Розроблено спосіб утилізації твердих рослинних відходів, а саме твердої оболонки кісточок Prunus armeniaca, в ефективні сорбційні матеріали. Встановлено закономірності процесу обробки рослинного матеріалу за різних технологічних параметрів з використанням методу математичного планування. Визначено оптимальний режим процесу (концентрація окисника, тривалість), що забезпечує високий вихід сорбційного матеріалу з низьким вмістом залишкового лігніну та високими сорбційними характеристиками

Ключові слова: шкаралупа кісточок Prunus armeniaca, окисна обробка, сорбент, повний факторний експеримент, оптимізація

Разработан способ утилизации твердых растительных отходов, а именно твердой оболочки косточек Prunus armeniaca, в эффективные сорбционные материалы. Установлены закономерности процесса обработки растительного материала при различных технологических параметрах с использованием метода математического планирования. Определен оптимальный режим процесса (расход окислителя, продолжительность), обеспечивающий высокий выход сорбционного материала с низким содержанием остаточного лигнина и высокими сорбционными характеристиками

Ключевые слова: шкаралупа косточек Prunus armeniaca, окислительная обработка, сорбент, полный факторный эксперимент, оптимизация

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DEVELOPMENT OF EFFECTIVE TECHNIQUE FOR THE DISPOSAL OF THE *PRUNUS ARMENIACA* SEED SHELLS

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1. Introduction

One of the promising areas in modern chemical technology and environmental science is the development of new effective methods for the disposal of solid plant wastes from wood, pulp and paper, agricultural and food industries. Natural biopolymers of plant origin, specifically lignin and cellulose, have a number of valuable properties due to which they can be used in chemical, pharmaceutical, food and many other industries [1, 2]. Of a particular interest is the possibility to dispose of solid plant waste by chemical processing or modification in order to obtain sorption materials [3–5]. Relevant are the studies aimed at developing new techniques for obtaining lignin-cellulosic sorbents that may be of interest to various sectors of the national economy. Sorbents of plant origin can be safely used in the chemical industry, environmental science, medicine and veterinary medicine as a cheap alternative to inorganic sorbents.

2. Literature review and problem statement

The necessity to dispose of plant wastes is justified by the fact that thousands of tons of plant and fruit and berry crops are processed in the world annually, and thus a large amount of solid waste and by-products are produced in agriculture and food industry. The main areas to dispose of agricultural waste are using it as livestock and poultry feed [6], as well as fertilizers [7]. However, solid waste of the food industry, specifically canning, that is primarily the solid shell of seeds of fruit and berry crops, remain unused and require the development of effective ways to dispose of them. It should be noted that the specified techniques are not suitable for the processing of the solid shell of fruit and berry seeds because their structure is non-fibrous and dense.

The solid shell of fruit and berry seeds is a complex of organic polymers with valuable properties, including sorption, which are predetermined by functional groups of both lignin and cellulose. Promising from economic point of view of environmental protection is the use of secondary plant wastes as sorbents for solving environmental problems. In the raw form, such materials are characterized by low absorption properties [8]. The most common technique for processing a solid shell of the fruit and berry seeds is to carbonize it at high temperatures to obtain carbon sorbent materials [9]. The main disadvantage of this technique of disposal is the low yield of the product, which typically does not exceed 30 %.

Another common technique for obtaining sorbents from the food industry waste is to shred the materials, to be followed by the hydrolysis with mineral or organic acid, and activation with an alkaline solution [10]. As a result of this treatment, a product with high content of lignin is obtained. The yield of such sorbents is less than 40 %. The unresolved scientific problem is the low absorption capacity of materials thus obtained in terms of organic substances, as, for example, indicated in papers [11] and [12].

A promising technique for obtaining effective sorbents enriched with a polysaccharide component can be oxidative treatment of plant waste, for example, with hydrogen peroxide in an acetic acid medium. It is known that hydrogen peroxide is an effective reagent used in the process of delignification of plant raw materials [13]. Given this, the use of hydrogen peroxide for the oxidation of solid food waste can also be promising. It is expected that an increase in the content of cellulose in plant sorbents will make it possible to improve sorption capacity in terms of synthetic dyes. Fixation of cationic dyes on such materials occurs not only due to the adsorption in pores, but also due to a chemical interaction with functional groups of polysaccharides.

