Clarification of sunflower oil with nanocarbon sorbent and analysis of product quality indicators

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Abstract. The concept of Industrie 4.0 involves the introduction of innovative industrial technologies. Sunflower oil is the most common vegetable oil in Russia. Improvement of sunflower oil quality is required taking into account changes in the domestic and foreign markets of Russia. The process of oil clarification with nanocarbon structures is proposed in the article. The influence of fullerene-containing sorbent on the efficiency of sunflower oil clarification process was investigated in the work. The mathematical model of the process is developed with the complete factorial experiment. Colour, acid number, mass fraction of moisture and volatile substances were taken as quality indicators. Variable indicators were the amount of fullerene-containing sorbent, the particle size of the fullerene-containing sorbent and the clarification process temperature. Series of experiments were carried out. According to them the values of color and acid numbers, mass fraction of moisture and volatile substances of the oil were obtained. The indicators obtained were compared with the oil indicators after the traditional clarification method. According to the built mathematical models graphs, a comprehensive quality indicator was determined as well as the optimal values of the conditions for the clarification process. It was found out that the use of fullerene-containing carbon as a sorbent for sunflower oil clarification improves the acid number by 80%; the mass fraction of moisture and volatile substances – by 74%, and the color index – twice. Thus, the use of fullerene-containing carbon as an adsorbent makes it possible to obtain world-class sunflower oil.

1. Introduction

The production of high-quality world-class sunflower oil by Russian enterprises is based on the introduction of innovative industrial technologies taking into account the concept of Industrie 4.0 and it will contribute to increasing the efficiency of production in other food industry sectors [1, 2, 3].

With Russia's switch to market relations after entering the WTO and changes in relations, both on the domestic and foreign markets [4, 5], many paragraphs of GOST 1129-2013 [6] were outdated and the sunflower oil produced according to the specified standard does not meet modern world requirements for the oil quality [7], although the majority of the oil manufactures produce their goods at the world level and have the ability to increase the quality products manufacturing.

Nanomaterials studying over the past two decades showed that they possess a set of physicochemical characteristics that are used in various fields of science and technology [8, 9, 10]. Since their structure consists of carbon (like the structure of most organic compounds), their use in the food industry is not ruled out [11], in particular, as an adsorbent for sunflower oil clarification.

Thus, the study of the adsorption capacity of fullerene-containing carbon in relation to sunflower oil and the development of recommendations for its practical use is the main task nowadays.
Studies of sorption by carbon products obtained in carbon-helium plasma were carried out by various scientists. They proved the high adsorption capacity of fullerenes [12-15]. This is a prerequisite for the use of fullerene-containing carbon as a sorbent for sunflower oil clarification [16]. Therefore, to study the effect of the adsorbent on the cleaning quality, it is necessary to use such an adsorbent, which includes the necessary amount of fullerenes.

2. Materials and methods

Fullerene-containing carbon was used as a fullerene-containing sorbent for research. Its composition included carbon nanotubes, soot, carbon, but fullerenes were the main component. Fullerenes were obtained by thermal decomposition of graphite and subsequent fullerene molecule assembly.

A sample of sunflower oil obtained as a result of neutralization, in the amount of 50 g, was heated in a water bath to the required temperature (depending on the number of the experiment) and the required amount of adsorbent was added. This temperature was maintained with constant stirring for half an hour. Then the mixture was filtered through a paper filter. The resulting oil was cooled to room temperature, and the quality indicators specified in GOST 1129-2013 [6], the value of which should be influenced by the clarification process, were determined in it. The colour determination was carried out according to GOST 5477-2015 [17], the acid number was determined according to GOST 5476-80 [18], the mass fraction of moisture and volatile substances was determined according to GOST 11812-66 [19].

3. Results

A number of experiments were carried out to study the effect of fullerene-containing sorbent on the efficiency of the sunflower oil clarification process. A full factorial experiment was applied to build a mathematical model. The following parameters were chosen as independent variables affecting the efficiency of the adsorption process: the amount of the fullerene-containing sorbent, the particle size of the fullerene-containing sorbent, and the temperature of sunflower oil clarification. We chose two variations for these variables:
- the amount of the fullerene-containing sorbent – 0.025 g and 0.075 g;
- the particle size of the fullerene-containing sorbent – 50 μm and 100 μm;
- the temperature – 50 °C and 80°C.

