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Properties of Sorbents from Pine Bark Activated by Mechanochemical Methods

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Abstract

The influence of pine bark pre-activation conditions: 1) in a planetary mill AGO-2, 2) with water vapor under the conditions of explosive autohydrolysis (EAH), on the sorption activity of resulting sorbents with respect to methylene blue and gelatin was studied. It is shown that explosive autohydrolysis is a more efficient method to activate pine bark, and under certain conditions it leads to an increase in the sorption of methylene blue and gelatin at least by a factor of 1.8 and 3.8, respectively, compared with the sorbent from non-activated bark. The activating treatment of pine bark in a planetary mill makes it possible to increase the sorption of methylene blue and gelatin not more than by a factor of 1.3 and 1.2, respectively. A mathematical model is obtained that describes the effect of explosive autohydrolysis conditions (water vapour pressure and duration of pine bark treatment) on the sorption properties of the resulting sorbents. Optimal conditions providing the maximal sorption of methylene blue by the obtained sorbent are determined: temperature 155 °C; water vapour pressure 2.62 MPa; processing time 58.6 s. The sorption properties of the sorbent predicted by the mathematical model have been confirmed experimentally. Sorbents from pine bark, activated by explosive autohydrolysis, surpass the industrial enterosorbent Polifepan from hydrolytic lignin in their ability to absorb methylene blue and gelatin, which indicates the prospects for their use as enterosorbents in medicine and veterinary medicine. The results of the conducted research allow us to consider pine bark as an alternative raw material that can replace hydrolytic lignin in the production of effective enterosorbents.

Keywords: pine bark, activation, planetary mill, explosive autohydrolysis, sorbent, methylene blue, gelatin

INTRODUCTION

Pine is one of the basic forest-forming tree species in the Siberian region. The weakest link in the integrated forest resource processing is bark utilisation: not more than 20 % of the total amount of formed bark is further processed. The major part of bark wastes are burnt or transported to dumps, which causes technogenic pollution of the environment. Pine bark is a valuable renewable raw material to obtain products for various functional purposes, for example, slab materials, sorbents for water purification from heavy metals, oil skimming materials [1–3]. Chemical treatment of pine bark allows obtaining various extractive substances: tanning agents, proanthocyanidins, flavonoids, pectin, β-sitosterol, etc. [4–7].

Methods for obtaining various materials from pine bark, including its mechanochemical activation, have been described in the literature. For

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instance, the process of obtaining humic fertiliser from pine bark is based on preliminary cavitational mechanical activation of initial raw material [8]. To obtain efficient heat- and soundproof filling, it has been proposed to modify pine bark by processing it in a planetary ball mill [9]. Pine bark modification with explosive autohydrolysis (EAH) was applied to obtain slab materials [10]. The effect of pine bark activation by EAH and by mechanical treatment in a barrel mill on the yield and properties of tarry and pectin substances, as well as β-sitosterol, was studied in [11]. It is shown that EAH is the most efficient method to activate pine bark.

Activation of the wastes of birch bark under the conditions of EAH is known to cause a substantial increase in the sorption activity of the resulting sorbents with respect to methylene blue (MB) and gelatin [12]. The authors of this work determined activation conditions that allow obtaining the sorbent with sorption properties exceeding those of commercial enterosorbent Polifepan obtained from hydrolysis lignin. For this reason, it was interesting to apply this activation method to pine bark in order to obtain sorbents with high sorption activity with respect to MB and gelatin. Substantial differences in the physicochemical properties of the bark of different tree species determine the novelty and relevance of the studies aimed at determining the effect of pine bark EAH conditions on the properties of sorbents.

Due to a decrease in the output of the hydrolysis industry, the search for new kinds of raw material to replace hydrolytic lignin in the production of enterosorbents is highly urgent. This is especially important for veterinary, because the possibility of large-scale application of enterosorbents is substantially dependent on the availability and low cost of initial raw materials. For this reason, development of methods to obtain sorbents with high activity from tree bark is practically significant.

The goal of the work is to determine the effect of mechanochemical activation of pine bark in a planetary mill or under the action of steam under EAH conditions on the sorption activity of resulting sorbents, and to outline the possible ranges of their application.

