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Process Optimization for Preparation of Enterosorbents of Birch Bark Bast

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Abstract

The optimum conditions for the synthesis of enterosorbents of birch bark bast were determined by experimental and calculation methods. The regression equations describing the dependence of characteristics of enterosorbents from conditions of its synthesis were obtained. The optimum conditions for the preparation of an enterosorbent with the maximum sorption activity for methylene blue and containing less than 5 mass % of water soluble substances were calculated using these equations: NaOH concentration of 1.5 mass %, temperature of 80 °C, and treatment duration of 60 min. Calculated values correlate well with experimentally obtained results.

Key words: enterosorbent, birch bark bast, preparation, mathematical model, optimization

INTRODUCTION

The risks of ingress of various substances into the organisms of people and agricultural animals grow resulting from technogenic pollution of the environment. To eliminate their hazardous exposure enterosorbents that represent porous sorption materials are widely used in medicine and veterinary [1, 2].

A wide variety of raw materials including wood wastes, peat etc. is used for the preparation of enterosorbents [3–6].

Activated coal of birch bark and enterosorbents based on hydrolysis lignin (so called medicinal or therapeutic lignins – Polyphepanum *etc*.) produced on industrial scales is used in medical practice [7–9].

However, hydrolytic production volumes are currently reduced in Russia, which provides the grounds for a drastic contraction of production of enterosorbents based on hydrolysis lignin.

Thiolignins that by their sorption properties are not inferior to the enterosorbents Filtrum STI and Polyphepanum based on hydrolysis lignin can serve as alternative raw materials for obtaining medical lignin [10, 11].

Large-tonnage bast and birch bark wastes are promising raw materials for obtaining enterosorbents that by their sorption properties are not inferior to industrial analogues of hydrolysis lignin [12, 13]. Technological scheme for obtaining sorbents based on birch bark is closest to obtaining Polyphepanum, which greatly simplifies the replacement of raw materials at enterprises for the production of enterosorbents of hydrolysis lignin.

The process of obtaining enterosorbents of birch bark bast is multistage and includes the stages of alkaline treatment, neutralization of residual alkali in the sorbent followed by washing with water, and grinding of the material obtained [12]. The removal of alkali-soluble components of bast leads to the development of a porous structure of the enterosorbent obtained and exerts a determining effect on the formation of its sorption properties [14].

To quantify the activity of medical sorbents methylene blue modelling toxins with a molecular mass to 500 atomic mass units that are creatinine, barbiturates, and organophosphorus compounds etc. is used. It is important to note, that the content of water-soluble substances (WSS) in enterosorbents is a strictly regulated value - their amount should not exceed 5.0 mass % [7]. This imposes restrictions on the selection of conditions for obtaining enterosorbents with the maximum high adsorption properties and requires solving the task of optimizing parameters of the process for their preparation.

Mathematical modelling using experimentally statistic methods turns up quite efficient for the search of optimum conditions for carrying out various processes [15–17]. Such an approach allows reducing costs for conducting experimental studies based on serial variations of individual technological parameters.

The purpose of this work was the determination of optimum conditions for obtaining enterosorbents of birch bark bast having the maximum sorption activity for methylene blue and containing no more than 5 % water-soluble substances.

EXPERIMENTAL

Air-dry crushed bast obtained from industrial birch bark wastes (particle size of less than 0.5 mm) was used as initial raw materials for the preparation of enterosorbents. The content of basic components in it, % of the mass of absolutely dry bast: easy-hydrolysable polysaccharides – 26.8; low-hydrolysable polysaccharides – 22.3; lignin – 34.5; water-soluble substances – 13.5; ash – 2.9.

Enterosorbents were obtained by alkaline treatment of bast according to the scheme given in Fig. 1. The concentration of a sodium hydroxide solution from 0.5 to 5.0 mass % was varied at the stage of alkaline treatment of bast: temperature from 20 to 100 °C and treatment time from 30 to 120 min. Stirring intensity (130±5) rpm and the hydromodulus value equal to 5 remained constant in all experiments. An alkaline solution was filtered off upon completion of the process. Enterosorbents were rinsed with water 3 times under the following conditions: temperature of 20 °C, hydromodulus 4, stirring, the duration of each flush of 60 min.