The mathematical model is presented in the form of an incomplete quadratic regression equation of the relationship of the quality indicator (colour, acid number, moisture mass fraction) from the controlled parameters. For these factors, the equation has the form:

\[ y = b_0 + b_1 x_1 + b_2 x_2 + b_3 x_3 + b_{12} x_1 x_2 + b_{13} x_1 x_3 + b_{23} x_2 x_3, \]  

where

- \( x_1 \) is the amount of the fullerene-containing sorbent;
- \( x_2 \) is the particle size of the fullerene-containing sorbent;
- \( x_3 \) is the temperature.

A reproducibility check was carried out and significance factors were determined for them.

After converting the equation from coded to absolute values, the model for the acid number has the following form:

\[ y = -0.0435 + 1.0086 c_1 + 0.00072 c_2 + 0.00065 c_3 - 0.00783 c_1 c_2 + 0.00439 c_1 c_3 - 0.00001 c_2 c_3, \]  

where

- \( c_1 \) is the amount of the fullerene-containing sorbent, g;
- \( c_2 \) is the particle size of the fullerene-containing sorbent, μm;
- \( c_3 \) is the temperature of the clarification process.

After analyzing sunflower oil producers claims over the past 3 years, it was found out that the largest percentage of defects exists in terms of color, the value of which depends on the sorbent used and the clarification conditions [20].

Analysis of changes in the mass fraction of moisture and volatile substances of sunflower oil was carried out in the work (Figures 1, 2). To analyze the color change of sunflower oil, an experiment was carried out with the expert method and the values of the color number were obtained. Their comparative analysis is presented in Figure 3.
After the results reproducibility calculation, a model for the mass fraction of moisture and volatile substances was obtained. It has the following form:

\[ b = 3.64755 - 21.445c_1 - 0.03001c_2 - 0.03887c_3 + 0.1168c_1c_2 + 0.00033c_2c_3 + 0.133c_1c_3 \]  

(3)

The value of the mass fraction of moisture and volatile substances of the sample clarified by traditional sorbents (bleached earth and perlite) is 0.263. The acid number value of the sample clarified by traditional sorbents (bleaching earth and perlite) is 0.07. Therefore, the application of fullerene-containing carbon improves the quality of sunflower oil in terms of quality - acid number by 80% under the following conditions: the amount of fullerene-containing sorbent - 0.075 g; the particle size of the fullerene-containing sorbent - 100 \( \mu \)m; the temperature - 80 °C.

The consistency of participants’ views determines the accuracy of the evaluations. Expert opinions are agreed. As a result, the obtained model for color has the following form:

\[ a = 27.934 - 58.355c_1 - 0.08355c_2 - 0.3336c_3 - c_1c_2 + 0.00167c_2c_3 + 1.667c_1c_3 \]  

(4)

To determine the complex quality indicator, graphs of mathematical models were built for the color number, acid number and mass fraction of moisture and volatile substances at \( c_2, c_3 = \text{const} \), \( c_1, c_3 = \text{const} \), \( c_1, c_2 = \text{const} \) (Figure 4).

The graphs show that when the number and size of particles of the fullerene-containing sorbent as well as the process temperature changes, the values of the color number, acid number and mass fraction of moisture and volatile substances change in different ways. Since the quality of sunflower oil depends on the total values of all quality indicators, and not each separately, we introduce a complex quality indicator \( S \) equal to the sum of the squares of the deviations of the theoretical values obtained from the models from the standard values. To find the optimal values of the parameters of the clarification process, the value of the complex quality indicator should be minimal:
\[ S = (a - a_n)^2 (a_n)^2 + (b - b_n)^2 (b_n)^2 + (y - y_n)^2 (y_n)^2 \rightarrow \min, \]  

(5)

where \( y \) is the standard value of acid number,  
\( a_n \) is the standard value of color number,  
\( b_n \) is the standard value of the mass fraction of moisture and volatile substances.