3. The aim and objectives of the study

The aim of present study is to develop a technique for the disposal of the solid shell of *Prunus armeniaca* seeds to obtain a sorbent with a high content of the cellulose component and high sorption properties in terms of a cationic dye.

To achieve the set goal, the following tasks must be solved:

– to select and implement the plan of an experiment, to investigate the effect of the concentration of hydrogen peroxide and the time of the process of oxidative treatment of the solid shell of *Prunus armeniaca* seeds in an acetic acid medium on the properties of the sorbents;

– to propose mathematical models for the process of obtaining sorbents and to conduct a statistical test;

– based on the constructed mathematical models, to optimize parameters of the process of obtaining sorbents.

4. Materials and methods to study the process of obtaining sorbents from the shredded solid shell of *Prunus armeniaca* seeds

To conduct a laboratory study, the solid seeds of the apricot *Prunus armeniaca* were shredded to a size of 0.5 mm, with a content of cellulose of 28.1 %, lignin 48.3 %, ash 0.8 %, resins, fats and waxes 7.6 %, to be used as starting raw materials.

In order to reduce the experimental load and to study the effect of conditions of oxidative treatment on the properties of sorbents, we selected and implemented the plan of a full factorial experiment of type 2^2 [14]. Oxidative treatment of plant waste with hydrogen peroxide in an acetic acid medium under laboratory conditions was conducted at a temperature of 95 °C. The ratio "liquid:raw material" was 5:1. In the research, ice-cold acetic acid and hydrogen peroxide (35 % concentration), of pure grade, were used.

The factors that impact the indicators of sorbents under oxidative treatment of plant raw materials in an acetic acid medium were chosen to be the following variables (x_i): x_1 – concentration of hydrogen peroxide, %; x_2 – time of treatment, min. Initial data for compiling the matrix of planning the experiment of type 2^2 are given in Table 1.

Table 1

Levels and intervals of variance and encoding of factors x_i

Factors (x_i)	Levels of factor variance			Variance interval (Δx_i)
	(+1)	(–1)	(0)	
x_1 – concentration of hydrogen peroxide, %	9	3	6	3
x_2 – modification time	150	30	90	60

Conversion from natural to encoded values of variable parameters of the process is performed using formula (1).

$$x_{ik} = \frac{x_{iн} - x_{0i}}{\Delta x_i}, \qquad (1)$$

where x_{ik} is the encoded factor value, $x_{iн}$ is the natural factor value, x_{0i} is a zero level, Δx_i is the interval of factor variance.

The sorbents obtained in this way were washed by distilled water, dried in the air and determined their structural properties and sorption characteristics. The following indicators of sorbents were set as variable functions (y_i): y_1 – yield of the product, %; y_2 – cellulose content, %; y_3 – content of lignin, %; y_4 – the efficiency of sorption of methylene-blue, %. The yield of the product was determined by a gravimetric method, and the content of lignin and cellulose were determined in line with standard procedures [15]. Sorption of the organic cationic dye was carried out at a temperature of 25 °C from model solutions with a concentration of 100 mg/l. Starting and the equilibrium concentration of the dye were determined using a spectrophotometric method. Transmission spectra of solutions were registered by "Specord M-40" (Carl Zeiss, Germany) at a wavelength of 668 nm. The efficiency of sorption of methylene-blue was calculated from formula

$$Ef = \frac{C_0 - C_e}{C_0} \cdot 100, \qquad (2)$$

where C_0 is the starting concentration of the dye, mg/l, C_e is the concentration of the dye in the equilibrium state, mg/l.

Estimation of the coefficients of regression equations and a statistical analysis of the accuracy was conducted in line with a standard procedure for mathematical planning of experiments.

