Determination of an effective regimen for maceration of berry raw materials of the *Rubus* genus

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**Abstract.** This article presents the results of mathematical modeling of the process of maceration of berry raw materials of the *Rubus* genus. The optimal extractant concentrations and the duration of the process, which provide the maximum output of extractives, are determined. The quadratic regression, obtained at the preliminary stage of modeling, had a high relative error by smoothing the experimental data; the coefficient of determination of the quadratic regression was 82.55%, which is significantly lower than the threshold value of 95%. Because the use of polynomial and polynomial-logarithmic functions to represent the patterns of this extraction processes was insufficient, a two-stage modeling approach was chosen. As a result, a general model for the dependence of the output of extractive substances on the duration of extraction and ethanol concentration was developed, based on the proposed two-stage modeling approach with the use of fractional-rational functions.

1. **Introduction**

The importance of food consumption in relation to human health has increased consumer attention in nutraceutical components and foods, especially fruits and vegetables. Berries are a rich source of a wide variety of non-nutritive, nutritive, and bioactive compounds such as flavonoids, phenolics, anthocyanins, phenolic acids, stilbenes, and tannins, as well as nutritive compounds such as sugars, essential oils, carotenoids, vitamins, and minerals. Bioactive compounds from berries have potent antioxidant, anticancer, antimutagenic, antimicrobial, anti-inflammatory, and antineurodegenerative properties, both in vitro and in vivo [1].

In the framework of complex technologies for processing plant materials, cultivated and wild berries of the *Rubus* genus have a great potential as sources of valuable nutrients (vitamins, flavonoids, anthocyanins, etc.) [2], [3].

Functional foods commonly incorporate some plant extract(s) rich with biologically active compounds produced by conventional extraction. This approach implies negative thermal influences on extraction yield and quality with a large expenditure of organic solvents and energy [4].

To extract biologically active components from berry raw materials, various extraction methods can be used [5], [6], [7], [8]. The easiest way is the maceration method used in the manufacture of extracts, tinctures. The main advantage of this method is the ease of extraction and the maximum preservation of the useful properties of the obtained extracts, because heating and intense mechanical stress are not used
in their manufacture. The disadvantages of this method are the complexity, duration of the process and incomplete extraction.

The solution to this problem is a search for the optimal parameters of the maceration regime, which allow to obtain the maximum output of extractive substances.

This study presents the results of mathematical modeling in the process of maceration of berry raw materials of the Rubus genus.

2. Methods and results

Among the representatives of the Rubus genus cloudberry is of great interest. Cloudberries (Rubus chamaemorus) contain phenolics (mainly ellagitannins), which have recently been related to many valuable bioactivity properties [9], [10].

The objects of the research were: the Rubus chamaemorus berries, growing in the Turukhansky district of the Krasnoyarsk Territory, collected during the technical maturity of the harvest period 2019. Water-ethanol solutions of various concentrations were used as a solvent. The quantitative determination of extractives was carried out in accordance with the pharmacopoeia article [11]. Mathematical modeling was performed with the help of the Statistics package from the Maple computer mathematics system, while using the DataFit package.

3. Results and discussion

The extraction was carried out at 20 °C temperature through maceration at a mass ratio of raw material and solvent 3:100. Ethanol concentration was ranged from 40 to 70% vol., with an interval of 5% vol. The determination of the output of extractives was carried out every day.

At a preliminary level of research, the statistical processing of data on control and result indicators was performed: the duration of extraction (τ, h), ethanol concentration (η, % vol.), the extractives’ output (Q, %), including finding the numerical characteristics and constructing a quadratic regression. The duration of extraction (τ, h) with an average value of 92.07 h varied from 24 to 168 h, the concentration of an ethanol solution with an average of 55.17% vol. ranged from 40 to 70% vol., the output of extractives was on average 13.55% and limited to 5.29 ... 22.6%. The standard deviation from the average value of an ethanol solution with an average of 55.17% vol. ranged from 40 to 70% vol., the output of extractives was on average 13.55% and limited to 5.29 ... 22.6%. The standard deviation from the experimental data of these indicators was estimated by numerical values: 46.79 h, 10.00% vol., 4.57%.

The linear correlation coefficient between the output of extractives (Q, %) and the duration of extraction (τ, h) was estimated at 0.57, and with the ethanol concentration (η, % vol.) it was 0.66.

The obtained quadratic regression had a high relative error by smoothing experimental data: for 45 points out of the available 58, the relative error turned out to be higher than 5%. In addition, the coefficient of determination of quadratic regression is 82.55%, which is significantly lower than the threshold value of 95%.

