

SORBENTS FROM VEGETABLE RAW MATERIALS

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Abstract: The morphology of the surface, the functional composition of dispersed samples of wheat straw, husk of rice and beans are studied. Adsorption of heavy metal ions from aqueous solutions on dispersed samples of vegetable waste is considered.

Key words: Waste of vegetable raw materials, SEM (scanning electron microscopy), IR- spectroscopy, heavy metal ions, adsorption.

Introduction. Perspective sources of cellulose-containing raw materials are plant waste from agriculture: straw, husk, sunflower husks, etc. The use of crop waste, in which the content of cellulose is 35-47% it due to their availability, annual renewability, as well as the unsolved problem of their rational use [1]. So, after processing of cereals, two kinds of waste are received simultaneously - straw and husk. These waste are used mainly for agricultural needs, in construction as finishing roofing materials, burn directly on the fields or simply leave in places of processing for natural decomposition [2]. At the same time, the use as a cellulose-containing raw material waste of cereals and leguminous plants will expand the prospects for the use of non-wood vegetable raw materials.

Characteristics of research objects. Straw of wheat grade "K-10" (Kyrgyzstan), the harvest of 2016. The husk of the bean "Lopatka" (Kyrgyzstan), the harvest of 2016. The rice husks of the grade "Zros" (Kyrgyzstan), the harvest of 2017. The process of cleaning waste of plant raw materials from debris was carried out manually.

