

Research Article

Biomodification of Flax Fibrous Materials for Increase of Sorption to Organic Compounds

S. A. Koksharov, S. V. Aleeva, and O. V. Lepilova 

G.A. Krestov Institute of Solution Chemistry of the Russian Academy of Sciences, Scientific-Innovative Department, 153045 Ivanovo, Russia

Correspondence should be addressed to O. V. Lepilova; lov@isc-ras.ru

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This paper was focused on the method to increase of the sorption properties in the flax fibrous material. This method was based on the original approach which includes the application of enzymatic catalysis as a destruction regulator of the polycarbohydrate components in the bast. The formed reaction products were used as reagents for reductive destruction of lignin. The changes in the fiber sorption capacity to the molecular markers were controlled after changing both the polymer composition of the fiber and the size of its pore. It was determined that the flax sorbents increase the adsorption of phenol vapors to 9–12 times and organic dyes from aqueous solutions to 4 times.

1. Introduction

The problem of environmental pollution a the global significance because huge amounts of industrial emissions containing the heavy metal ions, petroleum products, compounds which are formed after organic synthesis, and many other toxic chemicals polluting the water resources, soil, and atmosphere. Therefore, addressing the problems of environmental protection includes purification of the wastewater and air emissions and requires elaboration sorbents for providing both high effectiveness and low cost.

Sorbents from synthetic and natural materials and their modified analogs are widely used for purification of the wastewater. It is known that after using these materials, the degree of purification determined by the sorption method is about 80–95% and depends on the chemical nature of the sorbing agent, its structure and composition, the specific surface area, the pore sizes, and its accessibility for sorption of pollutions. Synthetic sorbents have high sorption properties, but they are much costlier and as well require complex purification methods for reuse and special conditions of burial due their low ability to biodegrade naturally. Natural sorbents are widely used for removal of impurities from water such as the pesticides, dyes, surfactants, and many inorganic and toxic organic chemicals [1, 2]. The main advantage of the natural

sorbents is the low cost allowing in some causes to abandon the regeneration and simplify exploitation.

The textiles made from fibrous plant raw materials are perspective to creation of high-effective sorbents. For example, the sorbents made of nonwoven materials are the leaders in the purification of wastewater and air emissions. The easiness during manufacturing and technical realization during purification are the advantages of the fibrous sorbents from nonwoven materials. In addition, the main advantage of the sorbents produced from then plant raw material has a high level of cation-exchange capacity. Numerous scientific publications present examples of the successful extraction of the toxic metals ions of Hg, Pb, Cd, Cu, Zn, and Ni from wastewater when the biosorbents were produced from sawdust [3], fruit pulp [4], fruits of date and banana tree, palms, and papaya [5, 6], rice husk [7], and other plant materials. The level of their sorption capacity can reach very high values for metal ions of Cu, Co, Pb, and Hg in $\text{mg}\cdot\text{g}^{-1}$ of about 243.9, 322.6, 252.38, and 120.62, respectively [8]. It is comparable to ion-exchanging resins or silicates which are high-performance sorbents [9]. The high level of the cation-exchange capacity for fibrous cellulosic material takes place because the specific surface sharply increases when the fibrous cellulosic material is put in the aqueous media [10, 11]. For example, the value of cation-exchange capacity of dry cotton

fiber is about $1 \text{ m}^2 \cdot \text{g}^{-1}$. This value increases to $100\text{--}200 \text{ m}^2 \cdot \text{g}^{-1}$ in the case when the cotton fiber absorbs water.

The original nonmodified plant raw materials poorly absorb organic pollutants, e.g., technical oils or petroleum products. The oil sorption in $\text{g} \cdot \text{g}^{-1}$ by sorbents produced from wheat straw, cotton fiber, and bast-fiber materials (hemp) bases are 4.1 [12], 6, and $10\text{--}13$ [12]. For comparison, the levels of oil sorption capacity in the synthetic materials produced from foam rubber and polyester in $\text{g} \cdot \text{g}^{-1}$ are 36.9 and 46.3, respectively [13]. Inorganic materials (graphite and modified basalt fiber) have an oil sorption capacity of 35 to $60 \text{ g} \cdot \text{g}^{-1}$.

In this regard, search of methods to increase the versatility of plant sorbents primarily by increasing their ability to interact with organic compounds from aromatic varieties is an undoubted interest. An important scientific and practical problem consists of the development of a methodology for a differentiated assessment of the contribution of adsorption processes mechanisms, taking into account the role of the individual components polymer system. This is will be the basis to obtain the technological approaches to increase the sorption characteristics for renewable carbohydrate and lignin carbohydrate raw using the high-technology methods for modification of the chemical and morphological substrate structure. The present study focuses on improving of the flax fibrous sorbent properties by implementing the breakthrough techniques of the enzymatic catalysis.

Flax bast is a multicomponent system consisting of polymers having various compositions and complexes morphology (Figure 1).

At the production of flax sorbents, the main objective of the preparation stages is the improvement of the internal pore structure in the material and also the stimulation of its polymer components to different types of interparticles and intermolecular interactions.

The internal volume is a chemically active system to both the amorphous intercellular formations and incrusts. The branched hemicelluloses macromolecules contain a large number of hydroxyl, carboxyl, and carbonyl groups [14], which are not used to formation of intermolecular hydrogen bonds, but they can interact with sorbed compounds. The polyuronide compounds have the high ability of chemisorption too. Their activity mostly depends on the content of carboxyl groups in galacturonic units presenting in the main chain. A fragment of pectin structure is shown in Scheme 1 [15].

Therefore, it is clear that maximum preservation of pectin and hemicelluloses in the material structure after directed modification of elementary fibers and formation in the fibrous matrix of the additional mezo- and macropores is necessary to increase the sorption of chemicals by the fiber. In the present work, the quantitative estimate of the perspective for regulation of the changes in the inner volume of flax fiber depending on the quantity of the polymer companions of cellulose present therein was carried out at first time.