EXPERIMENTAL

Common pine bark for sorbent preparation was sampled from timber sawing wastes in Krasnoyarsk in August 2022. The sampled material did not contain rotten or contaminated parts, timber residues or foreign impurities. Bark was dried to the air-dry state under room conditions and stored in a dry room in closed containers. The time of bark storage was 1 month by the moment when the experiments were carried out. To prepare sorbents, air-dry pine bark (residual humidity 8.1 %, cork cambium content not more than 1 wt%) of the following fractional composition was used, wt%: 1–2 mm – 17.7; 2–3 mm – 33.3; 3–5 mm – 45.6; 5–7 mm – 3.4. Bark was ground in a rotary cutting mill RM 120 (Russia) and fractionated with the help of vibrating sieve GR 30 (Russia).

Sorbent preparation included mechanochemical activation of pine bark and treatment of the activated samples with a 2 % aqueous solution of NaOH.

Pine bark activation was carried out using two methods: 1) processing in AGO-2 planetary mill (Russia); 2) by EAH.

Explosive autohydrolysis was carried out in a set-up with periodic operation, with a reactor 0.8 L in volume, described in [13]. Process temperature was varied from 120 to 185 °C, the pressure of overheated water vapour was 1.5 to 3.5 MPa, treatment duration 30 to 90 s. To maintain pressure at the preset level, water vapour was additionally supplied into the reactor. After activation termination, rapid pressure relief in the reactor was made by opening a ball plug valve within 1 s in order to achieve an explosion effect. Autohydrolysed pine bark was dried at 50±5 °C.

Mechanochemical processing of pine bark was carried out in the planetary mill AGO-2 in aqueous medium (liquid-to-solid ratio 6 and 12) with the centrifugal acceleration of 60*g*. Processing time was varied from 5 to 45 min. The conditions of mechanochemical treatment were chosen by analogy with those described in [14], where the effect of these conditions on supramolecular structure and on the yield of water-soluble substances was determined for aspen wood as an example. It may be assumed that the changes of this kind can affect the sorption properties of sorbents based on pine bark activated under similar conditions. The activated pine bark samples were separated from water and dried at 50±5 °C.

Pine bark activated by the indicated methods was treated with a 2 % NaOH solution at a temperature of 70±5 °C according to the procedure described in [12]. Sorbent samples were dried at 50±5 °C and ground to particle size less than 250 μm.

The sorption activity of resulting sorbents was determined with respect to MB and gelatin (P-140

grade, type B) was determined according to the procedure described in [15].

The infrared spectra of sorbents based on pine bark were recorded using an IR Tracer-100 Fourier spectrometer (Shimadzu, Japan) within the wavenumber range 4000–400 cm^{-1}. The samples were prepared as tablets in KBr matrix. Sample mass was 3 mg per 1000 mg KBr. Investigation of pine bark sorbents by scanning electron microscopy (SEM) was carried out with a scanning microscope TM-1000 (Hitachi, Japan). Analysis of the obtained SEM images was performed with the help of Image-Pro Plus software, ver. 3.0.

The static exchange capacity of pine bark with respect to NaOH was determined according to the procedure described in [16].

Mathematical modelling and optimisation of pine bark EAH was performed using the software package Statgraphics Plus ver. 5.0 (Experimental Design unit). Significance level was 0.05.

RESULTS AND DISCUSSION

Effect of different methods and conditions of pine bark activation on the sorption characteristics of resulting sorbents

To choose the best activation method, we prepared sorbents based on pine bark activated preliminarily in the planetary mill AGO-2 or by EAH. During activation in AGO-2, the liquid-to-solid ratio and activation time were changed, while for EAH temperature, water vapour pressure and treatment time were varied. The samples were tested for MB and gelatin adsorption, and studied by means of SEM and IR spectroscopy. To choose the above-indicated marker substances, the following considerations were taken into account:

– cation dye MB modelling the substances with molecular mass up to 500 Da (for example, phosphorus- and chlorine-containing organic compounds, pesticides, cation dyes of similar type, creatinine, barbiturates) is traditionally used to determine the sorption characteristics of various sorbents and makes it possible to evaluate their efficiency in purification of waste waters and biological media;

– gelatin, a polydisperse mixture of polypeptides with molecular mass up to 100–300 kDa, is usually applied to determine the sorption activity of enterosorbents with respect to the toxic substances of proteinic nature (microorganisms and their toxins, intestinal polypeptides, etc. [15]), however, its sorption amount also may be used to evaluate sorbent efficiency for the purification of waste waters from the pollutants of protein nature.

