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Separation of vitamin C by reactive extraction
2. Mathematical modeling of extraction process

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Abstract

Using the statistical analysis and a second order factorial experiment, a mathematical correlation between the vitamin C reactive extraction degree and the main parameters influencing the process (Amberlite LA-2 concentration, pH-value, duration) has been established. For both extraction systems, the considered variables control the extraction process in a 91.1% extent, the former two parameters exhibiting the most important influence.

Keywords: reactive extraction, vitamin C, Amberlite LA-2, mathematical modeling, regression equation, regression coefficients, determination coefficients.

Introduction

Vitamin C deficiency leads to scurvy, a disease characterized by weakness, small hemorrhages throughout the body that cause gums and skin to bleed, and loosening of the teeth [1,2].

Vitamin C is a water-soluble compound, being obtained by extraction from plants, by chemical synthesis, by biosynthesis and by mixed chemical/biochemical methods [1-4]. Its separation and purification require a lot of difficult stages, with high material and energy consumption.

For these reasons, in the previous paper the separation of vitamin C by reactive extraction with Amberlite LA-2 in butyl acetate has been studied [5]. The studies indicated that the separation occurs by means of an interfacial reaction between the vitamin C and the extractant, the extraction process being controlled by the extractant concentration in organic phase and pH-value of aqueous phase. The separation efficiency was enhanced by addition of a phase modifier, namely 2-octanol, the extraction yield being increased with about 6 - 23%. The phase modifier increases the solvent polarity and, consequently, exhibits a favorable effect on interfacial product solubilization into organic phase.

The previous experiments have been continued by mathematical modeling of vitamin C reactive extraction process, using the statistical analysis, respectively the factorial experiment of second order. The proposed model takes into account the cumulated influences of Amberlite LA-2 concentration in organic phase, pH-value of aqueous phase and the duration of extraction process on the extraction yield.

Materials and Method

The experiments have been carried out using an extraction column with vibratory mixing, this laboratory equipment being described in previous paper [5]. The phase mixing was made by mean of a perforated disk with 45 mm diameter and 20% free section. The vibrations had a frequency of 50 s^{-1} and 4 mm amplitude. The mixer position was maintained at the initial contact interface between the aqueous and organic phases. The extraction time was varied between 5 and 15 s at a constant temperature of 24^{o}C. The resulted emulsion was evacuated at the base of the column and broken in a centrifugal separator at 4000 rpm.

The vitamin C initial concentration in aqueous solution was of 7.6 g l^{-1}. The organic phase was a solution of Amberlite LA-2 in butyl acetate, the extractant concentration varying between 40 and 160 g l^{-1}.

The pH adjustment of the initial vitamin C solution has been made with a solution of 5% sulfuric acid or 5% sodium hydroxide, function on the prescribed pH value (the pH-value of vitamin C solution was of 3.5) The pH values were determined by using a digital pH meter of Consort C836 type and have been recorded throughout each experiment. Any pH change was noted during extraction experiments.

The extraction degree has been calculated by means of the vitamin C concentrations in the initial solution and in the raffinate. The vitamin C concentrations have been determined using the iodometric titration [6].

Results and Discussion

As it was concluded in the previous paper, the increase of extractant concentration in butyl acetate exhibits a significant influence on vitamin C extraction degree, by increasing the interfacial product hydrophobicity, either by solvation or by entrapping it into the aminic micelles [5].

Another important factor is the pH-value of aqueous solution, its lower values leading to the significant increase of extraction yield, especially because the acidic pH avoids the formation of dehydroascorbic acid, compound that has not the capacity to react with Amberlite LA-2 [5].

The cumulated effects of extractant concentration and pH-value on vitamin C extraction efficiency are plotted in Fig. 1.

