1. Antonina MALYUSHEVSKAYA[1], 2. Anna YUSHCHISHINA[1], 3. Olena MITRYASOVA[2], 4. Volodvmvr POHREBENNYK[3], 5. Ivan SALAMON[4]

Institute of Impulse Processes and Technologies of NAS of Ukraine, Ukraine (1), Petro Mohyla Black Sea National University, Ukraine (2), Lviv Polytechnic National University, Ukraine (3), University of Presov, Slovak Republic (4)
ORCID. 1. 0000-0003-0703-6105, 2. 0000-0002-5691-0885, 3. 0000-0002-9107-4448, 4. 0000-0002-1491-2356, 5. 0000-0001-5379-3989

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Optimization of Extraction Processes of Water-Soluble Polysaccharides under the Electric Field Action

Abstract. *The process of water extraction of polysaccharides was experimentally investigated when pulsed, alternating and direct current passes through the suspension "hyssop grass - water".*

Streszczenie. *Eksperymentalnie zbadano proces ekstrakcji wody polisacharydów, gdy przez zawiesinę „trawa hyzopowa – woda" przepływa prąd pulsacyjny, zmienny i stały.* (***Optymalizacja procesów ekstrakcji rozpuszczalnych w wodzie polisacharydów w działaniu pola elektrycznego***)

Keywords: pulsed electric field, extraction, polysaccharides, vegetable raw materials
Słowa kluczowe: pulsacyjne pole elektryczne, ekstrakcja, polisacharydy, surowce roślinne.

Introduction

The principles of sustainable development are a roadmap for the development of modern green technologies and industries [1-4]. The urgent need to transfer production to the principles of sustainable development, an increase in demand for environmentally friendly products with improved properties causes the development of new technologies for extracting biologically active substances from plant raw materials. Green technologies allow to reduce the negative impact on the environment, improving, first of all, the state of water resources and contributing to the sustainable development of ecosystems [5-9]. Biologically active substances isolated from plants have great potential for use in pharmacology (for example, galenic preparations), cosmetology (aromatic oils and various complex extracts), food industry (natural dyes, sweeteners, etc.). But the existing extraction methods are not perfect, and do not allow efficient, safe and rational extraction of target components, therefore, it is necessary to develop new intensive approaches.

The extraction process is a mass transfer process of extracting components from a mixture with the help of solvents (extractants), most often the rate of this process is increased by increasing the temperature and dispersing phases, that is, the process becomes heat and mass transfer. A promising way to enhance the process of heat and mass transfer is the effect of electromagnetic fields of various intensities and configurations on the "extractant - raw material" system. The purpose of this intensification is to increase the rate of the extraction process, increase the completeness of the extraction of target substances, reduce energy costs, and ensure the safety of bioactive components. Achieving this goal will reduce the severity of the problem of storing and maintaining the quality of vegetable raw materials during storage, rationally load industrial capacities of the food or pharmaceutical industry, reduce energy costs for such industries and approach sustainable development technologies.

The creation of an effective technology for extracting biologically active substances from plant materials under the influence of an electromagnetic field of an electric current and devices for its implementation is hindered by the lack of data on the conditions for ensuring enhanced heat and mass transfer while simultaneously maintaining or improving the quality of the final product (extract, filtrate).

Polysaccharides of plant and animal origin have antibiotic, antiviral, antitumor, anti-sclerotic and other medicinal properties. Methods for the isolation of polysaccharides from natural raw materials are very diverse and it is impossible to describe a standard procedure, but there are several general requirements and approaches. The selected extraction method must meet two main requirements:

firstly, it must be accompanied by the lowest possible cost of resources at all stages;

secondly, the polysaccharide must undergo as few changes as possible during the extraction process - taken into account as degradation caused by the chemical agents used and the possible influence of the enzymes present in the source.

Now there is a new round in the development of some methods aimed at intensifying the extraction of substances of plant origin. These include mainly the following methods: electric-discharge, magnetic-pulse, centrifugal extraction [10], extraction under the action of a microwave field [11-15] and some biological [16].

All existing methods for the extraction of target substances from plants can be divided into methods of isolation and distillation, the choice of the method is mainly determined by the properties of the compound that is extracted. Another principle of the classification of extraction methods is their division into static and dynamic, in the first case, the raw material is poured with an extractant and insisted for some time, in the second, either only the extractant or the extractant and the raw material are constantly replaced. Traditionally used extraction methods are described in the State Pharmacopoeias, for example [17]. Classical methods include maceration or infusion (used in the production of tinctures, extracts) [18], countercurrent method [19], percolation method [20], Soxhlet method [21].

