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Properties of Enterosorbents Obtained from Autohydrolyzed Bark

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Abstract

Preliminary birch bark activation by steam under the conditions of explosive autohydrolysis was studied. It has been established that as the result of the preliminary processing the sorption activity of obtained enterosorbents with respect to methylene blue and gelatin exhibits a significant increase. The properties of enterosorbents resulted from autohydrolyzedyh phloem and silver birch bark have been compared. Conditions for the activation of birch bark by explosive authohydrolysis to obtain enterosorbents have been determined those could be better than commercial enterosorbent Polyphepan according to the sorption activity with respect to methylene blue and gelatin

Key words: birch bark, phloem, silver bark, explosive authohydrolysis, enterosorbent

INTRODUCTION

Waste bark formed in the course of wood harvesting, represent a valuable renewable raw material for obtaining the products of different practical purpose such as fertilizers feed additives, tannins, sorbents, etc. The most promising line in utilizing the birch bark is considered to consist in obtaining biologically active compounds (betulin, anthocyanidin dyes *etc.*) [1-4]. Birch bark and phloem were used for obtaining enterosorbents, those compete with an industrial analogues "Polyphepan" made of hydrolytic lignin [5, 6]. Interest with respect to enterosorbents in modern medicine is increasingly growing due to the potentialities of using them in order to remove toxins of different nature. Currently, much attention is paid to the development of methods for modifying known enterosorbents those provide an increase in the sorption activity and selectivity thereof [7, 8].

The purpose of this work consisted in studying the influence of birch bark preliminary activation by steam under the conditions of explosion autohydrolysis upon the sorption properties of the enterosorbents obtained.

EXPERIMENTAL

In order to obtain enterosorbents we used grinded air-dry birch bark (residual moisture 6.5 %) containing $(35\pm1) \%$ of silver birch bark. The fractional composition of the feedstock is demonstrated in Fig. 1.

The samples of birch bark with silver bark content equal to $(25\pm1)\%$ was obtained by removing (sifting) a 5-7 mm fraction consisting

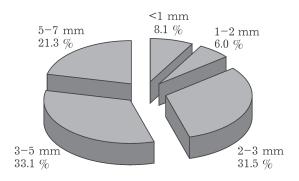


Fig. 1. Fractional composition of birch bark.

of silver bark only, from the original bark. Samples containing (50 ± 1) and $(70\pm1)\%$ of silver bark were prepared by introducing an additional amount of silver bark having a particle size of 2–3 mm into the feedstock.

Preliminary activation of the feedstock was performed in the course of the explosive autohydrolysis using a set-up described in [9]. The temperature was varied between 130-190 °C, steam pressure amounted to 2.5 to 4.0 MPa, the treatment time ranged from 30 to 120 s. The depressurization of the reactor after the activation was carried out with the help of a ball valve during 1 s in order to create the "explosion" effect.

The air-dry activated birch bark was used for obtaining enterosorbents according to a scheme presented in Fig. 2.

The separation of the autohydrolyzed birch bark into silver bark and phloem was performed *via* flotation in the water using apparatus (2). Feeding the activated bark into the apparatus (2) and into reactor (3) was performed from hopper (1). In order to obtain enterosorbents we treated the autohydrolyzed air-dry samples of bark, phloem and silver bark by 2 % NaOH solution in reactor (3) at a temperature of (70 ± 5) °C, at the water duty value equal to (5), under stirring for 1 h. After completing the process the alkaline solution was separated using filter (4), the enterosorbent was trice washed with water in reactor (5). Water washing conditions are they: temperature (20 ± 2) °C, water duty value (4), stirring, the duration of each washing procedure amounting to 40 min. The enterosorbent was separated from the washing water via filtration. The alkali residue in the enterosorbent was neutralized with 1 % HCl in a netralizer reactor (6), to wash then with water in reactor (5)as described in [5]. The samples of enterosorbents were dried at (50 ± 5) °C (7) and grinded (8) to obtain a particle size less than 250 µm.

The sorption activity of enterosorbents was determined using marker substance traditionally used to characterize these materials: iodine (A_{I_2} , GOST 6217–74), methylene blue (A_{MB} TU 6-09-29–76) and gelatin (A_{gel}). The sorption of gelatin (pH 6.5) was performed as described in [10].

All results presented in this paper (as calculated for absolutely dry mass (a. d. m.) of the sorbent) represent an average value of three measurements.