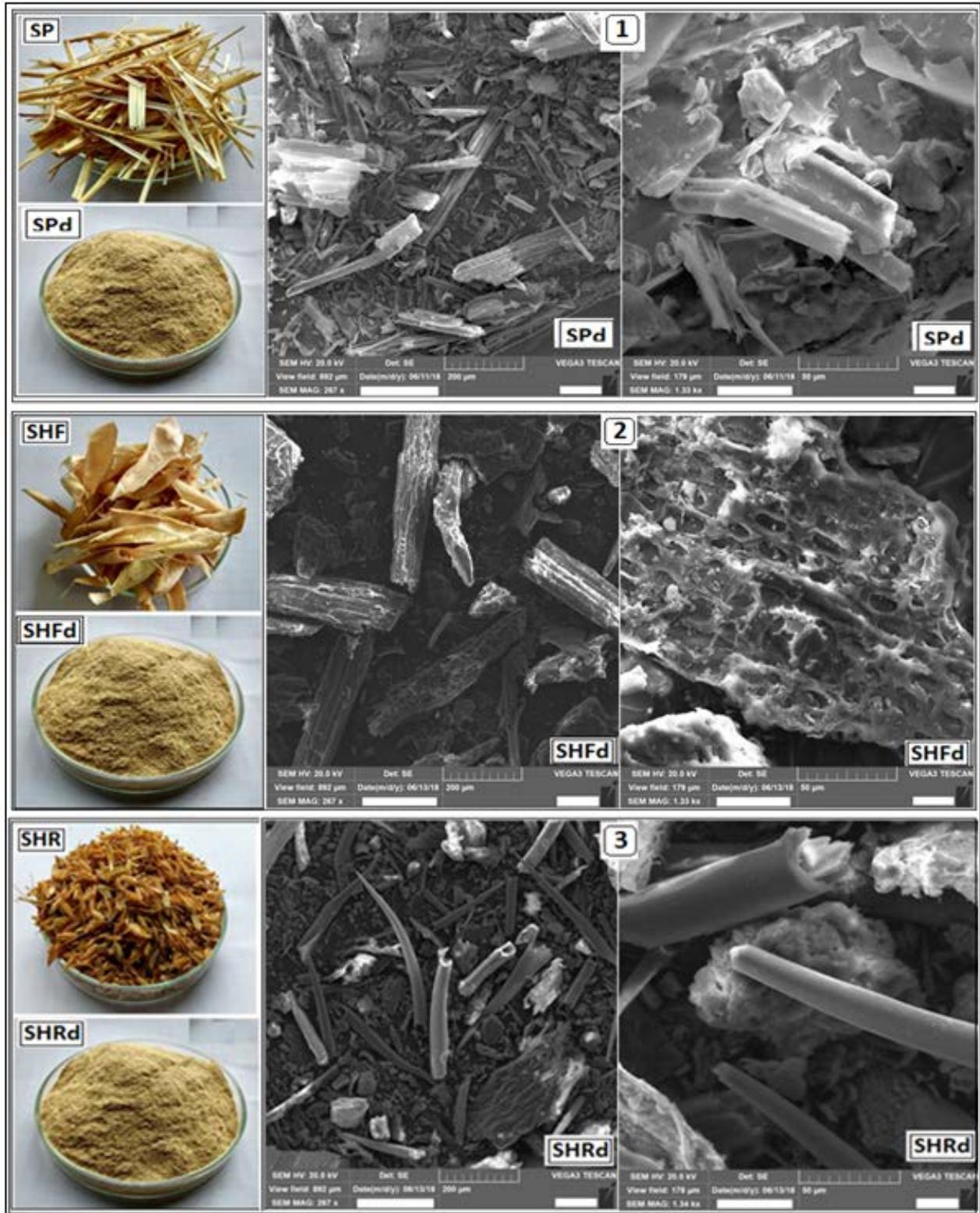


Fig.1. Appearance, morphology of the surface of vegetable waste: 1- initial (SP) and dispersed (SPd) samples of wheat straw of grade "K-10" (Kyrgyzstan); 2- initial (SHF) and dispersed (SHFd) samples of the husk of the bean "Lopatka" (Kyrgyzstan); 3- initial (SHR) and dispersed (SHRd) samples of the husks of rice grade "Zros" (Kyrgyzstan)

The test objects were dried at a temperature 100-105⁰C for 2 hours. Wheat straw and husks of beans were grounded to a size of 3-5 cm. Air-dry samples of plant material wastes were

dispersed. The resulting powders were sieved on sieves with a pore size of 0.25 mm (60 mesh). Figures of the appearance of the initial samples of vegetable waste and their dispersed forms are shown in Fig. Humidity, ash content of vegetable wastes was determined according to generally accepted methods [3]. The results are shown in tabl. 1.

Table 1 - Ash content and humidity of dispersed samples of plant material waste

Object of study	Humidity (W ^a), %	ash content (A ^a), %
Straw of wheat (SPd)	4,5	8,42
Bean husks (SHFd)	5,6	4,97
Rice husks (SHRd)	4,7	23,8

Along with the appearance of dispersed samples of plant material waste, figure 1 shows their micrographs. Analysis of the morphological structure of dispersed samples of wheat straw, bean husk, rice husks was carried out at SEM «VEGA3 TESKAN». Samples were scanned at different magnifications. Images of scanned objects were saved as a standard file in TIFF format with the parameters of the experiment. Micrographs show that a dispersed wheat straw sample (SPd) is a flat particle, layered structure, elongated shape, the longitudinal dimension of which is much greater than the transverse. The particle sizes range from 20 to 400 µm in length and from 5 to 100 µm in width. The dispersed sample of bean husk (SHFd) is a lamellar-scaly particle with large shallow pores. The longitudinal particle size ranges from 200 to 600 µm, the transverse particle size ranges from 20 to 200 µm. The dispersed rice husk sample (SHRd) is both a particle-layered structure with sizes from 50 to 400 microns, and hollow smooth cone-shaped tubes with a length from 150 to 600 microns and a diameter at the base of 40 microns. It should be noted that in all three initial samples, the presence of fine particles of irregular shape with a size of not more than 20 µm is observed, which are supposedly non-fibrous components of raw materials (lignin, ash).

