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Obtaining Porous Materials from Birch Bark Bast for Various Purposes

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Abstract

The possibility of obtaining a polydisperse porous material from the birch bark bast with subsequent separation into an enterosorbent and a porous substrate is demonstrated. A technological scheme is developed for processing birch bark bast, which allows one to obtain polydisperse porous material with a yield of 43.5 %. It is proposed to use the fraction of the size less than 0.25 mm as an enterosorbent, and the fraction of 0.25–1.0 mm as a porous substrate to obtain biocomposite fertilizers. It was established that the enterosorbent from birch bast is not inferior in its properties to the industrial enterosorbent "Polyphepan" from hydrolytic lignin. It is shown that, on the basis of the porous substrate, it is possible to obtain a complex biocomposite fertilizer with a growth-promoting effect and increased resistance to the washing out of active components by water. Slow leaching of macro- and microelements from the fertilizer determines the effect of its prolonged action. Thus obtained fertilizer is superior in its resistance to leaching of phosphates and potassium to the industrial granular fertilizer brand "Kemira Universal-2". Taking into account the particle size, lignin content and swelling ability, the porous substrate can also be used as a structuring additive in the soil. To obtain porous materials from the birch bark bast for various purposes, the enlarged plant is proposed, which allows processing up to 12 kg of the raw material in one technological cycle.

Keywords: birch bark bast, enterosorbent, porous substrate, biocomposite fertilizer

INTRODUCTION

Birch is one of the major forest-forming deciduous wood species over the territory of Siberia and the Far East. It is traditionally stored on a large scale. The wastes of birch bark formed during wood processing are mainly burnt or transported to dumps causing environmental pollution with the products of incomplete combustion and bark extractives. Meanwhile, birch bark is a valuable renewable raw material for the production of various materials. The most relevant raw material resource is birch bark, which is traditionally used in folk arts and crafts, and in the production of birch tar. An essential direction in birch bark processing is the production of unique biologically active substances, in particular, betulin, lupeol [1]. The bast of birch bark is also of interest for obtaining tanning agents, dyes, growth stimulators, sorbing materials [1, 2]. On its basis, enterosorbents were obtained, with the sorbing properties being not worse than those of industrial analogues made of hydrolytic lignin [1]. It should be noted that a trend to the reduction of hydrolysis works in the Krasnoyarsk Territory will have a negative effect on the production of enterosorbents based on hydrolytic lignin. Under these conditions, the problem connected with the search for new kinds of raw materials for the production of analogous sorbents is of great practical importance. The possibility to make efficient enterosorbents based on available wood waste promotes large-scale use of these materials in veterinary for prophylactics and treatment in cattle breeding and poultry. Another area of the application of the sorbing material made of bast is the development of biocomposite fertilizers in which this material is used as a porous substrate for the deposition of nutrient elements. The authors of [3] demonstrated the possibility to make a phosphorus-potassium fertilizer possessing prolonged action. It should be stressed that the development of the fertilizers of prolonged action based on wood substrates hold great significance because it allows skilful utilization of bark wastes and a decrease in technogenic load arising from the use of traditional water-soluble fertilizers (for example, soil salinization and groundwater pollution) [4].

The methods of obtaining enterosorbent and porous substrate from birch bark bast described in [1, 3] are close to each other and differ mainly by the size of bast fragments under treatment. This creates objective prerequisites for obtaining porous materials of various purposes within a single technological cycle. The development of a united scheme is of great practical importance for the industrial implementation of integrated processing of birch bark wastes.

The goal of the present work was to obtain enterosorbent and porous substrate for biocomposite fertilizers within a single technological cycle, to study the sorption activity and content of residual water-soluble substances in the enterosorbent, and to determine waterproofness of biocomposite fertilizers and their growth stimulating effect.

EXPERIMENTAL

The initial raw material for obtaining enterosorbent and porous substrate was air-dry (moisture content 7.5±0.5 %) bast from the industrial wastes of the bark of birch (*Betula pendula* Roth.) with particle size 0–200 mm. The bark dried to the air-dry state was subjected to mechanical separation into bast and bark. The residual content of bark in bast assigned for processing did not exceed 1.0 mass %. The bast was fragmented preliminarily in an 8255 Nossen disintegrator (Germany) and crushed to the necessary size with an RM-120 rotor knife mill (Russia).

