Corn Oil Enrichment with Waste Orange Peel Polyphenols and Its Effect on Oxidative Resilience: Stirred-Tank Versus Ultrasonication Mode

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Article

Corn Oil Enrichment with Waste Orange Peel Polyphenols and Its Effect on Oxidative Resilience: Stirred-Tank Versus Ultrasonication Mode

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Abstract: The use of synthetic antioxidants as edible oil stabilizers against oxidative rancidity is the method of preference for the relevant industries, yet these additives have been a subject of intense debate regarding adverse effects of their long-term consumption. In the search of natural replacers, interest has been focused on residual plant materials that could be used as cost-effective sources of oil antioxidants. In this line, this investigation aimed at studying the effect of enrichment of corn oil using waste orange peels (WOP), targeting at fortifying the oil with natural polyphenolic antioxidants, to provide effective shielding against oxidation. Initial comparison of two modes, a stirred-tank and an ultrasound-assisted one, evidenced that the latter was more efficacious in enriching corn oil with total polyphenols. However, detailed examination of the polyphenolic composition revealed that the oil enriched with the stirred-tank mode may have almost two times higher polyphenolic content, which mounted up to 109 mg per kg of oil. The major polyphenolic constituents identified were polymethylated flavones, but also ferulic acid and naringenin. Oil stability trials including the monitoring of peroxide value and p-anisidin value, demonstrated that the oil enriched with WOP polyphenols using the stirred-tank mode exhibited significantly higher oxidative resilience compared to control (neat oil), but also compared to the oil enriched using ultrasonication. Furthermore, it was observed that when neat oil was ultrasonicated, it also displayed exceptional stability against oxidation. Based on the outcome of this study, it is recommended that WOP, owed to their richness in lipophilic flavonoids, might be an ideal candidate for edible oil fortification, which could provide the oil with natural powerful antioxidants. Such a process could lend oils high oxidative resilience, but also functional ingredients.

Keywords: antioxidants; edible oils; food waste valorization; orange peels; polymethylated flavonoids

1. Introduction

The ever increasing agricultural and food production, tightly associated with the burst in global population, has pushed eco-systems to unprecedented limits, due to high waste load generation and environmental aggravation. The realization that current models of economy development may offer little to provide viable solutions to this problem, has brought out bioeconomy as the most promising route for reversing detrimental consequences and paving the way for establishing sustainable strategies for the agri-food sector. Basic principles of bioeconomy embrace philosophies that dictate the adherence to "zero-waste" processes, and in this regard, recycling and/or reuse of wastes produced from agricultural practices and food manufacturing have become indispensable elements for the development of sustainable technologies [1, 2].

The activities pertaining to crop and food production are inevitably the source of a large volume of biowastes, which may originate from farming practices (pruning, exfoliation, etc.), post-harvest screening and/or losses (e.g. rejection of defected products), and food processing (peeling, de-seeding

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etc.). As a result, a vast amount of plant biomass may be accumulated and destined for dumping, including disfigured and/or damaged fruit/vegetables, roots, stems, leaves etc. [3, 4]. However, these residual plant tissues are the pool of an enormous number of biomolecules, which could be used for the development of a spectrum of high value-added commodities, such as functional food and cosmetic ingredients, and pharmaceutical formulations [5, 6]. On this basis, food waste valorization has been a field of ongoing research, which aims mainly at establishing green processes within wider biorefinery frames, for effective biomass exploitation and bio-product commercialization.

One of the most precious classes of bioactive molecules that could be recovered from agri-food wastes is polyphenols. This peculiar group of secondary metabolites has several subclasses, such as simple phenolics (e.g. hydroxycinnamates), and flavonoids (e.g. flavanones, flavones, etc.). Numerous of these phytochemicals have been claimed to express important biological effects, including chemoprotective and cardioprotective activities, but they may also act as anti-inflammatory, antioxidant, and antimicrobial agents [7, 8]. Hence there has been a wide spectrum of investigations on the development of technologies for valorizing rejected materials rich in polyphenolic substances [9, 10].

Citruses are worldwide one of the largest fruit crops, with orange production representing 60% of the total. Oranges are principally processed into juice, giving a yield of almost 43 - 50% on a fresh fruit weight basis, while the residual 50% corresponds to discarded/defected fruits, peels, pulp and seeds [11, 12]. The global production of oranges was almost 46 million tons in 2019, of which around 37% were processed into various products. These data showcase orange processing as a major generator of side streams. Therefore, emerging technologies targeting at the reuse/valorization of orange processing wastes as polyphenol sources become imperative, on the ground of several studies that soundly documented citrus flavonoid bioactivities [13]. It is to be emphasized that citrus flavonoid-containing commodities are currently commercialized as health supplements and nutraceuticals [14].

