Episperm Separation from Walnut Kernels: Optimization of the Techniques and Impact on the Products Stability

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Walnuts are characterized by the presence of a cuticle (episperm) that covers the kernels: although rich in fibers and antioxidants, it can negatively affect the derived products' taste, color, and rheology. The aim of this study was to investigate its removal through a simple and efficient technique: by applying a process that does not damage the product and simultaneously ensuring good chemical profile and rheological stability of its derivatives, in particular of the paste. Different treatments were applied on the walnuts such as: roasting, blast chilling, soaking with different solutions (HCl, NaOH, NaHCO$_3$, citric and ascorbic acid, at different concentrations), blanching (with pure water and NaHCO$_3$ solutions), and steam blanching. The walnuts were then blown with compressed air to be peeled. Once individuated two optimal techniques, the treated walnuts were processed to obtain a paste that was chemically characterized and analyzed from a rheological point of view through both rotational and oscillatory modes (flow curves, amplitude and frequency sweep tests). The roasting and chilling treatments exhibited a positive impact on thermal expansion coefficients of seed and seed coat. The pre-treatments consisting only in the roasting and the soaking technique with 1% of baking soda (followed by a final roasting) gave the best peeling rates on kernels: both methods yield pastes that were chemically and rheologically stable. Further studies are needed to investigate how the peeling treatment may affect product taste and shelf-life.

1. Introduction

Walnuts are nutrient-rich foods widely used in the Mediterranean diet (Silveira et al., 2020). They can be consumed in their natural form or as an ingredient in sweet and/or savoury preparations. Walnut bioactive compounds are attracting consumer interest thanks the benefits correlated to their consumption into a healthy nutrition (Qamar et al., 2020). Such compounds have shown the ability of suppressing oxidative stress and inflammation process at the root of various diseases (Ni et al., 2021). The kernels as an ingredient can be used in whole or skinless form. Pellicle removal may be essential for further processing, for technological and sensory issues (Liu et al., 2021). It should be considered that the walnut episperm constitutes 5% of the edible part but contains most of the hydrophilic antioxidants present in the drupe (Salcedo et al., 2010). The concentration of phenolic compounds (including hydrolysable and condensed tannins, flavonoids, and phenolic acids) (Dordoni et al., 2017) originates bitter taste and astringency in the final product but makes the cuticle an interesting by-product that can be used by food industry as stabilizer with interesting applications (Jin et al., 2022). On the other hand, the low percentage on total weight drastically reduces the positive effect on health, if we consider the intake by eating whole walnuts (Figuero et al., 2016); the separation of the pellicle from the kernel could allow the extraction of bioactive compounds making them more bioavailable (Sánchez-González et al., 2017). There are different chemical or physical techniques suitable for peeling. The chemical methods aim at dissolving or pyrolyzing the pectin which acts as a glue between the peel and the kernel, and generally involve the use of alkaline solutions and temperatures around 90-100 °C. The low cost and the possibility of being applied on a large scale are the main advantages of these methods (Liu et al., 2021). The side effect is that the polyphenol content in the skin drops to almost zero, making it unsuitable for further health-related uses (Song et al., 2015).

To better preserve the skin, avoid the use of chemicals (and the related waste), several physical methods for peeling are emerging. These methods leverage the different thermal expansion coefficients between kernel and episperm which, due to the temperature variation, can cause the pellicle to break, making it removable with a flow of air (Liu et al., 2021). The treatment can be carried out exploiting low or high temperatures; low temperature application is more expensive and difficult to scale for large productions but allows to preserve the bioactive compounds (Liu et al., 2021). On the other hand, while being more industrially feasible, high temperature usage can easily promote oxidation processes (Fu at al., 2016). Starting from these background conditions, the aim of this study was to identify the most promising peeling treatment to be used on walnuts to ensure chemical and rheological stability also of the derived products. Different techniques were tested and their effects on the walnut paste properties were monitored.

2.Materials and methods

2.1. Materials

Walnuts in shell with 34-38 mm caliber (*Juglans regia* Lara variety, Il Noceto S.C.A., Treviso, Italy) were purchased from a local market in Piacenza (Italy).