RESULTS AND DISCUSSION

Data concerning the sorption activity of enterosorbents obtained from birch bark, silver bark and phloem samples activated *via* explosive authohydrolysis, are presented in Table 1.

One can see that the sorption level of methylene blue by enterosorbents obtained from

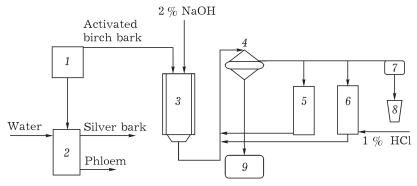


Fig. 2. Schematic diagram of obtaining the enterosorbents: 1 - hopper; 2 - flotation apparatus; 3 - alkali treatment reactor; 4 - filter; 5 - reactor for water-washing; 6 - neutralizer reactor; 7 - dryer; 8 - grinder; 9 - filtrate collector.

Original	Activation conditions	Sorption properties			
raw		$A_{\rm MB}$, mg/g	$A_{\rm gel},~{ m mg/g}$	$A_{\mathrm{I}_{9}}, \%$	
Birch bark	150 °C, 4.0 MPa, 60 s	126.9 ± 2.8	68.5 ± 2.4	29.8±1.2	
Phloem	150 °C, 4.0 MPa, 60 s	97.0 ± 2.1	38.1 ± 1.5	22.2 ± 0.9	
Silver bark	150 °C, 4.0 MPa, 60 s	52.1 ± 1.4	75.3 ± 2.8	34.1 ± 1.4	
Birch bark	170 °C, 2.5 MPa, 60 s	124.8 ± 2.6	53.8 ± 1.7	28.5 ± 1.3	
Phloem	170 °C, 2.5 MPa, 60 s	134.8 ± 3.2	38.1±1.2	24.1 ± 1.2	
Silver bark	170 °C, 2.5 MPa, 60 s	52.8 ± 2.1	104.8 ± 3.1	32.6 ± 1.5	
Birch bark	220 °C, 2.5 MPa, 30 s	118.3 ± 2.7	68.6 ± 2.6	25.1 ± 1.2	
Phloem	220 °C, 2.5 MPa, 30 s	129.7 ± 3.3	39.1 ± 2.2	21.4 ± 0.8	
Silver bark	220 °C, 2.5 MPa, 30 s	67.5 ± 2.6	121.5 ± 3.7	27.7 ± 1.3	
Birch bark	without activation	59.8 ± 2.2	45.5 ± 1.9	27.8 ± 1.2	
Phloem	« «	58.3 ± 2.2	40.6 ± 1.8	25.7 ± 1.1	
Silver bark	« «	56.7 ± 2.1	48.8 ± 2.1	35.9 ± 1.3	

Effect of birch bark, phloem and silver bark activation by explosive autohydrolysis exerted on the properties of the enterosorbents obtained. The content of silver bark in birch bark (25 ± 1) %

Note. Here and in Tables 2, 3: $A_{\rm MB}$, $A_{\rm gel}$, $A_{\rm I_2}$ are the sorption capacity values for methylene blue, gelatin and iodine, respectively (as calculated for the absolutely dry mass of the sorbent).

autohydrolyzed birch bark and phloem is about twice greater than that inherent in the samples of original bark. The sorption level of gelatin by enterosorbents resulted from autohydrolyzed birch bark is 1.2-1.5 times higher as compared to the sample of the original bark. Enterosorbents from original and autohydrolyzed phloem have approximately equal values of the the sorption capacity with respect to gelatin (within the range of 40 mg/g). A more significant increase in the sorption capacity with respect to gelatin (more than 2-fold value) was observed for the enterosorbents obtained from silver bark autohydrolyzed at 220 °C, at steam pressure of 2.5 MPa during 30 s.

TABLE 1

Preliminary activation by explosive authohydrolysis exhibits almost no effect on the sorption activity of enterosorbents obtained from birch bark, silver bark and phloem, with respect to iodine.

It is known that the sorption of iodine from an aqueous solution is used to assess the presence of micropores up to 1 nm [12]. Consequently, the observed increase in the sorption of methylene blue by enterosorbents obtained from the autohydrolyzedyh birch bark and phloem in the case of retaining iodine adsorption activity could be associated with an increase in the number of pores with pore size greater than 1 nm within the porous structure thereof.

