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Optimization of a process for discoloration of low-grade syrup

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Abstract. Color improvement of low-grade industrial syrup, on activated carbon, was optimized using a central composite design and response surface methodology. This study checks the effect of three experimental parameters: mass of adsorbent (activated carbon), contact time adsorbate-adsorbent (syrop - activated carbon), masses ratio of the flours constituting the filter cake (m_w/m_b), and their interactions on the response: ICUMSA Color. The exploitation of the established model in the space of the variables allowed defining optimal economic conditions of obtaining clear class syrup according to the International Commission for Uniform Methods of Sugar Analysis (ICUMSA).

Keywords: *Syrup, Discoloration, ICUMSA Color, Optimization, Experimental design, Response surface methodology.*

1. Introduction

Preparation of standardized sugar syrup includes three main steps: dissolving crystallized white sugar in water, filtering and discoloration. During the discoloration, the ICUMSA color value is measured to control the process and avoid disagreeable aromas [1-3].

During discoloration standardized sugar syrup, the crystallized sugar is usually dissolved in water at a concentration between 60 and 70 Brix [1,4]. The solution is then filtered, decolorized and used to produce soft drinks, lemonades and juices.

The ICUMSA color value determines the purity of the sugar solution. If it is greater than 25 IU (ICUMSA unit), the unpleasant residual aromas in the final product will be felt. After discoloration, the value should remain below 25 IU [1,4].

Use of a local syrup in the formulation of a colorless drink poses a problem with the coloring of the syrup and therefore of the drink [5,6]. In general, sugar dyes are macromolecules with weak acid behavior. They are in the form of long hydrophobic carbon chains and have a hydrophilic end, at the level of their weak acid function [7]. The ion exchange resin method [7,8] and the activated carbon adsorption method [9-11] are the most widely used methods for decolorizing sugar syrup.

In order to properly control the discoloration of sugar syrup by adsorption on activated carbon, it is necessary to study the parameters influencing this treatment such as the mass of adsorbent; activated carbon, the adsorbate-adsorbent contact time and the mass ratio of the flours constituting the filter cake, taking into account their interactions [10].

Experimental design methodology is a strategy for planning experiments to extract information corresponding to the initial objective. Analysis of collected information uses statistical methods [12].
The determination of the optimal conditions, which are the most economical in the present studies, is done by applying the response surface methodology [13]. This method allows establishing an empirical mathematical model that is a relationship between the output response and the input variables allowing optimizing the process parameters in order to achieve the desired response [14].

2. Materials and methods

2.1. Experimental method and materials

Into a closed and thermostatically controlled reactor equipped with a stirrer, we introduce 100 ± 0.01 g of sugar in 66 mL of demineralized water. The solution is brought to a temperature of 76 ± 2 °C for 20 min in order to obtain syrup of 60 ± 2 Brix [10,15], using densimeter type DMA 48. The obtained product is treated by adsorption on activated carbon (m ± 0.001 g) (Table 1) [10,15] and then filtered, using Buchner equipped with a pump, through a mixed layer (white-brown) produced by the following method: 9.2 ± 0.001 g of white flour are added to 60 Brix syrup, and then filtered. The resulting cake is called a white pre-layer. We add 2.9 ± 0.001 g of brown flour to the obtained filtrate and we filter through the cake just prepared [10].

The coloration of the filtred syrop is measured using a Jenway N9712 UV-visible spectrophotometer, with single-beam from 320 to 1000 nm, at the wavelength (λ) of 420 nm [15-18]. The value of the absorbency index multiplied by 1000 is reported as ICUMSA Color:

$$\text{ICUMSA Color} = \frac{1000 \text{ x } A_{420nm}}{\text{b x c}} \qquad (1)$$

where:

A_{420nm}: Absorbance of the solution at the wavelength 420 nm,
b: optical path-length in cm (= 1 cm),
c: concentration in g/mL.

The resulting values are referred to as ICUMSA Units (IU) [1].
The standard reference for zero coloration corresponds to filtered distilled water.