On the other hand, studies on various fat-containing products and oils indicated that orange peel polyphenol could be exploited as effective food antioxidants [15-17]. In fact, orange peels might be a unique material in this regard, considering that their composition includes significant amounts of polymethylated (lipophilic) flavonoids, which could be readily incorporated into lipid substrates [18]. Nevertheless, pertinent studies are rather scarce, and thus there is a lack of credible information to substantiate the usefulness of waste orange peels (WOP) as a source of food antioxidants. Recently, a detailed examination demonstrated that polyphenol-enriched WOP extracts, added into various edible oils as triacetin solutions, could display important protection against oxidative rancidity, although the level added was rather low [19]. Taking into account this outcome, the current study targeted at studying polyphenol enrichment of corn oil using WOP as a raw material. Enrichment was attempted using a conventional stirred-tank mode and ultrasonication, and thorough examination of oil composition and resilience to oxidation was performed. To the best of the authors' knowledge, such an examination is presented for the first time and may pave the way for industrial processes for oil fortification with natural antioxidants.

2. Materials and Methods

2.1. Reagents and Chemicals

Glacial acetic acid, gallic acid, ammonium iron(II) sulfate, Folin-Ciocalteu reagent and absolute ethanol were purchased from Panreac (Barcelona, Spain). Luteolin 7-*O*-rutinoside, ferulic acid, hesperidin, *p*-anisidine and hexane were obtained from Sigma-Aldrich (St. Louis, Burlington, MA, USA). Dichloromethane and isooctane were from Carlo Erba (Vaul de Reuil, France). Hydrogen peroxide (35%) was obtained from Chemco (Malsch, Germany). Sodium carbonate anhydrous and ammonium thiocyanate were from Penta (Prague, Czechia). Solvents used for chromatographic determinations were HPLC grade.

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2.2. Waste Orange Peel (WOP) Collection and Handling

A representative lot of orange processing residues, consisted essentially of orange peels, was collected from catering sites (Larissa, Central Greece) that daily process orange fruits to produce fresh orange juice. The collection was performed within a short period (3 consecutive days) and the material was stored at – 40 °C for no longer than a week. The collected residues were carefully screened to separate peels (flavedo + albedo) and remove unwanted material (foreign bodies, apparently infected tissues, pulpy material). Then, WOP were dried in a laboratory oven (Binder BD56, Bohemia, NY, USA), and comminuted and sieved according to a previously published detailed procedure [20].

2.3. Corn Oil Procurement

Commercially available corn oil (3 bottles of 1 L) was purchased from a local grocery store (Karditsa, Central Greece). Upon receipt, the oil was stored at ambient temperature, in a dry and dark chamber, and it was used shortly after opening. All experiments were carried out using corn oil from the same batch, to avoid measurement variations owed to variations in oil composition.

2.4. Stirred-Tank Mode of Enrichment

Amount of 1 g of WOP was combined with 10 g of corn oil in a 25-mL glass vial, and the mixture was stirred at 500 rpm, at room temperature or at 40 °C, for a period ranging from 3 to 24 hours, using a hotplate (Heidolph Instruments GmbH & Co. KG, Schwabach, Germany). After the completion of the treatment, the mixture was centrifuged at 4,000×*g*, to remove debris and suspended particles in the oil.

2.5. Ultrasound-Assisted Mode of Enrichment

Ultrasonication was carried out using a BIOBASE UCD-150 ultrasonic cell disrupter (Jinan, Shandong, China), operated at a fixed frequency of 50 Hz, with maximum nominal power of 150 W. The probe tip used (emitting surface) had a diameter of 6 mm. An exact mass of 10 g of corn oil was mixed with 1 g of WOP in a 25-mL glass vial, and the ultrasonication probe was immersed in the vial at approximately 3 mm above the bottom. Ultrasonication was conducted in pulse mode, with a duty cycle of 2/2 (2 s on/2 s off), by properly adjusting both the amplitude and time. Temperature was tracked using a thermal sensor placed within the ultrasonication chamber, which was in direct contact with the surface of the mixture (oil + WOP), to provide constant temperature measurement during ultrasonication. Throughout treatments, the glass vial was immersed in an ice bath to avoid large temperature increases, brought about by the energy dissipated in the mixture. The initial treatment temperature was usually 15 °C, and by the end of the treatment it increased to approximately 21 °C.