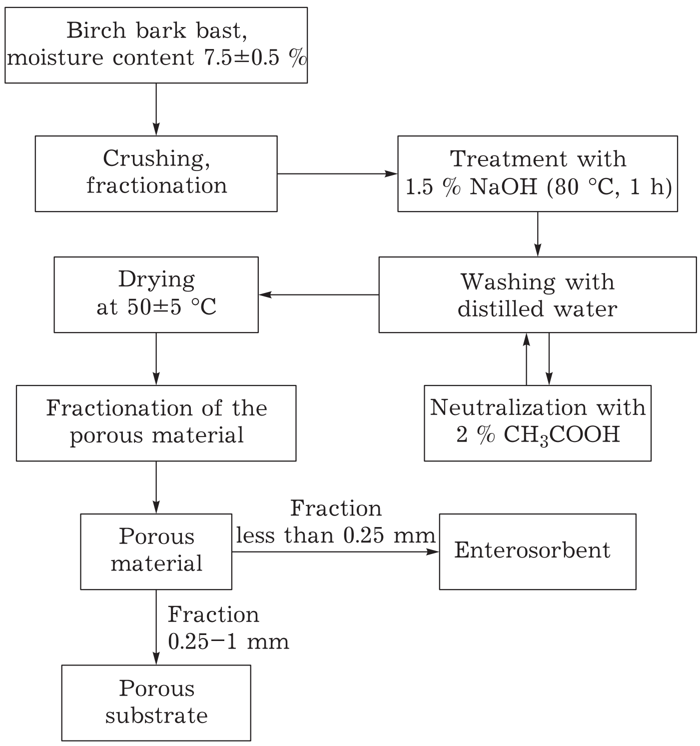

Fig. 1. Scheme of the process of obtaining enterosorbent and porous substrate from birch bark bast.

To carry out experiments, we prepared a technological mixture of fractions with the mass concentration, %: less than 0.25 mm – 51.2, 0.25–0.50 mm – 21.1, 0.50–1.00 mm – 27.7. Separation of bast and the products was carried out with a GR-30 separator (Russia).

The major stages of the technological process of bast processing into enterosorbent and porous substrate are shown in Fig. 1.

To carry out the alkaline hydrolysis of bast and subsequent stages of hydrotreatment, we used an extended laboratory installation with the reactor 60 L in volume (*V*), equipped with an anchor-type mixer allowing one to process 4–12 kg of initial raw material in a single technological cycle (Fig. 2).

The bast was treated with the alkaline solution in an Abat KPEM-60-OMP reactor (Russia, *V* = 60 L) (*1*) under the following conditions: alkali (NaOH) concentration 1.5 %, temperature of alkaline treatment 80 °C, treatment time 60 min, mixing intensity 130±5 r.p.m. The reactor was heated with the help of a water-heated jacket; mixing was carried out with an anchor mixer. After the process was completed, the installation was switched off. The alkaline solution was separated from the solid bast residue by filtering through a vacuum Nutsche filter (*V* = 30 L) (*2*). Aqueous phases were separated similarly at all subsequent stages. Filtrates were collected in a receiver tank (*V* = 60 L) (*3*). Then the residue was transferred from the filter into the reactor (*1*) and washed three times to remove residual alkali. Washing was carried out under the following conditions: temperature 20±2 °C, hydromodulus 4, continuous mixing, each washing operation lasted for 60 min. The solid residue was separated from the liquid phase and residual alkali and then neutralized with a 2 % solution of acetic acid at the hydromodulus equal to 5, for 30 min. After the separation of the acid solution by filtering, the product was washed two times with water at the hydromodulus equal to 4, for 30 min. Neutralization and subsequent washing were carried out under the following conditions: mixing intensity 130±5 r.p.m., temperature 20±2 °C.

Fig. 2. Enlarged laboratory installation for processing birch bark bast: *1* – reactor (*V* = 60 L), *2* – vacuum Nutsche filter (*V* = 30 L), *3* – receiver tank (*V* = 60 L).

