

Empirical Models Applied for Kinetics Extraction of β -carotene from *Rosa canina*

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*β -carotene from rose hip (*Rosa canina*) has been extracted under different experimental conditions. The investigated process factors were: temperature, solid/liquid ratio and extraction solvents. It was proven that the extraction solvent strongly influences the amount of β -carotene extracted from the vegetable material. Four empirical models were considered for describing the kinetics of β -carotene extraction. The models parameters were identified using experimental data.*

Keywords: β -carotene, solid-liquid extraction, extraction kinetics

Carotenoids are natural pigments widely spread, which can be found in all parts of a plant (leaves, fruits, stems, roots, seeds etc) with or without chlorophyll. They have various colours: yellow, red, magenta etc.

The carotenoids content in vegetables depends from the species and the cultivating and harvesting conditions [1]. Usually, carotenoids content in vegetables is reduced, varying between 0.1 – 2 mg carotenoids/100 g plant material. For this reason, when carotenoids extraction from vegetable is desired, several factors like vegetable source, processing method of solid material, solvent selection and extraction techniques, should be carefully considered.

Carotenoids are widely used in food industry as colouring agents, due to their high colouring capacity, colour stability in the presence of ascorbic acid and stability to frosting-defrosting cycles. A special attention is paid to β -carotene, due to its antioxidant activity and vitamin A precursor function. β -Carotene provides about 70 % of this vitamin in the human diet [2]. Epidemiological data have shown that antioxidants such as vitamin E and carotenoids (beta-carotene, lycopene, lutein, and zeaxanthin) contribute to preventing degenerative diseases such as cardiovascular diseases, diabetes, and several types of cancer [3,4].

Carotenoids are present in some vegetables and fruits, wastes from vegetables and fruits processing, algae like *Dunaliella salina* and shrimps. Carotenoids were identified also in some herbals like *Echinacea pallida* and *purpurea* [5]. The extraction from plant material is frequently carried out by means of the most common solvent-based procedures, in Soxhlet apparatus or, easier, in laboratory flask at the solvent boiling temperature under reflux. Modern alternative extraction methods can also be used: (1) ultrasonication, (2) microwave-assisted solvent extraction in closed and open systems, (3) accelerated solvent extraction and (4) supercritical fluid extraction [6-11].

β -Carotene can be extracted with organic solvents (hexane, cyclohexane, petroleum ether, etc), vegetable oils (sunflower oil, peanut oil, soy oil, coconut oil) or supercritical fluids [12-18].

The increasing demand of carotenoids in general and β -carotene in particular, led to an increased interest in extracting these compounds from different natural sources [12].

Kinetics models

Many studies have been conducted to describe the kinetics and the mechanism of the extraction process. Even if the principle of solid-liquid extraction is relatively simple, when this technique is applied for vegetal tissues, it entails a complex mechanism, because of the cellular structure of vegetables bodies. For this reason, it is difficult to explain with a single theory all the phenomena that take place during the solid-liquid extraction. Many mathematical models have been proposed by several authors to describe the extraction of different substances from vegetal materials. Some models are simply empirical equations that fit to experimental data; others are based on mass transfer theory and use mass balance equations. In that solid liquid extraction is concerned, a problem which must be explained is the fact that the initial period of extraction is very fast and cannot be explained by diffusion equations. That is why a two-stage mechanism of extraction has been proposed. The first stage corresponds to the rapid solute extraction by convection. It is a washing stage, in which a fast transfer of solute takes place from the solid surface and from the outer broken cells to the solvent. The second stage is characterized by a slower solute transfer from the inside of the solid by a diffusion process. These two mechanisms can be described by the different proposed models.

