

Досліджено хімічну природу та поверхневі властивості дисперсних наповнювачів рослинного походження: гречаного (ГЛ) та вівсяного (ВЛ) лушпиння, деревного (ДБ) та хвойного (ХБ) борошна. Методом ІЧ-спектроскопії встановлено, що у складі компонентів наповнювачів переважають кисневмісні атомні групи  $-\text{OH}$ ,  $-\text{C}-\text{O}-$ ,  $-\text{C}=\text{O}$ . Виявлено, що на поверхні повітряно-сухих наповнювачів присутній гідроксильно-гідратний шар функціональних груп. Методом потенціометричного титрування водних суспензій за способом Паркса – Бобиренка встановлено, що усі наповнювачі відносяться до типу «поліфункціональне тверде тіло». Показано, що гідроксильно-гідратний поверхневий шар складається з функціональних груп, які мають близькі величини кислотно-основних характеристик. На поверхні наповнювачів додатково виявлені функціональні групи кислотного характеру: на поверхні ГЛ групи з  $\text{pK}_a \approx 4,37-5,66$ , на поверхні БХ групи з  $\text{pK}_a \approx 4,49-4,90$ , а на поверхні ДБ групи з  $\text{pK}_a \approx 3,91-4,30$ . В результаті потенціометричного титрування показано, що кислотність поверхні наповнювачів знижується у ряду  $\text{ДБ} > \text{ХБ} > \text{ГЛ} > \text{ВЛ}$ , який співпадає з рядом, в якому зменшується сумарний вміст целюлози і лігніну та зростає стійкість наповнювачів до термоокислювальної деструкції. Виявлено, що швидкість гідролітичних процесів у водних суспензіях на межі поділу фаз зменшується у ряду  $\text{ВЛ} > \text{ХБ} > \text{ГЛ} > \text{ДБ}$  та оберненопропорційно залежить від концентрації функціональних груп на поверхні наповнювачів, а також, що зміна швидкості гідролітичних процесів на межі поділу фаз в залежності від вмісту наповнювачів описується ступеневими функціями. Встановлено, що для ефективного застосування досліджуваних дисперсних відходів у композиційних матеріалах та в якості адсорбентів для вилучення забруднюючих речовин з рідин необхідні дисперсійні середовища з наступними діапазонами водного показника: для ГЛ –  $\text{pH} > 4,4$ ; ВЛ –  $\text{pH} > 6,4$ ; ДБ –  $\text{pH} > 3,9$ ; БХ –  $\text{pH} > 4,5$ . Отримані результати дозволяють прогнозувати та регулювати кислотно-основні міксофазні взаємодії, а також обґрунтовано підходити до розробки нових ефективних технологій

Ключові слова: рослинні відходи, поверхня, хімічна природа, функціональна група, кислотно-основні характеристики

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# A RESEARCH OF CHEMICAL NATURE AND SURFACE PROPERTIES OF PLANT DISPERSE FILLERS

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## 1. Introduction

Recently, the use of plant disperse fillers has become popular in the development of «green» technologies and materials. The use of waste and processing products of the agricultural and woodworking industries is especial-

ly relevant. Among them, disperse products of processing large-tonnage grain crops: rice [1–3], buckwheat [4–12], oat [9, 10, 13], wheat husk [13]. Products and waste of some crops: flax fiber [14], cotton [15] and sunflower stalks. Wood waste: conifer flour [9, 10], palm [16] and pineapple leaves [17].

It is known that the influence on physical-mechanical, rheological, operational and other characteristics of composite materials is related to many properties of plant disperse fillers. The most important of them are the chemical composition, particle surface size and morphology, pre-treatment method, storage conditions, content and method of addition to the composite. The influence of these factors on the characteristics of filled composites has been studied by many researchers [1, 9, 12]. However, the chemical nature and acid-base characteristics of surface functional groups of particles of plant disperse fillers, which directly affect the interfacial interactions in the composite material and give rise to most of the properties, have not been studied enough. In turn, the chemical nature and characteristics, including acid-base ones, of functional groups of the surface layer of particles are obviously determined by the chemical composition, storage conditions, method of preliminary chemical, physical or mechanical treatment of disperse fillers [2, 9, 12, 18].

Plant disperse fillers are multicomponent amorphous materials, have a complex chemical composition and, obviously, unstable structure and surface properties. Particular attention is needed to study the acid-base properties of the surface. Acid-base characteristics are important because acid-base interactions occur between the functional groups of the filler surface and the matrix during the formation of composites at the interface. This is confirmed by theoretical and experimental studies on the acid-base nature of interfacial interactions in composites [19, 20]. Information on the acid-base characteristics of surface functional groups allows predicting interfacial interactions and controlling the properties of filled composites [21].

The study of the properties of the surface layer of promising plant disperse fillers is one of unresolved chemical and technological problems. In most cases, chemical and physicochemical methods are used for determining the chemical nature and preliminary assessment of the surface properties of filler particles. In order to interpret and find the nature of the particle surface, it is especially important to study the qualitative and quantitative chemical composition of fillers and determine correlations in the «chemical composition – surface properties» system. In this case, it is possible to determine the nature of certain individual atoms or atomic groups that are part of molecules and can potentially be located on the surface and cause both local and general acid-base characteristics. For example, in the composition of functional groups, the individual atoms of oxygen :O=, nitrogen :N≡, sulfur :S= predetermine alkalinity, and the atoms of metals  $Me^{n+}$ , carbon  $\equiv C^+$ , silicon  $\equiv Si^+$  predetermine the Lewis surface acidity. At the same time, some functional groups: hydroxyl –OH, carboxyl –COOH, aldehyde –COH cause the Brønsted surface acidity or alkalinity. In addition, by analogy with inorganic fillers [19–21], water molecules can be adsorbed on the surface, which form a hydroxyl-hydrate layer of the Brønsted functional groups (OH groups) with a wide range of acid-base characteristics. Therefore, in the study of surface properties, the first priority is to determine the qualitative and quantitative chemical composition of plant disperse fillers.

## 2. Literature review and problem statement

Chemical composition and surface properties of some plant disperse materials have been studied in [22–27].

