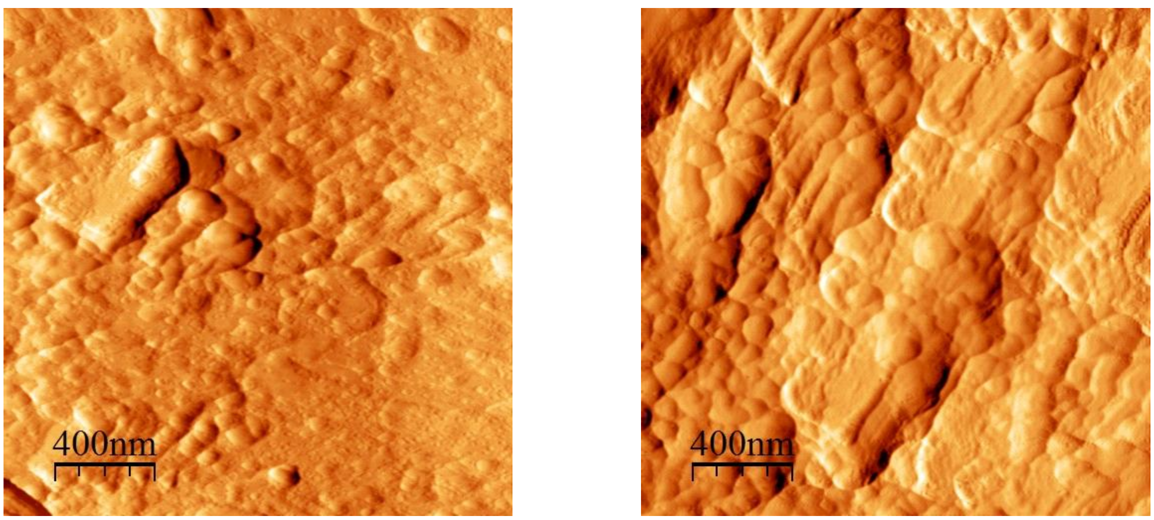


Fig. 3 FTIR spectra of raw (1) and modified (2) barley husk.



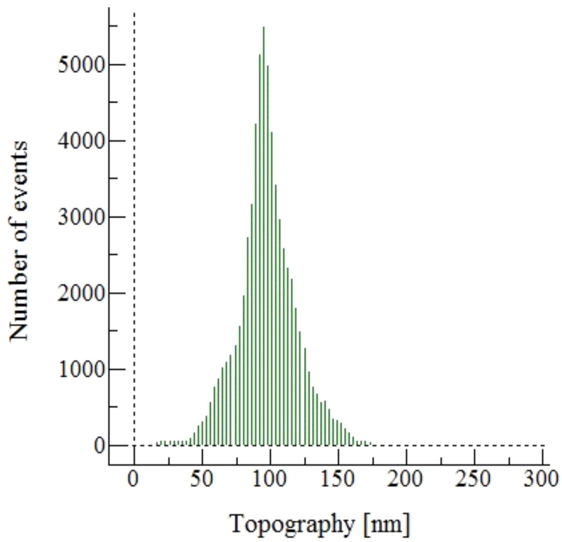
The surface morphology and the histograms of the surface distribution over the heights of native and modified fruit shells of wheat, oats and barley grains, determined by atomic force microscopy, are presented on Figures 4-9, respectively.

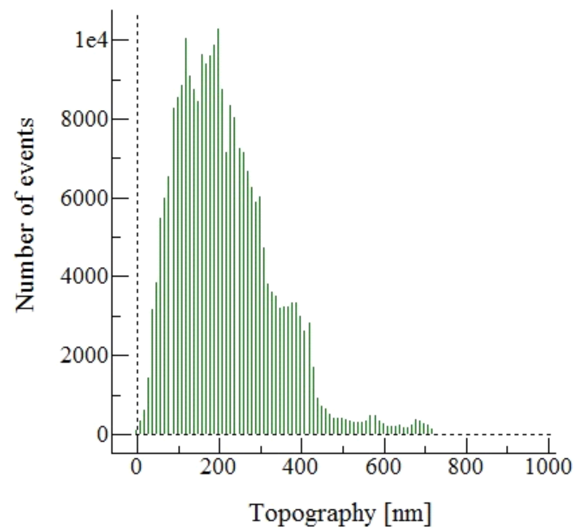
Fig. 4 AFM images of raw (a) and modified by 5% sulfuric acid solution (b) wheat husk.



