CHEMICAL ENGINEERING TRANSACTIONS
VOL. 75, 2019
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it
Guest Editors: Sauro Pierucci, Laura Piazza

ISBN 978-88-95608-72-3; **ISSN** 2283-9216
DOI: 10.3303/CET1975053

Freeze-dried Products Based on Walnuts: Interaction between Fat Fraction and Dietary Fiber

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Walnuts are appreciated all around the world by consumers and food industries because of their different and positive properties including flavouring, texturizing and nutritional qualities. Walnut paste production and use are commonly associated to confectionery or traditional products but may find space in different innovative foods, as fat replacer and functional component. The aim of this work was to increase the nutritional value of walnut paste and, at the same time, limit its oxidative degradation by developing a freeze-drying process with addition of polysaccharide matrices including dietary fiber. The effects of different formulations and technological treatments on product stability were evaluated. Shelled walnuts were roasted at 165 °C for 15 minutes, grinded, and refined; the obtained walnut paste was mixed with betaglucan, inulin and pectin, singly or combined with tragacanth gum and DE12 maltodextrin. The different formulations were added to water, emulsified and dehydrated by freeze-drying. Lyophilized samples were finally stored at 60 °C for 15 days. Walnut paste, samples just after lyophilization, and lyophilized samples after storage were evaluated in terms of moisture, peroxide number, acidity and pH, conjugated dienes and trienes, total phenols and tocopherols. Further analyses (color, 410 and 420 nm absorption, and total phenols content after ethanol precipitation) were carried out on freeze dried samples before and after storage. The results showed that the freeze-drying process affected the nutritional profile of the walnuts, limiting the onset of oxidative phenomena. After storage the content of total phenols and tocopherols was significantly higher already in the freshly lyophilized walnut paste, compared to the untreated one. The addition of polysaccharide compounds aided to preserve total phenols. However, when betaglucan, inulin, or pectin were individually included, a significant depletion of tocopherols was observed. Maltodextrin and tragacanth gum played a fundamental role in maintaining high levels of both total phenols and tocopherols. Nevertheless, formulations including also dietary fiber were slightly more oxidized. Among them, the inclusion of betaglucan provided the overall best results.

1. Introduction

Despite their interesting functional and sensory profile, the use of walnuts on industrial scale is limited by their high susceptibility to oxidation which leads to losses in terms of both nutritional value, and palatability. For this reason, only a small share of walnuts is usually allocated for industrial processing: besides the oil, there are relatively few walnut-based products which, in most of the cases, are flavoured walnut surrogates. In this context, the interest in using walnut paste is broad and growing (Tahmasebi et al., 2016). Walnuts are nutrient-dense food, source of polyunsaturated fatty acids and antioxidant compounds, such as phenolics and tocopherols (Martinez et al., 2010). Following a roasting and grinding process, walnut kernels become a semi-fluid paste that can be encapsulated in order to preserve its nutritional properties and increase stability and convenience (Dordoni et al., 2017). Mixtures of gums and carbohydrates are the most commonly used coating materials because of their ability in protecting sensitive active ingredients and interacting with fiber and other biopolimers (Vasisht, 2014; Othman et al., 2018). Dietary fiber includes cellulose, noncellulosic polysaccharides such as hemicellulose, pectic substances, gums, mucilages and the non-carbohydrate component lignin. Its physico-chemical properties can be manipulated through different treatments (chemical, mechanical, thermal etc.) to improve functions and activities. Considering also the proved health benefit

Paper Received: 9 April 2018; Revised: 12 July 2018; Accepted: 24 September 2018

Please cite this article as: Dordoni R., Duserm Garrido G., Gruppi A., Spigno G., 2019, Freeze-dried Products Based on Walnuts: Interaction Between Fat Fraction and Dietary Fiber, Chemical Engineering Transactions, 75, 313-318 DOI:10.3303/CET1975053

deriving from its consumption (Dhingra et al., 2012), innovative healthcare products can be obtained by incorporating dietary fiber into matrices high in nutrients, such as walnut paste. The aim of this work was to limit the oxidative degradation of walnut paste and increase its nutritional value by developing a freeze-drying process with addition of different polysaccharide matrices (including dietary fiber). Process impact and storage stability of the different formulated samples were evaluated.