2.2. Protocol of optimization

The goal of the experimental design methodology is to establish a mathematical model between the measured response and a number of variables that influence it [19]. In this work, we propose to establish a mathematical model between the response: ICUMSA Color and the factors influencing discoloration: mass of activated carbon (m_{ch}), contact time (t_c) and the ratio of flour masses (m_w/m_b), taking into account their interactions by constructing a central composite design [13]. This matrix has several advantages, particularly high resolution and a minimum number of tests [20]. For three factors, achieving a complete factorial design with 5-level requires 5^3 = 125 experiments, while our central composite design requires only 20 experiments [12]. Indeed, the realization of the latter depends on the number of explanatory variables to be studied.
Table 2 gathers the 20 tests which constitute the central composite design. The values of the coded variables X_j are grouped in Table 1.
The equation of the theoretical model is written:

$$\hat{Y} = \beta_0 + \sum_{j=1}^{3} \beta_j X_j + \sum_{j=1}^{3} \sum_{j'=1, j' \neq j}^{3} \beta_{jj'} X_j X_{j'} + \sum_{j=1}^{3} \beta_{jj} X_j^2 \quad (2)$$

where:

$\hat{Y}$ is the response function,

β_0 is the polynomial constant that expresses the general average effect,

β_j ,β_{jj}, $\beta_{jj'}$ are the coefficients of the linear effect, quadratic and interaction, respectively,

X_j and $X_{j'}$ represent the independent coded variables.

The method of least squares makes it possible to determine the β_U coefficients of the model [13]:

$$\beta_u = \frac{Y_u}{\sum_{i=1}^{n} X_{iu}^2} \quad (3)$$

$$Y_u = \sum X_{iu}\, y_i \quad (4)$$

with X_{iu} and Y_i are the values of X_u and Y for the i_{th} experiment.

The degrees of significance of the coefficients were determined using the student test.

2.3. Statistical software

The studies of the experimental design, the matrix calculations, as well as the statistical analysis experimental data were carried out using the JMP software, version 7 [21].

Table 1. Experimental range

Natural variables	Coded variables: X_1, X_2, X_3				
	-1.6818	-1	0	1	1.6818
$x_1 = m_{ch}$ **(g)**	1.3182	2	3	4	4.6818
$x_2 = t_c$ **(mn)**	7.9092	12	18	24	28.0908
$x_3 = m_w/m_b$	1.8227	2.3	3	5.7	4.1772

3. Results and discussions

3.1. Statistical analysis of the results

The set of results relating to the determination of ICUMSA Color of syrups are given in Table 2. The estimated values of the coefficients of the model and the significance are given in Table 3. So, the equation of this model is written as follows:

$$\begin{aligned} Y_{est.} = {} & 7.124 + 4.2605\, X_1 - 2.3375\, X_2 + 0.7088\, X_3 \\ & - 0.6125\, X_{12} - 0.6125\, X_{13} + 2.2075\, X_{23} \\ & + 2.1875\, X_1^2 + 1.2056\, X_2^2 + 0.8352\, X_3^2 \end{aligned} \quad (5)$$

From this equation, it is possible to calculate the estimated values ($Y_{est.}$) and the corresponding residues (Table 2). The comparison between the experimental and calculated values shows that there is a good estimate of the model.

In addition, the results in the form of analysis of variance (ANOVA) are given in Table 4. The results analysis shows that the model explains perfectly the experimental results [22].
From Table 3, it appears that only the mass of activated carbon, the contact time of activated carbon-syrup and the contact time of activated carbon-syrup – mass ratio of the flours constituting the filter cake (t_C–m_w/m_b) and the mass of the activated carbon – mass of the activated carbon (m_{ch}-m_{ch}) interactions are significant. Therefore, for a significance level of 90%, the mathematical model equation is written:

$$Y_{est.} = 7.124 + 4.2605\ X_1 - 2.3375\ X_2 + 2.2075\ X_{23} + 2.1875\ X_1^2 \qquad (6)$$

Table 2. Experiment matrix of central composite design and analyze results

Order	Values of coded variables			$es_{exp.}$	$es_{est.}$	Residues
	X_1	X_2	X_3	$Y_{exp.}$	$Y_{est.}$	e_i
1	-1	-1	-1	11.41	9.70	1.71
2	1	-1	-1	25.81	20.67	5.14
3	-1	1	-1	5.23	1.84	3.39
4	1	1	-1	9.33	10.36	-1.03
5	-1	-1	1	12.09	7.93	4.16
6	1	-1	1	17	16.45	0.55
7	-1	1	1	7.7	8.90	-1.20
8	1	1	1	17.2	14.97	2.23
9	0	0	0	7.34	7.12	0.22
10	0	0	0	7.39	7.12	0.27
11	0	0	0	7.12	7.12	-0.004
12	0	0	0	7.34	7.12	0.22
13	0	0	0	7.39	7.12	0.27
14	0	0	0	7.12	7.12	-0.004
15	-1.6818	0	0	2.77	6.15	-3.38
16	1.6818	0	0	18.28	20.48	-2.20
17	0	-1.6818	0	9.015	14.47	-5.45
18	0	1.6818	0	6.48	6.60	-0.12
19	0	0	-1.6818	4.72	8.29	-3.57
20	0	0	1.6818	8.68	10.68	-2.00

$Response_{exp.}$: experimental ICUMSA Color; $Response_{est.}$: estimated ICUMSA Color; $Y_{exp.}$: experimental response; $Y_{est.}$: calculated response; e_i : residues of the i^{th} experiment.