The mathematical model proposed describes the two mechanisms by a two exponential equation [19]:

$$c^* = c_w^* \cdot (1 - e^{-k_w t}) + c_d^* \cdot (1 - e^{-k_d t}) \quad (1)$$

where $c^* = c / c_\infty$, c is the solute concentration in solution at any time during the extraction process, c_∞ is the theoretical equilibrium solute concentration, $c_w^* = c_w / c_\infty$, c_w is the final solute concentration (hypothetical) in solution due to the washing stage alone, $c_d^* = c_d / c_\infty$, c_d is the final solute concentration (hypothetical) in solution due to the diffusion stage alone, k_w is the kinetic coefficient for the washing stage, k_d is the kinetic coefficient for the diffusion stage and t is the time. The total amount of extracted solute is equal to the sum of the amounts extracted during the washing and diffusion stages. This model has been used to describe extraction data of sugar from beet tissue and for aqueous extraction from carrots, both vegetables being treated by pulsed electric field [20, 21].

Power law model is used for the diffusion of an active agent through non-swelling devices and is described by equation:

$$q = B \cdot t^n \quad (2)$$

where B is a constant incorporating the characteristics of the carrier-active agent system and n is the diffusion exponent. For the extraction from vegetal material, the diffusion exponent is less than 1 ($n < 1$) [22].

The hyperbolic model is known also as Peleg model and was proposed in 1988 for the description of moisture sorption curves [23]. The mathematical expression of this model is given by equation:

$$q = \frac{K_1 \cdot t}{1 + K_2 \cdot t} \quad (3)$$

where K_1 and K_2 are parameters of the hyperbolic model. The equation 3 was used to model the experimental data obtained for resinoid extraction from aerial parts of St. John's wort and for total polyphenols extraction from soybeans [22, 24].

Weibull's equation can be also applied for plant extraction in the following form:

$$q = 1 - \exp\left[-\left(\frac{t}{\delta}\right)^m\right] \quad (4)$$

where δ is the scale parameter, which is related to the reciprocal of the extraction rate constant, and m is the shape parameter. If $m < 1$, as in the case of extraction, the curve is parabolic with a high initial slope followed by an exponential shape [22].

In the present paper we have studied the kinetics of β -carotene extraction from rose hip (*Rosa canina*) in different experimental conditions. The empirical models presented – the model with two exponential equations, the power law model, the Peleg model and Weibull's equation – were used to fit experimental data obtained for different solvents, temperatures and solvent to solid ratios.

Experimental part

Materials and methods

A batch extraction laboratory set-up was used for performing all the extraction experiment. The stirring speed was set at the appropriate level, in order to ensure the suspension of solid in the liquid phase.

For β -carotene extraction from rose hip, vegetal material, powdered rose hip fruits with a maximum 10% humidity content and particle size distribution in the range of 0.1 – 0.5 mm, was subjected to saponification with sodium hydroxide solution prior to extraction. This step was needed for removing the lipids and chlorophylls, which otherwise could have been extracted together with β -carotene from the vegetal material. Ethylic ether, petroleum ether and n-hexane were the solvents used in this experimental research. The solid liquid ratio was set at 1/10, 1/20 and 1/40 respectively. Extractions were carried out at three different temperatures: 25, 35, 45 and 55°C.

The β -carotene content in the extracts was determined spectrophotometrically, using an UV-VIS Cintra 6 spectrophotometer (GBS, Australia). The analytical method is based on the fact that β -carotene has an absorption maximum at 448 nm wavelength in ethylic ether and petroleum ether, and at 450 nm in hexane. The amount of β -carotene extracted was determined using calibration curves for tested solvents.

Results and discussions

Effect of solvent

Three different solvents were used to evaluate their extraction efficiency. The β -carotene extraction capacity of n-hexane, ethylic ether and petroleum ether is presented in figure 1.

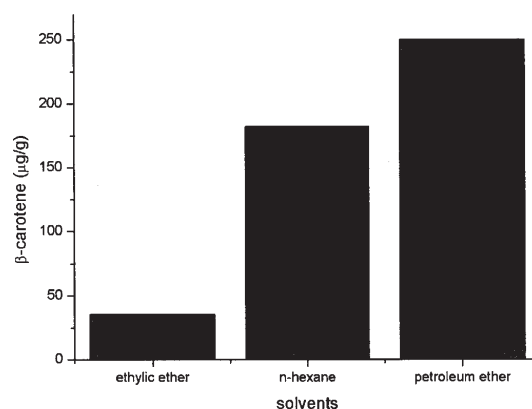


Fig. 1. The amount of β -carotene extracted from rose hip in different solvents (temperature: 35°C, solid/liquid ratio: 1/20 and extraction time: 4 h)

In figure 1 one can see that the highest extraction yield is obtained when petroleum ether is used as solvent.