Comparison between the data shown in Table 1 reveals a less efficient influence of pine bark activation in the planetary mill AGO-2 on the sorption properties of resulting sorbents in comparison with EAH. Bark activation in AGO-2, independently of liquid-to-solid ratio, leads to an increase in MB and gelatin sorption on the sorbents by not more than 31.5 and 24.5 %, respectively, in comparison with the sorbent made of non-activated bark. Sorbents obtained with liquid-to-solid ratio 6 and 12 only slightly differ from each other in sorption activity.

As a result of pine bark activation by EAH, the sorption activity of the sorbents with respect to MB and gelatin increases not less than by a factor of 1.8 and 3.8, respectively, in comparison with the sorbent prepared from non-activated bark. Sorption values for these substances by the sorbents based on pine bark after EAH are much higher than the values for sorbents prepared from bark activated in AGO-2 (see Table 1).

An increase in the time of pine bark treatment in AGO-2 up to 45 min, independently of the liquid-to-solid ratio, has no effect on gelatin sorption (Fig. 1) but causes a decrease in MB sorption by 15.2 and 23.4 % (liquid-to-solid ratio 6 and 12, respectively). In combination with the data shown in Table 1, this is evidence that pine bark activation in AGO-2 to obtain sorbents is unreasonable.

Investigation of the conditions of EAH variation shows that pine bark activation using this method within temperature range 150–185 °C and water vapour pressure 2.5 MPa allows obtaining sorbents that combine the highest MB and gelatin sorption in comparison with the sorbents obtained under other conditions (Fig. 2).

Within the studied temperature range, a decrease in water vapour pressure from 2.5 to 1.5 MPa during EAH treatment causes a decrease in MB and gelatin sorption by the obtained sorbents. The ability of these sorbents to adsorb gelatin is substantially lower than that of the sorbents prepared from bark autohydrolysed at water vapour pressure 2.5 and 3.5 MPa. An increase in vapour pressure from 2.5 to 3.5 MPa within the temperature range 120–150 °C is efficient to enhance gelatin sorption, but an increase in MB sorption is observed at a temperature not higher than 145 °C. The highest sorption values for the chosen marker substances are characteristic of the sorbent prepared from pine bark activated by EAH at a

TABLE 1

Effect of preliminary activation of pine bark on sorbent properties

Sorbent	Activation conditions	Sorption, mg/g	
		MB	Gelatin
PBS	Without activation	85.6±2.4	45.3±1.9
	Activation in planetary mill AGO-2		
PBS_{AGO}-1	Liquid-to-solid ratio 6, treatment time 25 min	112.6±2.7	54.2±2.1
$СКС_{AGO}$-2	Liquid-to-solid ratio 12, treatment time 25 min	109.3±2.4	56.4±2.2
	Activation by explosive autohydrolysis		
PBS_{EAH}-1	Temperature 165 °C, water vapour pressure 1.5 MPa, treatment time 60 s	158.7±3.1	174.4±5.8
PBS_{EAH}-2	Temperature 155 °C, water vapour pressure 2.5 MPa, treatment time 60 s	195.2±3.7	240.4±6.7
PBS_{EAH}-3	Temperature 140 °C, water vapour pressure 3.5 MPa, treatment time 60 s	182.5±3.3	238.2±6.3

Note. PBS – pine bark sorbent; MB – methylene blue.

temperature of 155 °C and water vapour pressure 2.5 MPa (treatment time 60 s) (see Fig. 2).

It is known that EAH involves mechanical destruction of the particles of wood material and thermochemical transformation of the organic mass under the action of increased temperature and pressure in water vapour medium [17].

A consequence of the mechanical destruction of pine bark tissues during EAH is the change of morphology of the sorbent prepared from bark activated using this method at a temperature of 155 °C and water vapour pressure 2.5 MPa for 60 s. The sorbents prepared from initial (non-activated) and activated bark have macroporous structure. However, smaller pores 10 to 20 μm in size prevail on the surface of sorbent prepared from activated pine bark, and some pores 3–5 μm in size are also present. The surface of sorbent prepared from initial bark is composed of pores 15–50 μm in size (Fig. 3).