To determine the actual power (P) dissipated to the mixture and the ultrasonic intensity, the following equations were used [21]:

$$P = mC_P\frac{dT}{dt} \quad (1)$$

$$\mathrm{UI} = \frac{P}{S} \quad (2)$$

$$\mathrm{AED} = \frac{P}{V} \quad (3)$$

where m is the mass of the ultrasonicated mixture (oil + WOP), C_P the specific heat capacity of corn oil (1.956 J g^{-1} K^{-1} at 20 °C) [22], and $\frac{dT}{dt}$ the temperature rise per s, computed by fitting temperature change (dT), measured by a thermocouple, *versus* time [23]. UI is the ultrasonication intensity (W cm^{-2}), S the area of the emitting surface of the transducer (cm^2), and V the volume of the oil used (L). AED is the acoustic energy density, expressed as W L^{-1}. To convert the mass of the oil into volume, a density (d) value of 0.9159 g mL^{-1} was used [24].

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2.6. Ultrasound-Assisted Enrichment Optimization

The experimental design chosen was a Box–Behnken with three central points. This design aimed at constructing a predictive model, on the basis of response surface methodology. Taking into consideration the data derived from the single-factor experiments, the actual levels of the ultrasonication settings (independent variables) amplitude (% Ampl) and time (*t*) were codified, as described in detail elsewhere [25]. Both codified and actual values are given in Table 1.

Table 1. The process (ultrasonication) variables used in this examination, and their values (coded and actual).

Variable	Code	Levels		
		-1	**0**	**1**
Ampl (%)	X_1	45	60	75
t (min)	X_2	5	7.5	10

The model constructed was assessed using lack-of-fit and analysis of variance (ANOVA) tests, which permitted to estimate of the overall model significance, and the significance of each individual term of the model. The non-significant terms ($p > 0.05$) of the mathematical expression (equation) that described the predictive model were omitted, so the final equation contained only significant terms.

2.7. Total Polyphenol Analysis

The total polyphenol content of oil samples was determined using a published protocol [26]. Exact mass of 1g of oil was dissolved in 2 mL hexane and mixed with 2 mL of a 60% aqueous methanol solution. The mixture was vortexed and then centrifuged at 4,500 rpm for 5 min. Following this, 0.1 mL of the aqueous phase was carefully withdrawn from the mixture and combined with 0.1 mL of Folin-Ciocalteu reagent. After exactly 2 min, 0.80 mL of 5% w/v Na_2CO_3 solution was added, and the mixture was incubated in a thermostated water bath (Falc Instruments LBS2, Treviglio, Italy), at 40 ºC, for 20 min [27]. The absorbance was recorded at 740 nm in a Shimadzu UV-1700 PharmaSpec spectrophotometer (Kyoto, Japan), and the determination of total polyphenol content (C_{TP}) was performed using a gallic acid calibration curve (10-100 mg L^{-1} in methanol). C_{TP} was expressed as mg GAE per kg of oil.

2.8. Determination of Peroxide Value (PV)

The IDF method 74A:1991 [28], slightly modified, was used for PV determination. An amount of 0.05 g of oil was dissolved in 2 mL dichloromethane/ethanol (3:2, *v*/*v*) by vortexing for 2-4 s. Then 0.02 mL oil solution was mixed with 0.196 mL of solvent (dichloromethane/ethanol) and 0.01 ammonium thiocyanate solution (4 M in water) was added. The mixture was vortexed for 2-4 s, and 0.01 mL of ammonium iron(II) sulfate solution (25.5 mM in 10 M HCl) was added. After a further vortexing for 2-4 s and a 5-min incubation at room temperature, the absorbance was measured at 500 nm against suitable blank (reaction mixture without oil). PV was determined using a hydrogen peroxide (H_2O_2) calibration curve, constructed using six different concentrations (0.5-5 mmol L^{-1} in dichloromethane/ethanol). Results were expressed as mmoL H_2O_2 per kg of oil, as follows:

$$\text{PV}\left(\text{mmoL } H_2O_2/\text{kg Oil}\right) = \frac{C_{H_2O_2} \times V}{w} \quad (4)$$

where C_{H2O2} is the concentration of H_2O_2 (in mmol L^{-1}), V the volume of the dichloromethane/ethanol used to dissolve the oil (in L) and w is the weight of the oil sample (in g).

