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POLYPHENOLS AND NAPHTHOQUINONES EXTRACTION FROM WALNUTS *PELLICULA*: THE IMPACT ON KERNELS QUALITY

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Abstract. Walnuts change their appearance during storage, becoming brown and bitter. The aim of this paper was to determine the polyphenols and naphthoquinones extraction process parameters from the pellicle of kernels, and to assess the influence of extraction on the walnuts quality. It was studied the influence of NaOH, ethanol and polygalacturonase on the polyphenols and naphthoquinones extraction from walnut kernels pellicle. Small amounts of enzyme, (0.011±0.001) %, contribute to the extraction of colored substances from the pellicle by destabilizing of biopolymer matrix. Hydration, volume increase, the destruction of the bio-polymeric matrix - all contributes to the extraction, also to the pellicle release from the kernels surface. The hydration degree increases as the amount of ethyl alcohol in the extract became < 7.5 %. The oxidized and colored components are extracted according to the exponential models: $Y = Ae^{kx}$, $k \in (-0.40 \pm 0.06)$. The consecutive extraction of phenolic substances and naphthoquinones, carried out at room temperature, contributes to the improvement of colour and taste, increasing technological value of the processed walnuts.

Keywords: *walnut kernels processing, Box-Hunter experimental design, extraction, UV-Vis spectra, "step climb experience", sensorial analysis, juglone.*

Introduction

Walnut kernels is a source of nutrients and biologically active compounds: dietary fibers, vitamins (E, B_3, B_5, B_6), bio elements (K, P, Mg) that cause high product value [1, 2]. Walnut kernels contains great amounts of lipids with recognized biological activity such as linoleic acid (ω_6) and linolenic acid (ω_3), sitosterols and biologically active polymers [3-5]. Walnut kernels are covered with *pellicula,* also called "pellicle" and "film" – thin skin, rich in phenolic substances, especially in gallic acid derivatives (C_6-C_1), naphthols and naphthoquinones (C_6-C_4) [6, 7]. These compounds exhibit pronounced antioxidant activity and protect bioactive compounds in lipid tissues of the kernels from oxidative degradation [8, 9]. While exposed to light, the walnut kernels pellicle changes colour and chemical composition [10]. This process probably protects lipids from light-caused destruction. During the storage, walnut kernels change their appearance: colour becomes dark brown and taste – bitter. These undesirable transformations are caused by the phenolic

compounds of the pellicle. They interact with the molecular oxygen from air, suffering irreversible oxidation. As an example it may serve a transformation of colourless hidroxyjuglone (1, 4, 5-trihidroxy-naphtalene) into brown-reddish juglone (5-hidroxy-1,4-naphthoquinone) [6, 11]. The brown oxidized pellicles cause real sensations of bitterness and, moreover, expectations of a bitter taste to potential consumers [12]. Thus, extraction of polyphenols and naphthoquinones from the pellicle of walnut kernels will allow to improve their quality. The aim of our investigation was to determine the polyphenols and naphthoquinones extraction process parameters from the pellicle of walnut kernels, and to assess the influence of extraction on the appearance and taste of the walnuts.

Experimental design

There were used the Calarash variety of walnut fruits, purchased in 2018 from Iargora State Forestry. Weight of the single walnut fruit without mesocarp was in range of (16.7±2.3)g. Walnuts were kept whole in cotton bags at room temperature, (22±2)°C, and on relative humidity, H_R = (60±5)%, in darkness [10], for 15 months. The kernels were carefully removed from fruits in the form of halves or quarters. There were used: 96% food-grade ethanol ("*Kvint*", Moldova), food-grade citric acid ("*Condiprod-Prom*", Moldova), sodium hydroxide "*pro analyses*" ("*Stanchem*", Poland), Folin-Ciocîlteu reagent ("*Ecochimie*", Moldova), oenological polygalacturonase ("*Laffort*", France).