Thus, chromatographic analysis of aqueous, oxalate and alkaline extraction solutions found that buckwheat waste (husk and straw) contains hetero-chain natural polymers –

polysaccharides, as well as uronic acids and some metals [22]. The total yield of polysaccharides ranges within 3.2–6.3 % for husk and 7.6–12.2 % for straw. Polysaccharides found in alkaline extracts have a complex monosaccharide structure and contain rhamnose, arabinose, xylose, mannose, glucose and galactose residues, depending on the type of waste. Uronic acids are contained in all the polysaccharides obtained and are mainly represented by galacturonic acid.

As a result of the chromatographic analysis of water-alcohol extraction solutions, the amino acid composition of rice, buckwheat and sunflower husk was investigated [23]. The total amount of free amino acids in terms of absolutely dry matter was: in the husk of rice – 0.06 wt. %, buckwheat – 0.05 wt. %, sunflower – 0.08 wt. %. The qualitative composition of essential amino acids of the husk is represented by valine and leucine in rice and sunflower, leucine in buckwheat. The qualitative composition of nonessential amino acids of the husk is represented by aspartic and glutamic acids in rice, serine, phosphoserine and aspartic acid in buckwheat, asparagine, glutamic and  $\gamma$ -aminobutyric acids in sunflower. In addition, the analysis of the results shows that the husk of all the studied crops also contains urea in the amount of  $4 \cdot 10^{-5}$ ,  $1 \cdot 10^{-5}$ ,  $8 \cdot 10^{-5}$  g/kg in the rice, buckwheat and sunflower husk, respectively.

The authors [24, 25] investigated the qualitative and quantitative chemical composition of inorganic components of husk and straw of rice, oat, sunflower and buckwheat. The total amount of ash obtained after waste firing at a temperature of 400–650 °C is: oat – 3.5–5.1 wt. %, rice – 6–22 wt. %, buckwheat – 1.7–5.8 wt. %. The authors note that the main component of waste ash of rice and oat is  $SiO_2$ , and waste ash of buckwheat and sunflower consists mainly of carbonates of alkali and alkaline earth metals. In terms of acid-base characteristics, the content of oxides of different chemical nature in waste ash is interesting (Table 1).

Table 1 shows that in terms of the content of inorganic oxides in the ash, the highest acidity is characteristic of the husk and straw of rice and oat, buckwheat waste has alkaline properties, and sunflower husk and straw have amphoteric or slightly alkaline character.

In [22, 24], the chemical composition of inorganic components of buckwheat and oat waste extracts was investigated. In aqueous, oxalate and alkaline extracts of buckwheat husk and straw, ions of alkali and alkaline earth metals  $Mg^{2+}$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Na^+$  (1–1000 mg/cm<sup>3</sup>) and transition elements  $Mn^{2+}$ ,  $Fe^{3+}$ ,  $Zn^{2+}$ ,  $Cu^{2+}$ ,  $Si^{4+}$ ,  $Al^{3+}$  (0.04–9 mg/cm<sup>3</sup>) were found [22]. Aqueous extracts are characterized by a high content of  $K^+$  (120–1060 mg/cm<sup>3</sup>),  $Na^+$  (7–20 mg/cm<sup>3</sup>),  $Ca^{2+}$  (1–2 mg/cm<sup>3</sup>),  $Mg^{2+}$  (20–70 mg/cm<sup>3</sup>),  $Zn^{2+}$  (1–4.5 mg/cm<sup>3</sup>),  $Mn^{2+}$  (0.7–8.5 mg/cm<sup>3</sup>),  $Fe^{3+}$  (0.2–6.2 mg/cm<sup>3</sup>) ions. All of the above ions are found in aqueous and acidic extracts of oat husk and straw. Aqueous extracts are characterized by a high content of  $K^+$  (80 mg/cm<sup>3</sup>),  $Mg^{2+}$  (3 mg/cm<sup>3</sup>),  $Ca^{2+}$  (5 mg/cm<sup>3</sup>),  $Na^+$  (6 mg/cm<sup>3</sup>) ions and small amounts of  $Si^{4+}$ ,  $Zn^{2+}$ ,  $Cu^{2+}$ ,  $Mn^{2+}$ ,  $Fe^{3+}$  ions [24]. It should be noted that, compared to water, when using 0.1*n* and 1*n* aqueous solutions of strong acids (HCl,  $H_2SO_4$ ), the amount of substances entering the extract increases 2–5 times. The acidity of the extractant practically does not affect the amount of extracted  $Si^{4+}$ ,  $K^+$ ,  $Na^+$  ions. At the same time, the presence of strong acid ions allows increasing the amount of extracted  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Zn^{2+}$ ,  $Cu^{2+}$ ,  $Mn^{2+}$ ,  $Fe^{3+}$ ,  $Al^{3+}$  ions 10–30 times. Increasing the acid extractant concentration also contributes to an increase in the content of extracted substances in the extracts.

Table 1

Chemical composition of ash of disperse organic fillers (according to [24])

Oxide	Oxide content in husk and straw, wt. %			
	buckwheat	rice	oat	sunflower
Acid oxides				
SiO <sub>2</sub>	1.7–4.0	91.7–95.5	62.1–69.8	1.5
Total average acid oxide content	2.9	93.6	66.0	1.5
Oxides of alkaline and alkaline earth metals				
K <sub>2</sub> O	22.0–43.0	4.3–7.3	2.4–4.1	29.9
Na <sub>2</sub> O	0.1–0.7	0.1–0.6	0.2–0.6	1.9
CaO	1.0–2.9	0.2–1.0	3.2–11.7	10.4
MgO	6.2–16.7	0.4–0.6	3.5–4.6	11.4
Total average alkaline oxide content	11.6	1.8	15.3	13.4
Oxides of amphoteric elements				
Fe <sub>2</sub> O <sub>3</sub>	0.1–0.4	0.1–0.2	0.1–1.8	0.2
Al <sub>2</sub> O <sub>3</sub>	0.2–0.3	0.1–0.2	0.1–2.0	0.1
MnO	0.1–0.3	0.1–0.2	0.1–0.2	0.3
ZnO	0.06–0.12	0.01–0.03	0.02–0.06	0.06
CuO	0.004–0.030	0.001–0.002	0.004–0.008	0.04
Cr <sub>2</sub> O <sub>3</sub>	0.02–0.03	–	–	0.004
Ni <sub>2</sub> O	0.005–0.009	–	–	–
Total average amphoteric oxide content	0.03	0.12	0.47	0.12

The authors of [26] found soluble amino acids, ascorbic and folic acids, riboflavin, nicotinamide in aqueous extracts of oat straw.