2.9. Determination of p-Anisidine Value (p-AV)

The determination was carried out using the ES ISO 6885:2012 method [29]. An exact weight of 0.5 g of oil was transferred into a 10-mL volumetric flask and made to the volume with 10 mL of isooctane. Volume of 1 mL of this solution was mixed with 0.2 mL of glacial acetic acid, shaken vigorously, and kept in the dark for 10 min. Following this, the absorbance (A_0) was obtained at 350

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nm, using isooctane as a blank. In addition, 1 mL of the oil solution was mixed with 0.2 mL of *p*-anisidine reagent (0.5% in acetic acid) and shaken vigorously. After exactly 10 min in the dark, the absorbance (A_1) of the solution was measured at 350 nm. The same was done by mixing 1 mL of isooctane with 0.2 mL of *p*-anisidine reagent, and this absorbance was termed as A_2. *p*-AV was computed using the equation:

$$\text{p-AV} = \frac{100\,Q\,V}{m}\,0.24\,[(A_1 - A_2 - A_0)] = 12\left(\frac{A_1 - A_2 - A_0}{m}\right) \quad (5)$$

Q is the oil concentration in the initial isooctane solution (0.05 g mL^{-1}), V is the volume of the oil solution (10 mL), m is the mass of the oil mass used (in g), A_0 is the absorbance of the unreacted test solution, A_1 the absorbance of the reacted solution and A_2 the absorbance of the blank. The value 0.24 is the correction factor for the dilution of the test solution with 0.2 mL of the reagent or acetic acid.

2.10. High-Performance Liquid Chromatography (HPLC)

Polyphenol extraction from the oil samples was carried out as described in paragraph 2.7. The polyphenol-containing extract was analyzed with HPLC, as described in full detail elsewhere [30]. Briefly, a Shimadzu CBM-20A liquid chromatograph coupled to Shimadzu SPD-M20A diode array detector (DAD) (both purchased from Shimadzu Europa GmbH, Duisburg, Germany) were employed, using a 20-μL injection loop. Separations were accomplished on a Phenomenex Luna C18(2) column (Phenomenex Inc, Torrance, CA, USA), 100 Å, 5 μm, 4.6 mm × 250 mm, which was constantly kept at 40 °C. The mobile phase was (A) 0.5% aqueous formic acid (A) and 0.5% formic acid in acetonitrile/water (6:4) (B), delivered at a flow rate of 1 mL min^{-1}. The gradient elution program implemented was as follows: from 0 to 40%, B for 40 min; then to 50%, B for 10 min; and to 70%, B for another 10 min and then constant for 10 min. Analytical information regarding peak identification and quantification have been reported in a previous study [31].

2.11. Data Processing and Statistics

At least two experiments were conducted for every enrichment process examined. The quantitative analyses (chromatographic, spectrophotometric) were performed in triplicate. The results given are mean ± standard deviation (sd). SigmaPlot™ 12.5 (Systat Software Inc., San Jose, CA, USA) was employed to accomplish linear regressions and to depict the course of oil oxidation. JMP™ Pro 13 software (SAS, Cary, NC, USA) was employed to setup the experimental design and compute the statistics for the response surface methodology (analysis of variance, lack-of-fit). A Shapiro–Wilk test was performed to test the normality of the experimental data. The IBM SPSS Statistics™ 29 (SPSS Inc., Chicago, IL, USA) was used to investigate statistically significant differences, based on the Kruskal–Wallis test.

3. Results and Discussion

3.1. Stirred-Tank Enrichment Mode

Prior to deploying ultrasonication for investigating corn oil enrichment with WOP polyphenols, a control assay was carried out using a conventional stirred-tank methodology. To study the degree of enrichment in total polyphenols, corn oil was mixed with dried WOP powder at a proportion of 10/1 (oil/powder, *w*/*w*), and the mixture was stirred for 1 – 24 h, at 25 and 40 °C. As can be viewed in Figure 1, stirring at 25 °C for 24 h was by far the most effective combination ($p < 0.05$), providing corn oil with a total polyphenol content of 31.7±2.2 mg GAE kg^{-1} oil. To the contrary, stirring at 40 °C for 1 h gave a level of enrichment of only 6.2±0.4 mg GAE kg^{-1} oil. The outcome of this assay strongly indicated that switching treatment temperature from 25 to 40 °C did not favor higher corn oil enrichment in polyphenols but stirring at 25 °C sufficed to achieve the highest enrichment level.