The changes revealed in the texture of the sorbent based on bark activated under the indicated conditions cannot explain the observed increase in MB sorption by a factor of 2.3 (see Table). It has been stressed previously that pine bark EAH at a temperature of 130–190 °C (water va-

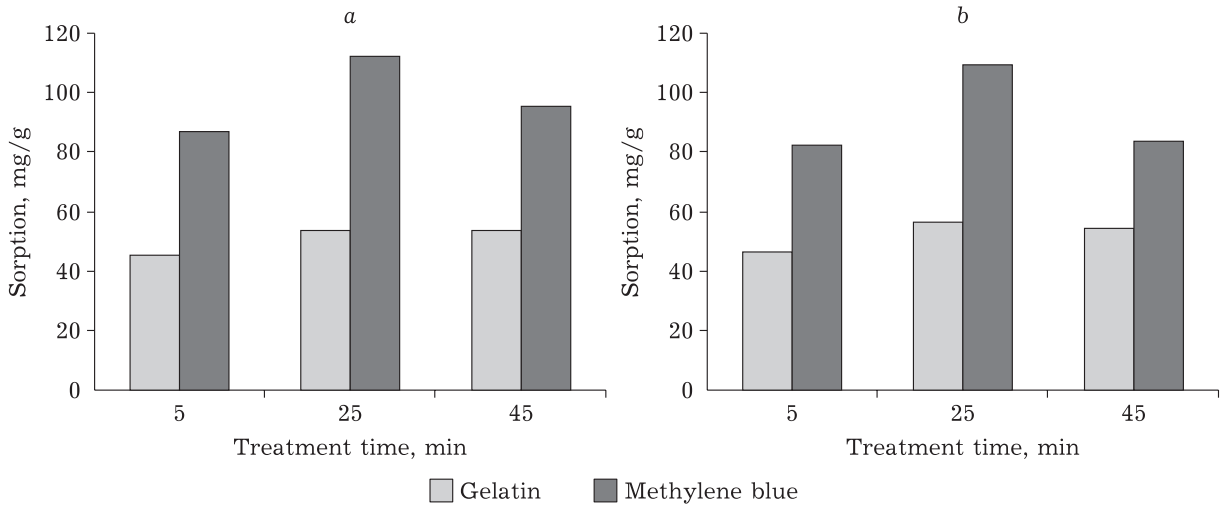

Fig. 1. Gelatin and MB sorption on the sorbents based on pine bark activated in planetary mill AGO-2 for different activation time: *a* – liquid-to-solid ratio 6; *b* – liquid-to-solid ratio 12.

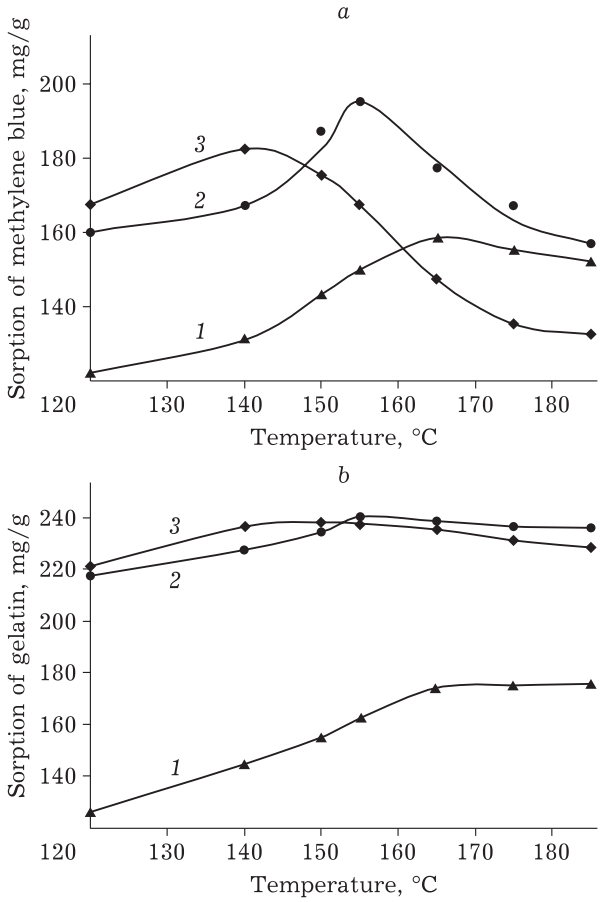

Fig. 2. Effect of the conditions of pine bark activation by explosive autohydrolysis on the sorption of methylene blue (*a*) and gelatin (*b*) on the resulting sorbents (treatment time 60 s). Water vapour pressure: 1.5 (*1*); 2.5 (*2*); 3.5 MPa (*3*).