(a) (b)

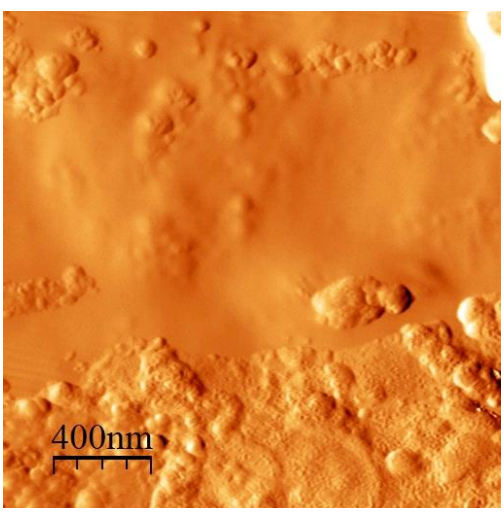
Fig. 5. Topographic histograms of raw (a) and modified by 5% sulfuric acid solution (b) wheat husk.

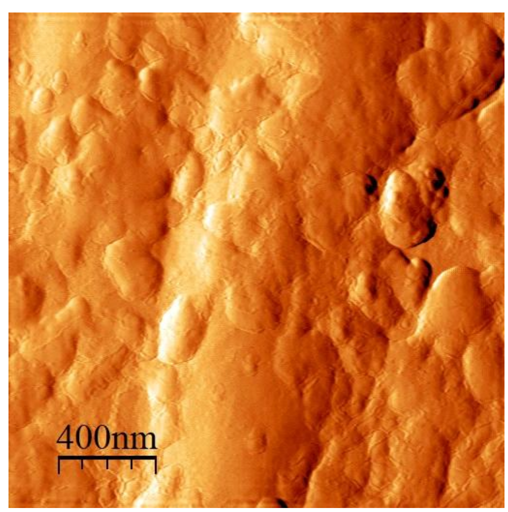




(a) (b)

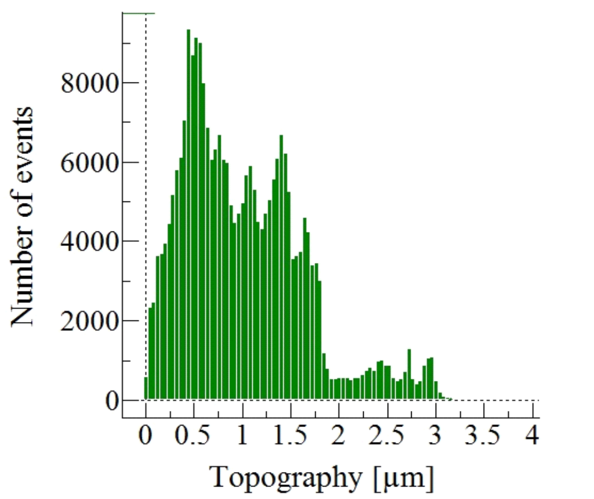
Fig. 6. AFM images of raw (a) and modified by 5% sulfuric acid solution (b) oat husk.