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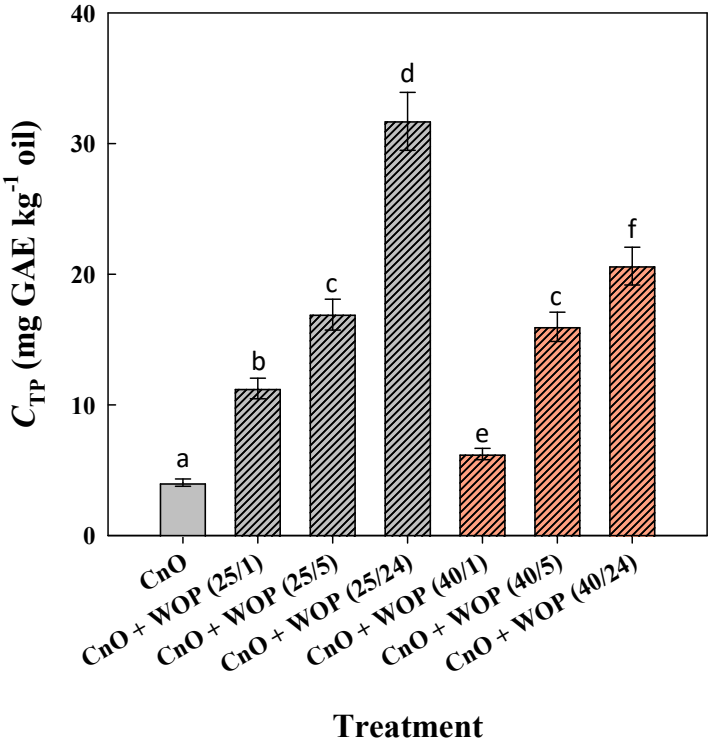

Figure 1. Bar plot presenting the content in total polyphenols (C_{TP}) of corn oil samples enriched with WOP using the stirred-tank mode. Assignments: CnO, corn oil (neat); CnO + WOP (25/1), corn oil enriched with WOP at 25 °C for 1 h. Likewise, "40" corresponds to a temperature of 40 °C, and 5 and 24 to stirring for 5 and 24 h. Bars designated with different letters (a, b, c, d, e and f) are statistically different values ($p < 0.05$). .

3.2. Ultrasound-Assisted Enrichment (UAE)

The effect of UAE was investigated by irradiating mixtures of corn and WOP powder at the same mass proportion mentioned in paragraph 3.1, employing a sonicator with a fixed frequency of 50 Hz. As previous studies demonstrated the pivotal effect of both amplitude (% Ampl) and time (t) of ultrasonication on WOP polyphenol extraction [32, 33], the preliminary single-factor trials included initially the examination of the effect of irradiation amplitude, and the results obtained are depicted in Figure 2.

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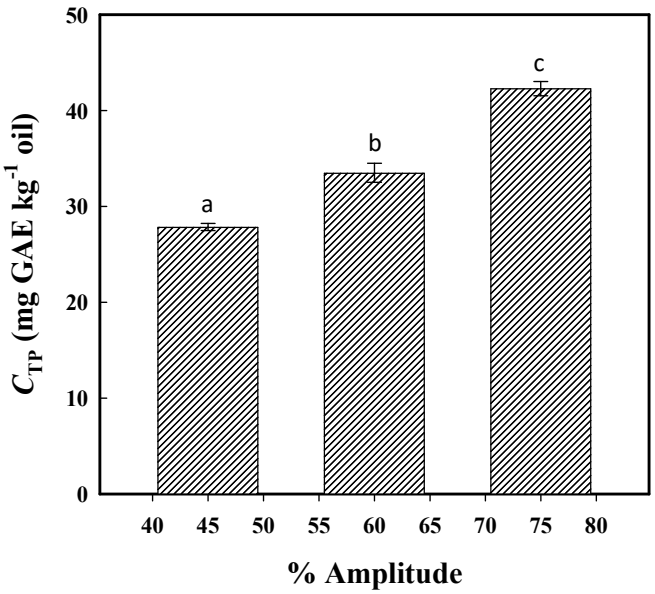

Figure 2. The effect of ultrasonication amplitude (%) on the content of corn oil in total polyphenols. Samples were ultrasonicated for 10 min. Bars designated with different letters (a, b, and c) are statistically different values ($p < 0.05$). .

By maintaining ultrasonication time (t_{US}) at 10 min, the increase of % Ampl from 45 to 75% yielded a significant increase in C_{TP} ($p < 0.05$). Thus, 75% Ampl was chosen as the desired setting. Levels higher than 75% were avoided, considering i) the adverse effect of ultrasonic radiation on polyphenolic substances [21], and ii) erosion of the ultrasonication probe [34]. As a following step, % Ampl was kept constant at 75% and the effect of ultrasonication time (t_{US}) time was examined (Figure 3).