After the separation from washing water, the product was dried to the air-dry state at 50±5 °C. The resulting polydisperse porous material was separated into two size fractions: less than 0.25 and 0.25–1.0 mm. For the examination of sorption properties, fraction 0.25–1.0 mm was separated into fractions 0.25–0.5 and 0.5–1.0 mm.

Specific surface S_{sp} was determined by means of low-temperature nitrogen adsorption with a Sorbtomer-M analyzer (Russia); the limiting pore volume W_s was determined from the sorption of benzene vapour under static conditions according to the procedure described in [5]; the total pore volume V_Σ was determined as described in [6].

The sorption activity *A* of different fractions of the porous material of birch bark bast was determined using methylene blue (MB) and gelatin, which are usually used to study the characteristics of sorbents for medical purposes and model toxins of different types. Sorption was studied from 0.15 % MB solution and 0.60 % gelatin solution at pH 5.5 according to the procedure described in [7]. The content of water-soluble substances (WSS) was determined according to the procedure described in [8]. The industrial sorbent of Polyphepan grade (JSC Sayntek, St. Petersburg, Russia) was chosen as a reference sample. Its properties were studied in a similar way.

The fraction 0.25–1.0 mm served as a porous substrate for a complex biocomposite fertilizer of the following composition, mass %: phosphorus 3.5, potassium 8.9, boron, copper and zinc 0.1 each. For this purpose, the porous substrate was impregnated with the aqueous solution containing known water-soluble fertilizers: potassium hydrophosphate, boric acid, copper and zinc sulphates. The fertilizer was prepared according to the procedure described in [3]. The temperature at which the substrate was dried after impregnation with the salt solution was 200 °C, and the concentration of HNO_3 solution for treatment was 0.1 mol/L. According to the procedure described in [3], washing-out of the active components from the fertilizer with water was determined. The aqueous extract of the porous substrate was prepared under conditions similar to those for the tests of fertilizers. Investigation of the amounts of water-soluble elements was carried out by means of mass spectrometry with the help of an ICP-MS 7500 Agilent instrument (USA).

Granular fertilizer with the trade name Kemira Universal-2 (JSC Fertika, Moscow, Russia) was used as a reference sample to compare the stability against washing phosphorus and potassium containing compounds out. This fertilizer contained 7.6 % P_2O_5 and 13.5 % K_2O.

The total ash content in the enterosorbent, lignin content (according to the procedure proposed by Komarov) in the porous sorbent and the ability of the substrate to swell were determined using the procedures accepted in wood chemistry [9].

Germination of the oats seeds of Megion variety was carried out according to GOST (state standard) 12038–84 [10]. Fertilizer made of birch bark bast in the amount of 5 g was applied on a roll of filtering paper wetted with boiled and cooled tap water. Seeds were placed on the substrates, 100 seeds per one substrate. Then the seeds were kept for 7 days at a temperature of 23±2 °C. In the reference experiment, only filtering paper wetted with boiled water was used. The resulting effect was evaluated as the seed germination capacity, the length of roots and sprouts.

TABLE 1

Properties of porous materials from birch bark bast

Size of the particles of porous material, mm	S_{sp}, m^2/g	V_{Σ}, cm^3/g	W_s, cm^3/g
<0.25	2.36	0.38	0.11
0.25–0.5	2.40	0.38	0.10
0.5–1.0	2.32	0.37	0.08

RESULTS AND DISCUSSION

The treatment of birch bark bast with a 1.5 % aqueous solution of NaOH according to the proposed method allows obtaining macroporous materials with different particle sizes, which is evidenced by the corresponding specific surface values (Table 1).

The volume of macropores was calculated as the difference between the total volume V_{Σ} and the limiting pore volume Ws (the latter is equal to the sum of micro- and mesopores [5]). Macropores account for 71 to 78 % in the structure of porous materials. It should be noted that the materials with different particle sizes only slightly differ from each other in the degree of structure development (see Table 1). The presence of micro- and mesopores in combination with macropores playing the transport role provides the sorption activity of the materials obtained from bast.

The possibility to use the porous material as an enterosorbent is determined by its sorption activity and the amount of residual WSS. The content of these substances in enterosorbents is strictly standardized and should not exceed 5 mass % [11]. The high content of water-soluble phenol compounds in the porous substrate can also have unfavourable effect on seed germination and the development of plants [12].