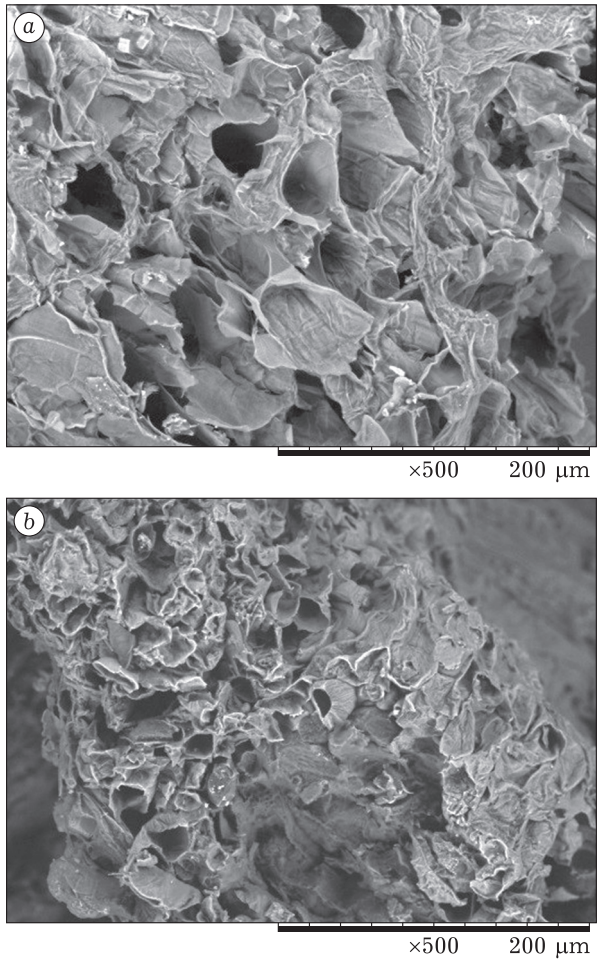

Fig. 3. SEM images of the sorbents based on initial (non-activated) pine bark (*a*) and bark activated by explosive autohydrolysis (*b*). Here and in Fig. 4, 5: the conditions of explosive autohydrolysis are: temperature, 155 °C; water vapour pressure, 2.5 MPa; treatment time, 60 s.

pour pressure 2.5 MPa, treatment time 60 s) allows obtaining the sorbents with high static exchange capacity (SEC) with respect to NaOH equal to 1.3–1.5 mmol/g [18]. The value of SEC with respect to NaOH for the sorbent prepared from non-activated pine bark is 0.85 mmol/g. Comparison between these values provides evidence that the amount of functional groups capable of cation exchange (since MB is a cationic dye) has increased.

Comparison between the IR spectra reveals an increase in the intensity of absorption bands (a. b.) at 3420 cm^{-1} (stretching vibrations of OH groups of different kinds) and at 1618 cm^{-1} (the vibrations of aromatic ring, C=C bond in alkenes and cyclic olefins, stretching vibrations of C=O in enol fragment [19]) for the sorbent based on EAH-activated bark in comparison with the sorbent based on initial bark (Fig. 4). The presence of a set of a. b. at 1618 и 1369 cm^{-1} in the spectrum of sorbent based on activated bark relates to antisymmetric and symmetric stretching vibrations of C–O bonds in carboxylate anion COO^- [19].

Comparison between the IR spectra of sorbent based on activated bark before and after MB sorption revealed the appearance of a. b. characteristic of this marker substance, for instance, at 1597 cm^{-1} (in-plane stretching vibrations of C=C-bonds in the aromatic ring of MB); at 883 and 667 cm^{-1} (out-of-plane bending vibrations of C–H-bonds of the aromatic ring of MB [19]). A low-frequency shift of a. b. at 1618 cm^{-1}, which is present in the IR spectrum of the sorbent prior to interaction with MB solution, by 21 cm^{-1} is detected (Fig. 5, *a*). This may be a result of the interaction of marker substance with carboxylate anions of the sorbent. Change in a. b. profile in the spectrum of the sorbent after MB sorption within the range of 3000–3600 cm^{-1} agrees with the spectral pattern