Modern intensive methods for extracting bioactive substances from plant materials include: accelerated liquid extraction [22], supercritical fluid extraction [23], subcritical water extraction [24], ultrasonic extraction.

The use of ultrasound makes it possible to increase the rate of the extraction process, to increase the yield of extracted substances, to ensure the extraction of inaccessible substances, in some cases to carry out the extraction at room temperature. Ultrasound enhances diffuse processes in tissues, changes the concentration of hydrogen ions in them, and causes the splitting of high-molecular compounds. The main driving force of ultrasonic treatment of plant objects for the extraction of target components from them is considered to be cavitation, which causes the appearance of a large number of ionized molecules in a liquid working medium. Ultrasonic extraction can be used to extract essential oils, lipids [25, 26] and dietary supplements from plants. But, it was found that when using the method of ultrasonic extraction, the material itself is influenced, which is inextricably linked with changes in its structure, which are not always desirable. At present, the dependence of the degree of destruction of biologically active substances of various origins on the parameters of ultrasonic treatment has not been precisely established.

Now there is a new round in the development of some methods aimed at intensifying the extraction of substances of plant origin. These include mainly the following methods: electric-discharge, magnetic-pulse, centrifugal extraction, extraction under the action of a microwave field and some biological [27-29].

The aim of this study is to study the process of extracting water-soluble polysaccharides from hyssop under the influence of fields generated by electric current.

Results and discussions

As an object of research, we used air-dry ground (leaves, stems, flowers) hyssop (Hyssopus officinalis L.). Freshly harvested raw materials contained 72% wt. water. Drying was carried out immediately after the collection of raw materials [30] to prevent the destructive action of enzymes and the development of mold, but in such a way that the target substances were preserved. Therefore, the temperature of the drying process was 40-50°C, while the herbaceous raw materials were laid out in a thin layer at the rate of 1 kg per 1 m^2 of drying area. The residual water content in the raw material did not exceed 14%. To prepare experimental samples, the crushed ground part of the plants was sifted through a sieve with a cell diameter of 7 mm, the sifted dry raw material weighing 50 g was poured with 1.5 dm^3 water, and the raw material was dynamically rehydrated for 12 hours at room temperature. To prepare the suspension, we used tap water from Mykolaiv with a specific electrical conductivity of 0.45 μS/cm and a redox potential of 268 mV, pH=6.7. The filtrate of such samples obtained at the end of the rehydration process was used as a zero sample ("Zero"). The rest of the prepared suspensions were treated with pulsed, alternating, and direct current electromagnetic fields in a chamber with an interelectrode distance of 10 cm at an initial suspension temperature of 25°C. The duration of treatment was varied in such a way that the final temperature of the processed sample did not exceed 40°C, trying to preserve bioactive extractives. The pulsed current treatment modes were varied by changing the pulse repetition rate. They tried to keep the total energy introduced into the working volume in the range from 6 to 9 kJ/kg when processing the suspension with pulsed, alternating and direct current, and in the latter two cases by varying the voltage. Sampling for the content of polysaccharides was carried out immediately after the end of the treatment with electromagnetic fields, and also, to clarify the hypothesis about the inertia of the extraction processes caused by the influence of the electromagnetic field, additional infusion of already processed samples was carried out for 90 minutes.

To experiment on processing plant materials with current pulses, the scheme shown in Figure 1 was used.

An array of experimental processing modes is presented in Table 1. Control samples of aqueous extract of polysaccharides from medicinal hyssop ("Control") were prepared according to [31]. The ground part of hyssop medicinal plants with a dry weight of 50 g, ground and sifted, as indicated above, was placed in a pre-heated container, filled with tap water of room temperature with a volume of 1.5 dm^3, covered with a lid and heated in a water bath, stirring occasionally, for 25 min. After the end of the heat treatment of the hyssop-water suspension, it was cooled at room temperature for 90 min, filtered through a double gauze layer, squeezing out the rest of the plant material, and the filtrate was examined for the content of polysaccharides.