Lignin has a special status among the polymer components of flax fiber, and it can reach 7 wt.% or more. Lignin is a hydrophobic polymer despite the fact that many hydrophilic and hydrated groups in the macromolecule

structure are present. Figure 2 depicts a variety of forms for structural units of lignin [16].

The main reaction centers in lignin are hydroxyl (6.5–8.78%), carbonyl (3.31–7.25%), metaxyl (4.27–4.47%), and carboxyl (2.49–of 6.5%) groups. However, most of these groups are located inside a three-dimensional net-like structure of the polymer. This structure has a complex network of short and nondeformation links between phenylpropane units. This is the reason the lignin formations in flax fiber have a small internal free volume, and this free volume does not increase when the flax fiber gets into an aqueous medium. However, the simple ether linkage between phenylpropane units can be hydrolyzed in alkaline medium [17]. This effect in combination with oxidation treatment is used for delignification of the fibrous materials and wood pulp. This delignification process mechanism is shown in Scheme 2.

The treatment of flax raw materials in the presence of reducing agents can stimulate the increase of the lignin reactivity. The reducing agents for the sulfite cooking process in the pulp and paper production [18] may consist of sodium sulfite or sodium bisulfite. Redox-transformations of lignin after interaction with a reducing agent take place because C=O bonds are present in its propane links. This is shown in the example of sodium hydroxymethanesulfonate [19] according to Scheme 3 depicted below.

These changes in the polymer state fix in longer wavelengths with a maximum at 350 nm by the method of differential UV-spectroscopy applied to aqueous and alkaline solutions of dioxane-lignin [20]. At that time, a disproportionate increase in the intensity of maximums at 250 and 300 nm was revealed. These maximums characterize that, in alkaline medium, the ionized phenolic lignin fragments are presented in the form of *n*-coumaryl (I) and coniferyl (II) alcohols as shown in Scheme 4.

After reducing treatment, a chromophore system of lignin is more efficiently oxidized under the action of hydrogen peroxide and sulphuric acid [21] according to schemes depicted below (Scheme 5).

It is a fact that both reactions take place if the phenylpropane units are present in a free phenolic form [17, 22]. The increase in confirmations of the numbers of structural fragments in the free phenolic form was obtained by three independent methods. These methods are allowed to determine the mechanism of initiated lignin transforms. The mechanism of lignin reduction was the same as in case the use of sodium borohydride according to the scheme: the mechanism of initiated lignin transforms is analogically similar to the mechanism taking place when sodium borohydride is used, described according to Scheme 6.

Directly, the reduction of the carbonyl group is a typical example of the nucleophilic addition [22]. The result of this reduction is destruction of ether bond and the formation of an additional number of units having the free phenolic hydroxyl groups in the coniferyl alcohol form. Similar transformations significantly influence the general changes in lignin structure because about 30% of ether bonds in the lignin macromolecule can be destructed as a result of reduction modification.

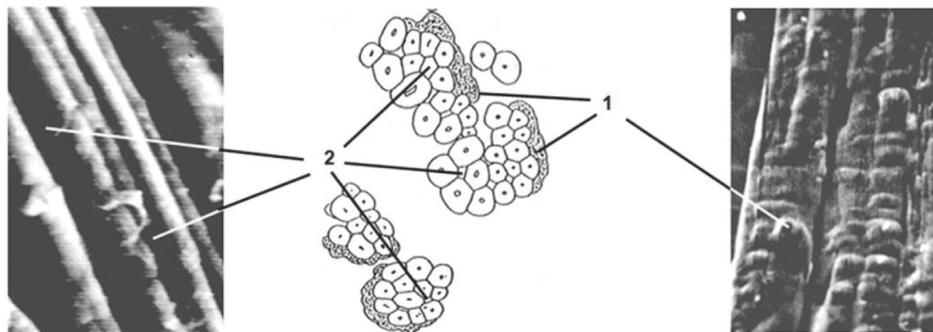
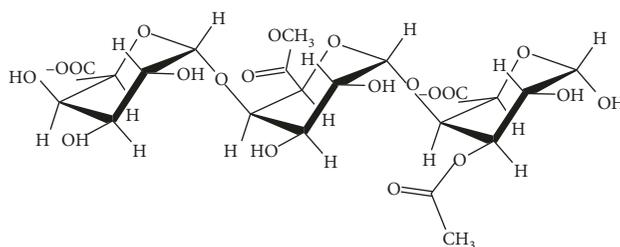


FIGURE 1: Incrusts (1) and inside intercellular space formations (2) from binders in the structure of the flax complexes.