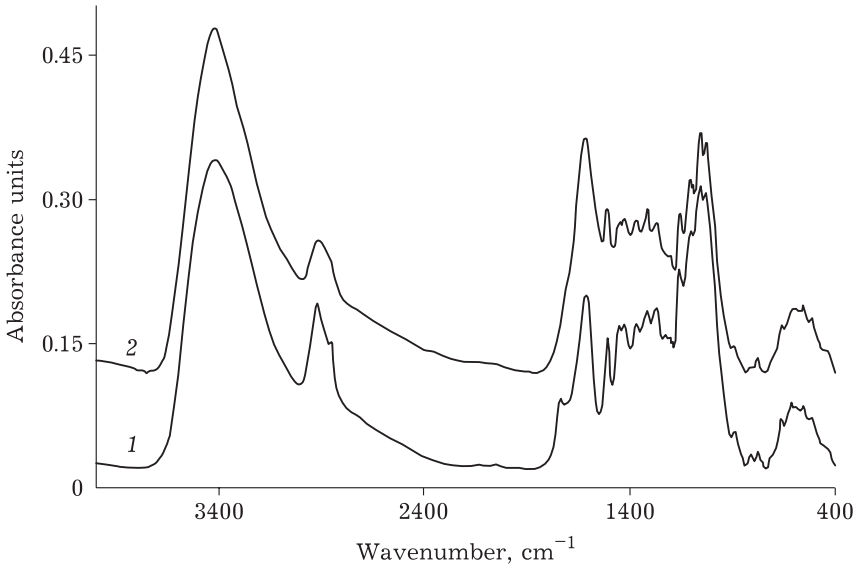

Fig. 4. IR spectra of the sorbents based on initial pine bark (*1*) and bark activated by explosive autohydrolysis (*2*). For the conditions of explosive autohydrolysis, see Fig. 3.

of the marker substance (see Fig. 5, *a*, curves *2* and *3*), which allows assuming the absence of MB interaction with the hydroxyl groups of the sorbent.

After gelatin sorption, a. b. characteristic of the marker substance are observed in the spectrum of the sorbent: at 2922 and 2855 cm^{-1} (stretching vibrations of C–H bonds in CH_3- and CH_2-groups bonded to heteroatoms O, N and S); a. b. with increased intensity at 1632 cm^{-1} (stretching vibrations of C=O – amide I) and 1512 cm^{-1} (bending vibrations of NH – amide II) [19]. The presence of a broad a. b. in the region of 3000–3600 cm^{-1} with a shift to lower frequencies maybe evidence of the formation of hydrogen bonds between OH groups of the sorbent and the functional groups of gelatin (see Fig. 5, *b*).

A decrease in absorption intensity in this region after the sorption of gelatin and MB is likely to proceed as a result of the transition of water-soluble substances containing OH groups from the sorbent into water (see Fig. 5). A similar phenomenon was observed for the sorption of MB by the sorbent based on the bast of birch bark [20].

Mathematical optimisation of the explosive autohydrolysis of pine bark

It is known that sorption activity of sorbents, based on birch park subjected to preliminary EAH, for MB and gelatin depends not only on temperature and water vapour pressure but also on treatment duration [12]. For this reason, to evaluate the effect of the time of EAH treatment and to determine the optimal EAH conditions, we planned and carried out a complete factorial experiment of 3^2 type [21]. On the basis of the above-described data on bark activation by EAH (see Fig. 2), fixed temperature equal to 155 °C was chosen. The variable independent factors were accepted to be: X_1 – water vapour pressure during EAH, MPa; X_2 – treatment time, s. Output parameter: Y – MB sorption, mg/g. Sorption of MB was chosen for mathematical modelling because this substance is commonly used for the quantitative characterisation of functional activity exhibited by the sorbents of different kinds for application in various sorption technologies.

The data of the factorial experiment are shown in Table 2.

Variance analysis shows that the dependence of MB sorption (Y) by pine bark sorbents on the variable factors of preliminary activation of pine bark (X_1 and X_2) is approximated by the second-order regression equation with natural factor designations, in which the terms with significance level less than 0.05 are included 0.05 [21]:

$$Y = 170.6334X_1 + 3.8208X_2 - 32.5467X_1^2 - 0.0325X_2^2 - 146.2889$$

where Y is MB sorption, mg/g; X_1 is water vapour pressure during EAH, MPa; X_2 is treatment duration, s.