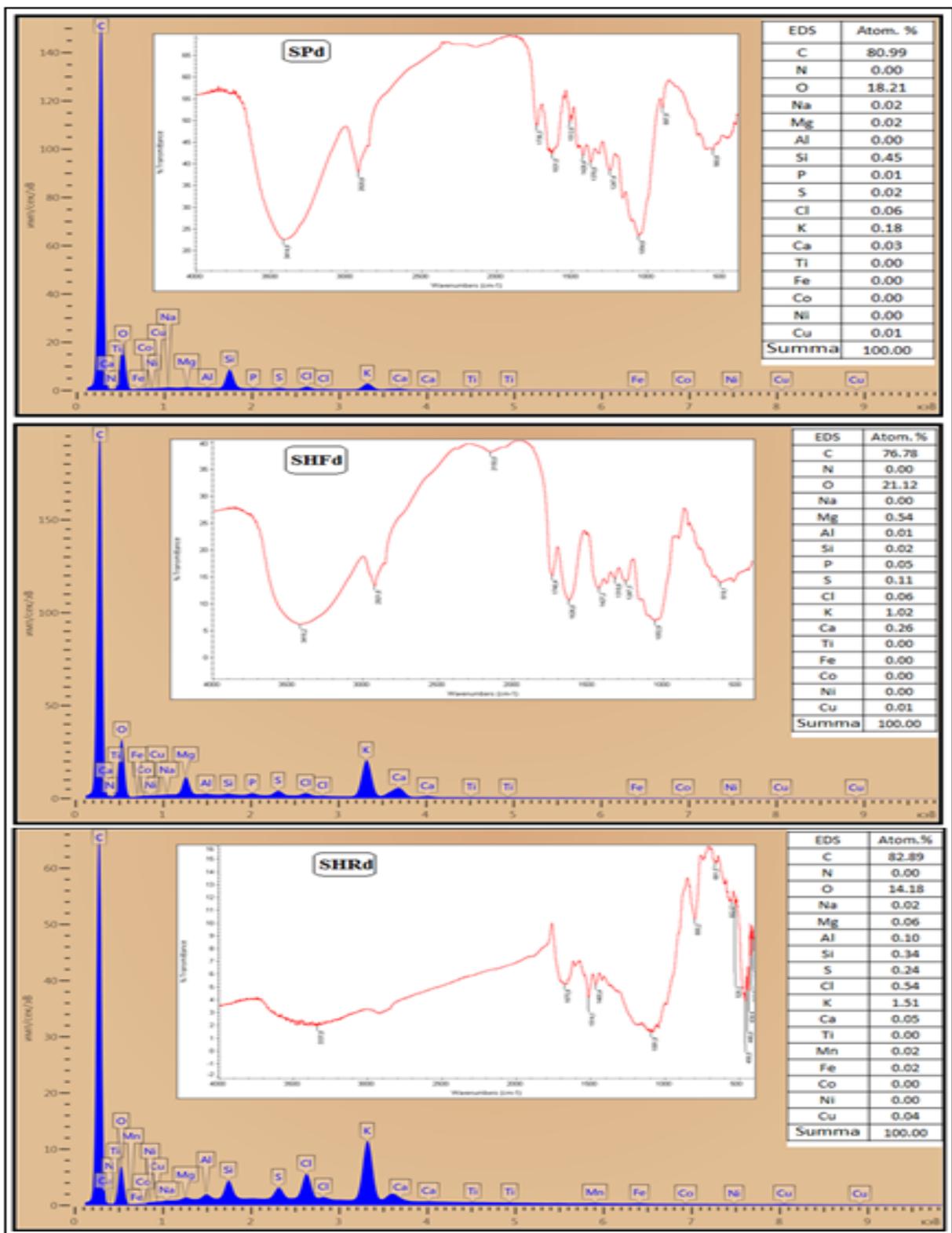


Fig.2. Energy dispersive and IR spectra of dispersed samples of wheat straw (SPd), bean husks (SHFd), rice husks (SHRd)

Figure 2 shows the energy-dispersive and IR spectra of the tested samples. The EDS analysis shows slight differences in the composition of dispersed samples of plant material waste by the macroelements C, O, Si. This is connected, apparently, with

differences, both in the structure of the raw materials, and with the presence in it of a different number of ash elements. IR - spectra of dispersed samples of wheat straw (SPd), bean hulls (SHFd), rice husks (SHRd) were taken on a NicoletAvatar 370 GDTS infrared spectrometer in a frequency range of 4000-450 cm^{-1} using the compression technique of the samples with bromide potassium. The analysis showed that in the spectra of all samples there are bands characteristic of cellulose:

- region 3700-3100 cm^{-1} - stretching vibrations of hydroxyl groups involved in intra- and intermolecular hydrogen bonds;
- region 3000-2800 cm^{-1} - stretching vibrations of C-H-bonds in methylene and methine groups of cellulose;
- 1680-1630 cm^{-1} area - adsorbed water absorption;
- area 1500-900 cm^{-1} - various vibrations of C-H-, C-O-, O-H-bonds, fluctuations of glycosidic bond and glucopyranose ring of cellulose;
- 900-700 cm^{-1} area - pendular vibrations of C-H bonds and pyranose links (asymmetric vibrations of the pyranose ring and C1 vibrations of the carbon atom in the glycoside structure).

It is known that vegetable raw materials in addition to cellulose, the main component, also contains hemicellulose, lignin and ash elements. In all spectra of the tested samples (SPd, SHFd, SHRd)), absorption bands are observed in the region of 1740-1700 cm^{-1} . These bands characterize the stretching vibrations of C = O in the ester groups of uronic acids of hemicelluloses and lignin. Bands of stretching vibrations of groups with multiple bonds C = C, C = O and CAr-CAr in saturated ketones or conjugated with an aromatic ring, characteristic of lignin lie in the same region. The peaks in the region 1514-1512 cm^{-1} refer to the skeletal vibrations of the benzene ring. They also characterize the presence of lignin. In addition, the spectra contain bands characterizing the presence of inorganic components in the samples (peaks in the range 700-450 cm^{-1} , They are due to stretching vibrations of Si-O, deformation vibrations of Si-O, Si-O-Me.). The highest intensity of these peaks is observed in the IR spectrum of rice husks [4,5].