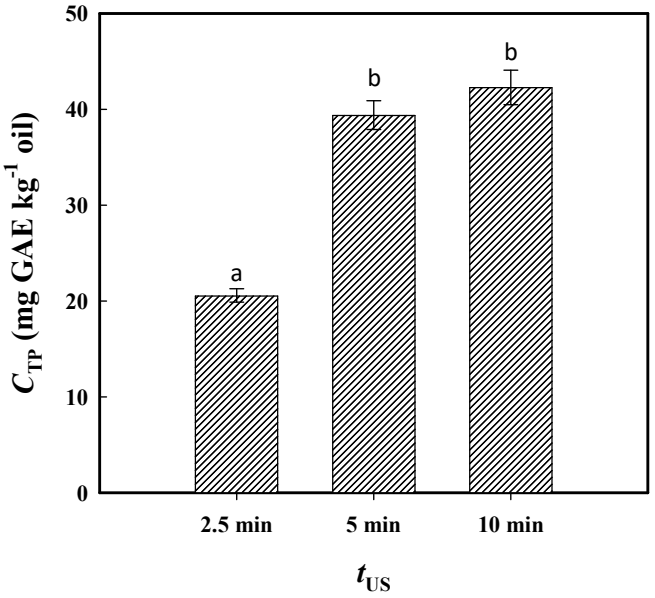

Figure 3. The effect of ultrasonication time (t_{US}) on the content of corn oil in total polyphenols. The % amplitude was set at 75%. Bars designated with different letters (a and b) are statistically different values ($p < 0.05$). .

At 2.5 min the C_{TP} determined was significantly low, but polyphenol entrainment into the oil was boosted by switching t_{US} to 5 min ($p < 0.05$). Further t_{US} extension to 10 min did not offer

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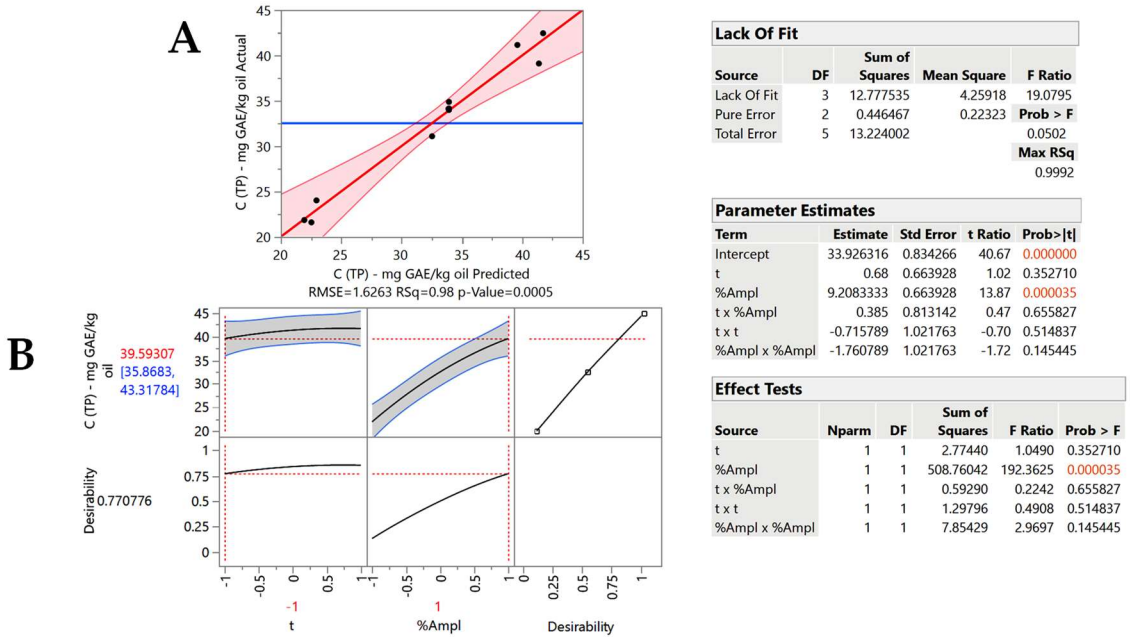
significant advantage for C_{TP} increase compared to 5 min ($p > 0.05$), and it was therefore concluded that the ideal t_{US} lied between 5 and 10 min.