It is known that buckwheat waste contains organic dyes of complex chemical structure, which obviously have a significant effect on the acid-base nature of the particle surface. The authors of [27] have developed an effective complex technology for extracting organic dyes and biologically active substances by complex aqueous acid extractants from buckwheat husk using liquefied carbon dioxide. It was found that the rate of extraction significantly increases with increasing temperature and degree of waste dispersion.

The main components of crop waste are cellulose polysaccharide (30–50 %) and a mixture of aromatic lignin polymers (20–30 %) [9, 18, 28, 29]. Using simple technologies, natural polymer materials are obtained – pulp, hydrolyzed lignin, which can be used as fillers and adsorbents [11, 12, 30, 31]. Cellulose and lignin do not dissolve or hydrolyze in water due to high molecular weight and formation of numerous intra- and intermolecular bonds. Polymer molecules contain a large number of different functional groups with a wide range of acidity, which upon reaching the surface determine the acid-base characteristic.

The information indirect method of surface characterization is the study of the sorption properties of disperse filler particles with respect to substances of different chemical nature [32–36]. The presence of functional groups and the acid-base nature of the surface of plant disperse waste were found in [32], which investigated the sorption properties of buckwheat and sunflower husk in relation to various organic and inorganic reagents. Pre-treatment by the acid-alkaline method has shown to increase the adsorption capacity of husk particles of both species 2–3 times. In [33, 34], kinetic patterns of adsorption on the surface of disperse materials are considered. All the above works studied the chemical nature of organic and inorganic compounds, which are part

of many popular plant wastes. And thanks to these studies, it is possible to get a fairly complete picture of the chemical composition of plant disperse materials. However, when using waste as fillers for composite materials, information about the surface properties of disperse particles, namely, the acid-base nature of surface functional groups that can interact with the material matrix, is essential. However, this issue is not considered in the presented studies. This may be due to the complexity of interpreting the results of experimental studies of the above disperse fillers by known physicochemical methods. This is because due to the natural origin of plant waste, the chemical composition and surface properties of filler particles are significantly dependent on many factors such as climatic conditions of plant cultivation, chemical treatment methods (pesticides, fertilizers, herbicides, etc.), features of processing technology to obtain the target product, storage conditions and methods of waste preparation for reuse. Also, the absence of the above studies can be explained by the fact that non-chemical interfacial interactions, which are considered to significantly affect the characteristics of composites are often neglected in the development of filled composites.

Earlier, the work [18] investigated the chemical composition, physicochemical, morphological and surface properties of disperse fillers on the basis of plant raw materials: buckwheat and oat husk, wood and conifer flour. The acid-base properties of the particle surface were studied using the potentiometric method of A. P. Nechiporenko. Patterns of changes in surface acid-base properties from the chemical composition and physicochemical characteristics of fillers are revealed. But the results provide only a generalized rough assessment of the acid-base properties of the filler surface and do not give an idea of the chemical structure and properties of functional surface groups. In addition, the results do not take into account the specific surface area of the fillers, i. e. do not give an idea of the concentration of functional groups per unit surface area of the disperse particle.

Thus, the issue of studying the chemical nature and acid-base characteristics of surface functional groups of plant disperse fillers remains unresolved. There is also little knowledge of the relationship between the acid-base characteristics of surface functional groups, chemical nature and quantitative content of organic and inorganic components of fillers.

### 3. The aim and objectives of the study

The aim of the study is to investigate the chemical nature and acid-base characteristics of surface functional groups of disperse fillers on the basis of plant raw materials of buckwheat (BH) and oat (OH) husk, wood (WF) and conifer (CF) flour. This will allow predicting and regulating the acid-base interactions between the filler surface and the dispersion medium.

To achieve the aim, the following objectives are formulated:

- using the IR spectroscopy method, to determine the chemical nature of functional groups and using potentiometric titration of aqueous suspensions to investigate the acid-base properties of the surface of plant disperse fillers;
- to investigate the relationship between the acid-base properties of surface functional groups, chemical nature and quantitative content of organic and inorganic components in the fillers;
- to formulate practical recommendations for the effective use of plant disperse fillers.

### 4. Materials and methods of the study

As materials for the study, disperse waste from the processing of multi-tonnage agricultural products and woodworking industry were selected. This is buckwheat (BH) and oat (OH) husk. For comparative characterization, wood (WF) and conifer (CF) flour is selected. The materials were milled and dried under the same conditions in an oven at 105 °C.

IR spectroscopy was used to study the chemical structure of filler components. Spectrograms were obtained on a SPECORD 75 UR spectrophotometer (Germany) at a temperature of 293–298 K in the wavenumber range of 4,000–500  $\text{cm}^{-1}$  with the following settings: monochromator slit width – 3 nm, recording time – 13.2 minutes, and time constant of recorder pen deviation – 1 second. Samples for IR spectra were prepared as pellets of filler powder and KBr with a filler weight content of about 1 %.

Potentiometric titration of aqueous suspensions of fillers according to the Parks-Bobyrenko method [37] was carried out at room temperature of 293–298 K using a portable SX 711 pH meter (China) with the measurement accuracy of hydrogen index  $\pm 0.001$  pH. In accordance with the method, the pattern of changes in the suspension pH during titration was investigated. Given that the investigated fillers are characterized by an acidic or weakly acidic surface [18], an alkaline solution of KCl is chosen as the electrolyte, and a 0.1 M HCl solution is chosen as the titrant. First, a blank experiment was conducted.  $25 \cdot 10^{-5} \text{ dm}^3$  of original alkaline electrolyte (0.1 M aqueous KCl solution with  $\text{pH}_0 \approx 10$ , the value of which was regulated by the addition of 0.1 M NaOH solution) were added to the potentiometric cell with glass and chloride silver electrodes. After stabilizing the potential of the glass electrode (after 2–3 minutes with continuous stirring with a magnetic stirrer), the solution was

titrated with 0.1 M HCl solution to reach the titration end point. The titrant was added in small portions of  $2 \cdot 10^{-5} \text{ dm}^3$  every 2–3 minutes after stabilizing the pH of the suspension. After that, a working titration was carried out.  $25 \cdot 10^{-5} \text{ dm}^3$  of 0.1 M aqueous KCl solution and a sample of the studied filler (0.10; 0.25; 0.50 g) were added to the potentiometric cell. The suspension was stirred with a magnetic stirrer until the pH was stabilized and the  $\text{pH}_{\text{susp}}$  value was recorded. The suspensions were then titrated as in the blank experiment.