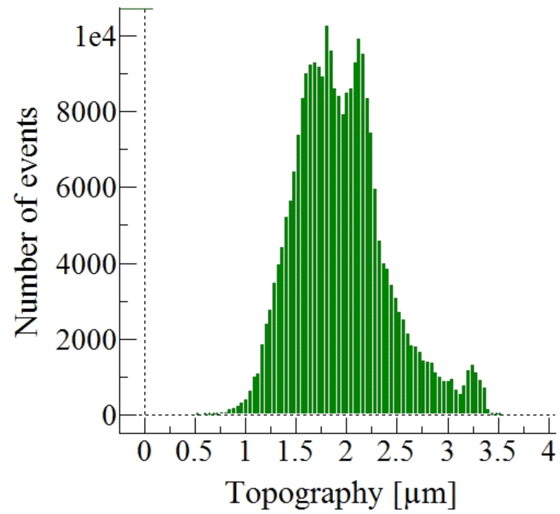




(a) **(b)**

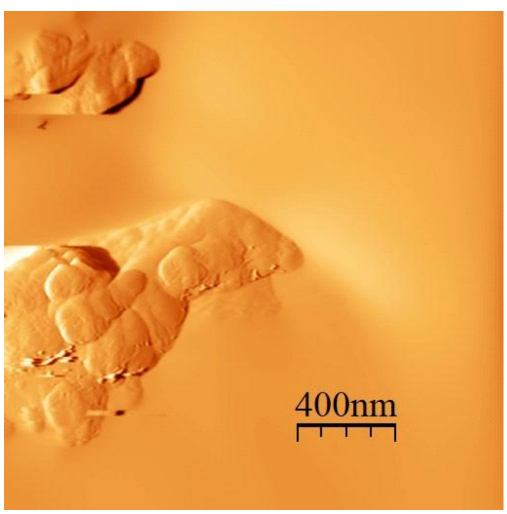
Fig. 7. Topographic histograms of raw (a) and modified by 5% sulfuric acid solution (b) oat husk

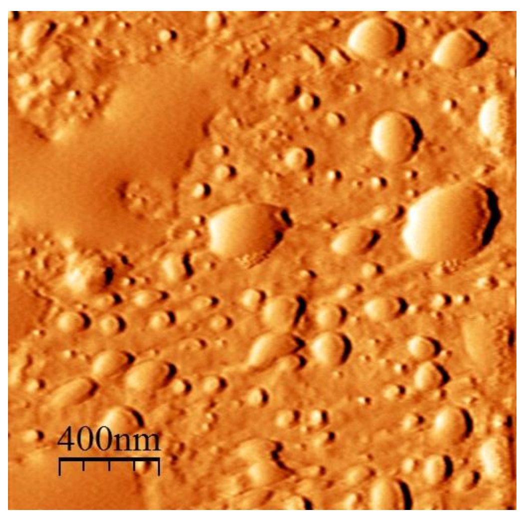




(a) **(b)**

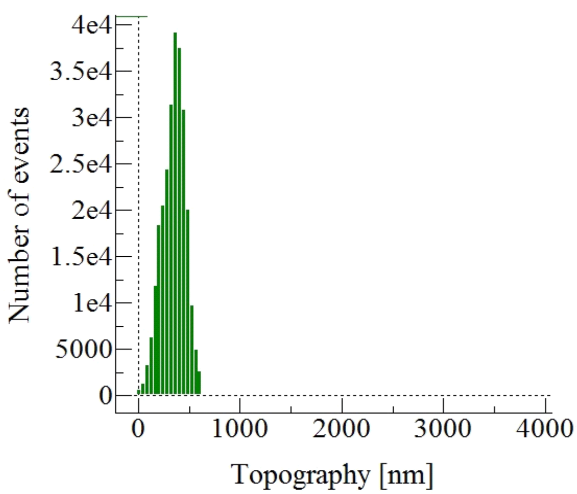
Fig. 8. AFM images of raw (a) and modified by 5% sulfuric acid solution (b) barley husk.



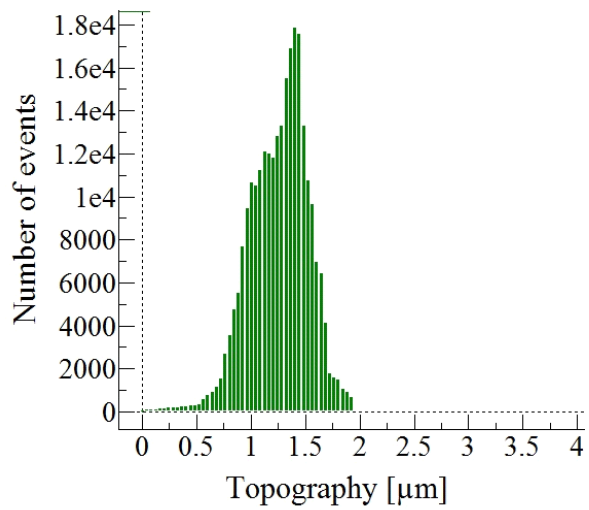


(a) (b)

Fig. 9 Topographic histograms of raw (a) and modified by 5% sulfuric acid solution (b) barley husk.