3.3. Optimization of the Ultrasound-Assisted Enrichment

Taking into account the above observations, response surface methodology was used to assess the effect of the independent variables (t and %Ampl) on the response (C_{TP}), and to reveal any cross (synergistic) functions between them. The ranges of the variables were chosen considering the single factor experiments, but also recent research data [35]. Response surface suitability and the model derived were evaluated by analysis of variance (ANOVA) and test for lack-of-fit (Figure 4), considering the closeness of the predicted and measured values (Figure 4A and Table 2). The mathematical equation (model), which included only the significant terms, was as follows:

$$C_{TP} = 33.9 + 9.2X_2 \ (R^2 = 0.98, p = 0.0005) \quad (6)$$



Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	3	12.777535	4.25918	19.0795
Pure Error	2	0.446467	0.22323	Prob > F
Total Error	5	13.224002		0.0502
				Max RSq
				0.9992

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	33.926316	0.834266	40.67	0.000000
t	0.68	0.663928	1.02	0.352710
%Ampl	9.2083333	0.663928	13.87	0.000035
t x %Ampl	0.385	0.813142	0.47	0.655827
t x t	-0.715789	1.021763	-0.70	0.514837
%Ampl x %Ampl	-1.760789	1.021763	-1.72	0.145445

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
t	1	1	2.77440	1.0490	0.352710
%Ampl	1	1	508.76042	192.3625	0.000035
t x %Ampl	1	1	0.59290	0.2242	0.655827
t x t	1	1	1.29796	0.4908	0.514837
%Ampl x %Ampl	1	1	7.85429	2.9697	0.145445

Figure 4. Correlation between the actual and predicted values of content in total polyphenols (graph A) and the desirability function (graph B). The inset tables contain the results of the statistical analyses for the response surface optimization of the process. Values appearing with different color are statistically significant ($p < 0.05$). .

Model square correlation coefficient (R^2), which represents an indicator of the total variability around the mean given by the model [36], and p value for lack-of-fit (assuming a 95% confidence interval) were highly significant. Thus, it could be supported that the equation (6) had very satisfactory adjustment to the measured (experimental) data. To depict an at-a-glance impression of the effect of the variables (% Ampl, t_{US}) on the response (C_{TP}), a 3D diagram was constructed based on the model, as shown in Figure 5.

Table 2. Total polyphenol content (CTP) of corn oil (measured and predicted values) enriched with ultrasonication, for every design point used in the experimental design.

Design point	Process variables		Response	
			C_{TP} (mg GAE kg^{-1} oil)	
	X_1 (t_{US}, min)	X_2 (%Ampl)	Measured	Predicted
1	-1 (5)	-1 (45%)	21.8	21.9
2	-1 (5)	1 (75%)	41.1	39.6
3	1 (10)	-1 (45%)	21.6	22.5

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4	1 (10)	1 (75%)	42.4	41.7
5	-1 (5)	0 (60%)	31.1	32.5
6	1 (10)	0 (60%)	34.1	33.9
7	0 (7.5)	-1 (45%)	24.0	23.0
8	0 (7.5)	1 (75%)	39.1	41.4
9	0 (7.5)	0 (60%)	34.9	33.9
10	0 (7.5)	0 (60%)	34.1	33.9
11	0 (7.5)	0 (60%)	34.0	33.9

Based on the statistical data given in the inset tables "Parameter Estimates" and "Effect Tests" (Figure 4), only the term X_2 (% Ampl) was significant. By contrast, t_{US} exerted no significant effect on C_{TP}, within the limits tested. This finding was in line with a recent study on sunflower oil enrichment with *Crithmum maritimum* polyphenols, where it was demonstrated that only the ratio oil/plant material was critical in obtaining a high degree of polyphenol incorporation, whereas time had a non-significant effect [37]. Thus, the lowest value used (5 min) was the optimum for maximizing C_{TP}, while the optimum % Ampl was 75%, according to the desirability function (Figure 4B). Under these settings, the maximum C_{TP} was 39.6±3.7 mg GAE kg^{-1} oil. This level was by almost 25% higher than 31.7±2.2 mg GAE kg^{-1} oil attained using the stirred-tank enrichment mode, as shown in paragraph 3.1. To gain an insight into the validity of the model, three individual experiments were carried out using the optimal settings, and the C_{TP} found was 41.1±3.4 mg GAE kg^{-1} oil. This value was virtually equal to the mean value predicted by the model (39.6.8±3.7 mg GAE kg^{-1} oil), confirming that the model could be used for credible predictions.