SCHEME 1

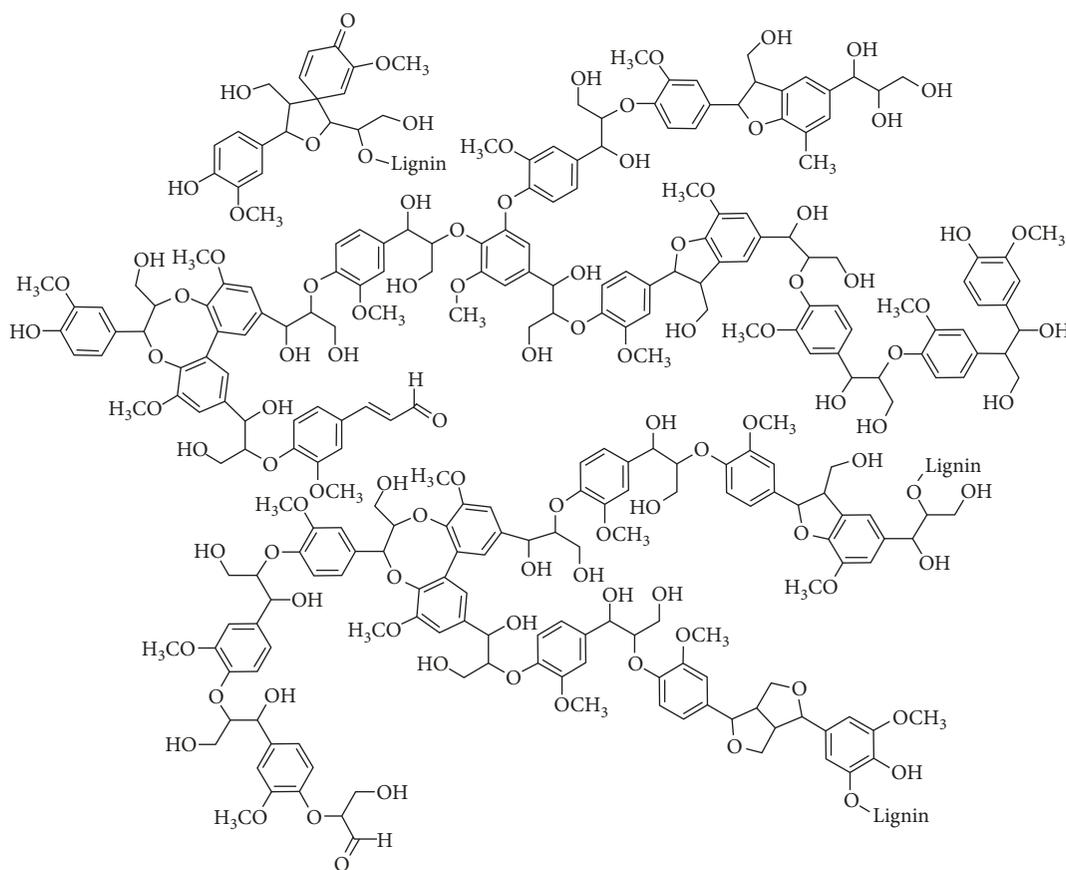
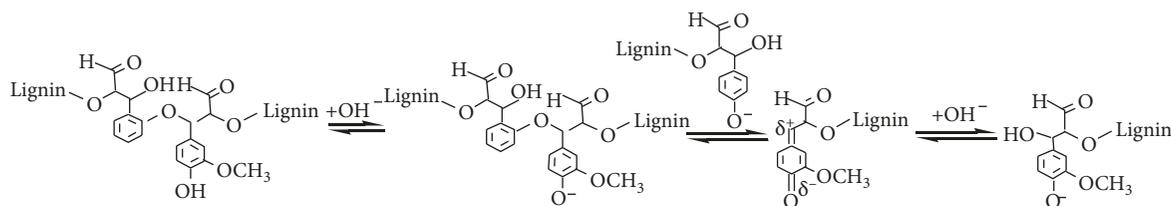


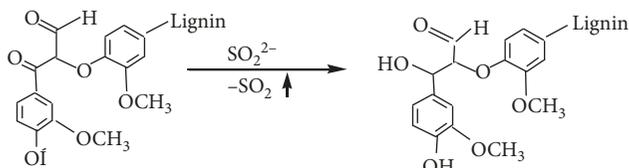
FIGURE 2: A fragment of the lignin structure according to Adler.

In the case when linen raw material was used for production of sorbents, lignin present in it does not require removal and therefore oxidative treatments are not needed.

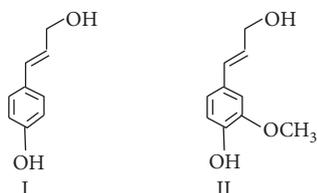
It is logical to believe that the destruction of a large number of internal links will increase the fragments mobility in the net structures of the lignin formations in air-dry condition



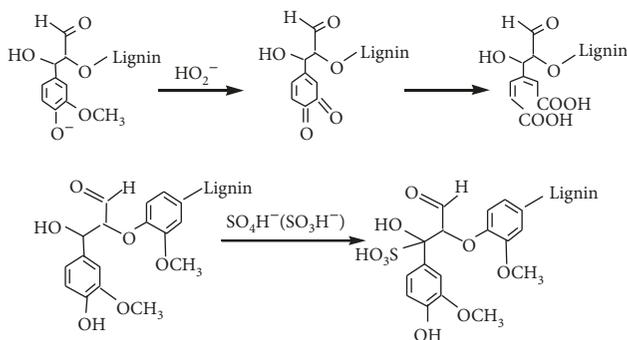
SCHEME 2



SCHEME 3



SCHEME 4



SCHEME 5

and, possible, in the moistening condition too. The transformation of the lignin structure will improve the accessibility of the active centers to chemisorption interactions. The active centers are not only hydrophilic groups but also aromatic and aliphatic fragments having oleophilic properties. The occurrence of the sorption binding of nonpolar organic substances is important. These theoretical conclusions are requiring the experimental verification. The objective of the present research study was to explore influence of the reducing destruction of lignin on the change of the sorption properties of flax fibers. At that the lignin solubility in 72% sulphuric acid was used as criteria which characterize the completeness of redox transformations in macromolecular lignin structure.

The basis for the present study is the scientific and technological author's groundwork including the new way to the use of enzymatic catalysis for delignification of flax

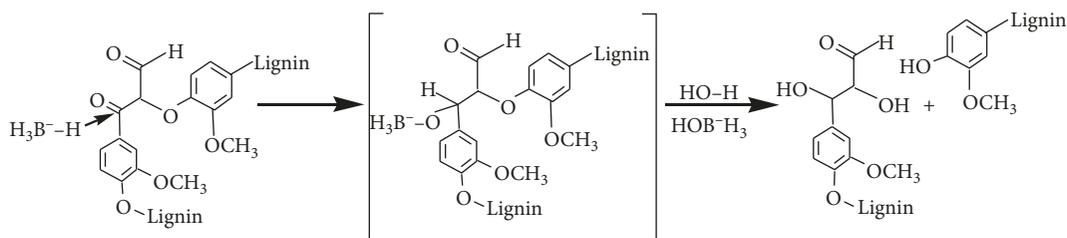
fibrous materials. Developments are base on the results of the studies in which the regularities of phenomena the reducing properties of aldose solutions were investigated [22]. It is established that structure of sugars in the pyranose form influence to its stability at the transition in the acyclic form which shown the reducing properties. At that the reaction of retroaldonic decay of aldoses takes place. This reaction initiated at heating and increasing of alkalinity in the solution. At that many reducing agents are formed. These reducing agents are provided the effective increase of reducing power in the solution. Retroaldonic decay reactions of aldoses can be described by the Scheme 7 depicted below.