2.2. Experimental plan

After manual shell removal, the kernels were characterized and treated using different peeling techniques: roasting (R), blast chilling (BC), soaking (S) with different solutions such as HCl, NaOH, $NaHCO_3$, citric and ascorbic acid at different concentrations, blanching (B) with pure water and $NaHCO_3$ solutions, and steam blanching (SB). The walnuts were then blown with compressed air to be peeled, and two optimal treatments were then selected; finally, the peeled kernels were used to produce the walnut pastes. The analyses were carried out on both the untreated and the treated samples (including pastes obtained from the unpeeled kernels and the peeled ones). The effect of the peeling treatment was evaluated monitoring the oxidative and rheological stability of the obtained pastes, compared to the untreated samples.

2.3. Walnuts' characterization

The kernels were characterized to obtain a specific chemical profile. The water activity (a_w) was monitored through the portable instrument Rotronic HygroPalm HP23 (Milan, Italy). Moisture, ashes, fat, and protein content were performed through the AOAC official methods (931.04, 950.48, 963.15, and 920.22, AOAC, 2005). The soluble and insoluble fiber were quantified using the enzymatic kit Megazyme Total Dietary Fibre (Megazyme, Wicklow, Ireland). Color was monitored using the D25 NC colorimeter (HunterLab, Virginia, USA). Total acidity and pH were evaluated following the methods reported by the Office International du Cacao, du Chocolat et de la Confiserie (OICCC, 1972). On defatted samples (Belšĉak et al., 2009), total phenolic content was determined through the Folin-Ciocalteau method (Ribéreau-Gayon et al., 2000), the FRAP assay was measured as indicated by Pulido et al. (2000), and the sugar content was evaluated using the enzymatic kit Megazyme K-FRUGL 09/13 (Megazyme, Wicklow, Ireland). The oxidative stability of the pastes was also monitored: conjugated dienes and trienes, and the peroxide value (PV) were determined according to the European Union Commission Regulation (1991).

2.4. Peeling techniques

Different techniques have been selected and applied for walnut pellicle removal. Each treatment was carried out on 10 g kernels.
1. Roasting (R): kernels were placed into a forced convention oven at 160 °C for 15 min and then blasted at -20 °C for 20 min.
2. Blast chilling (BC): sample was placed in a blast chiller at -20 °C for 20 min.
3. Soaking (S), kernels were immersed in different solutions at different concentrations, such as: water, ascorbic acid (at 0.5, 1, and 2%), citric acid (at 0.5, 1, and 2%), baking soda (at 0.5, 1, and 2%), sodium hydroxide (at 0.5, 1, and 2%), and hydrochloric acid (at 0.5 and 1%). Each soaking treatment lasted 2 hours: drained kernels were finally roasted (at 160°C for 15 min) and blasted at -20 °C for 20 min.
4. Blanching (B) with different solutions such as: pure water and baking soda at 3 different concentrations (0.5, 1, and 2%). Once prepared and boiled the solutions, kernels were placed into them and left for 2 min. After that, drained kernels were roasted (at 160°C for 15 min) and blasted at -20 °C for 20 min.
5. Steam blanching (SB): kernels were placed in forced convention oven at 160 °C for 15 min and steam was injected over them with a jet value of 3 and 5 at 5 min intervals.

After each treatment, 5 g of kernels were blown with compressed air at 2 atm into an 0.5 L Pyrex glass flask for 15 seconds. The yield of each peeling treatment was evaluated calculating the color change (ΔE) between the kernels before and after the peeling: ΔE was calculated as given in Eq. 1.

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

Two samples presenting the highest ΔE were selected to proceed with paste preparation and related analyses.

2.5. Walnut paste preparation

For each of the two selected treatments, two pastes were produced: one from peeled walnuts and one from unpeeled walnuts. Once treated, kernels were grounded using an all-in-one system (Roboqbo Qb8-4, Bologna, Italy) at 25 °C at 1000 rpm for 10 min, and at 2000 rpm for 10 min. The obtained samples were collected in plastic and opaque containers and finally stored at 4 °C until use.

2.6. Paste characterization

The obtained pastes were characterized in terms of moisture, fats, proteins, and fibers contents, a_w, pH and total acidity, color, total phenolic content, FRAP assay, PV, conjugated dienes, and trienes. The accelerated oxidative stability of the samples was evaluated by an Oxidation Test Reactor (Oxitest) at 100 °C and 6 bar oxygen pressure.