2. Materials and methods

2.1 Materials

Shelled Chile's walnuts (*Juglans regia* L.), harvested in 2013 and packed in polypropylene bag with a clear portion, were purchased from local market (I frutti del Convento, Alfano F.lli, Italy). Maltodextrin DE 12 (Glucidex® 12) was supplied from Roquette Italia (Italy); tragacanth gum powder (CEROTRAG 888) was procured from Roeper (Germany); barley betaglucan (Glucagel™) was provided by DKSH Italia (Italy); pectin from citrus peel (Pectin powder E440) and inulin from chicories roots (Inulin 90%) were purchased from A.C.E.F. (Italy). All chemicals used in the analytical determinations were high-purity commercially available reagents.

2.2 Experimental plan

Walnut paste preparation
Walnut kernels were roasted in a forced convection oven at 160 °C for 15 min (Vadya and Eun, 2013), ground by an electric domestic grinder (La Moulinette, Moulinex), and refined in a planetary micro mill (Pulverisette, Fritsch, Germany) at 500 rpm for 2 min. The obtained walnut paste was collected in plastic opaque containers, saturated with nitrogen, and stored at -18 °C until use.

Encapsulation and freeze-drying processes
Water and different combinations of polysaccharide matrices (betaglucan, inulin, pectin, maltodextrin, and tragacanth gum) were added to the walnut paste, according to the recipes shown in Table 1. Samples were homogenized for 5 min at 25 °C, placed into glass vessels, and frozen at -18 °C for 24 h (Dordoni et al., 2017). The emulsions were dried for 72 h by using a Christ Alpha 1-2 LD freeze dryer. During the process, the ice condenser was set at a temperature lower than -50 °C, and the pressure was around 0.120 mbar (Dordoni et al., 2015).

Table 1: Formulations of walnut paste and different carrier materials to be freeze dried.

Sample	Formulation
1	100 g walnut paste + 150 mL H_2O
2	100 g walnut paste + 5 g maltodextrin + 0.5 g tragacanth gum + 150 mL H_2O
3	100 g walnut paste + 5 g maltodextrin + 0.5 g tragacanth gum + 150 mL H_2O + 1 g betaglucan
4	100 g walnut paste + 5 g maltodextrin + 0.5 g tragacanth gum + 150 mL H_2O + 1 g inulin
5	100 g walnut paste + 5 g maltodextrin + 0.5 g tragacanth gum + 150 mL H_2O + 1 g pectin
6	100 g walnut paste + 150 mL H_2O + 1 g betaglucan
7	100 g walnut paste + 150 mL H_2O + 1 g inulin
8	100 g walnut paste + 150 mL H_2O + 1 g pectin

Accelerate storage test
Aliquots (50 g) of each lyophilized sample were placed in open glass vials and stored in the dark at 60 °C for 15 days (Vadya and Eun, 2013). Walnut paste quality was evaluated before and after storage in terms of moisture, pH and total acidity, conjugated dienes and trienes, peroxide value, total phenols, and tocopherols. Analytical determinations on freeze dried samples were carried out just after lyophilization and after storage.

2.3 Analytical determinations

Moisture content was determined according to the method AOAC 931.04 (AOAC, 2005); pH and total acidity were measured following the methods recommended by the Office International du Cacao, du Chocolat et de la Confiserie (OICCC, 1972). Oil fraction and defatted powder were separated by the cold extraction procedure described by Calvo et al. (2011) for α-, γ-, and δ-tocopherols determination. Peroxide values, and conjugated dienes (K_{232}) and trienes (K_{270}) systems were determined on the oil fraction as reported by the regulation (European Union Commission Regulation, 1991). Total phenols content was measured on defatted sample powder according to Belscak et al. (2009). Color measurements were taken on a Konica-Minolta CR-

310 reflectance colorimeter in the CIE L*a*b* color system. As for the absorption at 410 and 420 nm, the sample was dissolved in boiling water in a 1: 5 ratio. After 2 h cooling, under regularly stirring, the sample was filtered throughout a folded (Whatman 595½) and a 0.45 µm (Acrodisc®, Sigma - Aldrich) filters. The absorbance of the sample was measured (Shimadzu UV- 1601) against water. Total phenols content after ethanol precipitation was determined by dissolving sample in boiling water (in a 1:5 ratio) and stirring at 100 rpm for 1 h at 24 °C (orbital shaker Infors HT). Dissolved sample was then added with ethanol in a 1:4 ratio, kept in the dark for 48 h, and centrifuged (Varifuge 20 RS, Heraeus Sepatech) at 3000 rpm for 15 min at 24 °C. The supernatant mixture was filtered (Whatman 595½) and examined according to the Folin-Ciocalteu assay (Moncalvo et al., 2016).