According to the titration results, the amount of excessively adsorbed OH ions on the surface of the fillers ( $\Delta G$ ,  $\text{mol/m}^2$ ) was calculated using the improved formula:

$$\Delta G = \Delta \text{pH} \cdot \Delta V \cdot C / m \cdot S, \quad (1)$$

where  $\Delta \text{pH} = \text{pH}_0 - \text{pH}_{\text{susp}}$  is the change in the suspension pH as a result of hydrolytic adsorption;  $\Delta V$  is the volume of titrant added,  $\text{dm}^3$ ;  $C$  is the concentration of HCl (titrant) solution,  $\text{mol/dm}^3$ ;  $m$  is the filler sample, g;  $S$  is the specific surface area of the filler,  $\text{m}^2/\text{g}$  (the factor added to account for the concentration of functional groups per unit surface area of the filler); specific surface area values of the fillers are 0.68; 0.75; 1.20 and  $0.92 \text{ m}^2/\text{g}$  for BH, OH, WF and CF, respectively [18].

According to the constructed graphs  $\text{pH}_{\text{susp}} = f(V)$  and  $\Delta G = f(\text{pH}_0)$ , the following characteristics and values were determined:

- 1) by the nature of the graph  $\Delta G = f(\text{pH}_0)$ , the chemical nature of surface functional groups was evaluated according to the classification [37]: polyfunctional solid, monofunctional strong alkali, bifunctional surface with strong and weak alkaline groups; solid with a weakly alkaline surface;
- 2)  $\text{pH}_{\text{eq}}$  – the pH of the suspension, at which adsorption of an equal number of  $\text{H}^+$  and  $\text{OH}^-$  ions on the filler surface occurs; defined as the intersection point of the potentiometric titration curves of the electrolyte solution (blank experiment) and the suspension (working titration) on the graph  $\text{pH}_{\text{susp}} = f(V)$ ;
- 3)  $\text{pH}_{\text{IIP}}$  – the pH of the suspension at the isoadsorption (isoionic) point, which indicates the preference of surface functional groups with a certain acid-base characteristic ( $\text{p}K_a$ ); defined as the intersection point of three graphs  $\text{pH}_{\text{susp}} = f(V)$  for different filler samples and, to obtain a more accurate value, as the intersection point of the graph  $\Delta G = f(\text{pH}_0)$  with the abscissa axis, that is, at  $\Delta G = 0$ ;  $\text{pH}_{\text{IIP}}$  was thought to indicate the preference of surface functional groups with  $\text{p}K_a$ , that is,  $\text{pH}_{\text{IIP}} \approx \text{p}K_a$ ;
- 4)  $v$  – the value of the exchange capacity of surface functional groups of the filler (characteristic of the speed of hydrolytic processes at the interface), defined as the slope of the straight line  $\Delta G = f(\text{pH}_0)$ , i. e. the value of the factor  $k$  in the equation  $\Delta G = k \cdot \text{pH}_0 \pm b$ .

### 5. Experimental results of the study of the chemical nature of components and acid-base surface properties of plant disperse fillers by IR spectroscopy and potentiometric titration of aqueous suspensions

Using the IR spectroscopy method, the chemical structure of functional groups included in the compounds – filler components before and after heat treatment at  $T = 523 \text{ K}$  for 2 hours was investigated. The resulting filler spectrograms are presented in Fig. 1.

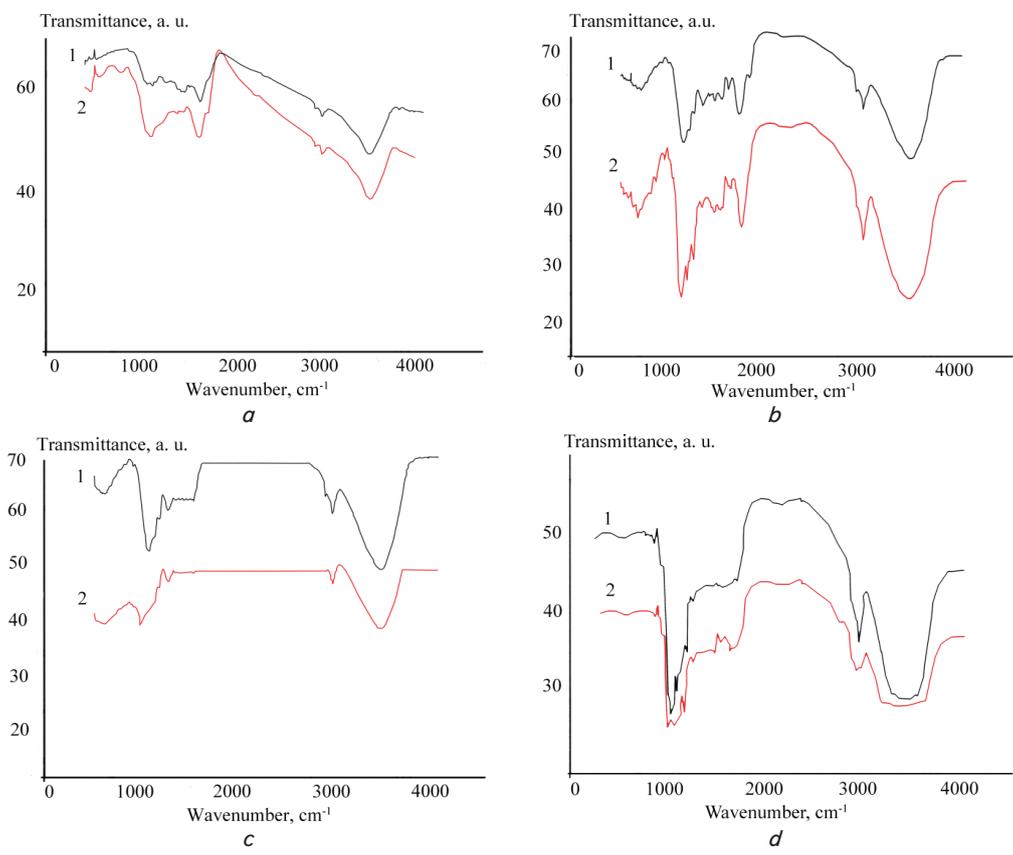


Fig. 1. Spectrograms: a – BH, b – OH, c – WF, d – CF: 1 – without treatment, 2 – after heat treatment