Effect of solid / solvent ratio

Because the most efficient solvent was petroleum ether, the next experiments were performed using this solvent. As it can be seen from figure 2, when the solid to solvent ratio is increased, the amount of β -carotene extracted increases also.

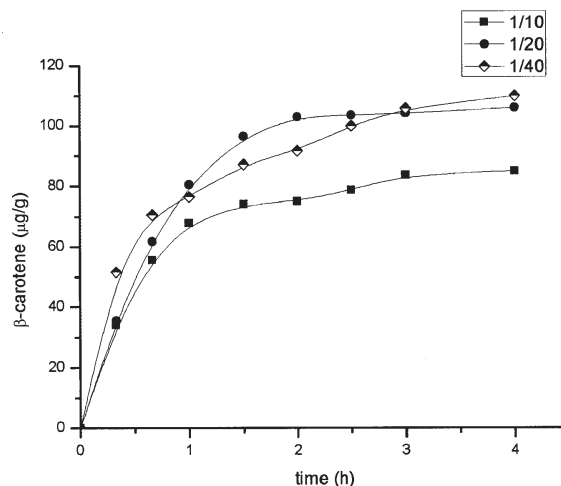


Fig. 2. The amount of β -carotene extracted from rose hip in petroleum ether at different solid/liquid ratios (temperature 25°C)

Because the difference between the amount of β -carotene extracted when solid / solvent ratio varies from 1/20 to 1/40 is not very large, in the next experiment the value 1/20 was preferred.

Effect of temperature

The effect of extraction temperature on the amount of β -carotene extracted is presented in figure 3. As it was expected, the increasing temperature has a positive effect on the amount of the extracted solute. But at 55°C the amount of extracted β -carotene diminishes, possibly because of the solute decomposition.

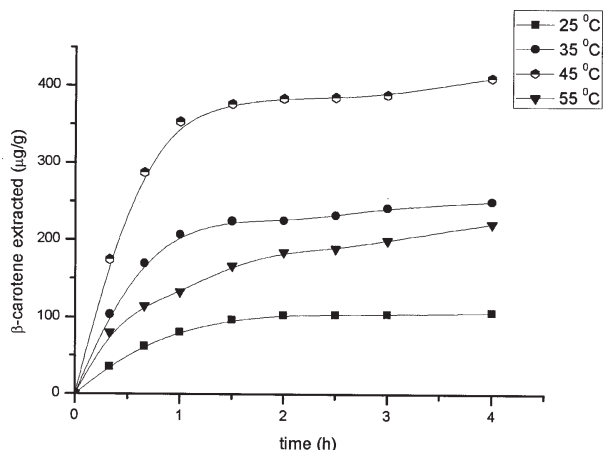


Fig. 3. The amount of β -carotene extracted from rose hip in petroleum ether at different temperatures (solid/liquid ratio: 1/20)

The experimental results were analyzed using the empirical models already described by the equations 1-4. The model parameters were calculated by linear regression using Mathcad®2001 software. The concordance between experimental data and calculated values was determined by the correlation coefficient (R) and by the root mean square (RMS) calculated as follows:

$$RMS = \sqrt{\frac{1}{N} \cdot \sum_{i=1}^N \left(\frac{c_{exp} - c_{calc}}{c_{exp}} \right)^2} \quad (5)$$

The calculated parameters for the empirical model with two exponential equations are presented in table 1.