Afterwards, enterosorbents were separated from rinse waters by filtration. Alkaline remnants in enterosorbents were neutralized with a 2 % acetic acid solution with the hydromodulus of 5 for 30 min. The enterosorbent was rinsed twice with water at hydromodulus 4 for 30 min after separating the acid solution. The stages of washings and neutralization were carried out

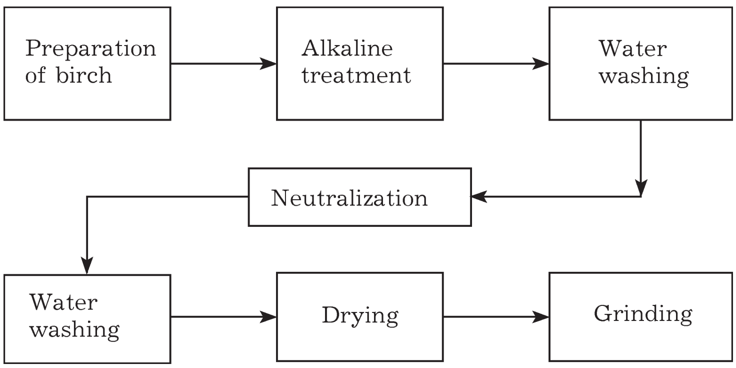

Fig. 1. Enterosorbent preparation scheme from birch bark bast.

with stirring with an intensity of (130±5) rpm. After separation from rinse water, enterosorbents were dried to the air-dried state at (50±5) °C and crushed to a particle size of less than 250 μm.

Sorption activity of enterosorbents in relation to methylene blue (A_{MB}) was determined by the method of work [18]. The content of water-soluble substances (WSS) therein was assessed according to the method described in work [19].

The effect of conditions for the stage of alkaline treatment of bast on properties of the obtained enterosorbents was determined by mathematical modelling methods. The following parameters of the alkaline treatment stage were selected as independent variables (factors): X_1 is the concentration of the NaOH solution (%); X_2 is temperature (°C); X_3 is treatment duration (min). As independent variables (factors), the following parameters of the alkaline treatment stage were selected: the sorption activity of enterosorbents for A_{MB}; the content of WSS.

The Statgraphics Centurion XVI software package, DOE unit (Design of Experiment) was used for mathematical processing of results [20].

To solve the optimization problem enterosorbent sorption activity $A_{MB} \rightarrow$ max with the condition of 5.0 mass % WSS is the criterion function in the region of factor space limited by variability intervals in the experiment. The task was solved by Microsoft Excel [21].

RESULTS AND DISCUSSION

The effect of conditions for treatment of birch bast (alkali concentration, temperature, process length) on sorption activity of enterosorbent samples in relation to methylene blue was determined (Tables 1 and 2).

TABLE 1

Temperature effect on treatment of bast by NaOH solutions of various concentrations on sorption of methylene blue (A_{MB}) by the enterosorbents obtained (treatment length of 60 min), mg/g

Concentration	Treatment temperature °C				
of NaOH solution, %	20	40	60	80	100
0.5	28.36	31.82	39.85	43.34	62.50
1.0	32.61	40.67	49.87	56.85	68.87
1.5	37.05	47.65	56.91	60.97	65.23
2.0	44.84	55.70	60.76	52.66	44.85
2.5	52.12	57.68	60.77	47.12	36.73
3.0	56.89	59.96	60.77	39.38	32.58
3.5	55.81	60.26	60.76	37.92	30.26
4.0	54.47	60.85	60.76	34.85	30.26
5.0	52.66	61.13	60.75	32.39	30.24

TABLE 2

Effect of preparation conditions of enterosorbents from bast on their activity in methylene blue sorption, mg/g

Time length	Treatment conditions of bast		
of alkaline treatment, min	2.0 % NaOH, 60 °C	1.5 % NaOH, 80 °C	1.0 % NaOH, 100 °C
30	32.75	57.23	60.77
45	44.51	59.41	64.76
60	60.76	60.97	68.87
75	59.72	60.72	68.75
90	56.37	58.64	68.54
105	54.44	56.12	67.15
120	53.17	54.25	65.21

Thus, an increase in temperature from 20 to 100 °C during treatment of bast by 0.5–1.5 % NaOH solutions is accompanied by an increase in adsorption of methylene blue (MB). Dependence of adsorption of MB on temperature acquires the extreme nature resulting from using more concentrated alkali solutions (see Table 1).

The data of Table 2 demonstrate that the effect of time length of alkaline treatment on adsorption of MB is also of an extreme character, regardless of alkali concentration and temperature.

Tables 1 and 2 were united in one data set for mathematical processing and analysis of the effect of preparation conditions on the sorption activity of enterosorbents for MB.