In the process of modifying plant raw materials using a variety of oxidants, structural components of natural polymers can simultaneously participate in different chemical transformations. Reactions of delignification are always accompanied by a partial hydrolytic destruction of the polysaccharide component, specifically low-molecular hemicelluloses. The intensity of the progress of these processes is determined by the conditions of oxidative treatment. The simultaneous effect of several factors on the properties of the product is controversial. For example, increasing the concentration of reactants within the same time has a larger effect on the reactions of oxidation of natural polymers than an increase in the time within a single concentration. Thus, it is known in advance that the impact of conditions for oxidative treatment on the indicators of products has a non-linear character. Therefore, to reproduce the experimental data, the polynomial experimental statistical model of the third order was used as a mathematical model (2). This would also make it possible to improve the accuracy of reproducibility of experimental data.

$$y_i = b_0 + b_1x_1 + b_2x_2 + b_3x_1x_2 + b_4x_1^2 + \\ + b_5x_2^2 + b_6x_1^2x_2 + b_7x_1x_2^2 + b_8x_1^3 + b_9x_2^3, \quad (3)$$

where y_i are the sorbent indicators, b_0–b_9 are the coefficients of a mathematical model, x_1 and x_2 are the values of factors in the encoded dimensionless form.

The optimization of technological parameters for the process of obtaining the sorbents was made using a multicriteria evaluation method applying a generalized Harrington desirability function [16]. Parameter values y_i were converted into the appropriate desirability (d_1, d_2, d_3, d_4). The scales of desirability in the range from 0 to 1, that is, from "very bad" (d=0.20–0.00) to "very good" (d=1.00–0.80) were used for this purpose. The generalized desirability function was calculated as a geometrical mean from formula (3).

$$D = \sqrt{d_1d_2d_3d_4}. \quad (4)$$

To determine the optimal values of parameters of oxidation treatment of plant materials in the medium of acetic acid, the one-sided Harrington desirability profiles were chosen. Search for an optimum in the generalized function of desirability was performed by the scanning method with a step of 0.001.

5. Effect of treatment conditions for the shell of seeds *Prunus armeniaca* on sorbent properties

The matrix of planning and research results for two factors are given in Table 2. The value of y_i in Table 2 is given as the average value of three experiments. Relative error for all cases is less than 10 %. The results obtained show that increasing the concentration of hydrogen peroxide in the solution from 3 % to 9 % at a time of 30 min contributes to the progress of delignification reactions. As a result, the content of lignin is reduced by 23 %. Under these conditions, the yield is reduced by 25 % because, in addition to lignin, the extractive and mineral substances are removed as well. The content of cellulose at the same time increases by 10 %. By increasing the concentration of hydrogen peroxide from 3 % to 9 % at a process time of 150 min, a reduction by 32 % in the content of lignin is observed, while the yield in this case is reduced by 37 %. It is obvious that, in addition to the reactions of delignification, there are also reactions of degradation of low polysaccharide components occurs. Content of the high-molecular polysaccharide component increases by 30 %. Increasing the content of cellulose leads to the improvement of sorption properties of the obtained plant sorbents in terms of organic dyes; the extraction efficiency of methylene-blue from an aqueous solution reaches 92 %.

Table 2

Planning matrix for two factors

No of experiment	Parameters		Indicators			
	x_1	x_2	y_1	y_2	y_3	y_4
1	1	1	47.33	59.20	11.49	91.90
2	1	0	52.25	50.79	18.49	90.10
3	1	–1	62.21	37.83	34.90	78.50
4	–1	1	75.35	41.54	35.73	69.75
5	–1	0	77.63	36.91	39.61	68.42
6	–1	–1	82.59	33.74	45.05	51.54
7	0	0	65.59	44.22	28.49	79.70

Based on the results of processing obtained experimental data, regression equations were obtained that adequately describe the process of oxidative treatment of solid shell of *Prunus armeniaca* seeds. The estimated values of Cochran criteria for mathematical models y_1, y_2, y_3 and y_4 are 0.1529, 0.1052, 0.1134, and 0.1512, respectively. Because the calculated values of Cochran criteria are smaller than the tabular value (0.66), the variances are homogeneous.

The values of coefficients b_i (as well as those coefficients that were rendered insignificant based on the results of statistical test), obtained regression equations for the relevant indicators y_i, are given in Table 3. The relative errors for models y_1, y_2, y_3 and y_4 are 3.83, 2.92 2.90, and 1.67 %. Estimation of the obtained mathematical models was performed taking into consideration the Student criteria (t-criterion). The value of t-criteria for each factor of the corresponding regression equation, as well as a conclusion about significance, are given in Table 3. Tabular value of t-criterion for this case is 2.36.