The value of determination coefficient (R^2 = 94.7 %) provides evidence of a rather good prognostic capacity of the obtained regression equation. The significance of Fisher criterion ($F(4, 4)$ = 17.91) for this equation is 0.0081, which is smaller than the chosen significance level 0.05. This confirms that the obtained regression model

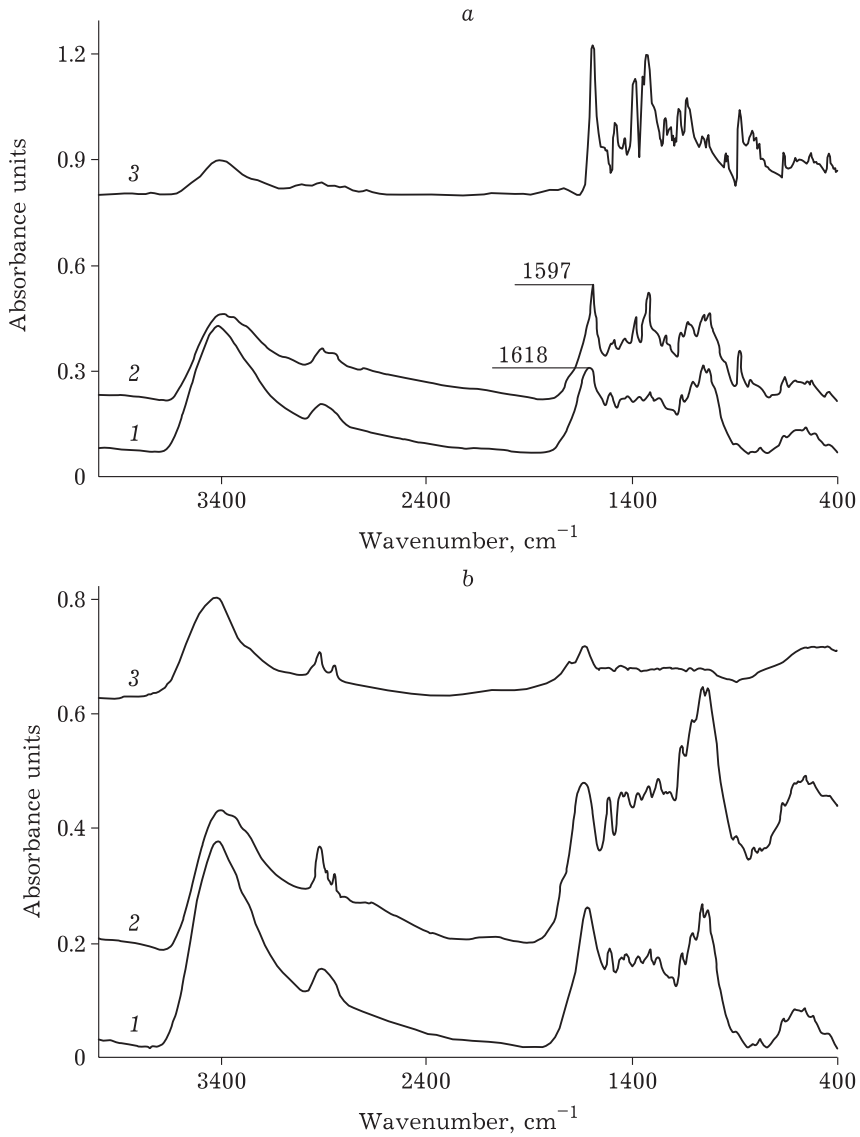

Fig. 5. IR spectra of the sorbent based on pine bark activated by explosive autohydrolysis, before and after sorption of methylene blue (*a*) and gelatin (*b*): *1* – sorbent spectrum before sorption; *2* – sorbent spectrum after sorption; *3* – spectra of methylene blue (*a*) and gelatin (*b*). For the conditions of explosive autohydrolysis, see Fig. 3.

is statistically significant [21]. The yield surface of output parameter Y under variation of variable factors X_1 and X_2 is presented in Fig. 6.

For the obtained regression model, the optimal conditions of pine bark EAH allowing the formation of sorbent with maximal MB sorption are determined: temperature 155 °C; water vapour pressure 2.62 MPa; treatment time 58.6 s. The predicted MB sorption value is 189.7 mg/g.