(a)



(b)

The sorption isotherms of bright green anionic dye by native and modified fruit shells of wheat, oats, and barley grains are shown on Figures 10, 11, 12, respectively.

Fig. 10 Isotherm of dye sorption by the fruit shells of wheat: 1) native species 2) treated with hydrochloric acid 3) treated with nitric acid 4) treated with sulfuric acid.

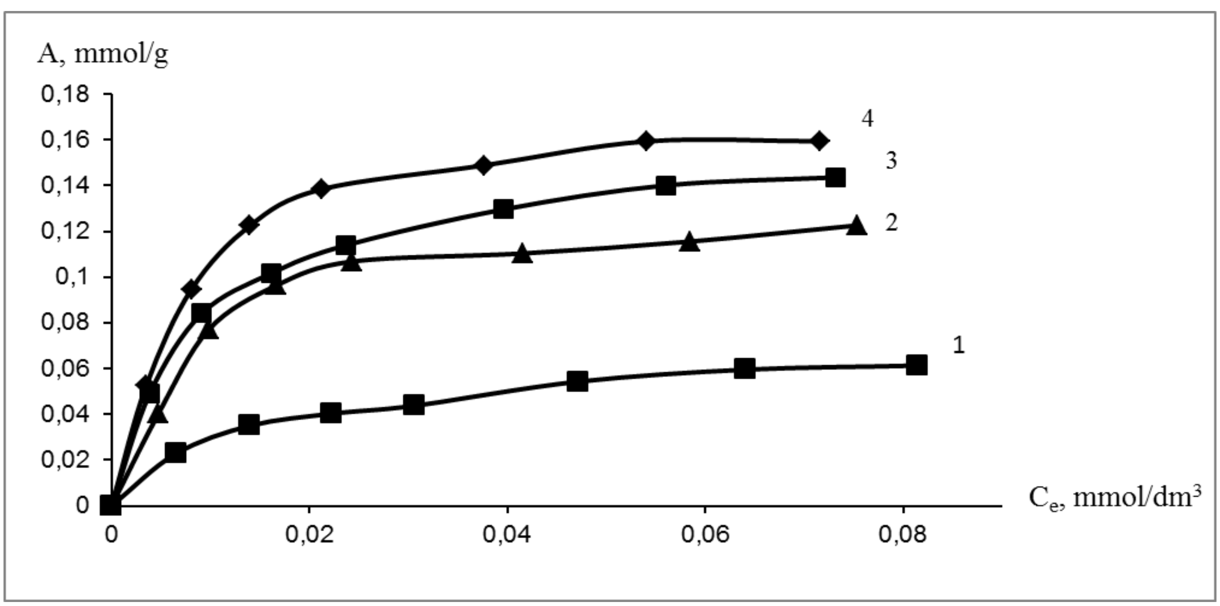


Fig. 11 Isotherm of dye sorption by the fruit shells of oat: 1) native species 2) treated with hydrochloric acid 3) treated with nitric acid 4) treated with sulfuric acid.