2.4 Statistical analysis

Results are reported as mean values of three replicates with their corresponding standard deviations. Student's t-test and analysis of variance (ANOVA) followed by Tukey's post-hoc test were performed at the $p \leq 0.05$ level using statistical software SPSS®(version 21.0, SPSS Inc., Chicago, IL, USA).

3. Results and discussion

Initial walnut paste showed pH and total acidity values of 6.30±0.00 and 53±0 $meq_{NaOH}/100\ g_{dm}$, respectively. After storage, pH decreased to 6.20±0.01 and total acidity increased to 84±2 $meq_{NaOH}/100\ g_{dm}$ suggesting the onset of fat hydrolytic rancidity (Ziaolhang et al., 2017). As expected, the accelerated aging at 60 °C induced the raise of conjugated dienes and peroxide values, and the reduction of total phenols and tocopherols contents (Table 2). However, no significant differences in the conjugated trienes were observed, indicating a non-substantial development of secondary oxidation products (Ferreira et al., 2018).

*Table 2: Characterization of walnut paste (WP) before and after 15 days storage at 60 °C. Different superscript letters indicate statistically different values within each column (Student's test).*n.d.: not determined.** toco: tocopherol.*

Sample	Moisture %	Dienes K_{232nm}	Trienes K_{270nm}	Peroxides m_{eqO_2}/kg_{oil}	Total phenols $mg_{GAE}/100g_{dm}$	α-toco** mg/kg_{dm}	γ-toco mg/kg_{dm}	δ-toco mg/kg_{dm}
WP before	0.48±0.01	1.306±0.002^{b}	0.144±0.003^{a}	n.d.*	37.13±0.13^{a}	2.12±0.22^{a}	61.51±5.29^{a}	0.47±0.04^{a}
WP after	n.d.*	2.067±0.076^{a}	0.129±0.019^{a}	9.38±0.03	17.03±0.15^{b}	0.39±0.04^{b}	25.88±2.28^{b}	0.17±0.00^{b}

Walnut paste was added with different polysaccharides (including dietary fiber) with the dual objective of acting as coating materials and further increasing the nutritional value of the product. As strong interactions were postulated between starch derivatives and polysaccharide gums (Vasisht 2014), the applied encapsulation process exploited the formation of a network among maltodextrin, tragacanth gum and other endogenous and/or exogenous polysaccharide compounds (Dordoni et al., 2015). Processes (such as grinding, heating, drying) and also environmental conditions (such as temperature, pH, ionic strength, dielectric constant of the surrounding solution and nature of the ions) can modify the physical properties of the fiber matrix. More branching (like tragacanth gum), the presence of ionic groups (e.g. pectin methoxylation) and the potential for inter unit positional bonding (like β-glucans with mixed β-1-3 and β-1-4 linkages) increase the solubility and can, therefore, influence the characteristics of final products (Dhingra et al., 2012). Samples were examined in order to evaluate the impact of encapsulation / dehydration process and storage on oxidation-related parameters. Just after lyophilization (Table 3), a residual moisture content was determinable solely in the samples with only fiber addition (6, 7, and 8). Higher acidity (90±2 and 86±1 $meq_{NaOH}/100\ g_{dm}$) and lower pH (6.06±0.01 and 6.12±0.00) in samples 8 and 5, respectively, were clearly linked to the properties of the added pectin (pH = 3 - 4 from data sheet). Samples with inulin showed higher pH values (6.38±0.01 and 6.33±0.01 in 7 and 4, respectively), but rather high acidity levels (79±1, and 84±2 $meq_{NaOH}/100\ g_{dm}$). Peroxide values were always negligible, indicating no significant differences among the different formulations. As peroxides, conjugated dienes reflect the degree of lipid oxidation at the primary level (Martinez et al., 2010), oxidative effect was minimal (Ferreira et al., 2018), but slightly higher in sample 8. In general, comparing to the initial walnut paste (Table 2), total phenols were preserved through the lyophilization process, when polysaccharides were added. The α-tocopherol levels were always lower in the treated samples, while δ-tocopherols and, in particular, γ-tocopherols had significantly lower values in samples 6, 7, and 8, containing only fiber with no maltodextrin and tragacanth gum addition. However, a significant increase in γ-tocopherol content was observed in sample 1. According to Vadya and Eun (2013), tocopherols can be released during

processes due to breaking of both membrane and the bond between tocopherols and phospholipids or proteins. In order to investigate the effect of formulations on the oxidative stability of the samples, an accelerated storage test was performed. In general, pH reduction and increase in acidity were observed, particularly in sample 5 (102±2 meq_{NaOH}/100 g_{dm}, pH=5.74±0.01).