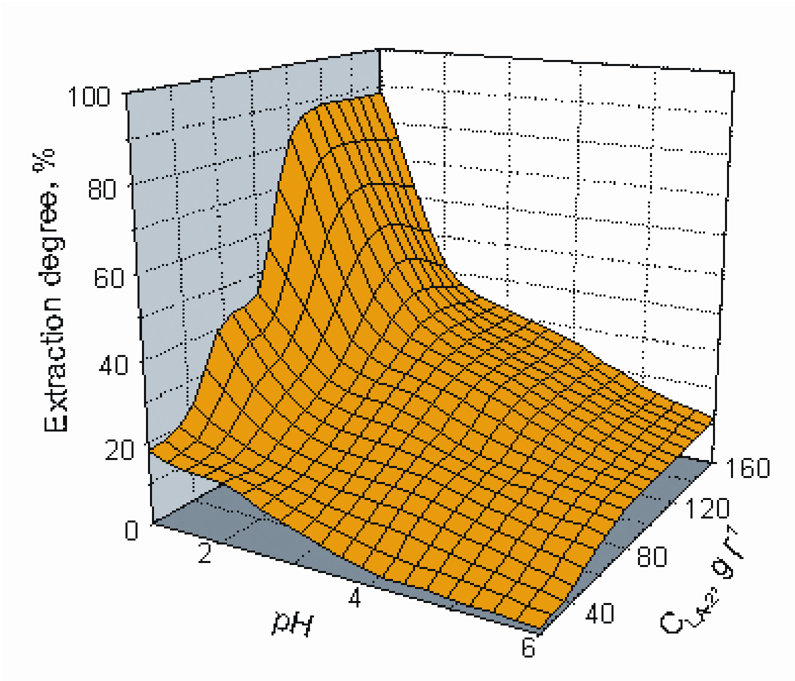

Fig. 1. Cumulated influence of extractant concentration in organic phase and pH-value of aqueous phase on vitamin C extraction degree.

From Fig. 1 it can be seen that the reactive extraction yields becomes of 88 - 90% for 160 g l^{-1} Amberlite LA-2 in butyl acetate and pH=1 (by adding of 15% vol. 2-octanol in organic phase, the extraction degree increased with about 6% [5]).

For mathematical modeling of reactive extraction of vitamin C with Amberlite LA-2, a factorial experiment of second order has been used. The mathematical model quantifies the influences of Amberlite LA-2 concentration in organic phase, pH-value of aqueous phase and duration of extraction process on the extraction yield, and it was established by statistical analysis. Thus, the real values of the process variables were chosen arbitrarily, their limits and coding being given in Table 1.

Table 1. The limits and coding of process variables for vitamin C reactive extraction.

Variable	Code	Variable level			Step
		-1	0	+1	
Amberlite LA-2 concentration, g l^{-1}	x_1	40	100	160	60
pH-value	x_2	1	3	5	2
Duration, s	x_3	5	10	15	5

In order to settle the correlation between the vitamin C extraction degree, Y, and the above mentioned parameters the following model of polynomial equation type has been proposed:

$$Y = b_0 + b_1 \cdot x_1 + b_2 \cdot x_2 + b_3 \cdot x_3 + b_{12} \cdot x_1 \cdot x_2 + b_{13} \cdot x_1 \cdot x_3 + b_{23} \cdot x_2 \cdot x_3 + \\ + b_{11} \cdot x_1^2 + b_{22} \cdot x_2^2 + b_{33} \cdot x_3^2 \quad (1)$$

where b_0,..., b_{33} are the regression coefficients.

The plan of the factorial experiment of second order is given in Table 2.

Table 2. The experimental matrix.

No. exp.	x_1	x_2	x_3
1.	-1	-1	-1
2.	1	-1	-1
3.	-1	1	-1
4.	1	1	-1
5.	-1	-1	1
6.	1	-1	1
7.	-1	1	1
8.	1	1	1
9.	-1	0	0
10.	0	0	0
11.	0	-1	0
12.	0	1	0
13.	0	0	-1
14.	0	0	1
15.	0	0	0
16.	0	0	0
17.	0	0	0

By means of the obtained data, the regression coefficients have been calculated using the following relations [7]:

$$b_0 = \overline{Y}_{15-17}, \quad b_j = \frac{\sum_{i=1}^{15} x_{ji} \cdot Y_i}{\sum_{i=1}^{15} x_{ji}{}^2}, \quad b_{jk} = \frac{\sum_{i=1}^{15} x_{ji} x_{ki} Y_i}{\sum_{i=1}^{15} x_{ji}{}^2 x_{ki}{}^2}, \quad b_{jj} = \frac{\sum_{i=1}^{15} x'_{ji} Y_i}{\sum_{i=1}^{15} \left(x'_{ji}\right)^2}$$

$$x'_{ji} = x_{ji}^2 - \frac{1}{15} \cdot \sum_{i=1}^{15} x_{ji}^2 \quad (2)$$

i = 1...15 number of experiments   j = 1...3 number of variables.

The obtained values of regression coefficients are listed in Table 3.