Upon carrying out a three-way analysis of variance, the A_{MB} dependence on variables X_1, X_2 and X_3 was approximated by a second order regression equation, where only components with the significance level of no higher than 0.05 were included:

$$A_{MB} = -23.95 + 19.82X_1 + 1.06X_2 + 0.530X_3 - 0.924X_1^2 - 0.255X_1X_2 - 00369X_2^2 - 0.00296X_3^2 \quad (1)$$

where X_1 is the concentration of NaOH solution, %; X_2 is temperature, °C; X_3 is treatment time, min.

It was determined that the approximation quality was characterized by the coefficient of determination $R^2 = 68$ %.

The data of Fig. 2 illustrate comparison of experimental and calculated A_{MB} values obtained on the ground of eq. (1).

The observed wide variations of experimental points along the direct line pointed out at the low predictive properties of the resulting mathematical model.

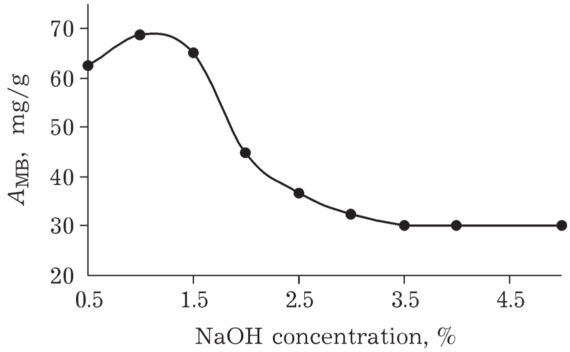

Fig. 3. Sorption activity of enterosorbents of birch bark bast for methylene blue (A_{MB}) *vs.* the alkali concentration (treatment temperature of 100 °C).

An insufficiently correct approximation using a parabolic eq. (1) of almost horizontal regions of the response surface at the border lines of the studied region of factor space may be the most probable cause of a low value of the coefficient of determination [20, 23].

For example, the presence of this region is detected when considering the dependence presented in Fig. 3 in the alkali concentration range of 3.5–5.0 %. Similar areas in the same region of a change in the alkali concentration can be distinguished for A_{MB} enterosorbents obtained at temperatures of 40 and 60 °C, which follows from the data of Table 1.

Variance analysis demonstrated that such parameters of the process as the alkali concentration and treatment temperature made the most substantial contribution into a change in

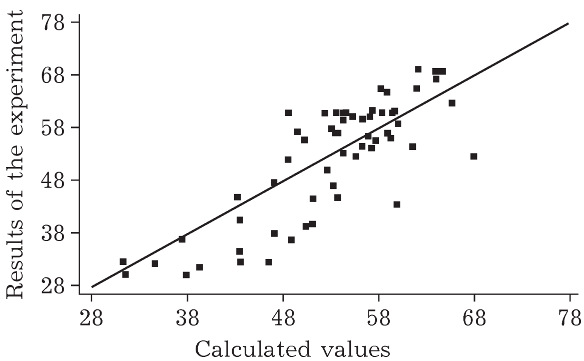

Fig. 2. Deviation of A_{MB} values observed in the experiment from their values predicted by eq. (1).

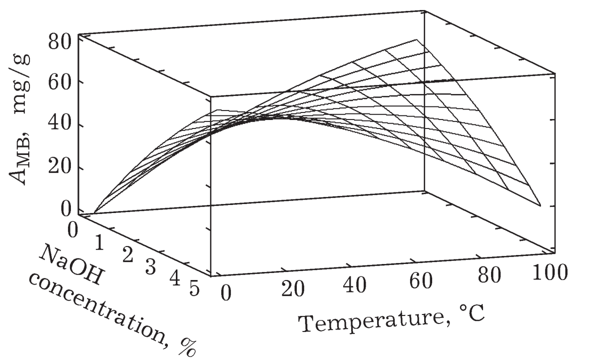

Fig. 4. Response surface A_{MB} in X_1–X_2 coordinates (X_3 = 75 min).

TABLE 3

Content of WSS in enterosorbents vs. conditions of alkaline treatment of bast, %

Time length	Conditions for treatment of bast			
of alkaline treatment, min	2.0 % NaOH, 40 °C	2.0 % NaOH, 60 °C	1.5 % NaOH, 80 °C	1.0 % NaOH, 100 °C
30	5.12	4.85	6.25	7.78
45	4.03	3.82	5.32	6.37
60	3.25	2.79	4.42	5.72
75	3.42	3.16	4.58	6.06
90	3.68	3.66	5.12	6.25
105	4.26	4.08	5.34	6.35
120	4.65	4.53	–	–

Note. Dash – no data.

the sorption activity of enterosorbents. Figure 4 presents the A_{MB} dependence on these factors as the response surface (with fixed treatment time of 75 min).