Various factors can influence the extraction process independently and jointly. In order to obtain information about directly influence and jointly interactions it was performed 2-Level, 3-Factorial Full Experiment, FFE 2^3[13]. There were studied influence of selected and codified factors, as ethanol (X_1, min. 10%, max. 25% (v)), NaOH (X_2, min 0,005%, max. 0.020%) and enzyme (X_3, min. 0.004%, max. 0.010%) to the extraction and to modification of walnut kernels quality. There were prepared water-ethanol solutions containing 10% (lower level) and 25% (upper level) of ethanol (factor X_1). Samples of 100mL of these solutions were distributed in hermetically sealed vessels with a volume of 150mL.

The corresponding quantities of NaOH (factor X_2) and enzyme (factor X_3) were introduced directly into the same vessels. Samples of walnut kernels, (25.00 ± 0.03)g, containing only halves and quarters were added to the resulting solutions. Samples were kept in extracting solutions for 24 hours at a temperature of (22.0 ± 1.0)°C. The obtained extracts were filtered immediately under the identical conditions, their filtration rates (V_f) were measured.

The amount of polyphenols (PPh) in the extract was determined by the standard Folin-Ciocîltău assay [14]. Walnut kernels, processed by extraction, were washed with 0.2% citric acid solution for 15 minutes, dried in a dark place for 3 days, when they were subjected to sensorial analyses.

Spectral and sensorial analysis

Spectra of strongly diluted extracts were recorded on a DR 5000 spectrophotometer in the range of 200...1000nm, using quartz cell with l = 10mm. The integral absorption, noted I_D, which characterizes the sum of extracted substances with active absorption in the studied region of spectrum, was also taken into account. Processed walnuts were analyzed by a group of five experts. The tasters appreciated the general appearance (colour) and the taste of the processed walnuts, attributing to the samples the general score in the 5-point system.

Statistic interpretations

The confidence interval of the sensory analysis results was appreciated accordingly to the 3σ-rule. It can be mentioned, that Box-Hunter experimental design presumes reducing of experiences number in the frameworks of whole experiment. In this context, for the statistical interpretation of the regression equations, the confidence level P = 0.95 was chosen. The reliabilities of linear and exponential mathematical models were estimated by the R^2 values.

Influence factors choice

It was observed that studies of a walnuts chemical composition are based on the overall quantity of the components from the whole kernels [1-4]. However, in some sources the pellicle, its chemical composition, the experimental data with the emphasis on separating and identifying the compounds of the pellicle, are discussed [6, 7]. The goal of this study was to appreciate the parameters of the extraction process of the water-soluble compounds from walnut kernels pellicle. Extracts obtained can be used to appreciate the amount of polyphenols and naphthoquinones, also to estimate the impact of the extraction process of these compounds on the formation of walnut kernels color, taste and quality.

It is known that phenolic substances are very sensitive to the pH, forming salts (phenolates) in an alkaline environment [15]. At the same time, significant amounts of alkali at elevated temperatures can expose the lipids of the walnut core to an absolutely undesirable saponification process.

Therefore, it was originally planned to carry out the extraction of phenolic substances at low concentrations of NaOH at room temperature. Pectolytic enzymes are widely used in winemaking to enhance the extraction of dyes from grape skins [16]. Therefore, they should act similarly in the water-alcohol phase extraction of polyphenols and naphthoquinones from the walnut kernel pellicles.

Therefore, the studied range of concentrations of the pectolytic enzyme (factor X_3) complies with the recommendations of the enzyme manufacturer, developed for winemaking processes.

The planning matrix for the Full Three-Factor Experiment and the response values are shown in Table 1.

Table 1

Plan matrix in codified and real coordinates, results (responses) of phenolic compounds extraction from walnut kernels pellicle: B – brown, Y – yellow.

Factors								Responses						
N	X_1 EtOH (%v)		X_2 NaOH (%m)		X_3 Enzime (%m)			Color, Transparency		V_f	I	$A_{(A)}$	$A_{(B)}$	$PPh_{(A)}$	$PPh_{(B)}$
1	+	25	+	0.020	+	0.010	B	clear		1.5	381.5	0.042	0.041	0.405	0.413
2	+	25	+	0.020	-	0.004	B	opaque		2.0	380.6	0.039	0.039	0.400	0.408
3	+	25	-	0.005	+	0.010	Y	clear		4.0	359.7	0.021	0.020	0.414	0.409
4	+	25	-	0.005	-	0.004	Y	opaque		4.0	353.4	0.024	0.023	0.370	0.378
5	-	10	+	0.020	+	0.010	B	clear		3.0	375.4	0.041	0.040	0.516	0.503
6	-	10	+	0.020	-	0.004	B	opaque		4.0	379.5	0.042	0.041	0.524	0.515
7	-	10	-	0.005	+	0.010	Y	clear		4.5	356.9	0.020	0.019	0.582	0.594
8	-	10	-	0.005	-	0,004	Y	opaque		3.0	347.3	0.023	0.022	0.497	0.502