Complete biocatalysis conversion of polycarbohydrates presenting in flax fibers by exogenous enzymes provide the generation of the highly reactive reducing agents [23]. Exogenous enzymes separate mono- or dimeric units in the end of polymer links inside fiber. This effect practically does not change the state of the high-molecular components in fiber. Exodepolymerases destruct the oligomeric fraction with a low polymerization degree. The products forming during enzyme treatment migrate in the technological solution. The conditions for the use of these internal reserves in the fibrous system to reach a level of reduction potential sufficient for redox transformations of lignin having been determined [24]. This method was realized in the biochemical technology to preparation of flax rove to spinning. The best effect of fiber delignification and improve the technological properties of the yarn were obtained when the exoxylosidases and exogalactosidases were part of the multienzyme composition. Therefore these kinds of exogenous enzymes were used in order to determine the efficiency of the structural lignin transformation in the flax fibrous sorbents.

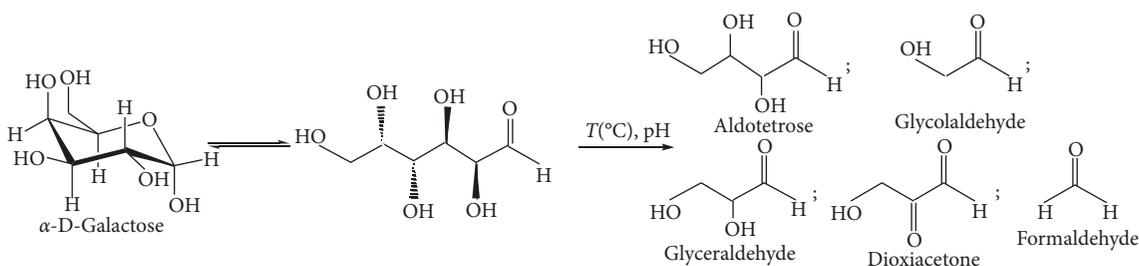
2. Experimental

2.1. Materials. The roving whose linear density is 625 tex made out from long fibrous kinds of flax was object of this research. Three types of enzyme preparations were used when carrying out the enzymatic processing of fibrous materials. The enzyme activity in preparations and processing conditions are listed in Table 1.

The initial preparation involves composition of cellulases (CP) in which endo-1,4- β -glucanase is the main component. The preparation, CP, modifies cellulose in the fibrillar structure of elementary flax fibers. Preparations, G and X, are the highly purified enzymes having an exogenous action. They were used as additives during the CP preparation. The action of enzymes to the flax fiber was compared with the results obtained after treatment of the material by solutions of



SCHEME 6



SCHEME 7

TABLE 1: Characteristics of enzyme preparations.

Preparation	Composition	Producer	Firm-supplier	Activity of enzymes		Processing conditions
				During preparation, U·g ⁻¹	During working solution, U·mL ⁻¹	
CP	Complex of cellulosic cellulolytic enzymes	<i>Aspergillus niger</i>	ZAO (enzyme) (Ukraine)	2000	20	T = 35–60°C pH 5.5–7.5
G	Homogenous enzyme exogalactosidase	<i>Trichoderma reesei</i>	ICN (USA)	20000	0.2	T = 37–45°C pH = 6.0–7.5
X	Homogenous enzyme exoxylosidase	<i>Aspergillus oryzae</i>	ICN (USA)	20000	0.2	T = 35–55°C pH 6.5–7.5

sodium hydroxide (NaOH), sodium borohydride (NaBH₄), and sodium hydroxymethanesulfonate (CH₃NaO₃S).

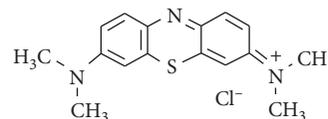
In order to evaluate the adsorption capacity of flax fibrous samples, methylene blue (methylthioninium chloride, 3,7-bis(dimethylamino)phenothiazin-5-ium), and crystalline phenol were used. Methylene blue was purchased from Chimmed (Russia). Its structural formula is shown in Scheme 8.

Crystalline phenol was purchased from Wuhan Creative Chemicals Co., Ltd. (China). All chemicals are of analytical grade.

2.2. Methods

2.2.1. Enzyme and Reducing Treatment of Flax Fiber. The technological process to treatment of flax fibrous materials consists of the following two stages.

Stage 1: enzymatic catalysis (Cat) including the treatment by solution of enzyme preparations at the temperature of 40 ± 0.1°C and pH 6.5. Phosphate buffer was used to help maintain a stable pH in solution. Bath module was 1 : 10. The time of treatment was 2 h, followed by washing by a cleaning solution and water; stage 2: activation of reducing agents (Red). The technological solution was heated to 95 ± 0.1°C



SCHEME 8

and maintained at pH 11 for 20 min in order for a reaction of the retroaldonic decay to occur in the generated reducing sugars. These conditions are providing the inactivation of enzymes.

2.2.2. Chemical Methods for Preparing Flax Fibers. Alkaline scouring of the rove was carried out for 2 h at the temperature of 95 ± 0.1°C. The bath module was 1 : 10. The technological solution contained 5 g·L⁻¹ of Na₂CO₃, 5 g·L⁻¹ of NaOH, and 1 g·L⁻¹ of wetting agent from ionogenic and nonionic surfactants.

Reduction treatment of flax rove was carried out for 1 h at the temperature of 95 ± 0.1°C. Sodium hydroxymethanesulfonate (6 g·L⁻¹) or sodium borohydride (2 g·L⁻¹) was used as the reducing agents. 5 g·L⁻¹ NaOH, 1 g·L⁻¹ of chelating agent, and 0.5 g·L⁻¹ of wetting agent from ionogenic and nonionic surfactant were also included in the technological solution.