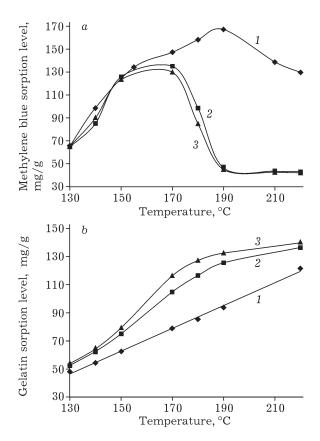


Fig. 3. Effect of birch bark phloem explosive autohydrolysis temperature exerted on the sorption activity the enterosorbents obtained with respect to methylene blue (a) and gelatin (b). Steam pressure 2.5 MPa; treatment duration, s: 30 (1) 60 (2), 120 (3).

Thus, the preliminary activation of the birch bark by explosive authohydrolysis exerts different effects on the sorption activity of enterosorbents with respect to methylene blue and gelatin obtained from birch bark components (phloem and silver bark). A significant increase in the sorption of methylene blue is observed only for sorbents obtained from autohydrolyzed phloem. Increasing the sorption of gelatin is inherent to enterosorbents obtained from autohydrolyzed silver bark. The sorption capacity with respect to gelatin inherent in the enterosorbents resulting from phloem does not exceed 39.1 mg/g, whereas that with respect to methylene blue for the enterosorbents from activated silver bark does not exceed 67.5 mg/g.

Varying the conditions of preliminary autohydrolysis (temperature, steam pressure and treatment duration) exerts different effects on the sorption activity of enterosorbents obtained from the phloem and silver bark. The temperature dependence of the level of methylene blue sorption by enterosorbents obtained from phloem activated *via* explosive autohydrolysis, exhibits an extremum (Fig. 3, *a*).

The maximum value of methylene blue sorption is achieved for enterosorbents resulted from phloem activated by authohydrolysis at 190 °C during 30 s. Increasing the duration of phloem activation results in reducing the sorption of methylene blue by the enterosorbent at temperature values above 170 °C. For example, increasing the duration of phloem autohydrolysis at 190 °C from 30 to 60 s is accompanied by a 3.6-fold decrease of methylene blue sorption.

The sorption of gelatin by enterosorbents obtained from activated silver bark exhibits an increase both with increasing the temperature, and with increasing the duration of explosive autohydrolysis (see Fig. 3, b).

The greatest increase in the sorption of gelatin is observed for enterosorbents obtained from silver bark autohydrolyzed within the range of 60-120 s. The highest adsorption capacity with respect to gelatin (139.8 mg/g) is exhibited by enterosorbents obtained from silver bark activated at 220 °C during 120 s.

We have studied the effect of steam pressure in the course of activation of phloem and silver bark exerted on the sorption of methylene blue and gelatin by enterosorbents obtained. In the case of phloem and silver bark activation at 190 °C during 30 s there is a clear correlation observed between the sorption properties of enterosorbents obtained and the steam pressure (Fig. 4).

Changing the steam pressure in the course of explosive autohydrolysis exerts different effects on the sorption properties of enterosorbents obtained from the phloem and silver bark. So, an increase in the steam pressure in the course of activation process from 2.5 to 4.0 MPa results in decreasing the sorption activity of enterosorbent obtained from phloem with respect to methylene blue by approximately 32 % and in increasing the sorption of gelatin by enterosorbent obtained from silver bark by 33 %.

Basing on the analysis of the experimental data obtained, we have determined optimal process conditions for explosive autohydrolysis those provide maximizing the value of methylene blue sorption for the enterosorbents from phloem and gelatin sorption for the enterosorbents from silver bark: 190 °C, 2.5 MPa, 30 s for the phloem and 220 °C, 4.0 MPa, 120 s for silver bark.

Table 2 presents data concerning the sorption activity of enterosorbents obtained from phloem, silver bark, and birch bark, as to compare with an industrial enterosorbent "Polyphepan".

The enterosorbent from birch bark activated via explosive autohydrolysis at 190 °C and steam pressure of 2.5 MPa during 30 s, is 2.5

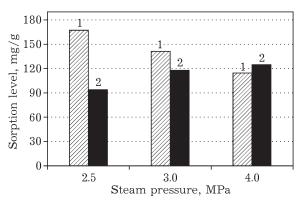


Fig. 4. Effect of steam pressure in the course of phloem and silver bark activation of at 190 °C during 30 s exerted on the sorption properties of the enterosorbents obtained: 1 - methylene blue sorption by enterosorbents resulted from phloem; 2 - gelatin sorption by enterosorbents resulted from silver bark.

