Optimization of the process CO_2 - extraction of plant raw material

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Abstract. The goal of optimization is to determine the best, i.e. the most advantageous state of the system. One of the optimization methods is the scanning method, the essence of which is to sequentially view the optimality criterion at a number of points belonging to the region of change of independent variables, and find among these points one in which the optimality criterion has the maximum (minimum) value. The main advantage of the scanning method is that the use of sufficiently "densely" located points of interest always guarantees the search for a global optimum. At the first stage, scanning is carried out with a large step, then the segment within which the largest value of the function is obtained is divided into smaller segments, a new segment is found, inside which the refined value of the maximum is located. The obtained data on the optimal operating parameters of the process of CO_2-extraction of licorice root are necessary for the engineering calculation of equipment for the implementation of this process, the optimal operating parameters of the liquorice root CO_2 extraction process were determined. In this case, the calculated and experimental values are equal to the extract yield of 35,7678 and 31,60, respectively, which confirms the adequacy of the generalized equation.

1 Introduction

Today, the main and fundamental purpose is the development of equipment and technologies that are adjusted to obtain environmentally friendly products of plant material used in the food, pharmaceutical, chemical and cosmetic industries.

Existing technologies for the extraction and concentration of biologically active substances and food additives from subtropical and medicinal plant materials lead to significant changes in the chemical composition of thermolabile components. First of all, this applies to essential fatty acids and vitamins. For example, essential oils obtained by steam distillation contain only highly volatile aromatic substances of the feedstock [16]. When extracts are obtained using organic solvents, the selectivity of the extraction of valuable components is not ensured, and when the solvent is distilled off, the heat-labile substances of the extracts are destroyed [13].

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In this regard, the improvement of the technology for the production of CO_2 extracts from local raw materials used in functional products is very relevant in the Republic of Uzbekistan.

2 Literature review

It was shown that the amount of extract that could be obtained from licorice roots ranged from 8,17 to 16,80%. These results can be compared with those literature data where extraction was combined with microwave treatment and they were 8,7%-16.8%. Some other literature data refer to supercritical CO_2 extraction [2]. However, these authors use a term defined as the ratio of supercritical CO_2 output to that of classical extraction methods. They found that supercritical CO_2 extraction gives a yield of 20÷85%, while in the classical method the yield ranges from 11÷43%. It should also be pointed out that supercritical CO_2 extraction of liquorice roots includes moisture-heat treatment of the material [3], which was absent in the methods used earlier in [4].

The literature [1] reported on the use of RSM - response surface methodology and CCRD (central composite rotatable design) for these purposes. The efficiency of the established conditions for supercritical CO_2 extraction, expressed by the content of glycyrrhizic acid in the extracts, was also compared with the yield of glycyrrhizic acid obtained by the traditional extraction method (water + ethanol).

Licorice root - Glycyrrhiza belongs to the Fabaceace legume family. Licorice root, the most ancient medicine. It contains substances useful for the human body: glycyrrhizic acid, phenolic compounds, glabridin and carbohydrates [5,6,7,8].

Currently, licorice root in many countries of the world is widely used in the food, pharmacological, and cosmetic industries. A processed product, that is, licorice root extract, which is obtained by Soxhlet extraction, maceration, percolation, turbo extraction (high-speed stirring) and sonication is very popular [9]. Recently, the so-called CO_2 extraction has become most widespread; carbon dioxide is used as a solvent in pre- and supercritical states [10].

In [11], the authors carried out studies on obtaining an extract of licorice root by CO_2-extraction.

Nonlinear programming methods are used to solve optimal problems with non-linear goal functions. The method of nonlinear programming combines a large group of numerical methods, many of which are adapted to solve optimal problems of the corresponding class. A number of non-linear programming methods are almost always used in combination with other optimization methods (for example, with the scanning method in dynamic programming).

The scanning method consists in sequentially viewing the optimality criterion at a number of points belonging to the region of change of independent variables, and finding among these points one in which the optimality criterion has a maximum (minimum) value. The accuracy of the method, of course, is determined by how “dense” the selected points are in the allowable range of independent variables [17].

3 Goals and objectives of the study

The purpose of our study is to identify the optimal conditions for the extraction of licorice root, summarizing the results obtained by other authors.

The task is to choose the most optimal conditions for extracting glycyrrhizic acid from licorice roots using modern methods of mathematical modeling [11,12,13,14,15,16].