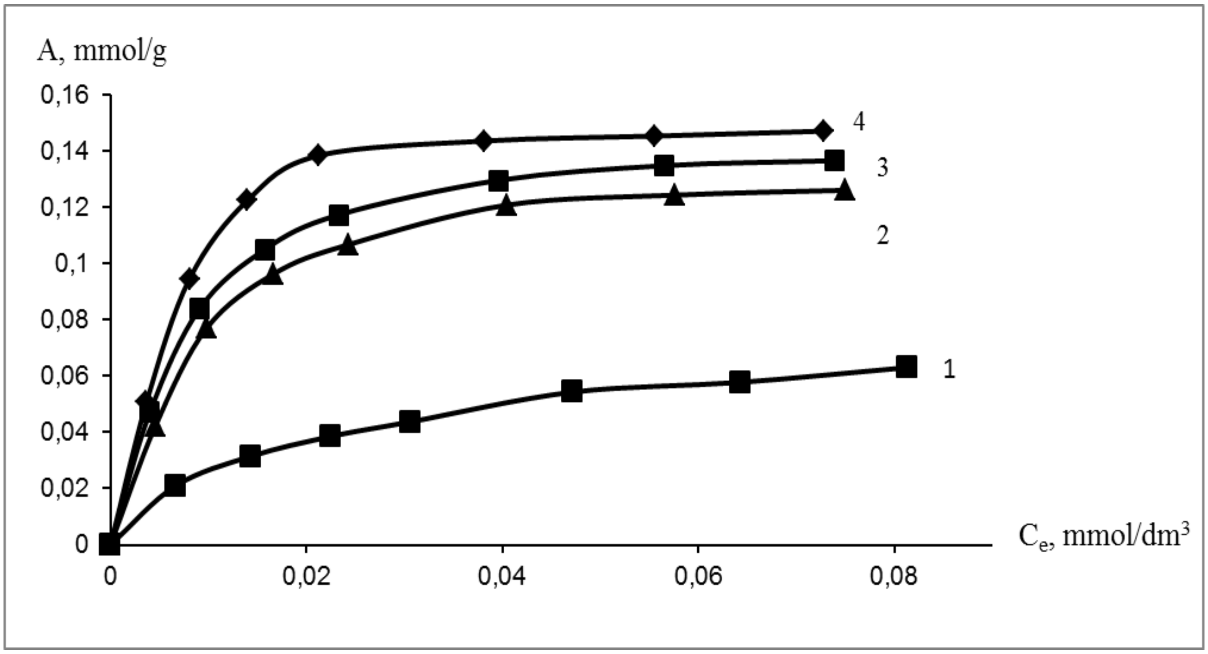
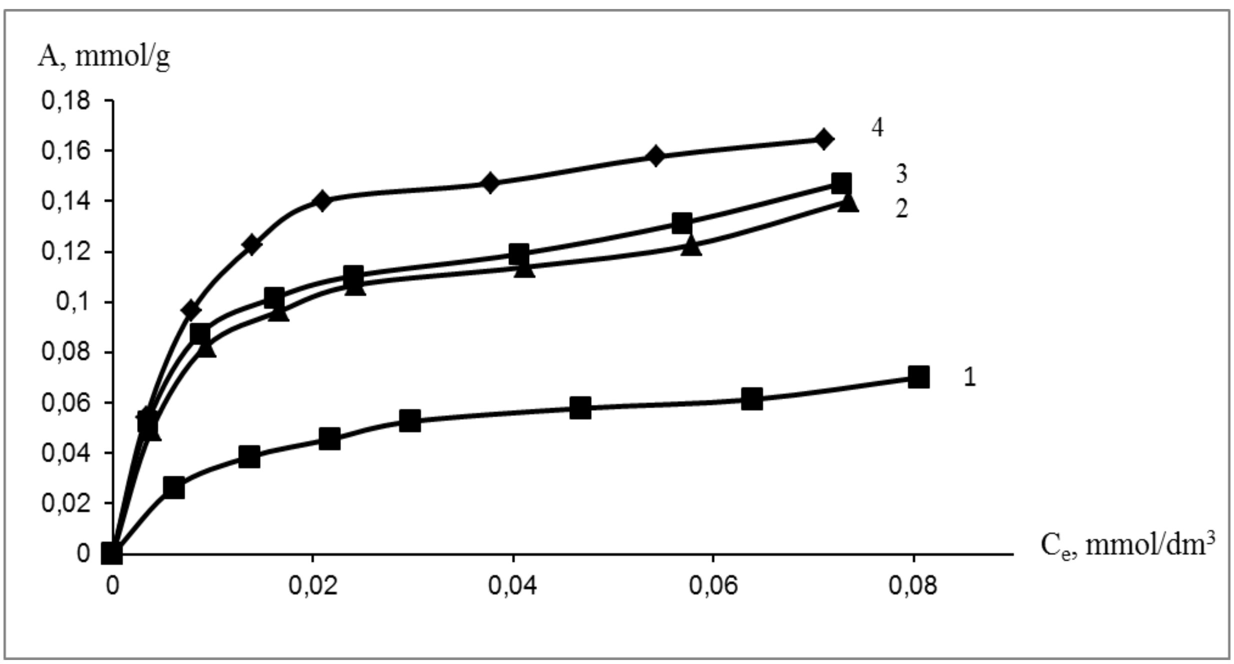