TABLE 2	
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Comparative characteristics of enterosorbents obtained from autohydrolyzed birch bark phloem, silver bark and industrial analogues thereof. Silver bark content in the birch bark (25 \pm 1) %

Enterosorbents	Activation conditions	Sorption properties			
		$A_{\rm MB}$, mg/g	$A_{\rm gel},~{ m mg/g}$	A ₁₂ , %	
Bark	190 °C, 2.5 MPa, 30 s	148.2 ± 3.1	53.6 ± 2.3	24.1±1.2	
Phloem	190 °C, 2.5 MPa, 30 s	167.3 ± 3.4	37.7 ± 1.7	22.6 ± 0.9	
Silver bark	190 °C, 2.5 MPa, 30 s	60.7 ± 2.1	93.8 ± 3.2	28.5 ± 1.2	
Bark	$220\ensuremath{^\circ \text{C}}$, 4.0 MPa, 120 s	45.3 ± 1.7	67.1 ± 3.1	24.4 ± 1.4	
Phloem	220 °C, 4.0 MPa, 120 s	43.1 ± 1.3	38.5 ± 2.8	21.4 ± 1.5	
Silver bark	220 °C, 4.0 MPa, 120 s	47.5 ± 1.6	146.9 ± 4.7	28.7 ± 1.8	
Polyphepan, JSC "Ecosphere"	-	56.8 ± 2.3	34.8 ± 1.4	26.5 ± 1.2	
Polyphepan, JSC "ScienTech"	-	57.1 ± 2.2	35.6 ± 1.5	29.2 ± 1.3	

Note. For designations, see Table 1.

and 1.5 times better than "Polyphepan" concerning the sorption of methylene blue and gelatin, respectively. The enterosorbent from phloem is better than Polyphepan with respect to the sorption of methylene blue superior being comparable with the preparation in the sorption of gelatin. The enterosorbent obtained from autohydrolyzed silver bark is characterized by a greater sorption activity with respect to gelatin than Polyphepan, which allows one to use it in order to efficiently remove the toxins of protein nature.

Table 3 presents data concerning the sorption activity of enterosorbents resulted from birch bark with different silver bark content activated at 190 °C, steam pressure 2.5 MPa during 30 s.

The data obtained indicate that increasing the content of silver bark in the feedstock results in increasing the sorption activity of enterosorbents with respect to gelatin. At the same time, the sorption level of methylene blue is

TABLE 3

Effect	of silver	bark	content	in	the	feedstock	exerted
on the	properti	es of	enteroso	orb	ents		

Content, mass %	Sorption activity, mg/g			
	$\overline{A_{ m MB}}$	$A_{ m gel}$		
25±1	148.2 ± 3.1	53.6 ± 2.3		
35±1	86.7 ± 2.8	58.8 ± 2.5		
50±1	74.2 ± 2.6	70.4 ± 3.1		
70±1	56.9 ± 2.1	80.9 ± 3.3		

Note. For designations, see Table 1.

lower to be comparable with the sorption of methylene blue by commercial samples of Polyphepan (see Table 2).

Thus, increasing the sorption of gelatin that simulates protein toxins by the enterosorbents from birch bark activated under the conditions of explosive autohydrolysis could be achieved via increasing the temperature, steam pressure and the duration of activation, as well as *via* increasing the silver bark content in the feedstock. It is obvious that increasing the content of silver bark in the feedstock costs less than changing the conditions of birch bark activation process.

CONCLUSION

It is demonstrated that the preliminary activation of the birch bark by means of explosive autohydrolysis allows one to significantly increase the sorption activity of the enterosorbents with respect methylene blue and gelatin.

Conditions for explosive autohydrolysis of birch bark and the value of silver bark content in the raw material have been determined those provide high values of the sorption level with respect to these markers by the enterosorbent under investigation: temperature 190 °C, steam pressure 2.5 MPa, processing time 30 s; the content of silver bark 25 %. Such an enterosorbent exhibits the sorption capacity with respect to methylene blue and gelatin 2.5 and 1.5 times greater, respectively, as to compare to industrial enterosorbent "Polyphepan". It has been found that increasing the content of silver bark in the feedstock represents an efficient way to improve the sorption activity of the enterosorbents obtained with respect to gelatin.

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