Because the use of polynomial and polynomial-logarithmic functions to represent the patterns of maceration technological processes was insufficient, a two-stage modeling approach was chosen, including: 1) constructing with the use of fractional-rational functions partial dependences of the output of extractives Q(τ, 40), Q(τ, 45), ..., Q(τ, 70) at ethanol concentrations of 40% vol., 45% vol., ..., 70% vol.; 2) constructing the general dependence of Q(τ, η) on two variables τ and η.

As a result of the implementation of the first stage of modeling, dependencies were obtained, which are represented by the following fractionally - rational equations (equations 1-7):

\[
Q(\tau, 40) = \frac{18.02685374\tau^2 - 3939.6336\tau + 260452.1927}{\tau^2 - 219.3437419\tau + 14113.29156\tau - 156318.2022} \times 10^{-1}
\] (1)

\[
Q(\tau, 45) = \frac{18.97300712\tau^2 - 3938.949182\tau + 235866.69}{\tau^2 - 206.1937419\tau + 11860.28007\tau - 89371.63986} \times 10^{-1}
\] (2)

\[
Q(\tau, 50) = \frac{20.8967418\tau - 4888.646532\tau + 428629.6245}{\tau^2 - 288.919565\tau + 17827.53214\tau - 1} \times 10^{-1}
\] (3)

\[
Q(\tau, 55) = \frac{17.28638258\tau^2 - 3123.405968\tau + 144744.9965}{\tau^2 - 168.9191109\tau + 7569.910406\tau + 186190.8249} \times 10^{-1}
\] (4)
The determination coefficients of regression dependences exceeded significantly the threshold value of 95%. The relative errors by smoothing the experimental data for the presented dependences did not exceed the threshold value of 5%.

To implement the two-stage modeling approach at the second stage of research, we constructed a general model for the output of extractives from private models, obtained at the first stage, corresponding to ethanol concentrations of 40%, 45%, ..., 70%.

The output of extractives (\(Q, \%\)), depending on the duration of extraction (\(\tau, \text{h}\)), and ethanol concentration (\(\eta, \% \text{vol.}\)), is represented as an interpolation polynomial (figure 1):

\[
Q(\tau, 60) = \frac{13.92615338 \tau^6 - 2160.702872 \tau^5 + 70387.04837 \tau^4 + 0.1602268246 \times 10^7 \tau^3 - 128.7781413 \tau^2 + 182.269186 \tau + 385624.0931}{\tau^6 + 182.269186 \tau^5 + 385624.0931 \tau^4 + 182.269186 \tau^3 + 70387.04837 \tau^2 + 2160.702872 \tau + 13.92615338}
\]

\[
Q(\tau, 65) = \frac{4.80862668 \tau^6 - 358.0258322 \tau^5 + 206532.4832 \tau^4 + 0.427048933 \times 10^7 \tau^3 - 1232.4429005 \tau^2 + 33217.04067 \tau + 610738.8387}{\tau^6 + 1232.4429005 \tau^5 + 33217.04067 \tau^4 + 206532.4832 \tau^3 + 358.0258322 \tau^2 + 4.80862668 \tau + 1}
\]

\[
Q(\tau, 70) = \frac{7.343448688 \tau^6 - 1036.989528 \tau^5 + 61281.32631 \tau^4 + 36614.6035 \tau^3 - 182.3153885 \tau^2 + 11762.41134 \tau + 1}{\tau^6 + 182.3153885 \tau^5 + 11762.41134 \tau^4 + 61281.32631 \tau^3 + 1036.989528 \tau^2 + 7.343448688 \tau + 1}
\]

Figure 1. The dependence of the yield of extractives (\(Q, \%\)) from the duration of the extraction (\(\tau, \text{h}\)) and the concentration of ethanol (\(\eta, \% \text{vol.}\)).

Polynomial interpolation scheme for nodes (\(\eta_k, Q(\tau, \eta_k)\)), \(\eta_k=40, 45, ..., 70, k=1, 2, ..., 7\), as well as checking the adequacy of the general model according to the Fisher’s F-criterion and the relevance of its coefficients by Student’s t-criterion (at a significance level of 5%) was implemented with the help of the Statistics package from the Maple computer mathematics system.

A computational experiment with the proposed model showed that the predicted output of extractive substances varies in the range 5.29 ... 22.77%, averaging 13.56% with a standard deviation of 4.57%.

The relative deviation of the experimental data from the predicted values of the output of extractive substances varied in the range -1.89...1.78%, with a standard deviation of 0.82, and in absolute value no more than 2%. Therefore, the relative error of approximation did not exceed the threshold value of 5%. The absolute error also did not exceed the value of 0.33%.

The coefficient of determination of this dependence, represented by the general model of the output of extractive substances, was 99.73%, which is significantly higher than the threshold value of 95%.