Alkaline treatment allows removing a complex of organic substances, including polyphenol compounds, from birch bark bast. This kind of treatment evidently causes a decrease in the content of WSS in the resulting porous material. Because of this, the conditions under which this stage is conducted (alkali concentration, process temperature and time) were chosen so that the WSS content in different fractions of the porous material did not exceed 5 mass %.

The sorption activity with respect to MB and gelatin for different fractions of porous materials obtained from birch bark bast and the data on WSS content in them are presented in Table 2. One can see that the sorption activity with respect to MB and gelatin decreases with an increase in the size of particles of the porous material. The adsorption of gelatin is stronger affected by

TABLE 2

Effect of the size of particles of the porous material obtained from birch bark bast on its properties

Particle size, mm	A_{MB}, mg/g	A_{gel}, mg/g	WSS, mass %
<0.25	58.7±1.8	37.2±0.8	4.70±0.05
0.25–0.5	54.1±1.5	31.5±0.4	4.80±0.05
0.5–1.0	48.6±1.5	14.4±0.6	4.60±0.05

Note. Here and in Table 3: A_{MB}, A_{gel} are sorption values for methylene blue and gelatin, respectively; WSS is water-soluble substances.

article size. The highest sorption of the marker substances under study is observed for particles less than 0.25 mm in size (see Table 2). Therefore, it is reasonable to separate this fraction from the polydisperse product and to use it as an enterosorbent.

It is important to stress that the content of residual WSS in the fractions of different sizes is less than 5 mass % (see Table 2). This allows us to use the whole polydisperse product and its separate fractions as enterosorbent. Relatively low sorption capacity of the fraction 0.5–1.0 mm with respect to gelatin is not critical because, for example, active carbon as a traditional enterosorbent practically does not adsorb this marker of protein nature [13].

The data presented in Table 3 show that the sample (enterosorbent-2) obtained as a result of grinding polydisperse porous material to a particle size below 0.25 mm is comparable with the fraction less than 0.25 mm (enterosorbent-1) isolated from this material in the sorption of MB and gelatin.

It was established that enterosorbents prepared from birch bark bast are comparable with the commercial enterosorbent Polyphepan in the sorption capacity with respect to MB, WSS and ash content, while their sorption capacity with respect to gelatin is higher by a factor of 1.6 as average (see Table 3). This characterizes their higher potential in removing the toxins of protein nature, microorganisms, *etc*.

The elemental analysis of enterosorbents prepared from birch bast (C 64.1 %, H 6.7 %, N 0.3 %, O 28.88 % and S 0.02 %) provides evidence of the presence of rather large amount of oxygen-containing functional groups, which implies the ability to interact with toxins of different types and is an essential factor of the efficient action of these enterosorbents [14].

On the basis of the porous substrate made of birch bark bast (see Fig. 1), a biocomposite fertilizer (BF) containing nutritious macroelements (potassium and phosphorus) and enriched with microelements (copper, zinc and boron) was obtained. It was established that the treatment of fertilizers with a diluted HNO_3 solution allows a substantial increase in its stability against washing the active components out with water [3].

The fertilizer on the basis of bast substrate exhibits higher stability against washing

TABLE 3

Characteristics of enterosorbents made of birch bark bast and the commercial analogue

Enterosorbent	A_{MB}, mg/g	A_{gel}, mg/g	WSS, mass %	Ash, mass %
Enterosorbent-1	58.7±1.8	37.2±0.8	4.70±0.05	2.3±0.1
Enterosorbent-2	57.5±1.6	36.4±1.1	4.80±0.06	2.0±0.1
Polyphepan	56.9±2.1	23.3±0.9	4.70±0.20	2.0±0.1

Note. For designation see Table 2.

TABLE 4

Washing out of phosphorous and potassium compounds from biocomposite fertilizers based on birch bark bast

Fertilizer	Washing out of phosphorous compounds*, %				Washing out of potassium compounds*, %			
	Time, days				Time, days			
	1	2	3	4	1	2	3	4
Birch bark bast fertilizer	32.6	34.9	39.2	41.9	29.8	32.4	35.6	38.3
Kemira Universal-2**	27.9	38.5	52.6	63.4	47.7	75.7	97.2	100.0

* From the initial content.