As noted earlier [18], to estimate the degree of integral (total) acidity of a solid surface, it is quite convenient to use the theory of «surface isostate». Surface isostate is defined as the equilibrium steady state of inertia of a solid surface in a suspension, which is characterized by the absence of mass transfer of charged ions at the interface [37]. The isostate is quantified by the isopoint in which the equilibrium between the solid surface ions and the liquid phase ions is maintained for some time. From the point of view of mass, the isoadsorption state (point of zero charge PZC) arises, and from the point of view of charge – the isoelectric state (isoelectric point IEP). The pH value in the isopoint indicates the preference of surface functional groups with a certain acid-base characteristic, which is reflected by the  $pK_a$  index.

In [18], the isoadsorption state and pH of aqueous suspensions at the isoionic point for buckwheat husk (BH), oat husk (OH), wood flour (WF) and conifer flour (CF) were in-

vestigated by the potentiometric method of A.P. Nechiporenko. Two types of functional groups are found on the surface of GL: weakly acidic and neutral. The OH surface is close to neutral. The surfaces of WF and CF have a general weakly acidic nature. It was found that the integral acidity of the filler surface decreases in the CF>WF>BH>OH series. It was found that, with the exception of CF, the surface acidity is directly proportional to the total content of cellulose and lignin in the fillers.

In order to expand the understanding of the properties of the isoadsorption state of aqueous suspensions and determine the acid-base characteristics of surface functional groups of the above-mentioned fillers, studies were performed by the Parks-Bobyrenko potentiometric titration method. Using the improved formula (1), the amount of excessively adsorbed OH ions on the surface was calculated.

Fig. 2–5 show the graphs  $pH_{susp}=f(V)$  and  $\Delta G=f(pH_0)$ , obtained by titration of aqueous suspensions of the fillers.

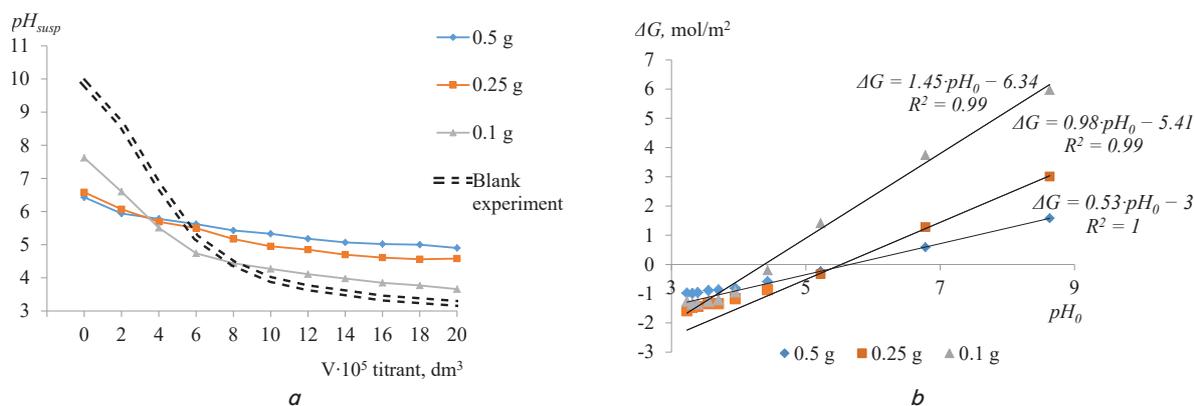


Fig. 2. Graphs: a –  $pH_{susp}=f(V)$ , b –  $\Delta G=f(pH_0)$  for titration of aqueous suspension of BH

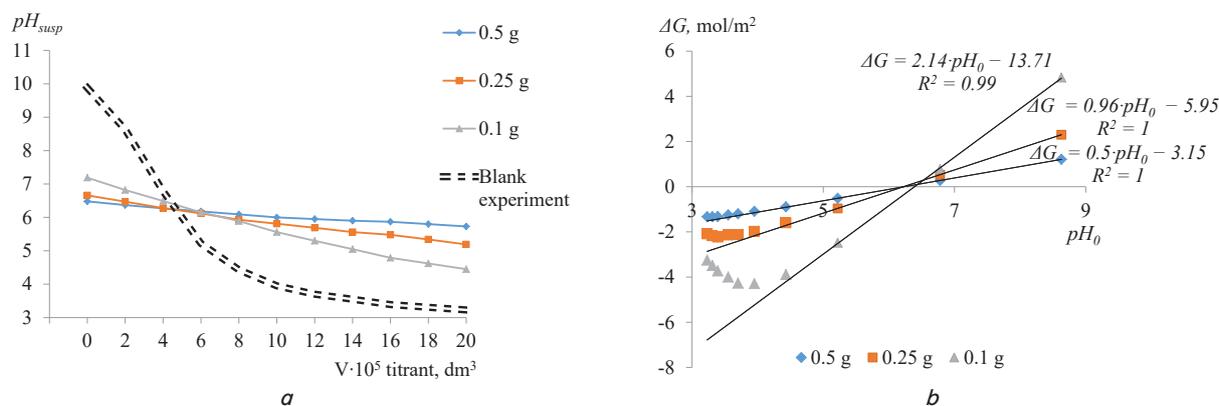


Fig. 3. Graphs:  $a - \text{pH}_{\text{susp}} = f(V)$ ,  $b - \Delta G = f(\text{pH}_0)$  for titration of aqueous suspension of OH