Experimental data interpretation

The external appearance of the obtained extracts clearly correlated with the design of some influence factors in the planning matrix. The brown (B) and yellow (Y) colour of the obtained extracts corresponded to the maximum (+) and minimum (-) values of the NaOH concentration (Figure 1).

The opacity, or the clarity of the extracts, corresponded directly to the quantity of the pectolytic enzyme. The extracts were transparent, when X_3 values were maximal (+). This observation correlates with emulsifying effect, which was found for high-methoxylated pectin, characteristic for walnuts [5]. Thus, the effect of the enzyme can be explained by its expected direct action on the partial hydrolysis of pectic substances, which are extracted from the pellicle together with the polyphenols. Because the clarity of the extract testifies to the lack of visible colloidal impurities, we can conclude, that the presence of the pectolytic enzyme contributes to obtain the extracts of polyphenols and naphthoquinones with better technological properties. Other direct correlations between the influencing factors values and the measured responses were not observed. Therefore, obtained data were subjected to regression analysis. The significance parameter (absolute error) of the regression coefficients, Δβ, was determined for the significance level P = 0.95. There were obtained four regression equations, describing the physical and chemical state and technological properties of the extracts. These equations characterize: extracts filtration speed; optical density at λ = 450nm; UV-Vis spectrum integral of the diluted extracts in the wavelength range 200...1000nm; the total concentration of polyphenols in the extracts which were obtained.

- ***Extract filtration speed***, V_f, mL/min.

$$V_f = 3.25 - 0.38X_1 - 0.62X_2 - 0.50X_{12} - 0.38X_{23} \qquad \Delta\beta = 0.31 \qquad (1),$$

where in X_{12} is the synergistic (super-additional) factor of ethanol and NaOH common influence, and X_{23} is the synergistic factor of NaOH and polygalacturonase influence.

The extract filtration speed depends on its chemical composition, temperature, and also, on the presence of fine colloidal impurities. These impurities are capable to block filter pores. The Equation (1) shows that all significant factors contribute negatively to filtration speed of the extract value. The negative influence of the alcohol on the filtration speed can be explained by the decrease of the extract density but also by changing the phase state of the biopolymers in its presence of ethanol. It should be noted that this influence in industrial technological processes can be shifted by filtration at high pressures.

The negative influence of NaOH was even greater. We assume that the slowing down of the extract filtration in basic media can occur due to the increase of the extract viscosity. Unexpectedly, the influence of factor X_3 (enzyme) on the extract filtration rate, expressed in

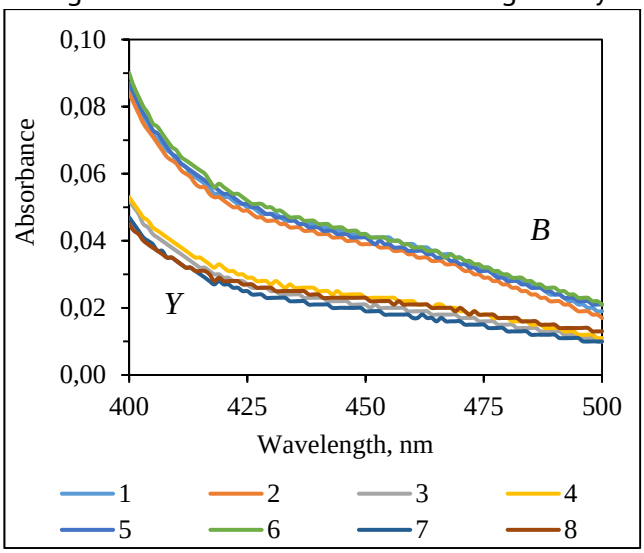


Figure 1. Fragments of the extracts spectra in the visible range: *B* – brown extracts (1, 2, 5, 6); *Y* – yellow extracts (3, 4, 6, 8).