Fig. 12 Isotherm of dye sorption by barley fruit shells of barley: 1) native form, 2) treated with hydrochloric acid, 3) treated with nitric acid, 4) treated with sulfuric acid.



Results and Discussion.

The study of native and modified cellulose-containing sorption material structure.

The change of IR spectrum pattern of the original shells of wheat, oats, barley and processed with 5% H_2SO_4 solution indicates the change in their internal structure. They noted the absence of the absorption band in the region of 1500 cm^{-1} and the change the spectrum pattern in the range of 1000–1250 cm^{-1} of an acid-treated sample of the sorption material. This circumstance may be conditioned by the change in the sorbent structure, due to the leaching of low molecular weight organic compounds from the pores of the fruit membranes of wheat, oats and barley grains when they are treated with the sulfuric acid solution.

The additional evidence of low molecular weight organic compound leaching from the pores of the sorption material, and, consequently, the formation of a more developed surface of the sorbent can be represented by atomic force microscopy data: AFM images of the surface and the histogram of the surface distribution by height are presented on Figures 4-9, respectively. They note the formation of a more pronounced surface relief, as well as the increase of peak height: from the interval of heights of 50-180 nm for wheat to the interval of 0-700 nm and the change in the amount from 5000 to more than 1000; from the interval of 0 to 3 µm to 0-3.5 µm for oats and the change of the amount from 1000 to over 1000; from the interval of 0-600 µm to the interval of 2 µm for barley and the change of quantity from 4e4 to 1,8e4.

The study of material sorption properties in relation to the bright green anionic dye.

Anionic bright green dye sorption isotherms with native and modified fruit shells of wheat, oats and barley grains belong to type 1 sorption isotherm, according to the BDDT classification [A. Dadrowski, 2001], and to type L, according to the classification of Gils sorption isotherms [F. Benmakroha, J.F. Alder, 1995], and describe the monomolecular dye adsorption dye on the sorbent surface (typical Langmuir sorption isotherm). It is clear from the sorption isotherm that during the material modification, their sorption properties increase with respect to the dye. The most effective sorption material in relation to the bright green anion dye is the fruit shell of barley, modified with the 5% solution of sulfuric acid (A∞ = 0.16 mmol/g). In order to describe mathematically the isotherms of monomolecular adsorption, the Langmuir, Freindlich, Dubinin-Radushkevich, Temkin equations are used usually [C. Hinz, 2001; L. Wojnarovits, Cs.M. Foldvary, E. Takacs, 2010]. The results of dye adsorption isotherm calculation with the studied materials are presented in Table 1.

Table 1 Results of treatment of isotherms for adsorption of dye by native and modified wheat husks, oat husks, barley husks

Adsorbent	Adsorption model	Adsorption equation	Correlation coefficient
Native wheat husk	Langmuir	y= 0,2803x+1,432	0,911
Wheat husk - HCl	Freundlich	y= 0,3193x+1,4272	0,974
Wheat husk – HNO_3	Dubinin-Radushkevich	**y=0,0406x+0,0007**	**0,996**
` Wheat husk – H_2SO_4	Temkin	y= 0,1627x+4,4062	0,941
Native oat husk	Langmuir	y= -0,1726x+3,628	0,951
Oat husk -HCl	Freundlich	y= -0,0353x-1,7303	0,958
Oathusk-HNO3	Dubinin-Radushkevich	**y= 0,00708x+0,0006**	**0,997**
Oathusk-H2SO4	Temkin	y= -0,185x+5,987	0,942
Native barley husk	Langmuir	y=17,687x +18,179	0,958
Barley husk- HCl	Freundlich	y=14,359x+23,469	0,954
Barley husk- HNO3	Dubinin-Radushkevich	**y= 0,0428x+0,0004**	**0,998**
Barley husk- H2SO4	Temkin	y=15,289x+19,345	0,957