2.2.3. Quantitative Analysis of Polyuronides and Hemicelluloses. The quantity of polysaccharides contenting in fibrous material was determined when the consecutive extraction methods was used. At first, pectin was extracted from flax rove (2 g) using 1% citric acid ammonium and boiled for 2 h. Then, the obtaining solution was filtered using a qualitative filter paper with medium filtering capacity. The dose 30 ml from ammonium citrate-extracted pectin solution was mixed with an equal volume of 8 N H₂SO₄ and boiled for 1 h. After that, this mixture was neutralized by 8 N NaOH. The neutralized hydrolyzate was placed in a 100 ml volumetric flask quantitatively. The flask was filled up to the mark with distilled water. The quantity of pectin in this solution was determined by the spectrophotometric method based on the formation of the colored complex of pectin and *o*-toluidine reagent [25]. The fibrous material that remained on the filter after analysis was washed and used for following step of analyses which was the determination of hemicelluloses quantity.

Hemicelluloses were extracted during the boiling of the fibrous material with 2% hydrochloric acid for 4 h. The hydrochloric acid-hemicelluloses filtrate neutralized by sodium carbonate was mixed with distilled water in order to obtain a solution volume was 500 ml. Further, hemicelluloses quantity in this solution was determined by the spectrophotometric method based on the formation of the colored complex of hemicelluloses and *o*-toluidine reagent [25]. The fibrous samples after sequence extraction of pectin and hemicelluloses were used for quantitative analysis of lignin.

2.2.4. Quantitative Analysis of Lignin in the Flax Fiber and Its Solubility in Sulphuric Acid. The lignin quantity in the fiber was determined by the gravimetric method as a ratio of the mass percent of acid-insoluble residual lignin to sample mass. Samples, after the preextraction of pectin and hemicelluloses, were washed and dried. The total lignin content L_0 was determined after extraction of cellulose by copper-ammonia solution according to the method of determination of degree polymerization of cellulose [26]. For determination of L_0 , 1.0 ± 0.0002 g (m_1) of fibrous material was treated for 4 h at $20 \pm 0.1^\circ\text{C}$ in 0.1% copper-ammonia solution. The solution has the following composition (g·L⁻¹): copper (powdery) -13 ± 0.2 ; ammonia -150 ± 5 ; and saccharose -2 ± 0.01 . After complete dissolution of the cellulose in copper-ammonia solution, the lignin precipitate was filtered off and dried in order to determine its weight m_2 . The value of L_0 (wt.%) was calculated using the following formula:

$$L_0 = \frac{m_2}{m_1} \cdot 100, \quad (1)$$

In order to calculate the content of acid-insoluble lignin (Klason lignin, L_K), the sample of lignocellulosic material was treated with 72 % sulphuric acid [27]. For this purpose, 1.0 ± 0.0002 g (m_1) of the fibrous sample was thoroughly mixed with 15 mL of 72% H₂SO₄ using a glass rod to homogeneous mass for 2.5 h at the room temperature. The obtained mixture was transferred to a flask. The hot distilled water was added to 100 mL in the flask too. Then, mixture was boiled for 1 h. After cooling the coagulated lignin was filtered using a qualitative filter paper of medium filtering

capacity. The weight of insoluble lignin residue m_3 (g) was determined. This value was used in order to calculate L_K (wt.%) by using the following formula:

$$L_K = \frac{m_3}{m_1} \cdot 100. \quad (2)$$

The content of acid-soluble lignin (L_S) was calculated as difference between L_0 and L_K :

$$L_S = L_0 - L_K. \quad (3)$$

The error analysis was $\pm 0.2\%$ when L_S was determined.

2.2.5. Gas Adsorption Method. The state of the pore structure in the flax fibrous samples was estimated by the method of low-temperature (77 K) nitrogen adsorption using a gas sorption analyzer NOVA 1200e Series. Sample having a mass of 0.25 ± 0.0001 g was placed in an analyzer cell. Further, both degassing under vacuum for 8 h at $100 \pm 0.1^\circ\text{C}$ and weighing of sample were carried out. Then, nitrogen was injected into the analyzer cell where the fibrous sample was placed. The gas molecules occupied the sample surface, forming a completed monolayer. The average area S_0 occupied by each nitrogen molecule in the completed monolayer at 77 K is usually taken as 16.2 \AA^2 . The measurements were carried out at $p/p_0 < 1.0$. For each sample, the adsorption isotherms of nitrogen were fixed. Porosity characteristics such as surface area S_A (M²·g⁻¹) and total internal pore volume V_P (cm³·g⁻¹) were automatically calculated for the analyzed materials using software NOVA Win-2.1.

2.2.6. Adsorption Capacity to Phenol. Adsorption capacity of the material to phenol was estimated by the gravimetric method. The predried and weighed flax fibrous sample having a mass $m_0 = 5.0 \pm 0.0002$ g was placed over a layer of crystalline phenol in the desiccator at $20 \pm 0.1^\circ\text{C}$ for 24 h for the flax fibrous sample to be adsorbed to the phenol vapor. After that, the increase of the sample weight m_4 was fixed. Adsorption capacity of flax fibrous samples to phenol Q_F (mol·g⁻¹) was calculated using the following equation:

$$Q_F = \frac{m_4 - m_0}{m_0 \cdot M_F}, \quad (4)$$

where M_F is molecular weight of phenol, g·mol⁻¹.

2.2.7. Adsorption Capacity to Methylene Blue. Adsorption capacity of the flax fibrous sample to methylene blue (Q_{MB} , mg·g⁻¹) was estimated according to the recommendations [28]. Methylene blue (MB) is a molecular marker which allows determination of the volume of mesopores in sorbents because the size of the MB molecules is large (of 1.97 nm^2). For this reason, the diffusion into the micropores having diameter less than 2 nm of the MB molecules is difficult.