Equation (1), proved to be null. However, polygalacturonase increase extract transparency, so improving its quality.

• ***Optical density integral*** in the analyzed wavelength range, I_D

$$I_D = 367 + 2X_1 + 12X_2 + 2X_3 + 2X_{23} \qquad \Delta\beta = 1 \qquad (2)$$

where in X_{23} is a synergistic influence factor of NaOH and pectolytic enzyme.

The integral absorption, I_D, represents the sum of the optical densities of the solution in the recorded range of the UV-Vis spectrum (200-1000nm). Thus, the I_D value correlates to some extent with the summary amount of all extract components, which manifest the light absorption in the studied spectrum's region. This response is positively influenced by all matrix generating factors, especially by NaOH, for which $\beta_2 = 12$. In this equation we observe the positive influence of the pectolytic enzyme, expressed by the statistically significant values of the factors β_3 and β_{23}. These values confirm the beneficial role of the pectolytic enzyme for the extraction of biologically active substances from the kernel's pellicle.

- ***The optical density of the extract*** at λ = 450nm, A_{450}

$$A_{450} = 0.0311 + 0.0096X_2 + 0.0009X_{23} \qquad \Delta\beta = 0.0006 \qquad (3)$$

Equation (3) quantifies colour differences, observed in the obtained extracts. According to Equation (3), the impact of factor X_2 on the extract colors is maximal and positive. The regression coefficient β_2, equal to 0.0096, exceeds 16 times the respective value of Δβ, equal to 0.0006. Therefore, the increase of NaOH quantity in the extracting system contributes to the increase of the extracted substances concentration. The impacts of direct factors X_1 and X_3 were statistically insignificant in case of this response.

- ***The amount of polyphenols, determined by the Folin-Ciocalteu method,*** PPh.

$$PPh = 0.46 - 0.06X_1 + 0.02X_3 + 0.01X_{12} - 0.02X_{23} + 0.01X_{123} \qquad \Delta\beta = 0.01 \qquad (4)$$

Equation (4) shows that the polyphenols extraction is negatively influenced by alcohol concentration increase. At the same time, NaOH does not significantly influence the extraction of polyphenols. The moderate, statistically significant positive influence of the enzyme, is expressed by the coefficient value $\beta_3 = 0.02$, which twice exceeds the value of $\Delta\beta = 0.01$.

Improving the processed nuts quality and sensory analysis

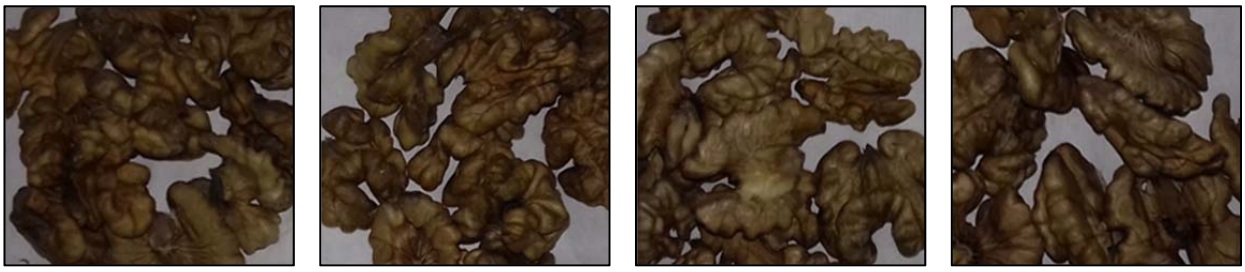
The obtained Equations (1)-(4) can be used to improve nuts processing technologies. The accumulation of oxidized substances in the core film contributes to the low sensory appreciation of the walnuts by consumers [12]. That is why, phenols and naphthoquinones extraction offers a possibility of the walnut kernels native aspect restoration. Based on the analysis of equations (1)-(4), the optimal conditions necessary for obtaining processed nuts were determined, using the "step climb experience" assay (SCE) [13]. The experiences counting, noted as N_{SCE}, was carried out in continuity of the FFE planning matrix counting, which includes 8 experiences (Table 1). The optimization plan of the extraction included the gradual decrease of the Ethanol and NaOH concentrations, and the increase of Polygalacturonase amount in the extract with respective "step climb" values, ΔX_{SCE} (Table 2). Experience $N_{SCE} = 9$ was not carried out.