** Reference sample.

Fig. 3. Results of germination of oats seeds of Megion variety: *1* – reference experiment (water), *2* – fertilizer based on the substrate prepared from birch bark bast.

phosphorus and potassium compounds out than that of commercial granulated fertilizer with the trade name Kemira Universal-2 (JSC Fertika, Moscow, Russia) (Table 4).

The data presented herein provide evidence that a larger (in comparison with reference sample) amount of active phosphorus-containing compounds is removed from the developed BF with water during 1 day. Then the process slows down, and the diurnal average rate of washing out with water is equal to 2.3 and 2.1 % per day for phosphorus and potassium, respectively (see Table 4). With these rates, 30 and 33 days, respectively, will be necessary to remove phosphorus and potassium compounds completely from the fertilizers.

The data obtained in the experiments on washing out showed that up to 65 % of copper and zinc and up to 41 % of boron are removed within 4 days from the fertilizer based on birch bark bast. This ability of the developed BF to release macro- and microelements slowly is the evidence of its high prolonged action.

Vegetation tests revealed a positive effect of the BF on the germination of the seeds of Megion oats variety (Fig. 3, Table 5). It was established that the application of the fertilizer prepared from birch bark bast causes an increase in oats sprout length by 24.5 % and the length of seedling roots by 11.6 % as average (see Table 5). The germinating capacity of the seeds was 100 % both in the reference experiment and in the experiment with the fertilizer.

The porous substrate made of birch bark bast is also the source of various water-soluble macro- and microelements that enrich the soil with additional nutrients. Aqueous extract washed out from the bast-based porous substrate within 4 days (pH 5.7) has the following composition, mg/100 g of the substrate: K 7.09, P 2.03, Ca 1.35, Fe 0.61, Mn 0.02, Mo 0.01, B 0.51, Cu 0.98, Zn 0.17, S 5.74, J 1.22.

In addition, the porous substrate obtained in the extended installation according to the scheme (see Fig. 1) contains lignin 28.6 mass %; its decomposition in the soil will promote an increase in humus content. The substrate is also characterized by the ability to swell and may absorb water up to 160 mass %. These properties of the porous substrate made of birch bark bast allow using it as a structuring additive to improve aeration and water-retaining capacity of the soil and to enhance the content of organic and mineral components.

CONCLUSION

A technological scheme has been developed for processing the birch bark bast to obtain food enterosorbent and a porous substrate for the biocomposite fertilizers of prolonged action. It

TABLE 5

Results of vegetative tests on the germination of oats seeds of the Megion variety

Experiment, version	Sprout length $X \pm S_x$, mm	Коэффициент вариации, %	Root length $X \pm S_x$, mm	Variation coefficient, %
Water (reference)	51.0±3.5	40	119.5±4.3	32
Fertilizer based on the substrate made of birch bark bast	63.5±3.5	34	133.4±4.3	28

Note. X is mean value, S_x – is the standard error of the mean.

was established that the proposed scheme allows obtaining polydisperse porous material with a yield of 43.5 %. The size fraction of <0.25 mm is proposed as enterosorbent, while the fraction 0.25–1.0 mm is proposed as a porous substrate for obtaining biocomposite fertilizers.

It was established that enterosorbents made of birch bark bast are not worse in their properties than the commercial analogue Polyphepan made of hydrolytic lignin.

A complex biocomposite fertilizer possessing growth-stimulating action and increased stability against washing active components out with water was obtained on the basis of the porous substrate. The slow release of macro- and microelements from the fertilizer by washing out with water provides its prolonged action. The fertilizer obtained in the present work exceeds the commercial granulated fertilizer of Kemira Universal-2 trademark in the stability against phosphate and potassium washing out. Taking into account particle size, lignin content and swelling ability, it is also reasonable to use the porous substrate as a structuring additive in soil.

Within the developed process, bast processing is carried out using standard inland technological equipment without dangerous concentrated chemical reagents, which greatly simplifies the introduction and performance of the method.

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