For analyses, stock solutions of $1.5 \text{ g} \cdot \text{L}^{-1}$ dye were prepared with distilled water, and the required concentrations were obtained by diluting. For equilibrium adsorption of methylene blue, a fiber sample (0.1 g) predried and weighed was soaked and stirred (by a glass rod) with 0.05 L (V) of an

aqueous solution of MB by shaking at 20°C for 20 min. Then, the centrifugation was carried out at 1000 rpm for 5 min. The aliquot 1 mL from discolored MB solution was moved into the volumetric flask. The distilled water was added to make up to the volume of 100 mL. The optical density (D) of the equilibrium MB solution was measured at 665 nm using a UNICO UV-2800 spectrophotometer. The D of the control MB solution was measured analogically but without fibrous sample. The D values of all MB solutions were measured using a 0.5 cm quartz cuvette. The D values of the MB solutions were used for the determination of final MB concentration by the calibration curve. The obtained results were used in order to calculate the adsorption capacity of flax fibrous samples to methylene blue using the following formula:

$$Q_{\text{MB}} = \frac{(C_1 - C_2) \cdot V}{m_0}, \quad (5)$$

where C_1 is the initial concentration of dye solution, $\text{mg}\cdot\text{L}^{-1}$; V is the volume of analyzed dye solution, L; and C_2 is the concentration of dye solution after contact with the fibrous material, $\text{mg}\cdot\text{L}^{-1}$.

2.2.8. Adsorption Capacity to Water. The gravimetric method was used for the determination of water adsorption by the flax fibrous samples. Flax fibrous sample ($m_0 = 2.0 \pm 0.0002$ g) was placed in a glass beaker containing water and remained for 30 min. Wet sample was weighed (m_w , g). Adsorption capacity of the each flax fibrous sample to water (Q_w ($\text{g}\cdot\text{g}^{-1}$)) was calculated using the following formula:

$$Q_w = \frac{m_w - m_0}{m_0}. \quad (6)$$

2.3. Mathematical Processing of Experimental Data. Mathematical processing of experimental data was carried out by the regression analysis method using the mathematical software of multivariate linear regressions with program Statgraphics PLUS 2000 Professional.

3. Results and Discussion

We believe that the composition of flax fibrous materials determines its properties. This is a general rule for all kinds of flax fibrous materials. For this reason, the effect after modifying treatment of flax rove to change the polymer composition and porosity of fiber in the dry state was investigated. The results are shown in Table 2.

It should be noted that the value of S_A index for fibrous material from flax rove is higher almost 15 times than the similar value for cotton fiber under the air dry condition. This is because the binders are present between the elementary bast fibers, that is, the binders are structurally organized in the amorphous carbohydrate-protein complex. The value of the specific surface area increases by 1.5 times when the alkaline cooking was carried out. This is a result of the removal of oily-wax impurities and low-molecular weight components and moderate hydrolysis of the polymers in the mesh structures of carbohydrate-protein binding.

The aim of action of the reducing agents is change of the chemical lignin structure. This is helping a sharp increase the ability of the polymer to the sulphiting reaction. This led to increase in 8 to 11 times lignin solubility in 72% H_2SO_4 . However, the treatment by alkaline solutions of reducers leads to adverse accompanying consequences such as both the loss of 70–82% polyuronide compounds and 60–69% of hemicelluloses. This means almost complete destruction of the amorphous formations takes place in binders present in the flax. In addition, these impurities are also extracted from the elementary fibers. This leads to the opening of the internal structure in areas between fibrils. Along with amorphisation of the rigidly cross-linked lignin structures, this allows avoiding the sharp decrease of the S_A value.

The opening of the internal structure in the elementary fibers effectively takes place when cellulolytic enzymes was used (CP; Cat). The index S_A increases by almost 2 times compared to initial level despite that the content of hemicelluloses decreases to 1.1 times. Sugars as product of biocatalytical reactions and reducing agents generated at the Red-activation stage modify only a small part of the lignin present in the fiber. When the exogalactosidase or exoxyllosidase were include for biopreparation composition, generation of the low molecular weight reducing sugars in the system was allowed. In these cases, the lignin acid solubility increased by 1.5 and 1.8 times, respectively. The mass fraction of acid-soluble lignin increases by 8 times in comparison with the level of the initial value when the combined additives G + X were used.

At the Red-activation stage, the alkalinity in the biomodifying system increases to 11. In these conditions, the partial hydrolysis of noncellulosic polysaccharides takes places. Oligomers with a low polymerization degree are formed, and they are migrated into the solution. However, this does not lead to a sharp decrease of S_A . Probably, the splitting and loss of a certain part of the amorphous formations in binders situated between the elementary fibers compensate by the transformation of rigidly cross-linked structures of lignin. The foregoing is confirmed by the fact that, with increasing L_S , the drop in S_A is logically reduced. Taking into account changes of V_p , it can be assumed that the increase of specific surface is a result of the formation of a developed pore system with smaller transverse sizes. When bonds between phenylpropane links of lignin are decayed and macromolecular chains of lignin are offset, this mechanism for pore formation is quite likely. The maximum effect of biochemical modification of lignin was achieved when three biocatalysts were used (Table 2). In this case, after redox transformations, the value of the internal specific surface area is increased and reduction of the pore spaces volume is minimum.

Mathematical processing of experimental data allowed revealing the model of multiparameter dependence. This model adequately describes the relationship between specific surface area in fibrous material that is available for nitrogen adsorption and content of the polymer companions in linen cellulose involving in the formation of the pores because R^2 indicates a high approximation. In the studied intervals of the independent variables (Table 2), the correlation model has the following form:

TABLE 2: Changes in the composition of not cellulosic polymeric components and in the pore structure of flax fibers after the chemical and biochemical modification.