Fig. 1 shows projections of the response curves from the resulting indicators y_1–y_4 in the process of obtaining sorbents along the plane of factorial space. The results given indicate that an increase in the values of technological factors leads to a decrease in the yield of sorbents, to reducing their lignin content, and to the increased content of cellulose. In addition, a change in both factors of the process of oxidative treatment has an equivalent effect on the specified parameters in the derived sorbents. At the same time, the sorption capacity of resulting products in terms of organic dyes does improve. With increasing values of parameters x_1 and x_2, there is an increase in the efficiency of removing the cationic dye methylene-blue from an aqueous solution.

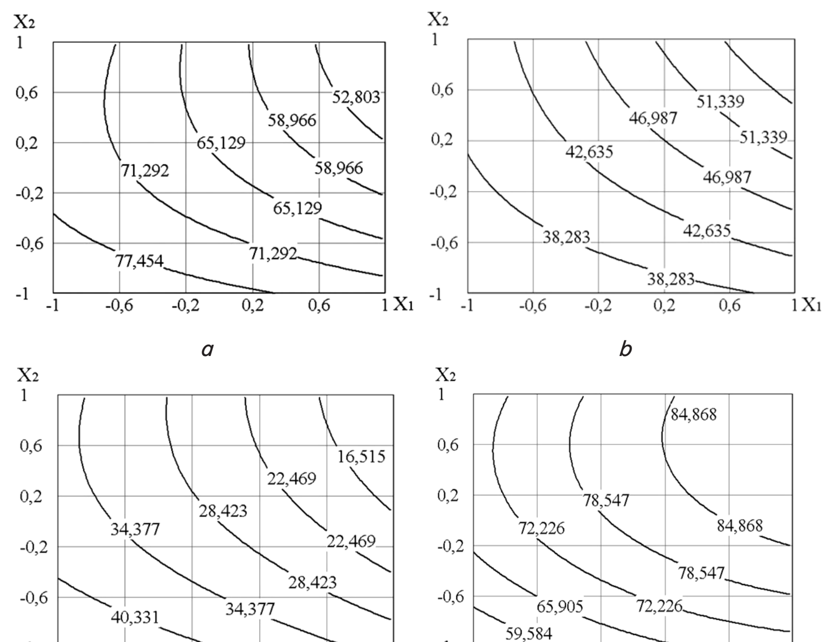
Fig. 2 shows 3D-surfaces of predicting the properties of sorbents based on the obtained regression equations. Data indicate that the maximum value of sorption capacity can be achieved under conditions of performing an oxidative treatment of plant material with a solution of hydrogen peroxide with a concentration of 9 % during 150 min.

Performing such a treatment will lead at the same time to a significant decrease in the yield of the resulting product, due to the removal of lignin, components of a non-cellulose character, as well as certain part of hemicelluloses. That is why the necessary requirement for research into effect of conducting the process is to find optimal parameters that would enable obtaining plant sorbents with high sorption characteristics at a maximally possible high yield.

Table 3

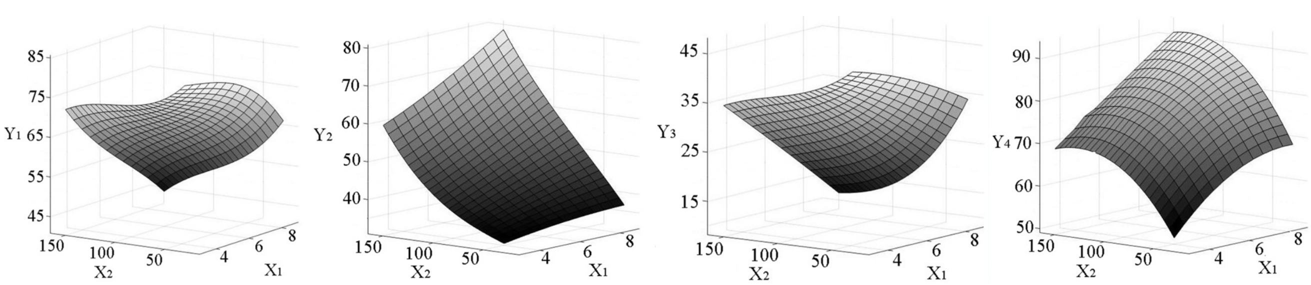
Values of coefficients for regression equations and evaluation of *t*-criteria for the coefficients of corresponding regression equations