2.7. Rheological tests

The paste rheological behavior was evaluated using the MCR 302 rheometer (Anton Paar, Austria) equipped with a Peltier system for the temperature control: analyses in both rotational and oscillatory modes were carried out to evaluate the viscosity (flow curves) and the stability of the product. The rotational analysis was performed using a flat-cone geometry probe (Cone CP50-1D, Anton Paar, Austria) with an angle of 1° and a diameter of 50 mm, the working gap was set at 0.101 mm, and the test was carried out at 25 °C applying a shear rate between 0.01 and 100 s^{-1}. The same conditions were used for the oscillatory tests: the linear viscoelastic region (LVER) was first evaluated through an amplitude sweep test, then the frequency sweep test was carried out (applying an angular frequency ω, between 0.01 and 1000 rad/s).

2.8. Statistical analysis

Results were reported as mean values of three replicates with their corresponding standard deviations. Data were then statistically elaborated through SPSS® software (SPSS Inc., version 25.0, Chicago, IL, USA).

3. Results and discussion

Before applying the different peeling techniques, the walnuts were characterized to highlight the nutritional values typical of the Lara variety (Table 1) and to understand how these parameters may be affected by applying the different peeling procedures.

Table 1: Lara walnuts' characterization. Values are expressed as mean ± sd (n=3). n.d.: not determined.

	Walnuts (Lara)
Moisture (%)	2.91 ± 0.05
Water Activity (-)	0.368 ± 0.005
Total acidity (g$_{oleicacid}$/100g)	1.13 ± 0.06
pH (-)	6.25 ± 0.03
Insoluble fiber (g/100g)	11.33 ± 0.0,34
Soluble fiber (g/100g)	0.42 ± 0.05
Conjugated dienes (K$_{232}$)	0.139 ± 0.026
Conjugated trienes (K$_{270}$)	n.d.
Peroxide Value (meqO/Kg$_{oil}$)	n.d.
Folin (mgGAE/100g)	96.7 ± 6.5
FRAP (mmolFe/100g)	3.446 ± 0.100
Fat (g/100g)	65.11 ± 6.69
Protein (g/100g)	19.68 ± 0.21
Glucose (g/100g)	0.069 ± 0.000
Fructose (g/100g)	0.119 ± 0.025
Ash (g/100g)	2.08 ± 0.02

According to previous studies (Peiyao et al., 2022; Chang and Zhongli, 2022), different gentle peeling techniques were applied on nuts to evaluate their feasibility and yield. The more widely used techniques on hazelnuts, peanuts, almonds, and cashews are based on abrasive action systems or immersion in different solutions (Liguori et al., 2011). Walnuts were then treated as explained in section 2.4. The large difference in color between the peeled and unpeeled product was related to the higher skin removal (data not shown). Therefore, only the treatments with the best results in terms of ∆E were considered for the paste production. Particularly: S with 1% of baking soda (19.619) and R (18.183) showed the ∆E highest values compared to the untreated walnut sample (7.665). Two different pastes (one from peeled walnuts and one from unpeeled ones) were then produced for each of the two selected treatments. In particular, the following samples were prepared in order to evaluate the impact of peeling and the role of episperm on the chemical and physical properties of the products:

- RU: from roasting of unpeeled walnuts
- RP: from roasting of peeled walnuts
- SU: from soaking with 1% of baking soda of unpeeled walnuts
- SP: from soaking with 1% of baking soda of peeled walnuts.

The results of the walnut paste characterization are reported in Table 2. As regard to the oxidative stability of the pastes, there was no evidence that the peeling processes could affect the conjugated dienes or trienes, but there is a significant difference between the R and the S treatments: conjugated dienes and trienes were slightly higher in the only roasted samples, compared to the soaked ones. Even though they were equally roasted and additionally immersed in an aqueous medium, the S samples were not found to be more prone to be oxidized.

All the samples were different in terms of polyphenols content and antioxidant capacity: roasting alone resulted in an increase compared to raw walnuts (Table 1) (Vinson and Cai, 2012), after that the different technologies applied (peeling and soaking) affected the Folin and FRAP values by reducing them both. As most of the hydrophilic antioxidants are contained in the episperm (Peiyao et al., 2022), it was expected that lower values were related to the peeled samples. The pastes obtained by soaked kernels showed halved values compared to their counterparts from only roasted kernels. In fact, it is conceivable that the phenolic compounds passed into solution during soaking (Chang and Zhongli, 2022; Liu et al., 2021). As a matter of fact, the phenolics loss can be so high that systems able to recover them from wastewater have already been developed (Song et al., 2015).