The response surface has a peak when increasing the alkali concentration from 1 to 5 % with a simultaneous decrease in process temperature from 100 to 40 °C. The sorption capacity remains at a high level in a range of 60–70 mg/g. This is in good agreement with experimental results given in Table 1.

To study the dependence of the content of WSS in enterosorbents on their preparation conditions the experimental results given in Table 3 were used.

Variance analysis detected the strongest influence of the alkali concentration on this indicator, to a much lesser extent – the effect of two other factors that are temperature and treatment time. The dependence of WSS on the selected factors was approximated by a second order regression equation (the significance level of members of no higher than 0.05):

$$\mathrm{WSS} = 15.38 - 2.30X_1 - 0.022X_2 - 0.144X_3 + 0.00801X_1X_3 + 0.00014X_2X_3 + 0.00081X_3^2 \quad (2)$$

A high value of the coefficient of determination ($R^2 = 96.4$ %) allows speaking of fine predicted properties of this equation (Fig. 5).

Dependence of WSS on the alkali concentration with fixed treatment time of 75 min is given in Fig. 6.

Calculation of variable values, with which the maximum sorption activity of enterosorbents for methylene blue can be reached with the condition of the content in it of WSS of no more than 5 %, is the task of optimization. This task was formulated in terms of nonlinear (quadratic) programming. Sorption capacity of enterosor-

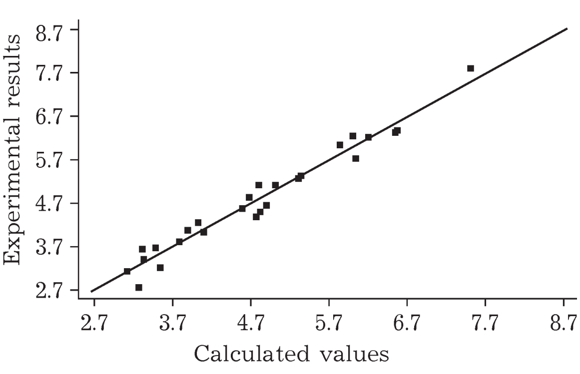

Fig. 5. Deviation of the values for WSS observed in the experiment from their values predicted by an eq. (2).

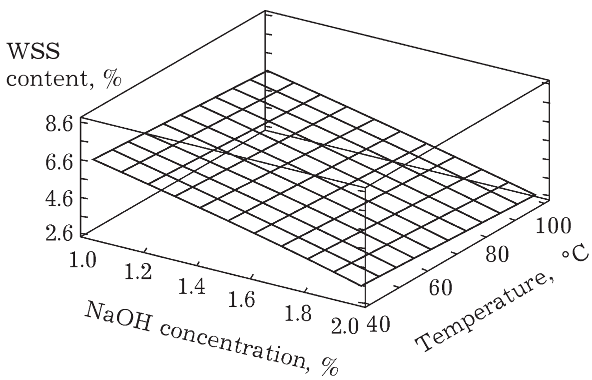

Fig. 6. Surface response of water-soluble substances (WSS) in X_1–X_2 coordinates (X_3 = 75 min).

bents acted as the target function $A_{MB} \rightarrow$ max under the condition WSS – 5.0 mass % in the region of the studied factorial space.

Microsoft Excel software [22] solved the task using equations (1) and (2): the alkali concentration X_1 = 1.5 %; the temperature of the alkaline treatment X_2 = 80 °C; treatment time X_3 = 60 min. The predicted results of the process under these conditions: A_{MB} = 57.0 mg/g; WSS is 4.79 %.

Enterosorbents, the properties of which were close to predicted were obtained during experimental verification of the optimum mode: A_{MB} = 56.1 mg/g (average error of 1.03 mg/g); WSS content is 4.82 % (error is 0.058 %).

CONCLUSION

The effect of conditions for the preparation of enterosorbents of birch bark bast on its characteristics was studied by experimental and calculation methods. Mathematical models describing the effect of conditions of alkaline treatment of birch bark bast on sorption activity of enterosorbents for methylene blue and the content of water-soluble substances in it were calculated.

The optimum conditions for alkaline treatment of birch bark bast allow obtaining enterosorbents with the maximum adsorption activity for methylene blue ((56.1±1.03) mg/g) with the content of water-soluble substances of less than 5 % ((4.82±0.058) mass %).

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