Table 2

Planning matrix and results of walnuts sensorial quality optimization by means of extraction conditions

Factor	Center X_0	Step climb ΔX_{SCE}	Conditions and responses in N_{SCE} 10	11	12	13
Alcohol, %	17.5	-2.5	12.5	10.0	7.5	5.0
NaOH, %	0.0150	-0.0025	0.0100	0.0075	0.0050	0.0025
Enzyme, %	0.007	0.001	0.009	0.010	0.011	0.012
Colour of walnuts surface after extraction			brown	brown	yellow	yellow
General opinion about taste of the samples			bitter	good	good	acid
Sensorial appreciation in five-points scale			4.0 ± 0.3	4.3 ± 0.3	4.7 ± 0.3	4.4 ± 0.3

The colours of the walnuts, processed under conditions of N_{SCE} = 10 and N_{SCE} = 11, remains dark. Better, light-yellow colours were obtained in N_{SCE} = 12 and N_{SCE} = 13 (Figure 2). The tastes of samples N_{SCE} = 10 and N_{SCE} = 11 caused disapprovals remarks from experts. Finally, walnut kernels samples, obtained in N_{SCE} = 12 and N_{SCE} = 13 gained high scores from all experts. The most successful sample in all aspects was one obtained under conditions of N_{SCE} = 12. These conditions are optimal for the kernels quality improving by extracting components that determine their bitter taste.



N_{SCE} = 10 N_{SCE} = 11 N_{SCE} = 12 N_{SCE} = 13

Figure 2. The external aspect of the walnuts kernels after extraction under the "step climb experience" conditions.

During the experiences, it was observed that the pellicle was partially detached from the kernels, due to the visible swelling of these. The walnut kernels, subjected to processing by extraction, were immediately weighted after extract decantation, being air-dried for 24 hours at room temperature.

The gravimetric measurements showed linearly changes of the samples hydration degree within the SCE, reaching the maximum values at N_{SCE} = 13 (Figure 3). As a result of the walnuts swelling, there were a partial release of the pellicle. This effect can be considered as a sign of the walnuts quality diminishing.

We consider that this fact is due to the linear decrease of the ethanol concentration in the respective extracts. Earlier it was reported that the walnut hydration process takes place for 4 hours, of which the most effective are the first 2 hours [17].

In order to improve walnut processing technology it is important to avoid or minimize the hydration of the walnuts, and simultaneously to accelerate the extraction process of the polyphenols and naphthoquinones from pellicle.

Drying of processed walnuts also requires additional time and energy. Therefore, we resorted to the repeated extractions of the walnuts under conditions, which correspond to the optimization experience N_{SCE} = 12. The resulted UV-Vis absorption spectra considerably differ from those obtained in the case of long-term extractions. The spectrum of the first extract contains well determined peaks at 256, 290 and 410nm (Figure 4). Following extracts spectra are pouring in peaks. At the second and third extraction the peaks at 256 and 410 nm manifest only as weakly shoulders. After the fourth extraction these shoulders completely disappear. We hypothesized that oxidized forms - substances that have already fulfilled their physiological role, are extracted firstly, but the un-oxidized substances, which still stay in reserve, are extracted more difficult. In this case, current physical and chemical state of polyphenols and naphthoquinones in the pellicle also bringing the contribution to extraction's kinetic.