Modifying agent (stage)	Content of noncellulosic polysaccharides (wt.%)		Content of acid soluble lignin in H ₂ SO ₄ (L _S , wt.%)	Specific surface area (S _A , m ² ·g ⁻¹)	Total internal pore volume (V _P ± 0.001, cm ³ ·g ⁻¹)	
	Polyuronides (Pu)	Hemicelluloses (Hc)				
–	3.3	13.3	0.6	14.7	0.007	
NaOH	2.0	8.1	0.8	21.9	0.012	
NaBH ₄	1.0	5.4	5.0	14.3	0.009	
CH ₃ NaO ₃ S	0.6	4.2	6.6	14.5	0.010	
CP	(Cat)	3.3	11.9	0.6	28.5	0.020
	(Red)	2.5	8.5	2.3	26.3	0.013
CP + G	(Cat)	3.3	10.9	0.6	28.1	0.020
	(Red)	2.5	8.5	3.6	27.6	0.015
CP + X	(Cat)	3.3	10.7	0.6	28.3	0.020
	(Red)	2.5	8.1	4.2	28.0	0.016
CP + G + X	(Cat)	3.3	10.3	0.6	27.8	0.020
	(Red)	2.5	7.6	4.8	28.1	0.017

CP=cellulolytic preparation; +G and +X=additives of exogalactosidase and exoxylosidase; processing step: (Cat)=enzymatic catalysis, (Red)=activation of reducing agents; total concentration of lignin in fiber is 7.3 wt.%.

$$S_A = 1.103 + 10.672 \cdot Pu + 2.031 \cdot Hc - 0.260 \cdot Gc^2 + 0.207 \cdot L_S, \quad (7)$$

$$R = 0.896.$$

The model of type (7) demonstrates that the value of the free member corresponds to the level of S_A for dry cotton fiber [29]. The role of polyuronide compounds is highly significant because the formation of the carbohydrate-protein complex structure and its association with the cell wall of elementary fibers occurs with their participation. The conclusion from this dependence is the recommendation to the maximum extent possible not to destruct pectin when sorbents from the flax fibrous materials will be produced. The factor of structural modification of lignin has the same unidirectional influence.

Also, equation (7) has two members which display the hemicelluloses role of formation of the specific surface area in the substrate. These members have a multidirectional action. Mathematically, this means that extremum takes place on either side of which a various factors have dominant influence. Linear and quadratic terms balance each other when Hc=7.7 wt.%. It can be assumed that the initial removal of hemicellulose fractions in the range of 13.3 > Hc > 7.7 having a low degree of polymerization and conservation of the skeleton in a high-polymeric branched neutral polysaccharides help to emergence of additional volume in the internal area. But, the destruction of the amorphous skeleton from binding compounds in flax material between the fibers area at the Hc < 7.7 wt.% inevitably leads to the partial loss of the sorption activity in the porous system.

Returning to the results of Table. 2, it may be stated that all variants of biomodification allowed to preserve hemicelluloses even after the process of Red-activation at a level not lower than 7.6 wt.%. that has a positive effect on the sorption process. This should provide a large contribution of polycarbohydrate components which is a part of the binder located between fibers of the flax, for physical sorption and

chemisorption of compounds to take place in the corresponding (electrically and neutral, polarized or ionized) chemical state.

The results of the assessment for the equilibrium phenol vapor sorption by analyzed fibrous samples are presented in Figure 3.

It was observed that the substrate sorption capacity relative to the aromatic volatile compounds increases to 10 times. This is confirming the correctness of the selected way for the lignin transformation. Correlation between the absorption characteristics for fibrous materials and rate characterizing the structural modification of lignin is quite expected. This correlation has the following mathematical form:

$$Q_F = 0.166 + 3.796 \cdot L_S, \quad (8)$$

$$R = 0.885.$$

The degree of approximation can be significantly improved when the pore volume will be added in mathematic formula as an additional independent variable:

$$Q_F = 0.035 + 3.790 \cdot L_S + 12.320 \cdot V_P, \quad (9)$$

$$R = 0.935.$$

Comparison of equations (8) and (9) shows that the contribution of the chemisorption ability for modified lignin component is bigger. Equation (3) shows the importance of both the conservation and increase of the lignin porosity which can become the catcher for gaseous aromatic toxins and also for organic pollutions removed from liquid-phase systems. The sorption of thiazinic dye methylene blue from aqueous solution was used in order to assess importance of the proposed methods for biomodification of the flax materials. The obtained results are demonstrated in Figure 4.

It is shown that the sorption of the dye increases by 3–3.5 times when the treatment of fibers in solutions of reducing agents was carried out. In the case when sodium hydroxymethanesulfonate is used, this result is achieved along with an increase in the minimal water sorption (to

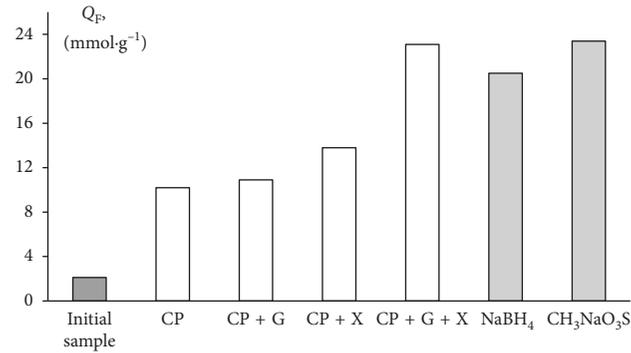


FIGURE 3: Equilibrium phenol vapor absorption by initial flax sample and samples after treatment by enzyme preparations and in solutions of reducers.