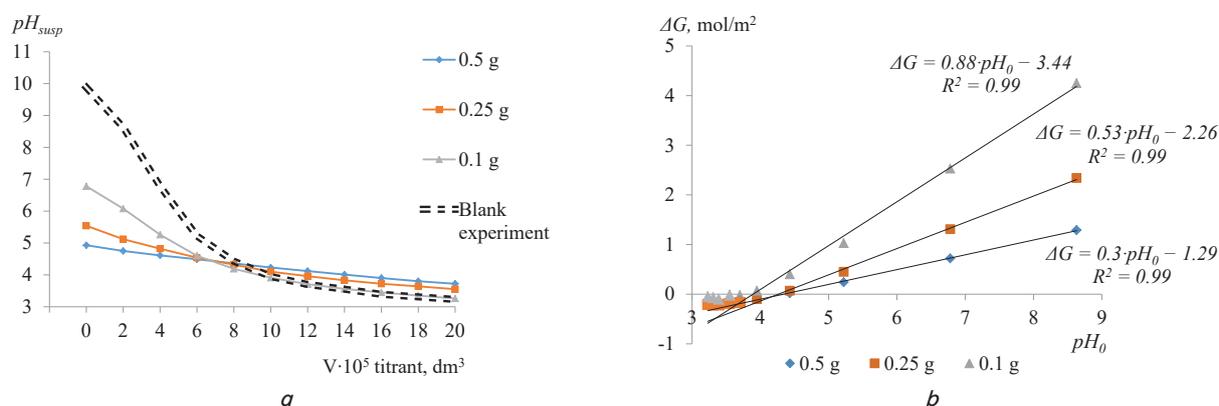


Fig. 4. Graphs:  $a - \text{pH}_{\text{susp}} = f(V)$ ,  $b - \Delta G = f(\text{pH}_0)$  for titration of aqueous suspension of WF

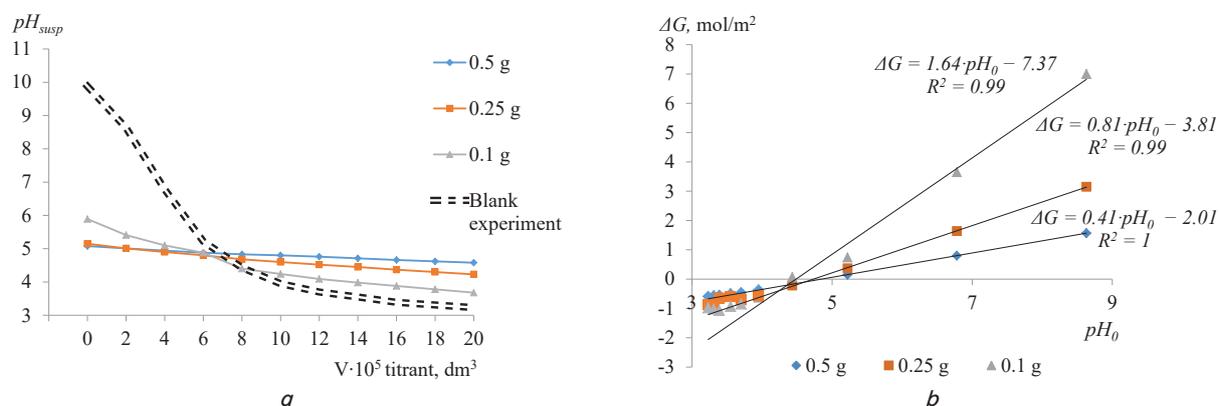


Fig. 5. Graphs:  $a - \text{pH}_{\text{susp}} = f(V)$ ,  $b - \Delta G = f(\text{pH}_0)$  for titration of aqueous suspension of CF

The graphs  $\text{pH}_{\text{susp}} = f(V)$  (Fig. 2–5,  $a$ ) are titration curves that reflect the change in the hydrogen index of aqueous suspensions as a portion of the titrant is added. The curves shown are based on the average  $\text{pH}_{\text{susp}}$  values calculated from the results of three parallel experiments.

## 6. Discussion of the results of the study of the chemical structure and acid-base properties of the surface of plant disperse fillers

Analysis of the IR spectra of all fillers revealed the absorption bands, characteristic of cellulose-containing materials.

Thus, the intense absorption band in the region of  $3,200\text{--}3,500\text{ cm}^{-1}$  is caused by valence vibrations of  $-\text{OH}$  groups

involved in hydrogen bonds, the band at  $3,000\text{--}2,800\text{ cm}^{-1}$  – valence vibrations of the bonds in  $-\text{CH}$  and  $-\text{CH}_2$  hydrocarbon groups, and at  $1,735\text{--}1,740\text{ cm}^{-1}$  – valence vibrations of  $-\text{C}=\text{O}$  groups. Absorption at  $1,160$ ,  $1,107$ ,  $1,060$  and  $1,033\text{ cm}^{-1}$  is caused by valence vibrations of  $-\text{C}-\text{O}-$  ether bonds, and at  $900$  and  $663$  – deformation vibrations of  $-\text{C}-\text{H}$  bonds. Absorption at  $1,630$  and  $1,650\text{ cm}^{-1}$  is caused by the presence of bound water in the fillers. After heat treatment, there is a significant decrease in the intensity of this band. Skeletal vibrations of the aromatic lignin ring appear at  $1,605$ ,  $1,510\text{ cm}^{-1}$ . The absorption band with a maximum at  $1,033\text{ cm}^{-1}$ , which relates to deformation vibrations of the  $-\text{C}-\text{O}$  bond in cellulose or hemicellulose, is equally strongly pronounced in the spectra of the original samples of all the fillers.

It is found that after heat treatment, there is a decrease in the intensity of the bands 3,600–3,100  $\text{cm}^{-1}$ , which are responsible for  $-\text{OH}$  valence vibrations with a maximum at 3330  $\text{cm}^{-1}$ , involved in the hydrogen bonding system and associated with the presence of moisture on the surface of all fillers. Thus, the presence of a hydroxyl-hydrate layer on the surface of the filler particles is obvious. It is also apparent that the functional groups of the hydroxyl-hydrate surface layer determine the acid-base interactions at the interface.

The differences in the chemical structure of BH and OH in comparison with WF and CF include the presence of a broad band of skeletal vibrations of functional groups with aromatic fragments in the region of 1,614–1,570  $\text{cm}^{-1}$ , which cause an increase in the thermal stability of these fillers. At the same time, the total amount of aromatic component for BH is higher compared to OH, which in turn may lead to increased thermal stability: thermal breakdown of BH begins only after  $T > 493$  K, and OH – after  $T > 473$  K. At the same time, thermal breakdown of WF and CF begins already at  $T > 433$ – $443$  K [18].