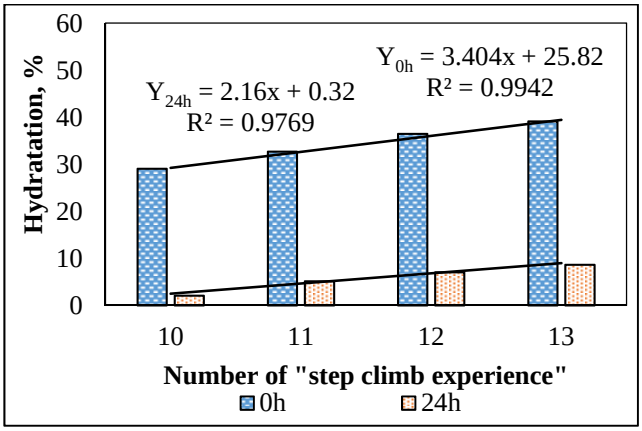


Figure 3. Walnuts hydration grade after extraction.

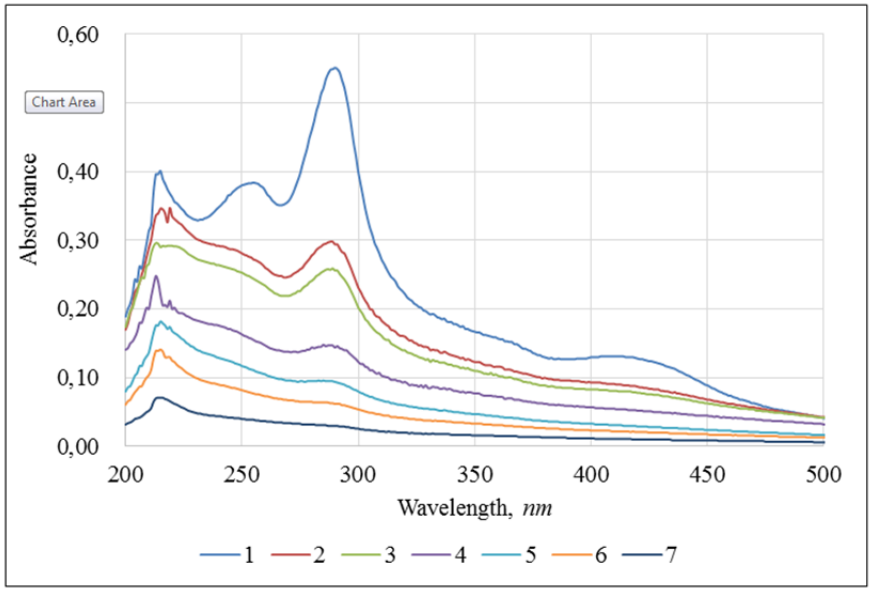


Figure 4. UV-Vis spectra of consecutive extractions.

The integrated absorption of extracts in the studied range corresponds to a linear model, which is confirmed by a high value of approximation credibility, R^2 = 0.9849 (Figure 5), Thus, we can conclude that the global content of extracted substances also slowly and linearly decreases. We suggest that the extraction of pellicles components is very difficult due to their attachment to the lipid part of the core.

Extract composition changes

Electronic absorption spectra make it possible to interpret the main components signals of the walnut kernel pellicle extracts. Particularly, the signals at 250 nm and 410 nm can be attributed to the juglone and other naphthoquinones [6, 18]. The signal at 290 nm corresponds to the polyphenols absorption, in particular, of some gallic acid derivatives [11].

It can be observed, that absorption values satisfy the descending exponential mathematical models, respective R^2 values being high (Figure 6). The colour intensity of the extracts decreases exponentially that is expressed quantitatively by light absorption in the visible range. As both polyphenols and naphthoquinones are responsible for forming the colour and taste of the walnut kernels, we can see that the amount of polyphenols and naphthoquinones in the pellicle decreases exponentially. Respectively, improving the quality of the kernels extraction takes place due to improving of their colour and diminution of the naphthoquinones-caused bitter taste.