Adsorption from solutions of heavy metal ions. Adsorption of Cu^{2+} , Ni^{2+} , and Cd^{2+} ions from aqueous solutions on dispersed samples of wheat straw, rice husks and bean husks was carried out under static conditions. For this purpose, a sample of an adsorbent with a mass of 0.1 g was added to a series of aqueous solutions of chlorides of doubly charged ions with specified concentrations, in a volume of 50 ml. The heterogeneous equilibrium in the adsorbent-adsorbate system was established for 24 hours in a TS-80M dry-air thermostat at $T = 298^{\circ}\text{K}$. At the same time, the phase were mixed every 15 minutes during the first 2 hours. After equilibrium was established, the phases were separated from each other using a syringe filter with pore sizes of 1-2 μm . The amount of matter adsorbed from the solution (the value of adsorption) on a solid adsorbent was calculated by the equation:

$$a = \frac{(C_0 - C_e) \cdot V}{m} \cdot 1000 (1),$$

where C_0 and C_e are the initial and equilibrium concentrations of the adsorbate, M ; V – volume of solution from which adsorption takes place, l ; m – amount of adsorbent, g ; 1000 is a conversion factor used for the resulting values to be expressed in mmol / g .

The concentration of Cu^{2+} , Ni^{2+} , Cd^{2+} ions after adsorption on dispersed vegetable waste was determined by trilonometric titration. For this, an aliquot in a volume of 5 ml was transferred to a titration flask, 0.5 ml of ammonia buffer solution, 0.01-0.02 g of the murexide indicator (in the case of Cu^{2+} and Ni^{2+} ions) and 0,01-0,02g eryochrom black T indicator (for Cd^{2+} ions) were added. Then, they titrated with a solution of Trilon B at a

concentration of 0.1 mol / l until the color transition from dark red to violet, characteristic of copper ions; from orange to violet - for nickel ions; from pink to blue in the case of Cd²⁺ ions. The ion concentration was determined from the equation:

$$C_{Me^{2+}} = \frac{C_{TB} \cdot V_{TB}}{V_{Me^{2+}}} \quad (2),$$

where C_{TB} is the concentration of Trilon B solution, 0.1 mol / l; V_{TB} - the volume of Trilon B used for titration, ml; $V_{Me^{2+}}$ - volume of aliquot part of solutions of chloride of copper, nickel, cadmium, respectively, taken for titration, ml.

The average values of adsorption, as a result of parallel tests, are visualized in Fig. 3, depending on the equilibrium concentration of heavy metal ions in the aqueous solution. It can be seen that adsorption isotherms of the Langmuir type are observed. At the same time, the adsorption of heavy metal ions on a dispersed rice husk sample is much larger than on dispersed samples of wheat straw and bean husks.

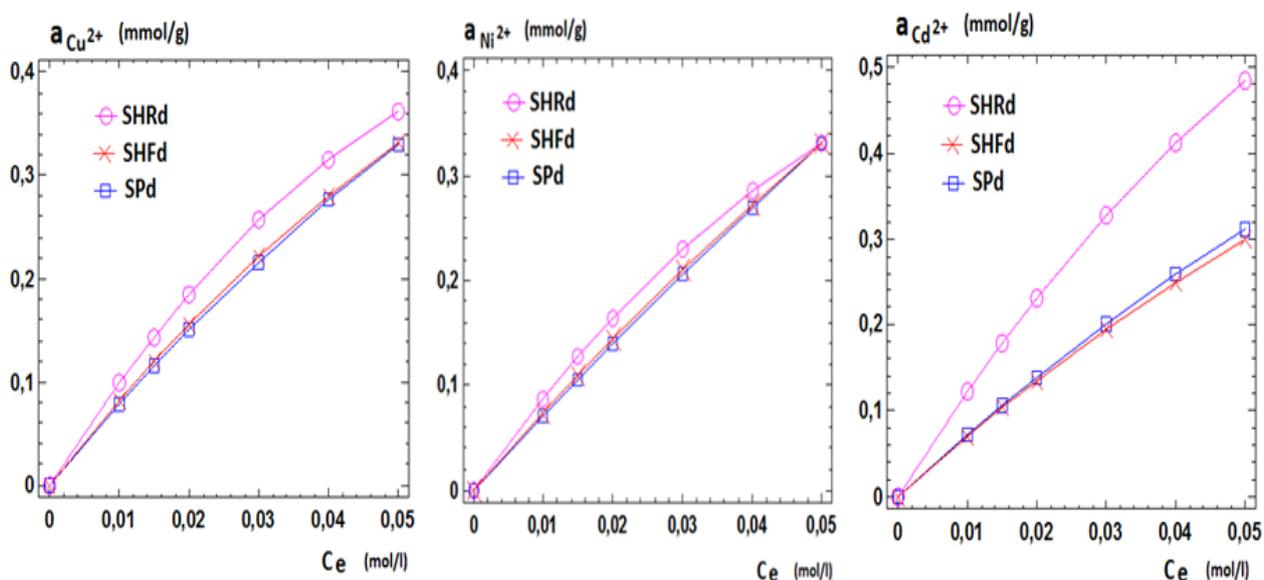
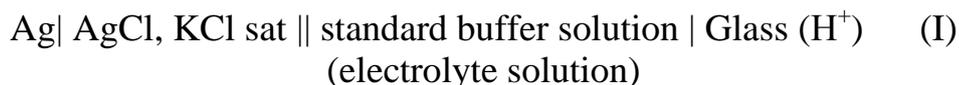