*Table 3: Characterization of walnut paste freeze dried samples just after lyophilization. Different superscript letters indicate statistically different values within each column (Tukey's test).*n.d.: not determined.** toco: tocopherol.*

Sample	Moisture %	Dienes K_{232nm}	Trienes K_{270nm}	Peroxides $m_{eq}O_2/kg_{oil}$	Total phenols $mg_{GAE}/100g_{dm}$	α-toco* mg/kg_{dm}	γ-toco mg/kg_{dm}	δ-toco mg/kg_{dm}
1	n.d.*	1.072±0.053^{c}	0.036±0.006^{c}	n.d.	18.97±3.00^{d}	1.75±0.06^{a}	141.04±0.89^{a}	0.52±0.02^{a}
2	n.d.	1.157±0.024^{bc}	0.065±0.008^{bc}	n.d.	30.28±0.67^{bc}	1.62±0.39^{a}	89.97±26.69^{b}	0.48±0.11^{a}
3	n.d.	1.218±0.037^{b}	0.082±0.016^{abc}	n.d.	23.23±2.12^{cd}	1.86±0.04^{a}	55.41±0.66^{c}	0.46±0.02^{a}
4	n.d.	1.245±0.041^{b}	0.068±0.013^{abc}	n.d.	34.83±8.55^{b}	0.43±0.04^{b}	31.46±13.39^{cd}	0.26±0.09^{bc}
5	n.d.	1.212±0.295^{b}	0.101±0.019^{ab}	n.d.	74.61±2.31^{a}	0.56±0.02^{b}	99.17±6.64^{b}	0.58±0.03^{a}
6	0.62±0.3^{a}	1.252±0.029^{b}	0.081±0.351^{abc}	n.d.	36.51±1.16^{b}	0.51±0.02^{b}	25.7±0.32^{d}	0.12±0.01^{cd}
7	0.49±0.4^{a}	1.108±0.036^{c}	0.116±0.015^{a}	1.74±2.47^{a}	30.34±1.78^{bc}	1.70±0.23^{a}	14.25±0.92^{d}	0.31±0.01^{b}
8	0.53±0.5^{a}	1.362±0.019^{a}	0.090±0.014^{ab}	1.24±1.75^{a}	28.69±2.78^{bcd}	0.23±0.00^{b}	11.31±0.33^{d}	0.07±0.00^{d}

On the basis of conjugated trienes and peroxide values (Table 4), samples containing maltodextrins, tragacanth gum and fiber (3, 4, and 5) showed the highest levels of oxidation. This could be due to the strong network formed with maltodextrin and gum, that can act as a barrier, slowing and/or limiting the activity of the antioxidant compounds naturally present in the product, such as total phenols and tocopherols. As a matter of fact, even after storage, these samples showed higher amounts of tocopherols compared to sample formulations including only fiber. However, in samples 2, 3, and 7 after storage, the total phenols were higher than just after lyophilization. This could be explained by a thermal effect during storage on the polysaccharide network leading to reduction of noncovalent interactions with negative effect on total phenols extraction by the Belskak's method (Zhu, 2018). To endorse this hypothesis, additional analyses were carried out to evaluate the total phenols content on supernatants of freeze dried samples subjected to ethanol precipitation. Since ethanol addition limits the hydrophobic interactions between polysaccharides and polyphenols (Renard et al., 2016), it was attempted to assess the increase in phenol solubility after storage (Table 5). Nevertheless, values significantly rose only in samples 2, 5, and 8, containing maltodextrin, tragacanth gum and / or pectin.
By comparing the initial walnut paste (WP before, Table 2) with the just lyophilized one (Sample 1, Table 3) it can be observed that freeze-drying process exerted an important effect on depletion of total phenols and increase in γ-tocopherol content. Even after storage (Table 4), the sample 1 showed a limited oxidative damage and the highest tocopherol levels.