Coefficients of regression equation	Mathematical models			
	y_1/*t*-criterion	y_2/*t*-criterion	y_3/*t*-criterion	y_4/*t*-criterion
b_0	66.75/750.24 (significant)	44.18/500.25 (significant)	27.98/365.66 (significant)	80.09/891.27 (significant)
b_1	−9.67/58.37 (significant)	7.33/36.06 (significant)	−11.33/63.93 (significant)	9.66/45.92 (significant)
b_2	−6.16/21.34 (significant)	5.04/22.19 (significant)	−6.79/37.87 (significant)	7.80/38.05 (significant)
b_3	−3.02/60.33 (significant)	3.87/43.69 (significant)	−3.02/37.89 (significant)	1.44/38.05 (significant)
b_4	−1.74/0.034 (insignificant)	0.25/2.19 (significant)	−0.71/8.61 (significant)	−2.23/20.32 (significant)
b_5	3.01/45.32 (significant)	−1.11/10.58 (significant)	4.01/40.53 (significant)	−7.26/67.24 (significant)
b_6	3.13/1.22 (insignificant)	0.89/7.83 (significant)	0.47/3.12 (significant)	2.07/13.23 (significant)
b_7	0.24/24.71 (significant)	−1.83/12.40 (significant)	2.60/20.44 (significant)	0.29/0.50 (insignificant)
b_8	1.99/0.68 (insignificant)	$2.67\cdot10^{-3}$/0.04 (insignificant)	$1.30\cdot10^{-13}$/0.23 (insignificant)	$5.39\cdot10^{-14}$/0.19 (insignificant)
b_9	−3.35/23.68 (significant)	1.58/9.10 (significant)	−1.17/9.26 (significant)	0.49/1.48 (insignificant)



a b c d

Fig. 1. Projections of response curves for resulting indicators y_1–y_4 onto the plane of factorial space x_1 and x_2: *a* – y_1; *b* – y_2; *c* – y_3; *d* – y_4



a *b* *c* *d*

Fig. 2. 3D-surfaces of predicting the properties of sorbent quality: *a* – yield, %; *b* – content of cellulose, %; *c* – content of lignin, %; *d* – efficiency of sorption of methylene blue

6. Determining optimal parameters of the process of oxidative treatment of the shell of *Prunus armeniaca* seeds

The task on searching for the optimal parameters of conducting an oxidative treatment of shredded solid shell of *Prunus armeniaca* seeds is a multicriteria problem. Thus, to find the compromise optimal solution, it was decided to apply the pooling of criteria (quality indicators) using a generalized function of desirability. Desirability scale for each of indicators y_1 is given in Table 4.

Based on the results of calculations, it was found that the optimal parameters for the process of oxidative treatment of apricot seeds shell with a solution in an acetic acid medium are the concentration of hydrogen peroxide of 9 % and the time of 120 min. It is for these technological parameters that the generalized Harrington desirability function is characterized by the maximum value, which is 0.7822. The calculated and experimental values y_1 at the optimum point are also given in Table 4. The compromise area for conducting the specified treatment, formed by the lines of indicators y_1 of sorbents, along the plane of technological factors x_1 and x_2, is shown in Fig. 3.

Table 4

Desirability scale for sorbent indicators and optimization results

Indicator y_i	Desirability scale		Value at an optimum point	
	Very good	Very bad	Calculated	Experi-mental
Yield of sorbent, %	82.6	47.3	50.3	50.8
Content of cellulose, %	59.2	33.7	58.2	56.2
Content of lignin	11.5	45.0	12.7	12.9
Efficiency of sorption of methylene-blue, %	91.9	51.5	91.4	91.0

