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WALNUT SHELLS BLEACHING USING OXIDIZING AND REDUCING AGENTS

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Abstract: *Walnuts with dark-colored shells, with blackish brown spots that are more or less punctuated, have poor consumer acceptability. To improve the appearance and the commercial quality of shell nuts, certain bleaching processes are applied by means of several oxidizing and reducing agents. Walnuts Juglans Regia L, variety Calarasi and Cogalniceanu, harvest 2015, Exploitation Iargara, Moldova were analyzed. The determination of chromatic characteristics according to CIELAB and effects of the reaction parameters on the color of the whitened shell by the method of the response surfaces of the color variables L*, a* and b* was made. Walnuts bleaching was performed with oxidative bleaching agents (hydrogen peroxide, calcium hypochlorite, sodium perborate and Okorn 12) and reductants (sodium dithionite and sulphurous anhydride) at different concentrations, pH values and temperatures. Based on the analysis of the effects of the independent whitening parameters (the pH of the environment, the concentration of bleaching agents and the temperature of the bleaching medium) and their interactive effects on the chromatic profile and the whitening process of the nut shell it was found that the oxidative whitening agents are more effective. Taking into account the whitening activityof the agents and their toxic emissions, the whitening of walnuts can be done with sodium perborate($C_{perborat}$=5%, τ=60 min, t=60^{0}C, pH=10), Okoron 12 ($C_{okoron12}$ =5%, τ=90 min, t=60^{0}C, pH=10) and with hydrogen peroxide (C_{H2O2}=10%, C_{NaOH} =2.2 %, t=60^{0}C, 90 min).*

Keywords: *walnts, bleaching, chromatic parameters, oxidizing and reducing agents*

1. Introduction

Walnuts are grown across the world [1]. Dark shell colored and stained walnuts have poor consumer acceptability [2].
Moldova ranks sixth among world exporters of walnuts, after the United States, Mexic and China, being the third among the European exporters of shelled nuts, after France and Germany, with an amount that worths $84.8 million dolars. [3]. In recent years, due to the adoption of the National Program for the walnut culture Development until 2020, to the more active involvement of state and non-governmental institutions are increasingly emphasized the paths of further walnut culture development.
During the harvesting of the walnuts, the wood peels are colored both by intact and crushed green, which is rich in tannins. Besides tannins, the green bark is also very rich in hydrogeldone glucoside, which, upon oxidation, releases juglone, causing the endocarp to stain.
The quality requirements for exporting walnuts require a clear, attractive product that can be obtained by using various oxidizing and reducing agents during the controlled washing and drying process.

Both oxidizing and reductive agents are used for bleaching cellulosic products like walnut shell. Data on walnuts bleaching with oxidative agents was presented in previous studies [4]. The bleaching activity of the agents is due to the hydrogen peroxide (HP)contained in their structure. When bleaching with hydrogen peroxide, direct action on whitening occurs due to peroxide ion (HO_2^-) resulting from the hydrolytic dissociation of peroxide. These ions are trained in reduction or oxidation reactions of the chromogenic lignin groups, thus contributing to the desired color change [5, 6-11].

2. Materials and methods

Walnut fruits, variety Calarasi, were collected from local walnut plantation, Iargara, Moldova. All chemicals used for experiments were at least analytical grade.
The walnut were cleaned to remove trash and damaged, sunburned, and broken walnuts.
For walnut bleaching were selected oxidising agents: H_2O_2, Okoron12, $Na_2B_2O_4(OH)_4$ and $Ca(ClO)_2$ (concentrations in the neighborhood of 1-10% being found satisfactory). The process was performed in the temperature range - 20-60^{0}C and at the pH range 3 to 10 (pH adjusted with HCl or NaOH to the desired value).
Prepared walnut samples were immersed in the solution of bleaching agent being agitated to insure complete contact, after which the walnuts were withdrawn from the solution and allowed to dry. Walnuts bleaching was performed at different concentrations, pH values (3, 7, and 10) and temperatures (20, 40, 60 ° C).
Color changes were judged after the total color difference between the initial (control) and bleached samples, calculated using the formula:

$$\Delta E^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2}$$

3. Results and Discussion

Previous research on walnut shell whitening is limited and provides the whitening only with solutions of hydrogen peroxide or various combinations of it with oxalic acid or sodium hydroxide and chlorine compounds [12 - 14].
The first question when performing experiences, was whether they are effective or not for bleaching walnuts and in how much time a 1 to 10% concentration of bleaching agents will manifest its effect. Below are the results for walnuts bleached with sodium perborate and Okoron 12 that have proven to be the best oxidative bleaching agents.
In table 3 are presented the obtained results for the walnuts bleached with sulfur dioxide.