From the analysis of the relative deviation and the coefficient of determination, we can conclude that the constructed general model can be used for forecasting purposes in the parametric area of the duration of extraction and ethanol concentration (equations 8):

\[
Q=\{ (\tau, \eta): 24 \leq \tau \leq 168.40 \leq \eta \leq 70 \}
\]

It is assumed that the selection of effective parameters for the indicators of the duration of extraction (\(\tau^*, \text{h}\)) and ethanol concentration (\(\eta^*, \% \text{vol.}\)) will provide the maximum output of extractives (\(Q^*, \%\)), that is (equations 9):
\[ Q^* = \max_{\Omega} Q(\tau, \eta) \] (9)

In this case, a couple \((\tau^*, \eta^*)\) will be the argmaximum of the output function \(Q(\tau, \eta)\), that is the solution of the following problem for optimizing the output function \(Q(\tau, \eta)\) in the parametric area \(\Omega\) (equations 10):

\[ (\tau^*, \eta^*) = \arg \max_{\Omega} Q(\tau, \eta). \] (10)

The maximum function of one variable \(Q(\tau, 49)\) is achieved at \(\tau^* = 144.66\) h, and the maximum function of two variables \(Q(\tau, \eta)\) is achieved at \(\tau^*=144.66\), \(\eta^*=49\%\) vol., and is equal to 23.10%.

Thus, an effective operating regime of the extractor is established by the ethanol concentration of 49% and extraction time of 144.66 hours, which ensures the highest output of extractives in an amount of 23.10%.

4. Conclusions
At the preliminary level of research, when performing statistical processing of data, the control and result indicators of the extraction processes from berry raw materials of the Rubus genus were distinguished: the coefficient of linear correlation between the output of extractives and the duration of extraction is estimated at 0.57, and with ethanol concentration it was of -0.66; indicators of the duration of extraction and ethanol concentration are slightly correlated, with a tightness of connection 0.04.

At the main level of research, a general model was developed for the dependence of the output of extractives on the duration of extraction and ethanol concentration based on the proposed two-stage modeling approach with the use of fractional-rational functions. The possibility and accuracy of predicting the laws of extraction in a given parametric area is justified by the values of the determination coefficient of 99.73% (> 95%) and the relative error of 1.89% (<5%).

As a result of mathematical modeling, an effective extraction regime of berry raw materials of the Rubus genus was determined, corresponding to the calculated optimum of the function of the general model in a given parametric area: at the ethanol concentration of 49% and extraction duration of 144.66 h, the highest output of extractive substances in the amount of 23.10% is achieved.

References
[1] Nile S H, Park S W Edible berries: Bioactive components and their effect on human health 2014 Nutrition 30(2) 134-44
[2] Teng H, Fang T, Lin Q, Song H, Liu B and Chen L. 2017 Red raspberry and its anthocyanins: Bioactivity beyond antioxidant capacity Trends in Food Science and Technology 66 153–65
[3] Luchina N A Technological Properties of Raspberries Grown in the Novosibirsk Region 2015 Food Industry 8 22–4
[4] Putnik P, Lorenzo J M, Barba F J, Roohinejad Sh, Jambrak A R, Granato D, Montesano D and Kovačević D B Novel Food Processing and Extraction Technologies of High-Added Value Compounds from Plant Materials 2018 Foods 7(7) 106
[5] Makila L, Laaksonen O and Kallio H Effect of processing technologies and storage conditions on stability of black currant juices with special focus on phenolic compounds and sensory properties 2017 Food Chem. 221 422-30
[6] Vagiri M and Jensen M Influence of juice processing factors on quality of black chokeberry pomace as a future resource for colour extraction 2017 Food Chem. 217 409-17
[7] Eremeeva N B, Makarova N V, Zhidkova E M, Maximova V P and Lesova E A 2019 Ultrasonic and microwave activation of raspberry extract: antioxidant and anti-carcinogenic properties Foods and Raw Materials 7 264-73
[8] Terletskaya V A, Rubanka E V, Zinchenko I N Influence of technological factors on the process of black chokeberry extraction 2013 Food Processing: Techniques and Technology 31(4) 127–
31

[9] Laine P, Kylli P, Heinonen M and Jouppila K Storage Stability of Microencapsulated Cloudberry (Rubus chamaemorus) Phenolics 2008 J. Agric. Food Chem. 56(23) 11251–61

[10] Thiem B Rubus chamaemorus L. – a boreal plant rich in biologically active metabolites: a review 2003 BIOL. LETT. 40(1) 3-13

[11] OFS.1.5.3.0006.15 Determination of the content of extractive substances in medicinal plant raw materials and medicinal plant preparations