*Table 4: Characterization of walnut paste freeze dried samples after storage at 60 °C for 15 days. Different superscript letters indicate statistically different values within each column (Tukey's test).*n.d.: not determined. ** toco: tocopherol.*

Sample	Moisture %	Dienes K_{232nm}	Trienes K_{270nm}	Peroxides m_{eqO2}/kg_{oil}	Total phenols $mg_{GAE}/100g_{dm}$	α-toco** mg/kg_{dm}	γ-toco mg/kg_{dm}	δ-toco mg/kg_{dm}
1	n.d.*	3.349±0.116^{a}	0.274±0.038^{bc}	5.67±0.33^{de}	21.84±2.41^{de}	0.98±0.07^{d}	114.91±0.09^{a}	0.51±0.02^{a}
2	n.d.	3.255±0.214^{a}	0.210±0.008^{d}	5.72±0.36^{de}	35.58±0.87^{de}	0.73±0.07^{b}	41.13±4.22^{d}	0.37±0.02^{c}
3	n.d.	3.466±0.076^{a}	0.320±0.017^{ab}	14.06±1.06^{c}	58.20±9.27^{c}	0.94±0.08^{a}	53.42±0.19^{c}	0.47±0.01^{b}
4	n.d.	3.486±0.066^{a}	0.305±0.017^{b}	22.35±0.68^{b}	22.96±0.53^{b}	0.39±0.01^{d}	26.54±1.71^{e}	0.34±0.00^{c}
5	n.d.	3.495±0.019^{a}	0.369±0.02^{a}	33.36±2.18^{a}	49.92±1.05^{a}	0.38±0.01^{a}	63.79±3.41^{b}	0.46±0.00^{b}
6	n.d.	3.201±1.094^{a}	0.245±0.017^{cd}	9.90±4.99^{cd}	28.87±1.80^{cd}	0.06±0.00^{bc}	4.05±0.49^{f}	0.05±0.00^{f}
7	n.d.	3.083±0.034^{a}	0.223±0.001^{cd}	6.72±0.38^{de}	35.74±0.48^{de}	0.08±0.01^{b}	10.33±0.70^{f}	0.10±0.00^{e}
8	n.d.	1.102±0.038^{b}	0.116±0.015^{e}	1.74±2.47^{e}	28.87±1.80^{e}	0.23±0.01^{bc}	26.02±2.95^{e}	0.17±0.02^{d}

Analysis of chemical parameter was integrated with color evaluations (Tables 6 and 7). In detail, 410 and 420 nm absorption was determined as indicator of possible browning polymers formation (Xu et al., 2017), that could have interfered with total phenols dosage. However, most of the samples showed a reduction in absorption at 420 nm after the 60 °C storage (Table 7). Therefore, the evaluation of total phenols level was not influenced by the formation of new compounds. This is also confirmed by the comparison between the CIE L*a*b* coordinates, where only minimal variations were observed.

Table 5: Total phenols content measured on supernatants of freeze dried samples subjected to ethanol precipitation. Different superscript letters indicate statistically different values within each row (Student's test), and different subscript letters indicate statistically different values within each column (Tukey's test).

Sample	Total phenols after EtOH precipitation (mg_{GAE}/100 g_{dm})	
	After lyophilisation	After storage
1	$20.15\pm1.29^{a}{}_{a}$	$21.70\pm0.54^{a}{}_{c}$
2	$22.46\pm1.66^{b}{}_{a}$	$27.64\pm1.27^{a}{}_{ab}$
3	$23.11\pm2.58^{a}{}_{a}$	$27.19\pm3.18^{a}{}_{ab}$
4	$23.88\pm0.30^{a}{}_{a}$	$24.01\pm0.76^{a}{}_{abc}$
5	$24.01\pm2.12^{b}{}_{a}$	$29.06\pm2.03^{a}{}_{a}$
6	$19.97\pm2.79^{a}{}_{a}$	$23.68\pm2.58^{a}{}_{bc}$
7	$20.28\pm1.85^{a}{}_{a}$	$21.77\pm1.62^{a}{}_{c}$
8	$21.37\pm1.77^{b}{}_{a}$	$26.77\pm0.76^{a}{}_{abc}$

Table 6: Color evaluation of walnut paste freeze dried samples just after lyophilisation. Different superscript letters indicate statistically different values within each column (Tukey's test).