Thus, the analysis of the IR spectra of the fillers leads to the following conclusions:

- spectral analysis revealed that among the atomic groups included in the components of the fillers and, apparently, determining the acid-base properties, the oxygen-containing groups  $-\text{OH}$ ,  $-\text{C}-\text{O}$ , and  $-\text{C}=\text{O}$  predominate; these atomic groups may in turn be within more complex functional groups such as carboxyl, complex ether or aldehyde;

- it is found that BH and OH contain aromatic compounds that increase the thermal stability of these fillers;

- the decrease in the intensity of the bands responsible for valence vibrations of  $-\text{OH}$  groups with hydrogen bonds after heat treatment indicates the presence of a considerable amount of adsorption water on the surface of air-dry fillers, which forms the hydroxyl-hydrate surface layer of the Brønsted functional groups;

- given the diverse chemical composition of plant fillers, it can be assumed that the Brønsted functional groups with a wide range of acid-base characteristics are present on the surface of the particles.

By the nature of the graphs  $\Delta G = f(\text{pH}_0)$  (Fig. 2–5, *b*) and according to the classification [37], all the investigated fillers are of the «polyfunctional solid» type. This is indicated by

the nature of the graph with two sections: the linear section of positive values of  $\Delta G$  and the nonlinear section of negative values of  $\Delta G$ . The region of positive values characterizes the process of adsorption of  $\text{OH}^-$  ions on the surface of fillers in suspensions with a certain hydrogen index  $\text{pH}_0$ . The number of adsorbed ions increases in direct proportion with increasing  $\text{pH}_0$ , that is, with increasing concentration of  $\text{OH}^-$  ions in the solution. The linearity of this section of the graph is due to the fact that at these  $\text{pH}_0$  values, the adsorption of  $\text{OH}^-$  ions mainly occurs in the suspensions, the rate of which is the highest in comparison with other hydrolytic processes. The approximation was carried out for these sections of the graphs. After crossing the abscissa axis at the isoadsorption point ( $\text{pH}_{\text{IIP}}$ ), the graph loses linearity and the nonlinear section of negative values of  $\Delta G$  appears. Thus, it can be argued that in the area of positive values of  $\Delta G$ , the adsorption process on the surface of the fillers in aqueous suspensions is dominant and actively occurs in the range of the hydrogen suspension index  $\text{pH}_0 > \text{pH}_{\text{IIP}}$ . The nonlinearity of the graph in the region of negative values of  $\Delta G$  is obviously due to the fact that in addition to the adsorption of  $\text{OH}^-$  ions, other hydrolytic processes are intensified. The adsorption processes of  $\text{OH}^-$  ions slow down. As the concentration of  $\text{H}^+$  ions increases, that is, the hydrogen index decreases, processes of desorption of  $\text{OH}^-$  ions and competitive adsorption of  $\text{H}^+$  ions occur. In addition, with increasing acidity of the medium, extraction processes may occur, the possibility of which is noted in [26, 27].

On solid surfaces of the «polyfunctional solid» there are no adsorbed impurities, the dissociation degree of which exceeds the dissociation degree of surface functional groups of the filler itself and can change the chemical equilibrium at the interface [37]. This means that all hydrolytic processes that are observed during the titration of suspensions occur at the interface and reflect the acid-base characteristics of surface functional groups of the fillers. It is also apparent that the definition of the investigated fillers as «polyfunctional solids» indicates that there is a hydroxyl-hydrate layer of functional groups with close values of acid dissociation constants  $\text{p}K_a$  on the surface of the particles.

Table 2 presents the results of the calculation of the characteristics of aqueous suspensions of fillers according to the obtained graphs of potentiometric titration  $\text{pH}_{\text{susp}} = f(V)$  and  $\Delta G = f(\text{pH}_0)$ .

Table 2

Characteristics of aqueous suspensions of fillers

Filler	Sample <i>m</i> , g	$\text{pH}_{\text{eq}}$ (Parks-Bobyrenko method)	$\text{pH}_{\text{eq}}$ (Nechiporenko method) [18]	$\text{pH}_{\text{IIP}}$ (Parks-Bobyrenko method)	$\text{pH}_{\text{IIP}}$ (Nechiporenko method) [18]	$\nu$
BH	0.10	4.43	5.53 6.16	4.37	5.83 6.30	1.45
	0.25	5.50		5.52		0.98
	0.50	5.62		5.66		0.53
OH	0.10	6.49	6.15 6.30	6.41	6.18 6.32	2.14
	0.25	6.28		6.22		0.96
	0.50	6.27		6.30		0.50
WF	0.10	5.56	5.29	3.91	5.52	0.88
	0.25	5.93		4.26		0.53
	0.50	6.09		4.30		0.30
CF	0.10	5.89	5.02	4.49	5.36	1.64
	0.25	6.12		4.70		0.81
	0.50	6.18		4.90		0.41

Table 2 shows that the use of the Parks-Bobyrenko potentiometric titration method in comparison with the Nechiporenko method provides refined  $\text{pH}_{\text{eq}}$  and  $\text{pH}_{\text{HP}}$  values. The method further revealed acidic functional groups on the surface of the fillers. So, groups with  $\text{p}K_a \approx 4.37\text{--}5.66$  on the BH surface, groups with  $\text{p}K_a \approx 4.49\text{--}4.90$  on the CF surface, and groups with  $\text{p}K_a \approx 3.91\text{--}4.30$  on the WF surface are detected. This is due to the fact that, first, the Nechiporenko method provides a general (integral) acid-base characteristic, which indicates the acidity of the functional groups that prevail on the surface. Thus, it can be argued that the number of acidic groups detected on the surface of the fillers is small and the effect of these groups on the overall acid-base character is negligible. secondly, only one sample of the fillers ( $\sim 0.2$  g) was investigated by the Nechiporenko method, and three samples (0.1; 0.25 and 0.5 g) were used in the potentiometric titration method, which yielded refined results. In general, according to the results of potentiometric titration, the surface acidity of the fillers decreases in the  $\text{WF} > \text{CF} > \text{BH} > \text{OH}$  series [18]. This series completely coincides with the one in which the total cellulose and lignin content in the investigated fillers decreases and the resistance of the fillers to thermal-oxidative breakdown increases [18]. Therefore, on the basis of the above, it can be concluded that the Parks-Bobyrenko potentiometric titration method is more informative for investigating the acid-base characteristics of the surface of plant disperse fillers.