3.2. Graphical analysis of the results

The graphical representation of the response (ICUMSA Color) in the space of the variables X_1 (mass of activated carbon) and X_2 (contact time of activated carbon-syrup) for a constant mass ratio of flour (X_3 = -1.6818) is shown on the Fig. 1. The contour plots given in this figure show that the response (ICUMSA Color) decreases to zero for a minimum value of the mass of the activated carbon and a maximum value of the contact time. In addition, we note that all the values of the ICUMSA Color represented by the isoresponse curves are less than 25 UI; value imposed by the International Commission for the Standardization of Sugar Analysis Methods [23]. This is due to the good choice of the studied experimental field which was based on preliminary studies in the laboratories.

So, the optimal conditions for obtaining bleached syrup, with the above criteria, are as follows: m_{ch} = 1.318 g (X_1 = -1.6818), t_c = 7.91 mn (X_2 = -1.6818) and m_w/m_b = 1.823 (X_3 = -1.6818). Under these conditions, the value of predicted response ($\hat{Y}$) is equal to 17.4.

Table 3. Coefficients of the estimated model

Effects and interactions	Coefficients (β_u)	t_{exp}	Significance
β_0	7.1239821	4.73	***
β_1	4.2604692	4.27	**
β_2	-2.3375330	-2.34	*
β_3	0.7087942	0.71	NS
β_{12}	-0.6125000	-0.47	NS
β_{13}	-0.6125000	-0.47	NS
β_{23}	2.2075000	1.69	<10%
β_{11}	2.1875474	2.25	*
β_{22}	1.2055528	1.24	NS
β_{33}	0.8352057	0.86	NS

*** : significant at a level of 0,1 % ; ** : significant at a level of 0.5 % ;
* : significant at a level of 5 % ; <10%: significant at a level of 10% ;
NS : not significant.

Table 4. Regression variance analysis

Source	Sum of squares	Degrees of freedom	Medium square	$F_{exp.}$	Significance
Regression	461.64648	9	51.2941	3.7657	*
Residue	136.21391	10	13.6214		
Total	597.86039	19			

*: significant at a level of 5%.

3.3. Experimental verification

In order to verify the optimization results, it is absolutely necessary to retry experiment under these optimal conditions to verify that the experimental measurements are in agreement with what has been predicted. In this context it was essential to do the experimental verification of the optimal point. The ICUMSA Color obtained experimentally $(Y)_{exp.}$ is 17.3. This data show that the difference between the predicted and the experimental values are very small. Consequently, the established model can be considered to represent the studied response.

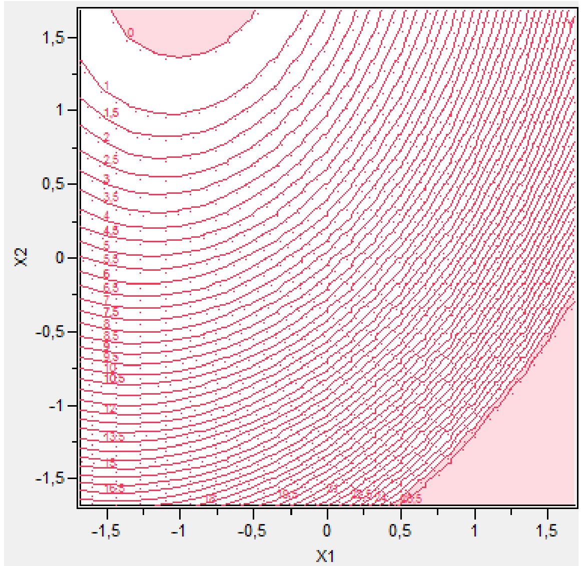

Figure 1. Response function contour lines with X_3 = -1.6818.

4. Conclusion

The use of an experimental design permitted us to build up a mathematical model representative of the phenomenon of the discoloration of sugar syrup by adsorption on activated carbon. The graphical portrayal of this model in the variable space permitted us to predict the conditions for acquiring an ICUMSA Color lower than the value imposed by the International Commission for the Standardization of Sugar Analysis Methods (25 IU) in the most economical conditions.

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