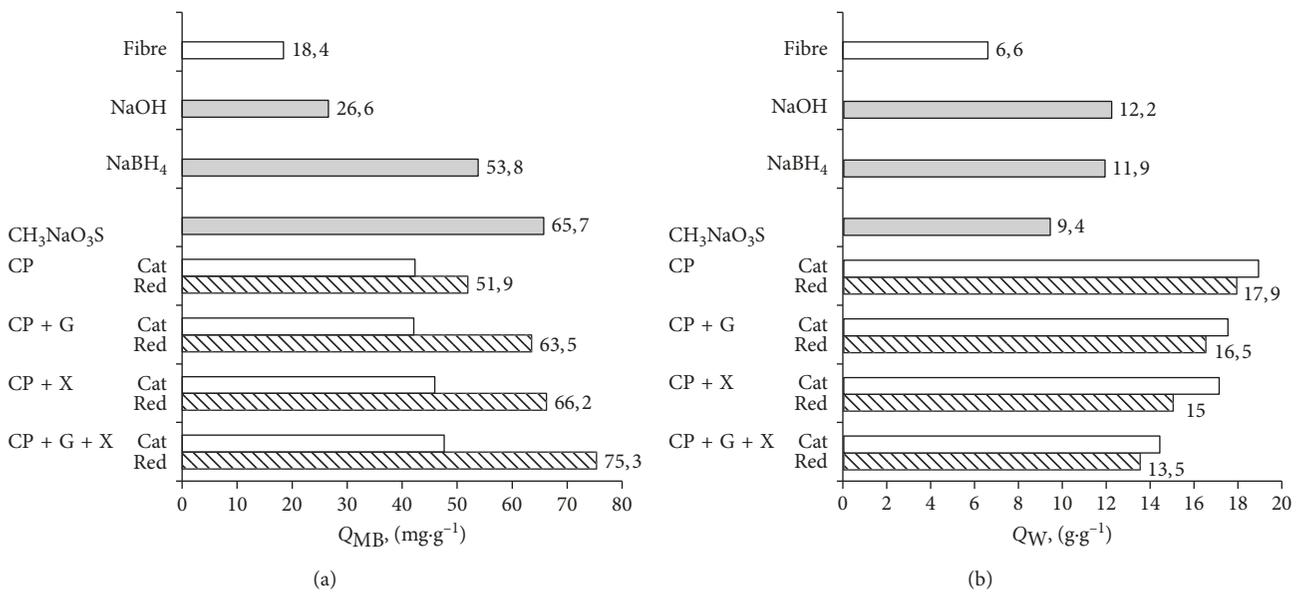


FIGURE 4: The sorption capacity to methylene blue (a) and water (b) of the initial flax sample and samples after treatments by sodium hydroxide, enzyme preparations, sodium borohydride, and sodium hydroxymethanesulfonate: □: after enzyme treatment; ■: after reductive destruction of lignin.

1.5 times). This result may indicate that the activity of lignin after reducing destruction was increased.

Then, the analysis of the experimental results for fiber samples shows that the changes in the sorption capacity to water and dye have opposite dynamics. However, this should not cause the confusions about role of the polycarbohydrate matrix for the extraction efficiency of the dye from the aqueous solution. Multidirectional deflection of Q_{MB} and Q_W values for analyzed objects group reflects only the inevitable losses of the fibrous system ability to the hydrophilic swelling when the modification effect is intensified. The Q_{MB} level for the fibers treated with sodium hydroxymethanesulfonate managed to exceed only, thanks to the retaining of high ability of biomodified fibrous materials to sorption of the aqueous solution and participation of polycarbohydrate components in interactions with the dye.

Mathematical processing of the experimental data is demonstrated in Figure 4, and the values of the content in

fibrous materials of the acid insoluble lignin presented in Table 2 provides a satisfactory view of the correlation model describing the complex participation of all structural fragments in the flax fiber to sorption of organic compounds which are soluble in water:

$$Q_{MB} = 0.082 + 6.949 \cdot L_S + 2.277 \cdot Q_W, \quad (10)$$

$$R = 0.856.$$

Analysis of equation (10) shows the best variant of mode prescription for flax rove biomodification by multi-enzyme preparation including three components. In this case, both the variable terms assure the identical investment to achievement of the end result. At that, both the hydrophilic and hydrophobic components included in fibrous structure are the activation factors to the adsorption of methylene blue. The increase in sorption capacity relative to its initial level more than to 4 times indicates that the

developed technological approaches for increase of the universality and effectiveness of sorption materials from the flax fibers have a high practical value.

4. Conclusions

The results of the experimental researches confirm that flax fibrous sorbents must undergo the complex modification in order to increase their sorption capacity to the pollutions having an organic nature. The increase of the chemisorption activity of the lignin and pore system in elementary fibers and also maximum retaining of the amorphous formations in binders presenting in the structure of the bast-fiber bunch are important.

The perspective of the use of reducing treatments for the increase of the chemisorption lignin ability was demonstrated. It is proposed that the content of lignin soluble in 72% sulphuric acid L_S may be used as criteria for assessment of the effectiveness of the lignin modification. The mathematical model to describe the dependence of the specific surface area of the dry flax fibrous sample to content in this sample of pectin, hemicelluloses, and acid insoluble lignin was revealed. This mathematical model allowed us to determine that the optimum concentration level of hemicelluloses should not be lower than 7.7 wt.% in fibrous sorbents from flax. The correlations which describe the relationship of sorption capacity in flax sorbent to aromatic organic compounds using two types of molecular markers were obtained. It was revealed that the sorption of phenol vapors is determined by the internal pore volume in the material and parameter L_S . Sorption of thiazinic dye methylene blue from aqueous solutions depends as on the L_S value and the value of the water sorption capacity material.

The variant of biochemical treatment for fibrous material was proposed. This biochemical treatment includes the enzyme action on the polycarbohydrate components without pectin destruction and also the use of products formed after biocatalytical processes, assuring reductive lignin destruction. The modifying treatment stimulates the increase in the specific surface area for dry fibers to 1.9 times and of their internal free volume to 2.4 times. At that, the reductive lignin transformation by products formed after biocatalytical processes is comparable with the action of the potent reducing agent which is sodium borohydride. This ensures the increase in the sorption capacity of the material to aromatic compounds vapors by 11 times. The maximum level of sorption of biomodified material was over $70 \text{ mg}\cdot\text{g}^{-1}$, which is comparable to the efficient sorption capacity but costly polymer sorbents, such as those based on polyvinylene chloride materials. Simultaneous activation of lignin and 2-fold increase in the ability of biomodified material to swell in water together provide a 4-fold increase in the sorption capacity of water-soluble dyes.

Mathematical equations are the basis for the choice of conditions of modification of linen materials for the production of effective sorbents of organic compounds. The obtained data may be considered as a key to improvement of technological processes for production of high-effective sorbents from linen fibrous materials, for example, production of

gas-air sorbents for purification of industrial emissions from phenol and also liquid filters for purification of wastewater from organic pollutants.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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