Table 2: Walnut paste characterization. Different superscript letters within each row indicate statistically different values according to post-hoc comparison (Tukey's test) at p ≤ 0.05. Values are expressed as mean ± sd (n=3). n.d.: not determined.

	RU	RP	SU	SP
Moisture (%)	n.d.[c]	0.316 ± 0.086[b]	0.898 ± 0.095[a]	n.d.[c]
Water Activity (-)	0.184 ± 0.000[d]	0.354 ± 0.008[c]	0.521 ± 0.001[b]	0.445 ± 0.002[a]
pH (-)	6.36 ± 0.71[b]	6.47 ± 0.01[b]	6.86 ± 1.14[a]	6.55 ± 0.18[ab]
Total acidity ($g_{oleicacid}$/100g)	1.26 ± 0.04[a]	0.81 ± 0.05[b]	0.69 ± 0.00[bc]	0.66 ± 0.28[c]
Insoluble fiber (g/100g)	10.995 ± 0.373[a]	6.782 ± 0.255[b]	6.965 ± 0.720[b]	7.372 ± 0.030[b]
Soluble fiber (g/100g)	0.406 ± 0.038[a]	1.257 ± 0.109[b]	0.219 ± 0.033[a]	0.470 ± 0.072[a]
Conjugated dienes (K_{232})	1.940 ± 0.051[a]	1.832 ± 0.021[a]	1.572 ± 0.022[b]	1.504 ± 0.035[b]
Conjugated trienes (K_{270})	0.230 ± 0.008[a]	0.214 ± 0.007[a]	0.170 ± 0.003[b]	0.175 ± 0.000[b]
Peroxide Value ($meqO/kg_{oil}$)	<10	<10	<10	<10
Folin (mg_{GAE}/100g)	664.295 ± 62.303[a]	132.284 ± 30.665[b]	193.158 ± 37.763[b]	69.090 ± 4.517[c]
FRAP ($mmol_{Fe}$/100g)	11.985 ± 0.210[a]	3.513 ± 0.288[c]	4.071 ± 0.270[b]	1.519 ± 0.053[d]

The Oxitest analysis evaluated the impact of peeling and soaking on the oxidative stability of the pastes. As shown in Figure 1, SU was characterized by an induction time almost double that of RU (with the lowest value). It can be deduced that the different technological processes applied to the kernels affected the paste resistance to oxidation: surprisingly, the best results were obtained from unpeeled but soaked kernels. One explanation could be that soaked samples were roasted immediately after draining and consequently maintained a high level of humidity, even higher in the sample with the peel. Part of the heat supplied during the roasting treatment was therefore used to evaporate the water content: this may have effectively reduced the impact of the heat treatment by preserving the antioxidant activity of lipophilic compounds (i.e.: tocopherols).
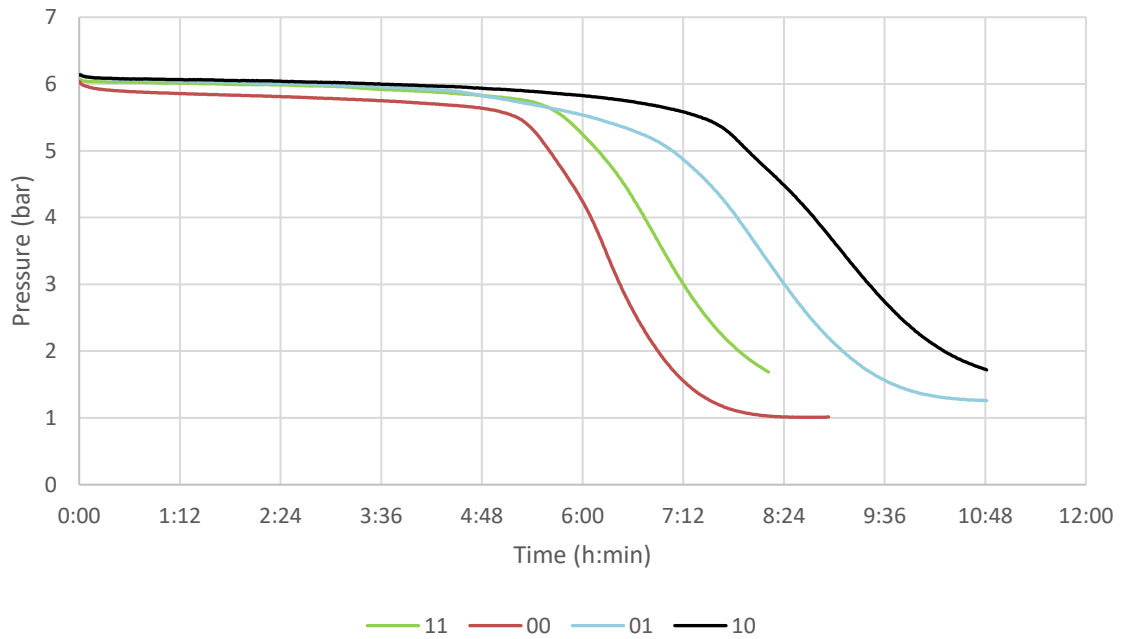
Figure 1: Oxitest analyses carried out on SP (green line, code 11), RU (red line, code 00), RP (blue line, code 01), and SU (black line, code 10) expressed as pressure [bar] as a function of the time [h: min].