The correlation coefficient is high in all experiments (0.968-0.997) and the root mean square deviation is in the range 0.033-0.105, which implies a good agreement between experimental and calculated data. Figure 4 shows the correlation between experimental values of extraction

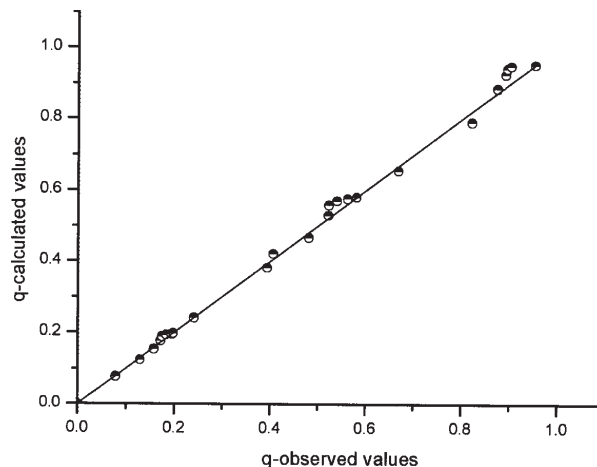


Fig. 4. Correlation between experimental values of extraction yield for β -carotene extraction versus calculated extraction yield using So and Macdonald equation (1) at different extraction temperatures (25, 35 and 45°C)

yield for β -carotene extraction versus calculated extraction yield using the model proposed by So and Macdonald (1) at different extraction temperatures. It can be observed a good agreement between experimental and calculated data.

The calculated parameters for the power law model (2) are presented in table 2.

The correlation coefficient is also high in all the experiments (0.924-0.991) and the root mean square deviation is in the range 0.03-0.124, which implies that this model fit also well the experimental data. The figure 5 sustains also this conclusion. The calculated parameters for the Peleg model (3) are presented in table 3. For the Peleg model, the correlation coefficient is also high in all experiments (0.981-0.995) and the root mean square

Table 1
PARAMETERS OF So AND MACDONALD MODEL (1) for β -CAROTENE EXTRACTION FROM ROSE HIP AT DIFFERENT TEMPERATURES AND DIFFERENT SOLID/LIQUID RATIOS, USING PETROLEUM ETHER AS SOLVENT

No.	Experimental conditions		Model parameters				Statistical correlation values	
	Temp. (°C)	S/L ratio	c_w^*	k_w [min ⁻¹]	c_d^*	k_d [min ⁻¹]	R	RMS
1	25	1/10	0.01	0.012	0.188	0.0256	0.992	0.037
2	25	1/20	0.0075	0.012	0.293	0.0230	0.997	0.039
3	25	1/40	0.01	0.011	0.246	0.0220	0.968	0.105
4	35	1/20	0.01	0.027	0.571	0.0270	0.993	0.035
5	45	1/20	0.01	0.027	0.943	0.0270	0.994	0.033
6	55	1/20	0.04	0.016	0.474	0.0160	0.986	0.092

Table 2
PARAMETERS OF THE POWER LAW MODEL (2) FOR β -CAROTENE EXTRACTION FROM ROSE HIP AT DIFFERENT TEMPERATURES AND DIFFERENT SOLID/LIQUID RATIOS, USING PETROLEUM ETHER AS SOLVENT

No.	Experimental conditions		Model parameters		Statistical correlation values	
	Temp. (°C)	S/L ratio	n	B (min ⁻ⁿ)	R	RMS
1	25	1/10	0.341	0.034	0.957	0.094
2	25	1/20	0.429	0.028	0.924	0.124
3	25	1/40	0.297	0.052	0.995	0.028
4	35	1/20	0.321	0.111	0.949	0.091
5	45	1/20	0.305	0.199	0.936	0.076
6	55	1/20	0.404	0.059	0.991	0.030