Fig.3. Isotherms of adsorption of heavy metal ions from aqueous solutions on dispersed samples of rice husks (SHRd), bean husks (SHFd), wheat straw (SPd)

pH-metric control of the solutions was carried out before and after adsorption on solid adsorbents to complete the characteristics of studied heterogeneous equilibria. The pH of aqueous solutions of electrolytes was determined by EMF method using galvanic transfer cell of type (I):



In the element (I), a saturated silver chloride electrode of the EVL-1 grade and a glass electrode with a hydrogen function of the ESL-43-07 grade were used. The PHS-2F pH meter was used as the measuring equipment.

Before the measurement was started, the glass electrode with the hydrogen function was calibrated using standard buffer solutions. Thus, for a given electrode, in the pH range from 1.68 to 6.86, the following relationship was obtained:

$$\text{pH} = \frac{390.309 - E}{58.5345} \quad (3),$$

where E – EMF of element (I).

According to the EMF data of the element (I), using the relation (3), the pH values of the aqueous solutions of electrolytes were obtained before and after adsorption on the investigated solid waste of vegetable raw materials, which are given in Table 2. Table 2 shows that there is some ambiguity in the acid-base manifestations of dispersed samples of wheat straw, rice husks and beans when they are in contact with aqueous solutions of electrolytes.

Table 2 - pH of aqueous solutions of heavy metal ions before and after adsorption on dispersed samples of wheat straw (SPd), bean husks (SHFd), rice husks (SHRd)

№	H ₂ O - CuCl ₂			H ₂ O - CdCl ₂			H ₂ O - NiCl ₂					
	pH ₀	pH _e (SPd)	pH _e (SHRd)	pH _e (SHFd)	pH ₀	pH _e (SPd)	pH _e (SHRd)	pH _e (SHFd)	pH ₀	pH _e (SPd)	pH _e (SHRd)	pH _e (SHFd)
1	4,91	4,16	4,67	4,03	5,98	5,36	6,01	4,75	6,46	5,64	6,65	5,00
2	4,60	4,07	4,50	3,89	5,91	5,31	5,87	4,72	6,30	5,09	6,53	4,91
3	4,43	4,02	4,53	3,83	5,94	5,27	5,81	4,69	6,11	5,40	6,46	5,00
4	4,23	3,92	4,38	3,77	5,79	5,24	5,79	4,63	6,03	5,45	6,40	4,86
5	4,10	3,86	4,31	3,71	5,92	5,19	5,76	4,53	6,03	5,29	6,30	4,81
6	3,96	3,81	4,26	3,67	5,37	5,12	5,68	4,45	5,95	5,52	6,40	4,89

The obtained result indicates the possibility of both ion exchange processes and the non-binding (selective) binding of heavy metal ions on the surface adsorption centers of tested sorbents.

Conclusions. Certain differences in the morphological structure of the raw materials (SPd, SHFd, SHRd) were revealed. In all samples, the presence of non-fibrous components was detected. The IR spectra of the samples (SPd, SHFd, SHRd) showed the presence of cellulose, lignin and ash elements in their compositions. At the same time, small differences in the macroelements C, O, Si are observed in the composition of dispersed samples of plant material waste according to EMF data. The suitability of tested wastes of plant raw materials as sorbents of heavy metals ions is shown.

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