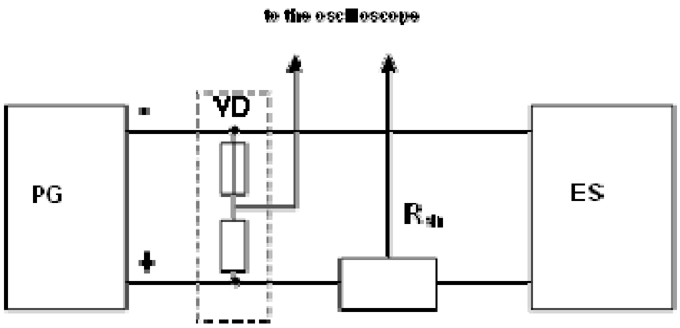

Fig. 1. Diagram of experimental equipment for pulse current processing. (PG - pulse current generator; VD - voltage divider; Rsh - shunt;
ES - electrode system)

Table 1. Experimental modes of processing samples of a suspension of hyssop-water.

Name of the sample	Voltage, V	Specific energy, kJ/dm^3	Source frequency current, Hz	Temperature at the end of processing, ° C	Processing time, min
1	2	3	4	5	6
Processing of samples with a pulsed current					
1	150	-	500	30	3.0
2	150	6,8	500	40	9.0
3	Sample 2 was kept at room temperature				90
4	150	-	250	30	3.0
5	150	7,73	250	40	9.0
6	Sample 5 was kept at room temperature				90
7	150	-	750	30	2.0
8	150	6,46	750	40	7.5
9	Sample 8 was kept at room temperature				90
10	150	-	50	30	3.0
11	150	9,0	50	40	9.0
12	Sample 11 was kept at room temperature				90
13	150	-	500	30	2.0
14	150	9,1	500	40	10.25
15	Sample 14 was kept at room temperature				90
16	150	-	1000	30	3
17	150	8,33	1000	40	9.75
18	Sample 17 was kept at room temperature				90
AC Sample Processing					
19	50 B, I=3 A	6,47	50	30	1.1
20	Sample 19 was kept at room temperature				90
21	100 B, I=6,5 A	6,93	50	32	0,27
22	Sample 21 was kept at room temperature				90
23	110 B, I=7,5 A	6,6	50	32	0.2
24	Sample 23 was kept at room temperature				90
Processing of samples with direct current					
25	20 B, I=1,5 A	6,67	-	30	6.7
26	Sample 25 was kept at room temperature				90
27	50 B, I=5,5 A	6,6	-	30	0.6
28	Sample 27 was kept at room temperature				90
29	100 B, I=8 A	6,4	-	30	0.2
30	Sample 29 was kept at room temperature				90

The processing of the suspension on the ground part of the hyssop/tap water using electromagnetic fields of currents of various types made it possible to obtain the following data on the content of the sum of polysaccharides in the filtrates of the suspensions (Table 2.).

Let us analyze the obtained data from the point of view of the relationship between the pulse parameters and the content of water-soluble polysaccharides in the extracts obtained after the pulsed current treatment of the hyssop herb - water suspension (Table 2).

The maximum content of soluble polysaccharides (1.9524 g/l) is demonstrated by extract "15", obtained after processing the suspension with a pulsed current at a generator frequency of 500 Hz. To elucidate the main operating factors of such an influence of the pulsed current, the influence of a continuous pulse on the extraction processes was studied. It turned out that the duration of the pulse is of great importance for the intensification of the extraction processes - when it is halved, the treatment of the suspension with a current turned out to be much less effective - in the extract obtained at such a frequency (sample 3), although the total the energy introduced into the treated volume (1.25·104J) is close to the energy used to obtain the sample “15” (1.37·104J), the content of water-soluble polysaccharides is only 0.5909 g/l. The content of polysaccharides in the extract "12" obtained at a frequency of 50 Hz (1.6231 g/l, energy of 1.35·104 J was introduced) also stands out among those studied. In this case, the shape of the current and voltage pulses in this case was distinguished by a greater ordering and symmetry, and, most importantly, the pulse duration is the longest - tens of milliseconds, in contrast to tenths of milliseconds. Perhaps it was this factor that made it possible to obtain such a content of target components, despite a significant gradual decrease in the average value of the current from the beginning of the processing process and almost until its very end (up to 0.3 A versus 0.45 A for the sample “15 ").