As you know, the goal of optimization is to determine the best, i.e. the most advantageous state of the system [17]. To this end, in this work, the least squares method was used to obtain regression equations, and the scanning method was used to optimize the extraction parameters.

4 Material and research methods

To solve optimal optimization problems, mainly the methods of studying the functions of classical analysis, methods based on the use of indefinite Lagrange multipliers, as well as the calculus of variations, dynamic programming, linear and nonlinear programming, etc. are mainly used. As a rule, it is impossible to recommend any one method for solving all without exception problems arising in practice. The best way to choose the optimization method most suitable for solving the corresponding problem is to study the possibilities of using various optimization methods [17].

In this regard, the main advantage of the scanning method is that the use of sufficiently "densely" located points under study always guarantees the search for a global optimum, since the entire range of independent variables is analyzed [17].

At the first stage, scanning is carried out with a large step, then the segment within which the largest value of the function is obtained is divided into smaller segments, a new segment is found, inside which the refined value of the maximum is located. It (the new segment) is again divided into smaller ones, etc., until the value of the segment containing the maximum value of the function is less than the specified error.

In this regard, to solve the problem of optimizing the process of extracting licorice root using CO_2, we chose the scanning method [17,18].

5 Research results and discussion

In [18] for the qualitative and quantitative characteristics of the extraction of glycyrrhizin from particles of licorice root (Glycyrrhiza glabra) crushed roots, the following results were achieved:

- the material is contacted with continuous stirring, using distilled water and ethyl alcohol-water as the extraction medium.

Solutions for licorice root were chosen as aqueous-alcoholic and ammonia-aqueous;

- low values of the distribution coefficient for some cases of extraction of glycyrrhizin showed a fast extraction;
- a mathematical model was proposed for modeling the release of glycyrrhizin inside the solid particles of licorice, respectively;
- for the extraction of glycyrrhizin with a cold ammonia-water solution, the chemical reaction that occurs in the surface of the particle brings the model under consideration to the form where only the effective diffusion coefficient is responsible for the dynamics of the process;
- the values of the effective diffusion coefficient were determined, comparing with the data on swelling, information on the structure of the porous solid.

Research by Bogdanovich and others reported on the use of RSM - response surface methodology and CCRD (central composite rotatable design) for these purposes. The efficiency of the established conditions for supercritical CO_2 extraction, expressed by the content of glycyrrhizic acid in the extracts, was also compared with the yield of glycyrrhizic acid obtained by the traditional extraction method (water + ethanol) [1].

In the present study, the response surface methodology was used to optimize the conditions for the extraction of phenolic compounds from licorice root using microwaves [20].

In this experiment, at a fixed extraction time, the yield of glycyrrhizic acid increased with increasing extraction temperature. Therefore, it can be considered that the solubility of glycyrrhizic acid increases with increasing temperature, and therefore the amount of extracted glycyrrhizic acid also increases. Moreover, it was found that the yield of glycyrrhizic acid increases with increasing extraction time, followed by a decrease with a further increase in extraction time. The extraction yield decreased, which may be due to bioactive degradation during prolonged ultrasonic activity [21].

The results of supercritical CO_2 optimization obtained in previous studies [11,12,14,15] as well as those available in the literature for various plants have proven that the extraction temperature has little or no effect on extraction (yield) glycyrrhizic acid. It is also important to note that this study provides for the first time data on supercritical CO2 extraction of glycyrrhizic acid from licorice roots [18,19].

In [11], empirical equations were obtained to formalize the particular dependences of the extract yield on the influencing extraction parameters: temperature t (^{0}C) and pressure P (MPa) of the compressed CO_2 extractant, as well as the duration of the process τ (min), obtained by processing the experimental data by the method least squares:
for factor 1 – extractant temperature:

$$y = -41.772 + 4.176 \cdot t - 0.058 \cdot t^2 ; \quad (1)$$

for 2 factors - process time:

$$y = 10.537 + 0.336 \cdot \tau - 0.0001 \cdot \tau^2; \quad (2)$$

for 3 factors - extractant pressure:

$$y = 75.080 - 0.2211 \cdot P + 0.7257 \cdot P^2 \quad (3)$$

We choose the extract yield as a criterion for the optimality of the CO_2-extraction process, and the pressure and temperature of the extractant, the duration of the material extraction as the influencing factors. Let's reveal them in an implicit form:

$$Y_{ex} = f(P, T, \tau) \rightarrow Y_{ex\ max} \quad (4)$$

To obtain a generalized equation for the technological process of extracting licorice root, the formula proposed by M.M. Protodyakonov [18]:

$$Y_{\Pi} = \frac{\prod_{i=1}^{n} Y_i}{Y_m^{n-1}} \quad (5)$$

where Y_Π is a generalized function; Yi is a partial function; $\prod_{i=1}^{n} Y_i$ is the product of partial functions; Y_m^{n-1} is the overall average of all considered values of the generalized function, to a power of one less than the number of partial functions. For our case, as the objective function we will take the generalized equation that was obtained in [11]:

$$Y_{ex} = \frac{(41{,}772 + 4.176 \cdot t - 0.058 \cdot t^2) * (10{,}537 + 0{,}336 \cdot \tau - 0{,}0001 \cdot \tau^2)}{32{,}5^2 * (75.080 - 0{,}2211 \cdot P + 7257 \cdot P^2)^{-1}} \quad (6)$$

where t is the temperature of the extractant, τ is the time of extraction, P is the pressure of the extractant.

When finding the optimal values of the objective functions, the restrictions are given in the form of the following expressions for the mathematical model (6) of extraction:

for extraction temperature, ^{0}C: $30 \leq t \leq 45;$

for extraction time, min: $90 \leq \tau \leq 150;$

for extraction pressure, MPa: $7{,}5 \leq P \leq 9{,}5.$

The lower and upper limits of the influencing factors are chosen according to the results of experimental studies carried out in [7].

Based on the test results, the working commission recognized that the proposed method of direct extraction using liquefied carbon dioxide as an extractant is highly effective, considers it appropriate to introduce the proposed installation for producing CO_2 - extracts into production.

A computer program has been created and a certificate of official registration of the program DGU 09833, 01/05/2021 has been received. [22].

for electronic computers of the Agency for Intellectual Property under the Ministry of Justice of the Republic of Uzbekistan (Optimization of the process of obtaining CO2 extract from licorice root DGU 09833, 01/05/2021). The program is designed to find the optimal parameters for the yield of extract from licorice root by CO_2-extraction according to experimental data.

On the basis of an experimental study of the influence of such factors as the temperature of the extractant (compressed carbon dioxide), the duration of extraction and the pressure of the extractant on the yield of extractives from crushed licorice root, empirical equations were obtained as a result of data processing by the least squares method.

The obtained empirical equations are checked for reliability using the methods of mathematical statistics.

At the same time, the approximation error, the coefficient of determination, and the Fisher criterion are determined.

On the basis of these empirical equations, a generalized formula was obtained that describes the dependence of the yield of extractive substances from the licorice root during CO2 extraction on the influencing factors: extractant temperature, extraction duration and extractant pressure, and using the scanning method, the optimal values were found, which gives a maximum yield of products at critical points.

The above algorithm (Certificate of official registration of the program for electronic computers DGU No. 098331) is implemented in the Delphi language. The input components are given default initial values. They can be changed. The execution of the task is divided into several stages according to the concept of the algorithm, which are implemented by the Button components.