Potentiometric titration of the three filler samples made it possible to determine the exchange capacity of the surface functional groups of the fillers, that is, the velocity characteristic of the hydrolytic processes on the surface  $v$ . This value was defined as the slope of the straight line  $\Delta G = f(\text{pH}_0)$  to the abscissa axis or as the value of the  $k$  factor in the equation  $\Delta G = k \cdot \text{pH}_0 \pm b$  (Table 2). The results show that the rate of hydrolytic processes at the interface in aqueous phase suspensions decreases in the  $\text{OH} > \text{CF} > \text{BH} > \text{WF}$  series and depends on the concentration of functional groups on the surface of the fillers. It is shown that the decrease in the concentration of functional groups increases the rate of interfacial hydrolytic processes. These data correlate with the specific surface area values of the fillers and with the time of equilibrium establishment in the suspensions [18]. The specific surface area and the time of equilibrium establishment in the suspensions of the fillers are reduced in the  $\text{WF} > \text{CF} > \text{OH} > \text{BH}$  series.

It is known that the rate of adsorption processes in aqueous suspensions of inorganic adsorbents, depending on the content of the disperse phase, varies by step functions [34, 35, 38]. Approximation of the obtained dependencies, even with limited data, revealed that on the surface of plant disperse fillers, this dependency is also described by equations of step functions (Fig. 6).

The obtained graphs show that in the aqueous suspensions of all studied plant disperse fillers, hydrolytic processes occur at the interface according to the same patterns. The rate of hydrolytic processes in aqueous suspensions decreases with increasing weight (content) of disperse fillers, which does not contradict the results of studies by other authors [35, 38].

Thus, the results obtained provide more complete information about the acid-base properties of the surface of the investigated fillers, which in turn allows predicting and regulating the interfacial interactions in disperse systems. Plant disperse waste is actively used to create composite materials, both in water-based concretes [4] and in organic-based polymers [1–7, 12–16]. These wastes can also be used

as adsorbents for removing contaminants from aqueous and organic liquid media [32–36]. In both cases, reliable information on the possible limits of using a particular disperse material is needed to create effective technologies. This is due to the need to provide the most intense acid-base interfacial interactions, which in the first case provides improved properties of composites, and in the second – effective removal of contaminants. It is found that the following ranges of the hydrogen index of dispersion media are required for the effective application of the investigated disperse waste in composites and as adsorbents: for BH –  $\text{pH} > 4.4$ ; OH –  $\text{pH} > 6.4$ ; WF –  $\text{pH} > 3.9$ ; CF –  $\text{pH} > 4.5$ . It should be noted that the higher the hydrogen index of the dispersion medium, the more intense the interface processes are. Also, as the graphs show, these limits may vary somewhat depending on the content of fillers in suspensions and further studies are needed to determine these limits. Considering the peculiarities of the experiments conducted (in aqueous suspensions), these recommendations are more suitable to apply in aqueous dispersion media. With some assumptions, they can also be used in organic low-polar media, but in this case additional experimental studies are required for effective use.

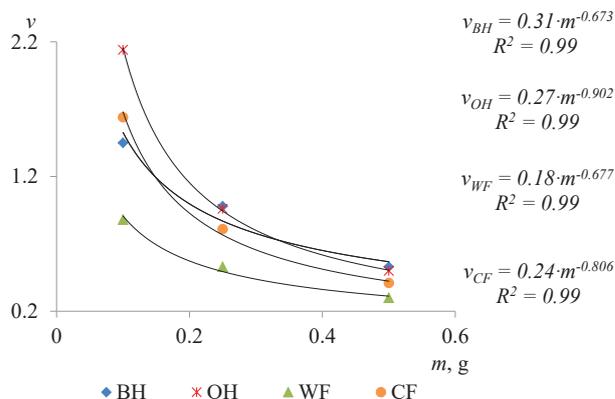


Fig. 6. Dependency of the rate of hydrolytic adsorption at the interface on the content of fillers in aqueous suspensions

## 7. Conclusions

1. Experimental studies of the chemical nature and surface properties of plant disperse fillers – buckwheat husk, oat husk, wood flour and conifer flour were carried out. IR spectroscopy studies revealed absorption bands characteristic of cellulose-containing materials. It is found that among the atomic groups, which are part of the filler components and determine the acid-base surface properties, the oxygen-containing groups  $-\text{OH}$ ,  $-\text{C}-\text{O}-$  and  $-\text{C}=\text{O}$  predominate. The atomic groups may in turn be within more complex functional groups such as carboxyl, complex ether or aldehyde. It is found that on the surface of air-dry fillers there is a hydroxyl-hydrate surface layer of the Brønsted functional groups with a wide range of acid-base properties.

2. Using the method of potentiometric titration of aqueous suspensions by the Parks-Bobyrenko method, the acid-base characteristics of surface functional groups of fillers were investigated. It was found that all the investigated fillers are of the «polyfunctional solid» type. Hydrolytic adsorption processes observed during titration of suspensions occur at

the interface and reflect the acid-base characteristics of surface functional groups. The hydroxyl-hydrate surface layer of the fillers is shown to consist of functional groups with close values of acid dissociation constants. Functional groups of acid character were additionally found on the surface of the fillers: groups with  $pK_a \approx 4.37$ – $5.66$  on the BH surface, groups with  $pK_a \approx 4.49$ – $4.90$  on the CF surface, and groups with  $pK_a \approx 3.91$ – $4.30$  on the WF surface. In general, the potentiometric titration results show that the acidity of the filler surface decreases in the  $WF > CF > BH > OH$  series. This series completely coincides with the one in which the total cellulose and lignin content decreases and the resistance of fillers to thermal-oxidative breakdown increases. It is found

that the change in the rate of hydrolytic processes in suspensions at the interface depending on the content (weight) of fillers is described by step functions. It is found that the rate of hydrolytic processes decreases in the  $OH > CF > BH > WF$  series and inversely depends on the concentration of functional groups on the surface of the fillers.

3. It is found that for the effective use of the investigated disperse waste in composite materials and as adsorbents for the removal of contaminants from liquids, dispersion media with the following ranges of hydrogen index are required: for  $BH - pH > 4.4$ ;  $OH - pH > 6.4$ ;  $WF - pH > 3.9$ ;  $CF - pH > 4.5$ . In this case, it is advisable to use dispersion media with the largest possible values of the hydrogen index.

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