Table 2. Influence of different types of treatment with an electromagnetic field of currents of different types on the degree of extraction of water-soluble polysaccharides from the ground part of medicinal hyssop

Extract name	Structure	Content of polysaccharides in terms of glucose, C, g/l
	Standard glucose solution: 1 ml of 1% picric acid, 3 ml of 20% Na_2CO_3, 5 ml of glucose solution (0.05 g in 250 ml), add dist. water up to 50 ml.	0.2000
Zero	1 ml of picric acid, 3 ml of 20% Na_2CO_3, 5 ml of the investigated extract, heated for 10 minutes at t=80-90^{o}C, allowed to cool, dist. water up to 50 ml	0.3643
Control	All extracts were prepared similarly to the sample "Zero", their names correspond to the names of the samples in Table 1	1.3196
3		0.5909
6		0.6566
9		1.3916
12		1.6231
15		1.9524
18		0.4860
22		0.9098
30		0.9665

At this stage of the research, the goal of investigating the dependence of the content of water-soluble polysaccharides in the extracts on the amplitude of the pulse current was not considered, all experiments were carried out at a generator voltage of 150 V and the initial electrical resistance of the suspension was assumed to be the same, this was confirmed by the approximate equality of the average values of pulse currents - from 0.28A to 0.35A. If we analyze the oscillograms, we can conclude that during the experiment the electrical conductivity of the suspension increases slightly and the average value of the current increases - from about 0.3 A at the beginning of the process to 0.35 A at its end. This effect can also be due to an increase in the temperature of the treated suspension. But when processing the sample "6" with a pulse current with a frequency of 250 Hz, the opposite process was observed - over the course of processing, the average value of the current decreased from 0.6 A to 0.3 A. This phenomenon requires further study and clarification.

To compare the energy consumption required to obtain extracts of is-sop polysaccharides by different methods, the following experiment was carried out. The initial suspension of hyssop herb and water (sample "Zero"), prepared by the method described above, was heated to a temperature of 40 to 90°C with a step of 10°C by the convection method and left at room temperature 25°C for infusion for 90 minutes. After that, the filtrates were obtained and the content of water-soluble polysaccharides in them was determined by the picric method. The results are summarized in Table 3.

Table 3. Content of water-soluble polysaccharides in extracts obtained by convection heating of hyssop / water suspension

The final temperature of the suspension, °C	Content of water-soluble polysaccharides, g/l
40	1.0432
50	1.5210
60	1.8521
70	1.9003
80	2.1004
90	2.2832

The closest to the best (extract "15" from Table 2) result is the heating of the suspension to 70^{o}C. Electricity consumption for such heating is about 28.2·104 J, while the cost of pulsed electric current treatment of a similar suspension to obtain sample "15" was 1.37·104 J. Thus, from the point of view of energy consumption, extraction , intensified by a pulsed electric current, in comparison with extraction by convection heating, has a twentyfold advantage.

The discussed method makes it possible to significantly expand the range of recoverable components in comparison with the electric-discharge (breakdown) method due to the possibility of using a wider range of extractants. In the case of pulsed electric current intensification of extraction, the range of electrical conductivity of the suspension is limited only by the requirements for the fundamental possibility of passing an electric current. The results of the work indicate the advantage of using a pulsed current for intensifying extraction when processing plant materials. Treatment with a pulsed current at a moderate electric field strength (E≤100 V/cm) and a short processing time (t = 400 ... 500 s) makes it possible to effectively influence the extraction processes of target substances, significantly reduce the temperature of the extraction processes, and avoid significant losses in the concentration of the target. -th product, i.e. the pulsed electric current method of processing plant raw materials directly in the extractant has great practical prospects.

Conclusions

Shown in principle the possibility of intensifying the process of extraction of polysaccharides from plant materials under. exposure to an electric field.

The effect of several types of electric fields - direct, alternating and pulsed currents - on the extraction process of medicinal hyssop polysaccharides has been studied.

It has been shown that under conditions of pulsed electric current treatment it is possible to increase the content of extracted polysaccharides by 48% in comparison with the traditional pharmacopoeial method of their extraction.

Low final temperature (up to 40°C) of the considered process, the treatment allows expanding the range of extractable substances while maintaining their biological activity.

Authors:
Antonina Malyushevskaya, PhD, Eng., Institute of Impulse Processes and Technologies of NAS of Ukraine, E-mail: ninutsa@ukr.net;
Anna Yushchishina, PhD, Ass.Prof., Institute of Impulse Processes and Technologies of NAS of Ukraine, E-mail: yushchishinaanna@gmail.com;
Olena Mitryasova, DSc., Prof., Dept. of Ecology, Petro Mohyla Black Sea National University, E-mail: eco-terra@ukr.net;
Volodymyr Pohrebennyk, DSc., Prof. Dept. of Ecological Safety and Nature Protection Activity, Lviv Polytechnic National University, E-mail: vpohreb@gmail.com;
Ivan Salamon, PhD, Prof., Dept. of Ecology, University of Presov,; E-mail: ivan.salamon@unipo.sk

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