Table 1.
The effect of Sodium perborate concentration, pH and temperature on chromatic parameters of walnuts shell

Agent	C, %	t, min	ΔE
$Na_2B_2O_4(OH)_4$	1%	10	21.26
		30	21.96
	5%	10	22.49
		30	23.19
Agent	pH	t, min	ΔE
$Na_2B_2O_4(OH)_4$ (5%)	3	10	42.03
		30	33.92
	7	10	41.55
		30	35.05
	10	10	45.19
		30	42.97
Agent	t, ^{0}C	t, min	ΔE
$Na_2B_2O_4(OH)_4$ (5%)	20	10	41.04
		30	42.67
	40	10	44.45
		30	55.17
	60	10	48.73
		30	73.90

The results show that the brightness of the walnut shell increases with the increase of the agent concentration, the yellow shade decreases (the value of the component b

increases). The maximum brightness value is reached after 30 minutes of bleaching.
In all cases, for each bleacing agent, bleaching rate increases significantly with increasing the temperature of the medium from 20 to 60 ° C. The sodium perborate bleaching mechanism is similar to the hydrogen peroxide bleaching mechanism, but the perborate alkalinity is higher than hydrogen peroxide and has more significant effects on the delignification and bleaching process at the same active oxygen concentration.

Table 2.
The effect of Okoron 12 concentration, pH and temperature on chromatic parameters of walnuts shell

Agent	C, %	t, min	ΔE
Okoron 12	1%	10	5.64
		30	6.32
	5%	10	3.76
		30	11.47
Agent	pH	t, min	ΔE
Okoron 12 (5%)	3	10	7.27
		30	9.38
	7	10	9.44
		30	10.91
	10	10	15.52
		30	19.54
Agent	t, ^{0}C	t, min	ΔE
Okoron 12 (5%)	20	10	22.71
		30	25.61
	40	10	25.03
		30	34.19
	60	10	31.39
		30	34.63

The effectiveness of whitening, as can be seen from the results presented in Table 4, largely depends on the pH value of the medium, which determines the decomposition of the hydrosulfite, but also the browning caused by the basic medium too strong.

Table 3.
The effect of sulfur dioxide concentration, pH and temperature on chromatic parameters of walnuts shell

Agent	C, %	t, min	ΔE
SO_2	1%	10	2.96
		30	4.22
	5%	10	3.14
		30	9.51
Agent	pH	t, min	ΔE
SO_2(5%)	3	10	12.47
		30	14.45
	7	10	6.72
		30	4.17
	10	10	4.41
		30	7.78
Agent	t, ^{0}C	t, min	ΔE
SO_2 (5%)	20	10	3.09
		30	7.12
	40	10	12.63
		30	20.77
	60	10	24.30
		30	30.22

Table 4.
The effect of Sodium dithionite concentration, pH and temperature on chromatic parameters of walnuts shell

Agent	C, %	t, min	ΔE
$Na_2S_2O_4$	1%	10	4.64
		30	11.33
	5%	10	12.95
		30	13.76
Agent	pH	t, min	ΔE
$Na_2S_2O_4$ (5%)	3	10	5.84
		30	6.67
	7	10	10.79
		30	16.77
	10	10	9.91
		30	15.49
Agent	t, ^{0}C	t, min	ΔE
$Na_2S_2O_4$ (5%)	20	10	12.95
		30	13.76
	40	10	18.72
		30	29.48
	60	10	27.32
		30	35.88

Whitening of walnuts is relatively low at pH≤5,0 and is caused by accelerated decomposition of hydrosulfite. At pH values greater than 6.0, the hydrosulphite is stable and the bleaching process is more pronounced. At the same time, with the further increase of pH, the formation of chromophores, which are little attacked by hydrosulfite, is amplified.

Results with a similar trend have been obtained with other whitening agents: Hidrogen peroxide and calcium hypochlorite.

It has been found that oxidative bleaching agents are more effective and that the bleaching process depends on the concentration of the agents, the temperature and the pH of the medium and the duration of retention of the walnuts in the bleaching medium. After the whitening process of the walnut shell, the agents studied form the following series: $Na_2B_2O_4(OH)_4$ >Okoron 12>H_2O_2 > Ca $(ClO)_2$> $Na_2S_2O_4$ > SO_2.

The obtained results are correlating with others researcher's data that mention that the effectiveness of the whitening process depends on the concentration, temperature, time, environment pH. All these factors must keep in balance to achieve the desired degree of bleaching [16, 17].

Taking into account the bleaching activity of the agents and the toxic emissions produced by them, whitening of the walnut can be done with sodium perborate (%$Na_2(H_4B_2O_8)$=5%, 60 min, t=60^0C, pH=10), Okoron 12 (%Okoron 12 =5%, 90 min, t=60^0C, pH=10) and hydrogen peroxide (%H_2O_2=10%, % NaOH =2,2 %, t=60^0C, 90 min).

5. Conclusions

Colour is one of the most important quality attributes influencing consumer food choices, perceptions and purchase behaviour. Colour measurement and analysis is therefore important in postharvest handling and biopro-cessing to optimize the quality and value of food. There were quantified chromatic characteristics of walnuts in shells by CIELAB system and conducted experimental studies on theyr bleaching with oxidizing and reductive agents. Taking into account the whitening activityof the agents and the toxic emissions produced by them, whitening of the walnuts can be done with sodium perborate ($C_{perborat}$=5%, τ=60 min, t=60^0C, pH=10), Okoron 12 (C_{okoron} =5%, τ=90 min, t=60^0C, pH=10) and with hydrogen peroxide (C_{H2O2}=10%, C_{NaOH} =2,2 %, t=60^0C, 90 min).

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