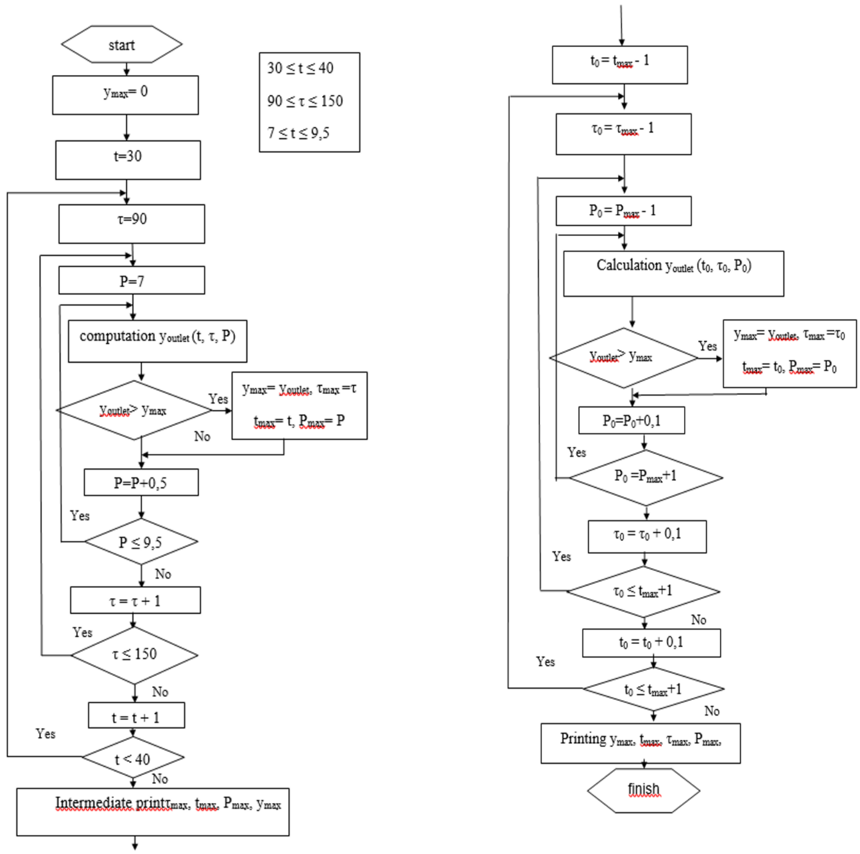

Fig. 1. Algorithm for solving the problem of optimizing the CO_2 extraction process.

In accordance with the scanning method, in the first stage, the maximum extraction yield is found in large steps, while the steps are taken as follows: ΔP=0,5 MPa; Δτ=1 min; Δt=1 ^{0}C.

As a result of solving the optimization problem, the optimal operating parameters of the process of CO_2 extraction of licorice root were determined: the specified extraction pressure P = 9,5 MPa, the extraction temperature

t=36 ^{0} C, extraction time τ=135 minutes. In this case, the calculated and experimental values are equal to the extract yield of 35,7678 and 31,60%, respectively, which confirms the adequacy of the generalized equation (3).

In the second step of solving the optimization problem, we find the maximum extraction yield in small steps, while the steps are taken as follows: ΔP=0.1 MPa; Δτ=0,1 min; Δt=0,1 ^{0}C; and the restrictions are as follows (adjacent values of the optimal parameters P=9,5 MPa, t=36 ^{0}C, τ=135 min):

for extraction temperature, ^{0}C: $35 \le t \le 37$;

for extraction time, min: $134 \le \tau \le 136$;

for extraction pressure, MPa: $9,4 \le P \le 9,6$.

With given small steps and restrictions, the maximum point was obtained at the following values: given extraction pressure P=9,5 MPa, extraction temperature t=36^{0}C, extraction time τ=135,5 minutes, i.e. only the extraction time has changed. In this case, the calculated value of the extract yield is 35,7681%, the difference of which is small with the value of 35,7678% during the primary optimization.

According to the results of the performed calculations, the dependences of the optimality function on the values of the influencing factors were obtained (Fig. 2,3,4). It can be seen from the graphs that the goal function approaches the maximum with a decrease in temperature from 37 ^{0}C to 35.

C, with an increase in pressure from 9,0 to 9,5 MPa, the extraction time from 136 to 134 minutes.

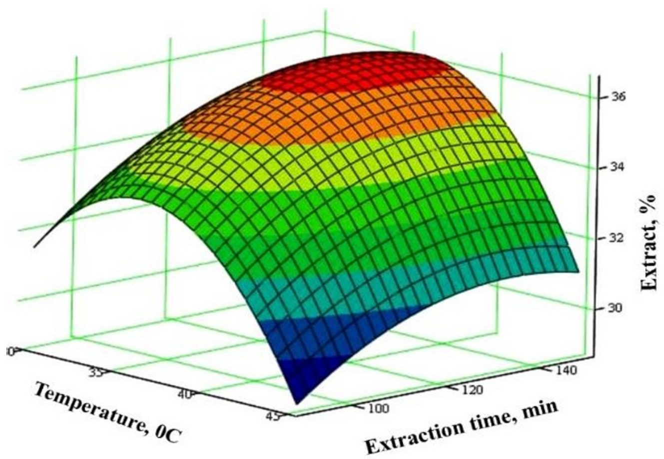

Fig. 2. Graph of the dependence of the extract yield on the temperature of the extractant and the duration of the process.

With increasing temperature, the solubility of solids in most cases increases. Very rarely, an increase in temperature leads to a decrease in solubility. But in our case, we cannot raise the temperature to preserve biologically active components.