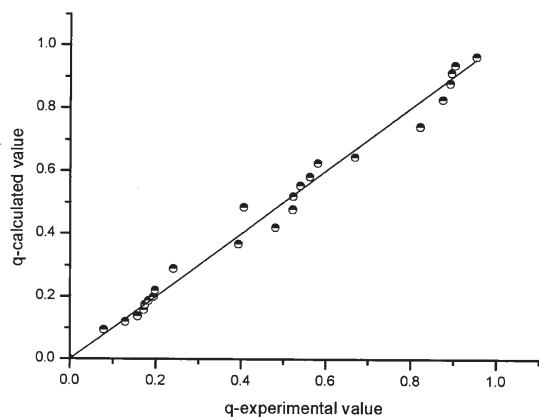


Fig. 5. Correlation between experimental values of extraction yield for β -carotene extraction versus calculated extraction yield power law model (2) at different extraction temperatures (25, 35 and 45°C)

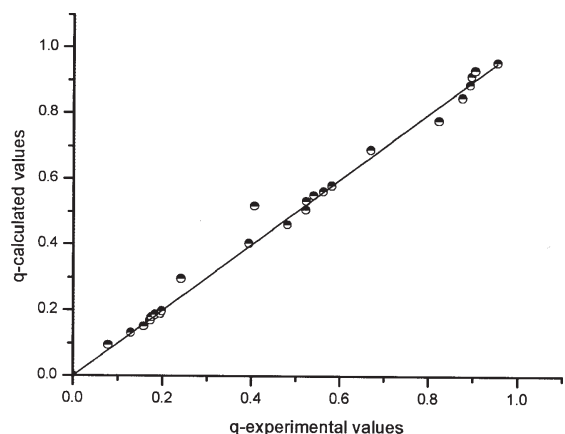


Fig. 6. Correlation between experimental values of extraction yield for β -carotene extraction versus calculated extraction yield using Peleg model (3) at different extraction temperatures (25, 35 and 45°C)

deviation is in the range 0.038-0.096, which implies a good agreement between experimental and calculated data.

Figure 6 shows the correlation between experimental values of extraction yield for β -carotene extraction versus calculated extraction yield using Peleg model. A good agreement between experimental and calculated data can be observed.

The calculated parameters for the Weibull's equation (4) are presented in table 4. For the Weibull's equation, the correlation coefficient is high in all experiments (0.932-0.996) and the root mean square deviation is in the range 0.028-0.118, which implies a good agreement between

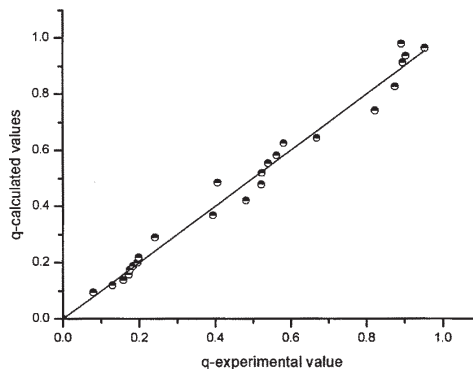


Fig. 7. Correlation between experimental values of extraction yield for β -carotene extraction versus calculated extraction yield using Weibull's equation (4) at different extraction temperatures (25, 35 and 45°C)

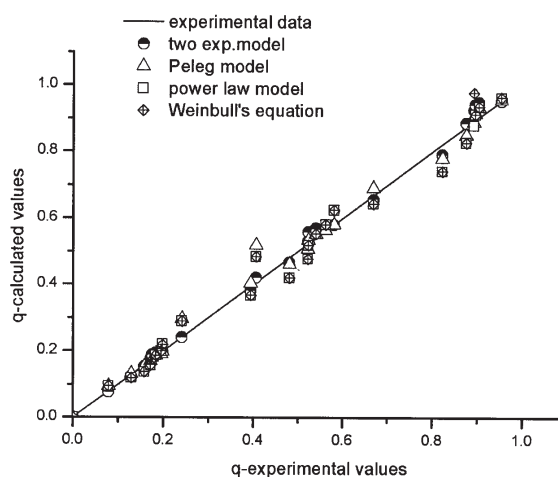


Fig. 8. Correlation between experimental values of extraction yield for β -carotene extraction versus calculated extraction yield using all the models at different extraction temperatures (25, 35 and 45°C)

experimental and calculated data. Figure 7 shows the correlation between experimental values of extraction yield for β -carotene extraction versus calculated extraction yield using Weibull's equation. A good agreement between experimental and calculated data can be observed. A comparison between experimental and calculated data with all the tested models is presented in figure 8. As it can be seen, it is rather difficult to recommend one model or another. Still, the empirical model with two exponential equations, which was proposed by So and Macdonald (1986), gave the best fit for the kinetics extraction of β -carotene from rose hip powder.