Table 3. The values of regression coefficients for vitamin C reactive extraction

Regression coefficient	Value
b_0	7.33
b_1	13.86
b_2	-14.13
b_3	8.83
b_{12}	-8.78
b_{13}	6.26
b_{23}	-5.48
b_{11}	4.40
b_{22}	12.40
b_{33}	3.76

For checking the normal results obtained in the program center the Q test was used [7]. Thus, the calculated Q value is:

$$Q = \frac{|a_1 - a_2|}{A} = 0.67 \quad (3)$$

where: a_1 - the uncertain value (7.5%);
a_2 - the closest to the uncertain value (7.3%);
A - the amplitude (difference between the most distant values, 0.3).

For a certain threshold of 0.05, Q = 0.77 was found in literature [7]. Since the calculated value of 0.67 is lower than the tabulated one, it could be concluded that the uncertain value of 7.5% is also a normal value. Consequently, all of the three obtained values for vitamin C extraction yield (experiments no. 15 - 17) were taken in calculation.

Hence, the regression equation may be written as:

$$\begin{aligned} Y = {} & 7.33 + 13.86 \cdot x_1 - 14.13 \cdot x_2 + 8.83 \cdot x_3 - 8.78 \cdot x_1 \cdot x_2 + 6.26 \cdot x_1 \cdot x_3 - 5.48 \cdot x_2 \cdot x_3 \\ & + 4.40 \cdot x_1^2 + 12.40 \cdot x_2^2 + 3.76 \cdot x_3^2 \end{aligned} \quad (4)$$

The experimental and calculated values of the vitamin C reactive extraction from aqueous solutions were tabulated in Table 4.

Table 4. The experimental, Y_{exp}, and calculated values, Y_{calc}, for vitamin C reactive extraction yield.

No. exp.	y_{exp}, %	y_{calc}, %
1.	11.2	11.33
2.	47.2	47.07
3.	12.0	11.59
4.	9.1	9.05
5.	27.4	27.43
6.	88.1	88.23
7.	5.9	5.77
8.	28.4	28.45
9.	10.7	10.87
10.	58.4	58.92
11.	47.1	46.86
12.	19.8	19.30
13	13.2	13.56
14	34.4	34.62
15	7.2	7.33
16	7.5	
17	7.3	

The limits between which these values, calculated with the regression equation, oscillate around the experimental value are determined with the relation [7]:

$$Y_{calc_i} = Y_{exp_i} \pm t \cdot S_{Yx}\ , \% \qquad (5)$$

The standard deviation S_{Yx}^2 was calculated using the following relationship [7]:

$$S_{Yx}^2 = \frac{\sum_{i=1}^{8}\left(Y_{exp_i} - Y_{calc_i}\right)^2}{n-(k+1)} = 0.0604 \qquad (6)$$

where n is the number of experiments and k the number of variables taking into account.

The t values are to be found in the tables for Student distribution [7], for a confidence threshold of 0.05 and 15 experiments, namely:

$$t = 2.131 \qquad \text{and} \qquad Y_{calc_i} = Y_{exp_i} \pm 0.523,\ \% \qquad (7)$$

The individual influence of the factors under consideration is estimated by means of the value of the correlation coefficient, r_{Yx} [7]:

$$r_{Yx_i} = \frac{\sum_{i=1}^{8}\left[x_i \cdot \left(Y_i - \overline{Y}\right)\right]}{\sqrt{\sum_{i=1}^{8} x_i^2 \cdot \sum_{i=1}^{8}\left(Y_i - \overline{Y}\right)^2}} \quad (8)$$

which describes the nature of dependence between the process variables and the extraction yield. The determination coefficient, which represents the square of correlation coefficient, indicates the fraction of vitamin C extraction yield that can be explained by variable x_i variation. In this case, the calculated values of determination coefficients are:

$$r^2_{Yx_1} = 0.336 \qquad r^2_{Yx_2} = 0.359 \qquad r^2_{Yx_3} = 0.216$$

These values suggest that the parameters taken into account influence the efficiency of vitamin C reactive extraction to an extent of 91.1%, the extractant concentration and pH-value being the most important factors. The rest of 8.9% can be attributed to the effect of other factors, namely: mixing intensity, temperature, volumetric ratio between aqueous phase and solvent etc.

Conclusions

The experimental results of the study on vitamin C reactive extraction with Amberlite LA-2 dissolved in butyl acetate indicated that the extractant concentration and pH-value control the separation efficiency.

By means of the statistical analysis and using a factorial experiment of second order, the vitamin C extraction has been modeled. Thus, a mathematical correlation between the extraction degree and the main parameters influencing the extraction (extractant concentration in organic phase, pH-value of the aqueous phase, duration) has been established. For the studied extraction system, the considered variables determine the extraction process in a 91.1% extent, the extractant concentration and the pH-value exhibiting the most important influence.

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