Sample	L*	a*	b*	410nm (a.u.)	420nm (a.u.)
1	48.73 ± 0.60^{d}	6.45 ± 0.14^{a}	23.17 ± 0.07^{bcd}	0.360 ± 0.000^{e}	0.300 ± 0.000^{d}
2	53.81 ± 0.24^{b}	5.40 ± 0.10^{de}	23.21 ± 0.05^{bcd}	0.700 ± 0.180^{bc}	0.930 ± 0.040^{a}
3	54.19 ± 0.32^{b}	5.34 ± 0.08^{de}	23.41 ± 0.11^{bc}	0.660 ± 0.040^{bc}	0.697 ± 0.045^{b}
4	53.63 ± 0.68^{b}	5.15 ± 0.11^{e}	23.02 ± 0.24^{cd}	0.570 ± 0.000^{cd}	0.540 ± 0.010^{c}
5	55.48 ± 0.26^{a}	5.38 ± 0.10^{de}	22.85 ± 0.08^{de}	0.970 ± 0.010^{a}	0.910 ± 0.010^{a}
6	54.31 ± 0.13^{ab}	5.69 ± 0.03^{c}	23.90 ± 0.11^{a}	0.707 ± 0.015^{bc}	0.690 ± 0.010^{b}
7	51.75 ± 0.27^{c}	6.09 ± 0.09^{b}	23.51 ± 0.27^{ab}	0.410 ± 0.020^{de}	0.320 ± 0.000^{d}
8	54.22 ± 0.53^{b}	5.50 ± 0.04^{cd}	22.53 ± 0.18^{e}	0.807 ± 0.006^{ab}	0.727 ± 0.006^{b}

Table 7: Color evaluation of freeze dried samples after storage. Different superscript letters indicate statistically different values within each column (Tukey's test).

Sample	L*	a*	b*	410nm (a.u.)	420nm (a.u.)
1	44.06 ± 0.34^{d}	6.59 ± 0.01^{b}	21.36 ± 0.19^{c}	0.425 ± 0.005^{g}	0.330 ± 0.010^{e}
2	48.84 ± 0.28^{c}	5.93 ± 0.01^{d}	22.73 ± 0.16^{a}	0.485 ± 0.005^{f}	0.430 ± 0.000^{d}
3	49.25 ± 0.10^{c}	5.67 ± 0.05^{e}	22.53 ± 0.13^{ab}	0.790 ± 0.010^{c}	0.430 ± 0.010^{d}
4	50.31 ± 0.57^{b}	5.76 ± 0.04^{e}	23.04 ± 0.25^{a}	0.645 ± 0.015^{d}	0.465 ± 0.005^{c}
5	51.31 ± 0.21^{a}	5.66 ± 0.06^{e}	22.54 ± 0.22^{ab}	0.955 ± 0.005^{a}	0.795 ± 0.005^{a}
6	48.70 ± 0.09^{c}	6.25 ± 0.04^{c}	22.75 ± 0.08^{a}	0.575 ± 0.035^{e}	0.465 ± 0.005^{c}
7	44.94 ± 0.58^{d}	6.80 ± 0.04^{a}	22.11 ± 0.23^{b}	0.420 ± 0.000^{g}	0.350 ± 0.000^{e}
8	51.27 ± 0.14^{ab}	5.93 ± 0.09^{d}	22.77 ± 0.14^{a}	0.845 ± 0.015^{b}	0.670 ± 0.020^{b}

4. Conclusions

Freeze-dried products based on walnuts were specifically obtained by roasting and grinding of kernels, and encapsulation of the resulting paste. Product stability seemed to be linked to the three-dimensional network that was built during the encapsulation/freeze-drying process and that could be supported by the addition of polysaccharide compounds. Even after storage, the only lyophilized walnut paste showed a significantly higher content of total phenols and tocopherols, compared to the untreated one. Maltodextrin and tragacanth gum addition allowed a good preservation of both total phenols and tocopherols content. However, if also dietary fiber were included, lower protection of fat fraction against the oxidation was observed. Moreover, significant depletion of tocopherols resulted by using betaglucan, inulin, or pectin individually. Among the different formulations, sample with maltodextrin, tragacanth gum, and betaglucan showed a limited increase in peroxide number, a slight decrease in tocopherols, and high values of total phenols, even after storage. Hence, the combination of these ingredients and the performance of the lyophilization process originate a

stable and versatile product with an increased nutritional value that can be applied in various food products, from confectionery, to bakery, to the meat industry and more.

Acknowledgments

This work was supported by the Fondazione Cariplo and Regione Lombardia through the research project Cremona Food-LAB, grant n. 2015/1341.

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