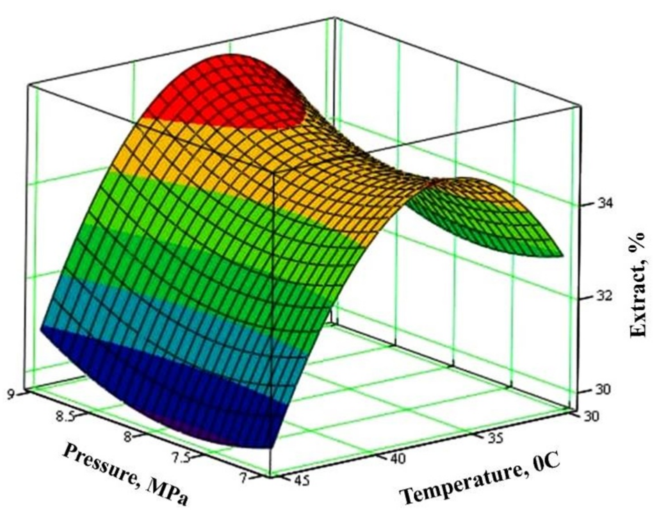

Fig. 3. Graph of dependence of extract yield on extractant temperature and process pressure.

From the data presented in graphs 3-4, it can be seen that with increasing pressure, the yield of extractive material increases. The results also show that a high yield of oil is observed at a pressure of 7,0 MPa (under subcritical conditions), while under supercritical conditions a high yield of licorice root extract is observed at 9-9,5 MPa. Therefore, for the extraction of licorice root, a pressure of 9,5 MPa is optimal.

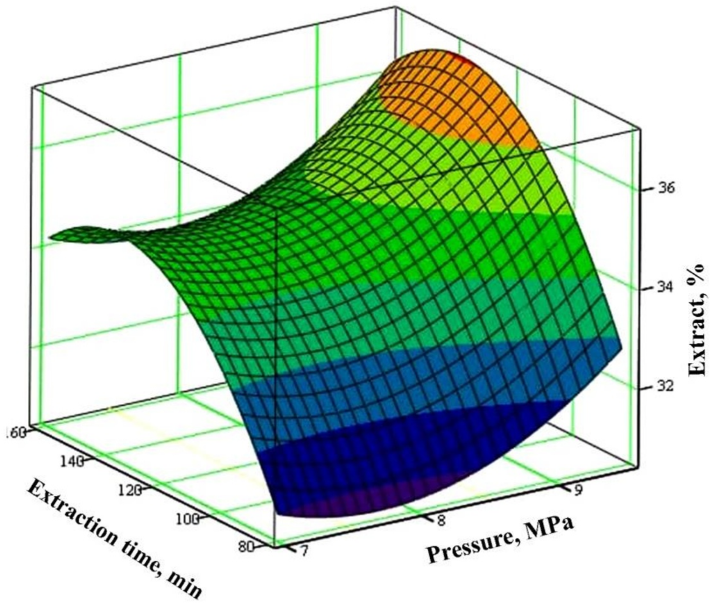

Fig. 4. Graph of dependence of extract yield on pressure and duration of the process.

Any production process is effective if it is short. The duration of the process affects the yield of the sum of extractive substances or individual substances. The kinetic regularities of the process of extraction with liquefied gases gives an idea of the rate of extraction of biologically active substances from plant materials.

For extracting licorice root extract, time is one of the main factors. Insufficient extraction time of the raw material with the extractant reduces the yield of the product; an increase in the contact time of the raw material with the solvent leads to an extract with a high yield. Therefore, it was advisable to study the kinetics of licorice root extraction.

Approbation of research results. Based on the obtained scientific results on the improvement of extraction equipment and modeling of an effective technological process of CO_2 extraction of licorice root, the following results were obtained: an efficient CO_2 extraction apparatus was introduced in Bukhara Roses LLC (Bukhara), economic efficiency was obtained in the amount of 315 million soums per year.

6 Conclusions

1) On a single methodological basis, the formalization of multi-level and multi-criteria tasks of optimizing the process of extracting licorice root was carried out. 2) An analysis of the optimization results shows that, according to the designs of the CO_2 extractor, it allows us to draw a conclusion about the effectiveness of the design. 3) The use of the recommended design of the extractor makes it possible to reduce the extraction time by more than 6 times, which significantly improves the quality indicators of the obtained ingredients. Thus, under appropriate conditions 4) The maximum yield of the extract was obtained at: extractant

pressure P=9,5 MPa, extractant temperature t=36 ^{0}C, extraction time τ=135 minutes. The yield of the extract is 35.77%. The obtained data on the optimal operating parameters of the process of CO_2-extraction of licorice root are necessary for the engineering calculation of equipment for the implementation of this process.

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