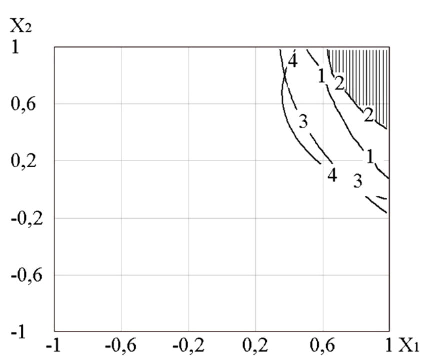


Fig. 3. Compromise area for conducting the treatment of solid shell of *Prunus armeniaca* seeds with hydrogen peroxide in a medium of acetic acid, limited by indicators: 1 – y_1; 2 – y_2; 3 – y_3; 4 – y_4

The experimental research conducted showed that values of the structural and sorption characteristics of sorbents differ slightly from the estimated values – the error is less than 10 %. Because calculated values of y_i agree well with the experimental values, it also indicates the adequacy of the obtained mathematical models.

7. Discussion of results of developing a technique for the disposal of shell of *Prunus armeniaca* seeds

As it was mentioned above, the main techniques for obtaining sorbents from plant raw materials are the carbonation or the hydrolysis, the main shortcomings of which are a low yield and low absorbing capacity in terms of organic dyes, respectively. In the framework of research reported in this paper, we devised a technique for obtaining sorbents with a high yield and high sorption capacity in terms of organic dyes, due to preserving the high-molecular, and part of low-molecular, polysaccharide component. As a result of oxidative treatment of plant materials with hydrogen peroxide in an acetic acid medium, dominant are the reactions of delignification, which lead to a decrease in the content of lignin. Such a technique makes it possible to obtain a sorption material enriched with cellulose and hemicelluloses. The sorption of organic dyes in such materials occurs both due to the physical adsorption and chemical adsorption through the interaction between functional groups of polysaccharide.

In general, the results obtained open up new ways for the effective disposal of solid plant wastes in food industry that are annually produced in large quantities and have no further application. The proposed technique makes it possible to obtain an effective sorbent with high sorption properties in terms of methylene-blue due to the preservation of high-molecular, and part of low-molecular, polysaccharide component. The dye methylene-blue is typically used as a marker for medium-molecular toxicants when studying the properties of medical materials. Due to high sorption properties of the specified toxicant, the obtained sorbent could find wide application not only for solving environmental problems, but also as enterosorbents in medicine and veterinary.

The results obtained indicate the prospects for practical multipurpose application of the received product and will form the basis for further research related to determining the sorption capacity of plant sorbents for high molecular toxicants and toxicants of protein nature.

8. Conclusions

1. We studied the effect of basic technological parameters in the treatment of solid shell of *Prunus armeniaca* seeds with hydrogen peroxide in an acetic acid medium on the structural-sorption properties of obtained sorbents using the methods of mathematical planning. It was established that increasing the concentration of hydrogen peroxide from 3 to 9 % within the same process time leads to a decrease in the yield of sorbent and the content of lignin in it by 24 % on average. At increasing the time from 30 to 150 minutes within the same concentration, the sorbent yield and its content of lignin reduce by 20 % on average. With a decrease in the content of lignin from 45.05 to 11.49 %, the cellulose content in sorbents and their sorption capacity for methylene-blue increases from 33.74 to 59.20 % and from 51.54 to 91.90 %, respectively.

2. We have derived mathematical models for the process of oxidative treatment of solid shell of *Prunus armeniaca* seeds for different values of concentration of hydrogen peroxide and the time of the process, which adequately describe the process for obtaining sorbents. Errors of calculation for the obtained experimentally-static models of third order,

for the indicators of sorbents, specifically the yield of the product, its content of cellulose and lignin, as well as the efficiency of sorption of methylene-blue, are 3.83, 2.92, 2.90, and 1.67 %, respectively.

3. Based on the results of solving a problem of multicriteria optimization, we established optimum process parameters for oxidative treatment of plant waste in a medium of acetic acid. Conducting the specified process at a concentration of hydrogen peroxide of 9 % for 120 min makes it possible to obtain sorbents with efficiency of extracting the methylene-blue larger than 90 % at the product yield exceeding 50 %. The proposed technology makes it possible to introduce a new technique for the disposal of solid plant waste in the food industry, with obtaining effective sorbents enriched with a polysaccharide component at the content of cellulose of about 56 %.

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