The sorption isotherms of native and modified materials based on fruit shells of wheat, oats and barley grains are best described by Dubinin-Radushkevich equations for all materials that describe the volumetric filling of sorbent micropores, and are a special case of TOZM equation for microporous adsorbents.

Calculation of bright green anion dye sorption thermodynamic values by native and modified cellulose-containing sorption materials.

By isotherm processing, Langmuir and Dubinin-Radushkevich sorption models were used to determine the constants of Langmuir and Dubinin-Radushkevich equations, which were used to calculate the thermodynamic values of the processes by the equations 2 - 3, presented in Table 2.

$$E = (-2\beta)^{-½} \tag{2}$$

$$\Delta G^{o} = - R\cdot T\cdot \ln K_{L} \tag{3}$$

According to the sources [N.S. Kumar, A.S. Reddy, VOL. M. Boddu, A. Krishnaiah, 2009;M. Doğan, M. Alkan, O. Demirbaş, Y. Özdemir, C. Özmetin, 2006; H. Arslanoglu, H.S. Altundogan, F. Tumen, 2009;A. Sarı, M. Tuzen, M. Soylak, 2007], the following values indicate the course of physical adsorption: the sorption energy less than 8 kJ/mol and Gibbs energy from -100 to 0 kJ/mol.

Table 2 Thermodynamic constants of adsorption process of dye by native and modified wheat husks, oat husks, barley husks

Adsorbent	E, kJ/mol	ΔG, kJ/mol	Adsorption mechanism
Nativewheat husk	6,601	-4,793	Physical adsorption
Wheat husk modified by HCl	6,677	-5,587	Physical adsorption
Wheat husk modified by HNO_3	6,705	-5,613	Physical adsorption
Wheat husk modified by H_2SO_4	6,717	-5,627	Physical adsorption
Native oat husk	6,908	-3,982	Physical adsorption
Oat husk modified by HCl	7,180	-4,931	Physical adsorption
Oat husk modified by HNO_3	7,208	-4,952	Physical adsorption
Oat husk modified by H_2SO_4	7,238	-4,983	Physical adsorption
Native barley husk	6,832	-4,154	Physical adsorption
Barleyhusk modified by HCl	7,081	-5,681	Physical adsorption
Barleyhusk modified by HNO_3	7,098	-5,673	Physical adsorption
Barleyhusk modified by H_2SO_4	7,105	-5,701	Physical adsorption

CONCLUSIONS.

Cellulose-containing sorption materials modified with weak solutions of hydrochloric, nitric, and sulfuric acid were obtained on the basis of fruit shells of wheat, oats, and barley grains. They studied the structure of native and modified sorption materials by IR Fourier spectroscopy and atomic force microscopy. They determined that the surface treatment of fruit shells leads to the leaching of low-molecular-weight organic compounds from the sorbent pores and the formation of a more developed surface of the material. It was revealed that the sorption properties of modified fruit shells of wheat, oats and barley grains in relation to a bright green anionic dye are 2; 2.3 and 2.6 times higher, respectively, as compared with the native form of the sorbent. The dye sorption isotherms with native and modified fruit shells of wheat, oats and barley grains are classified as type I isotherm according to IUPAC and L type according to Hills classification and describe the monomolecular sorption of bright green anion dye on the surface of materials.

The processing of isotherms in the framework of Langmuir, Freindlich, Dubinin-Radushkevich and Temkin models revealed that the dye sorption process by native and modified fruit shells of wheat, oats and barley grains is best described by the Dubinin-Radushkevich equations with the correlation coefficients of 0.996; 0.997 and 0.998, respectively. According to the calculated data of the sorption energy and Gibbs energy, it was noted that all the studied processes belong to the physical adsorption processes.

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