The rotational rheological analysis showed a pseudoplastic behavior for all the examined pastes. A slight decrease in viscosity was noted in the soaked versus roasted kernel samples (data not shown); the peeling process did not result to directly affect viscosity. Some differences among samples were observed by performing rheological analysis in oscillatory mode. As represented in Figure 2, all the samples showed the elastic modulus G' prevailing over the viscous modulus G''; they were quite stable despite the increase in the oscillation frequency as the curves did not exhibit any crossover points (usually related to phase separation and/or sedimentation over time). All the curves were well differentiated from each other: it can therefore be deduced that the different treatments applied to the walnuts can positively influence the rheological stability of derived products. In particular, the S treatment produced a more stable paste than the R one; peeling also had a positive effect on stability as the presence of episperm could cause a greater inhomogeneity of the product.
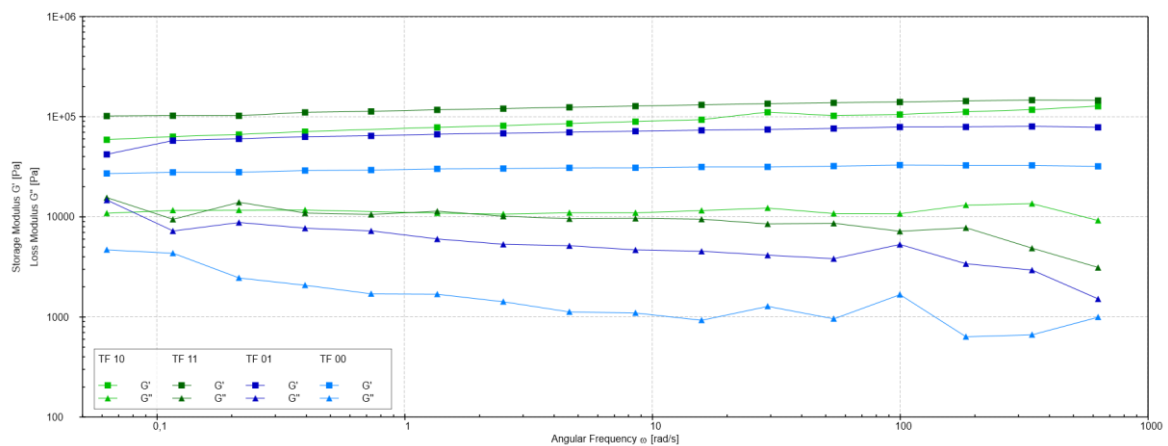

Figure 2: Frequency sweep test carried out on RU (light blue lines, code TF00), RP (blue lines, code TF01), SU (light green lines, code TF10), and SP (dark green lines, code TF11). The storage modulus G' [Pa] (squares) and the loss modulus G'' [Pa] (triangles) are expressed as a function of the angular frequency, ω [rad/s].

4. Conclusion

The data obtained bode well for a wider use of walnut paste: it is in fact possible to obtain peeled walnuts through treatments which maintain high stability in the derived products. This allows to offer the market semi-finished and finished products richer in fiber and antioxidants (from unpeeled walnuts) or more homogeneous and velvetier (from peeled walnuts), without sacrificing quality in both cases. Further studies will be useful to better investigate the impact of different peeling treatments on the taste and the long-time stability of products also through a sensory analysis and an accelerated shelf-life study.

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