To determine the minimum, we find the partial derivatives with respect to \( c_1, c_2, c_3 \) and equate them to zero:

\[
\begin{align*}
\frac{\partial S}{\partial c_1} &= 0, \\
\frac{\partial S}{\partial c_2} &= 0, \\
\frac{\partial S}{\partial c_3} &= 0.
\end{align*}
\]

(6)

Thus, the final mathematical model of the optimal parameters choice for obtaining oil of a given quality was derived in the work:

\[
\begin{align*}
\frac{1}{y_n} (2(-0.0435 + 1.0086c_1 + 0.00072c_2 + 0.00065c_3 - 0.00783c_1c_2 - 0.00439c_1c_3 - 0.00001k_c c_1 - \\
- y_n)(1.0086 + 0.00783c_2 - 0.00439k_c) + \frac{1}{b_n^2} (2(3,64755 - 21.445c_1 - 0.0300k_c - 0.03887c_3 + 0.1168c_2 + \\
+ 0.133c_1c_3 + 0.00033c_2c_3 - b_n)(-2.1445 + 0.1168c_1 + 0.133c_1) + \frac{1}{a_n} (2(27,934 - 58.355c_1 - 0.08355c_2 - \\
- 0.3336c_1 - c_1c_2 + 1.667c_1c_3 + 0.00167c_2c_3 - a_n)(-58.355 - c_2 + 1.667c_1)) &= 0, \\
\frac{1}{y_n} (2(-0.0435 + 1.0086c_1 + 0.00072c_2 + 0.00065c_3 - 0.00783c_1c_2 - 0.00439k_c c_1 - 0.00001k_c c_1 - \\
- y_n)(0.0072 - 0.00783c_1 - 0.00001k_c) + \frac{1}{b_n^2} (2(3,64755 - 21.445c_1 - 0.0300k_c - 0.03887c_3 + 0.1168c_2 + \\
+ 0.133c_1c_3 + 0.00033c_2c_3 - b_n)(-0.03001 + 0.1168c_1 + 0.00033c_1) + \frac{1}{a_n} (2(27,934 - 58.355c_1 - 0.08355c_2 - \\
- 0.3336c_1 - c_1c_2 + 1.667c_1c_3 + 0.00167c_2c_3 - a_n)(-0.08355 - c_1 + 0.00167c_1)) &= 0, \\
\frac{1}{y_n} (2(-0.0435 + 1.0086c_1 + 0.00072c_2 + 0.00065c_3 - 0.00783c_1c_2 - 0.00439k_c c_1 - 0.00001k_c c_1 - \\
- y_n)(0.00065 - 0.00439c_1 - 0.00001k_c) + \frac{1}{b_n^2} (2(3,64755 - 21.445c_1 - 0.0300k_c - 0.03887c_3 + 0.1168c_2 + \\
+ 0.133c_1c_3 + 0.00033c_2c_3 - b_n)(-0.03887 + 0.00033c_1 + 0.133c_1) + \frac{1}{a_n} (2(27,934 - 58.355c_1 - 0.08355c_2 - \\
- 0.3336c_1 - c_1c_2 + 1.667c_1c_3 + 0.00167c_2c_3 - a_n)(-0.3336 + 1.667c_1 + 0.00167c_1)) &= 0, \\
\end{align*}
\]

(\text{c}_1, \text{c}_2, \text{c}_3 > 0)

Since it is necessary to strive for a world-class level of quality to ensure the production and products competitiveness, we take the values from international standards as normative values of quality indicators: \( y_n = 0.3; a_n = 5; b = 0.001 \) [19].

After solving the final mathematical model, the optimal values of the conditions for carrying out the sunflower oil clarification process were found, the radicals closest in value to the experiment
conditions were chosen: \( c_1 = 0.05996 \, \text{g}, \ c_2 = 42.5 \, \mu\text{m}, \ c_3 = 82 \, ^\circ\text{C} \). The result of sunflower oil clarification with a fullerene-containing sorbent is presented in Figure 5.

Figure 5. Clarification results: 1 - sunflower oil after clarification with a fullerene-containing sorbent; 2 - sunflower oil after clarification with a traditional sorbent.

By maintaining the calculated values of the process parameters during sunflower oil clarification we will obtain a product with values of quality indicators corresponding to the world level, and the resulting mathematical model will allow us to determine the parameters of the clarification process for the given quality oil production.

4. Conclusion

Studies with traditional and fullerene-containing sorbents for the analysis of physicochemical parameters were carried out: color and acid numbers, mass fraction of moisture and volatile substances. It was found out that the application of fullerene-containing carbon as an adsorbent can improve the acid number by 80%, the mass fraction of moisture and volatile substances – by 74%, and the color index – twice.

Mathematical models in the form of incomplete quadratic regression equations were built for the practical application of fullerene-containing sorbent in the process of sunflower oil clarification on a production scale. Since the quality of sunflower oil depends on a combination of quality indicators values, a complex quality indicator was given in the work. The optimal values of the parameters of the clarification process were determined with its help, and the final mathematical model of the optimal choice of parameters for obtaining oil with specified characteristics was built.

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