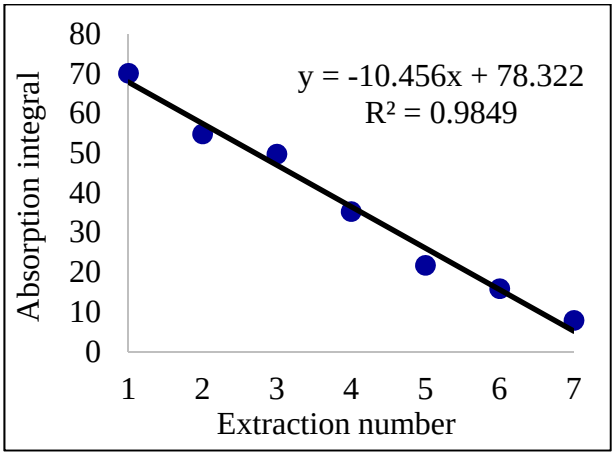


Figure 5. Linear model of light absorption integral.

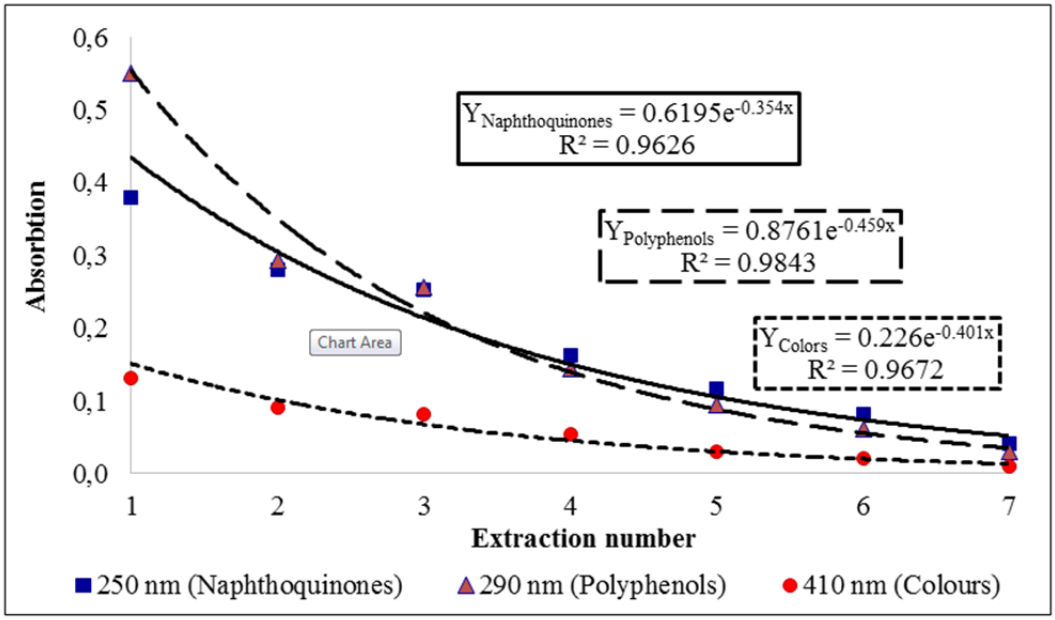


Figure 6. Changes in the UV-Vis absorptions in the consecutive extractions, exponential models.

At the same time, the exponential nature of the curves shown in Figure 6, demonstrate that more than 7-8 extraction cycles are necessary for the complete removal of polyphenols and naphthoquinones from the walnut kernel pellicles.

Conclusions

Efficient removing of polyphenols and naphthoquinones from the walnut kernel pellicles is performed in the basic medium, NaOH (0.005±0.001) %, in the presence of moderate amounts of ethyl alcohol (7.5±1.5) %. The presence of polygalacturonase (0.011±0.001) %, significantly contributes to the extraction of coloured substances from the pellicle. The role of enzyme is destabilization and hydrolysis of biopolymer matrix of the pellicle. The changes of the kernels quality during extraction is strongly influenced by the hydration and imbibing processes. Naturally, the degree of hydration increases as the amount of Ethyl alcohol in the extract decreases. Hydration, accompanied by the increase in volume, but also by the destruction of the biopolymer matrix, contributes to the extraction

of coloured substances, and to the pellicle release from the kernels surface. The oxidized and coloured forms of the pellicle components are extracted according to the descending exponential models: $Y = Ae^{kx}$, $k \in (-0.40 \pm 0.06)$. The consecutive extraction of phenolic substances and naphthoquinones, carried out at room temperature, contributes to the significant improvement of the external appearance (color) and taste of the processed walnut kernels.

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