Table 3
PARAMETERS OF THE PELEG MODEL (3) for β -CAROTENE EXTRACTION FROM ROSE HIP
AT DIFFERENT TEMPERATURES AND DIFFERENT SOLID/LIQUID RATIOS,
USING PETROLEUM ETHER AS SOLVENT

No.	Experimental conditions		Model parameters		Statistical correlation values	
	Temp. (°C)	S/L ratio	$K_1 \times 10^3$ (min^{-1})	K_2 (min^{-1})	R	RMS
1	25	1/10	8.241	0.038	0.992	0.065
2	25	1/20	7.185	0.023	0.984	0.072
3	25	1/40	9.510	0.035	0.992	0.038
4	35	1/20	28	0.044	0.988	0.078
5	45	1/20	53	0.051	0.981	0.096
6	55	1/20	12	0.019	0.995	0.041

Table 4
PARAMETERS OF THE WEIBULL'S EQUATION (4) FOR β -CAROTENE EXTRACTION FROM ROSE HIP AT DIFFERENT TEMPERATURES AND DIFFERENT SOLID/LIQUID RATIOS, USING PETROLEUM ETHER AS SOLVENT

No.	Experimental conditions		Model parameters		Statistical correlation values	
	Temp. (°C)	S/L ratio	m	$\delta(\text{min}^{-1})$	R	RMS
1	25	1/10	0.367	1.087×10^4	0.960	0.092
2	25	1/20	0.469	2.367×10^3	0.932	0.118
3	25	1/40	0.329	8.713×10^3	0.996	0.028
4	35	1/20	0.424	250.58	0.962	0.091
5	45	1/20	0.644	37.682	0.979	0.076
6	55	1/20	0.499	430.26	0.995	0.030

Conclusions

An experimental study of β -carotene batch extraction from rose hip (*Rosa canina*) under different experimental conditions was performed. The influence of different extraction conditions was also studied. The best solvent from β -carotene extraction was petroleum ether. The extraction yield increases with the increase of the solvent/solid ratio and with temperature. For a temperature higher than 45°C we have observed a destruction of β -carotene. The empirical models tested showed a good agreement between experimental and calculated data. For all the models high linear correlation coefficient ($R > 0.92$) and relatively low RMS values were obtained.

Notations

B - parameter of power law model [min^{-n}];
 c - amount of β -carotene extracted [$\mu\text{g/g}$ of plant material];
 c^* - dimensionless solute concentration of So and Macdonald model ($c^* = c / c_\infty$);
 c_d - final solute concentration (hypothetical) in solution due to the diffusion stage alone of So and Macdonald model [$\mu\text{g/g}$ of plant material];
 c_o - amount of β -carotene present in the vegetal material [$\mu\text{g/g}$];
 c_w - final solute concentration (hypothetical) in solution due to the washing stage alone of So and Macdonald model [$\mu\text{g/g}$ of plant material];
 c_e - amount of β -carotene extracted when the equilibrium is reached [$\mu\text{g/g}$ of plant material];
 k_w - kinetic coefficient for the washing stage [min^{-1}];
 k_d - kinetic coefficient for the diffusion stage [min^{-1}];
 K_1 - parameter of the hyperbolic model; extraction rate at the very beginning [min^{-1}];
 K_2 - parameter of the hyperbolic model; constant related to the maximum extraction yield [min^{-1}];
 n - diffusional exponent of the power law model;
 m - shape parameter of the Weibull's equation
 q - extraction yield ($q = c / c_o$)
 t - time [min]

Greek letters

δ - scale parameter of the Weibull's equation (4) [min^{-1}]

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