Taking into account the technical possibility to maintain and measure vapour pressure and treatment time, we carried out experiment on preliminary activation of pine bark by EAH under the conditions close to the optimal ones: water vapour pressure was 2.6 MPa, and treatment duration 58 s (process temperature 155 °C). The sorbent prepared from pine bark activated under these conditions sorbs 187.6 mg/g MB. This value, taking into account determination error ±3.4 mg/g, is close to the value calculated according to the regression equation (189.7 mg/g). The amount of gelatin sorption for the sorbent based on pine bark activated by autohydrolysis under the indicated conditions was determined to be 241.3 mg/g.

The data on MB and gelatin sorption by the sorbents based on pine bark, independently of the conditions of its activation by EAH, shown in Tables 1, 2 and in Fig. 2, are substantially higher than similar parameters reported in the literature for commercial enterosorbent Polifepan prepared

TABLE 2

Planning matrix for the complete factorial experiment of 3^2 type for pine bark activation by explosive autohydrolysis

Experiment No.	Variable factors on the natural scale		Output parameter, Y
	X_1	X_2	
1	1.5	30	122.44
2	1.5	60	139.69
3	1.5	90	125.59
4	2.5	30	160.92
5	2.5	60	195.19
6	2.5	90	152.95
7	3.5	30	138.34
8	3.5	60	167.56
9	3.5	90	129.22

Note. X_1 – water vapour pressure during explosive autohydrolysis, MPa; X_2 – treatment time, s; Y – sorption of methylene blue, mg/g.

from hydrolysis lignin (for this sorbent, the amounts of MB and gelatin sorption are 58.3 and 28.6 mg/g, respectively [22]). The residual content of water-soluble substances for the sorbents based on pine bark is within the range 3.6–2.8 wt%, which is smaller in comparison with Polifepan (4.2 wt% [22]). So, sorbents based on pine bark activated by EAH may be of interest for application as enterosorbent in medicine and veterinary.

CONCLUSION

The influence of two different methods of pine bark activation and their conditions on the sorption activity of sorbents with respect to MB and gelatin is investigated for the first time. Comparison of the obtained results shows that preliminary treatment of pine bark in the planetary mill AGO-2 has almost no effect of gelatin sorption by the resulting sorbents. Explosive autohydrolysis is a more efficient method of pine bark activation and leads to a substantial increase in the sorption of marker substances. Pine bark activation using this method within temperature range 150–185 °C and water vapour pressure 2.5 MPa for 60 s allows obtaining the sorbents that combine the highest sorption of MB (157.1–187.6 mg/g) and gelatin (234.6–236.1 mg/g).

A mathematical model describing the effect of the conditions of pine bark EAH on the sorption activity of the resulting sorbent with respect to MB is obtained for the first time as a result of factorial experiment. The optimal EAH conditions providing maximal MB sorption by the obtained sorbent are determined on the basis of this mathematical model: temperature 155 °C; water vapour pressure 2.62 MPa; treatment duration 58.6 s. It has been established that the sorption characteristics of the sorbent, predicted by the mathematical model, are in good agreement with the experimental results.

The sorbents based on pine bark activated by EAH are better in their sorption activity with respect to MB than the commercial enterosorbent Polifepan based on hydrolysis lignin, which defines the potential possibility of their use in medicine and veterinary.

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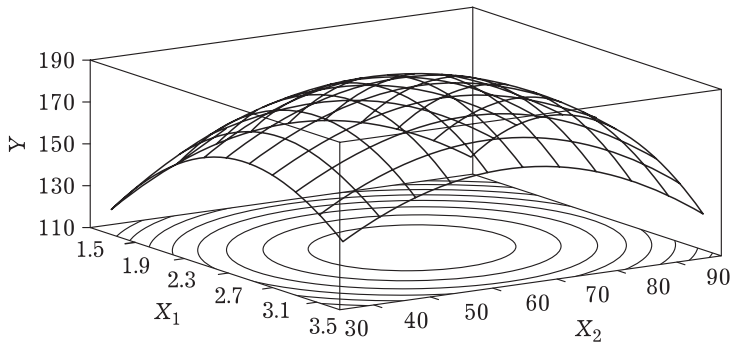

Fig. 6. The yield surface of output parameter Y (sorption of methylene blue by the sorbents based on pine bark, mg/g) under variation of the variable factors of explosive autohydrolysis: X_1 (water vapour pressure, MPa) and X_2 (treatment time, s).

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