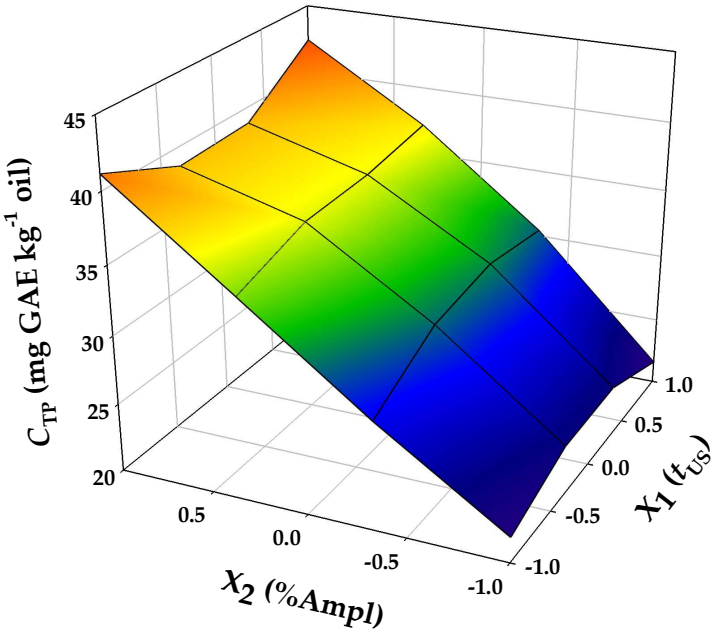

Figure 5. 3D graph representing the variations in total polyphenol content of corn oil enriched with WOP, as a function of the ultrasonication amplitude (% Ampl) and time (t_{US}). .

The level of the optimum %Ampl corresponded to an actual ultrasonication power of 26.7 W, an ultrasonication intensity (UI) of 23.6 W cm^{-2} and an acoustic energy density (AED) of 485 W L^{-1}. The effect of the amplitude applied is directly associated with the actual ultrasound power dissipated to the system and defines the ultrasonication intensity (UI) and the input of the specific ultrasonication energy. Increasing the amplitude would result in increased pressure amplitude of sound wave; this would enable more violent bubble collapse. A certain level of UI is necessary to achieve cavitation threshold [34], which may be pivotal for the extraction yield, because UI strongly affects extraction

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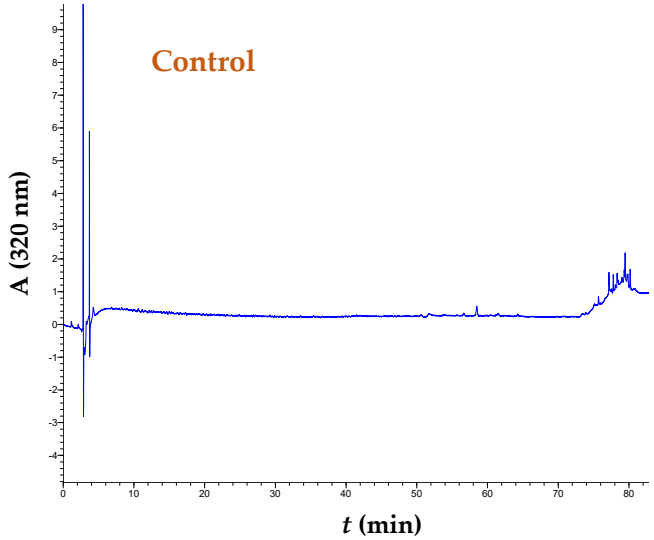
efficiency. Usually, increases in ultrasonication power result in enhanced polyphenol extraction yield, as previously observed for aqueous WOP polyphenol extraction [32, 38]. Nevertheless, setting ultrasonication power to higher levels does not necessarily entail a stronger effect on polyphenol extraction yield. It has been previously shown that increases in ultrasonication power may have a rather negligible effect on certain WOP polyphenols [39], or even negative [40].

On the ground of the response surface outcome, the process was time-independent, and thus t_{US}, beyond a certain limit, was not critical with regard to polyphenol enrichment of oil. Enrichment effectiveness within a short period of time was a very positive finding, showcasing the applicability of the methodology implemented. It should also be noted that, in model polyphenol solutions, intense sonication settings, including extended t_{US}, had negative impact on polyphenols, leading to degradation and polymerization [41]. Although such an effect has never been demonstrated to occur in a medium such as corn oil, studies on polyphenol extraction from mandarin peels suggested that prolonged t_{US} resulted in an important decline in naringenin extraction yield [42]. A similar outcome was reported for phenolic acids in the ultrasound-assisted extraction of orange peels [43]. Thus, short t_{US} might confine adverse effects on polyphenols and contribute towards higher enrichment levels.

3.3. Effect on Polyphenolic Composition

The oil enriched using the stirred-tank mode and the one enriched using ultrasonication were analyzed by HPLC to have a detailed image of the polyphenolic composition. As can be viewed in Figure 6, the non-enriched oil (termed as “control”) was completely deprived of any polyphenolic constituent. To the contrary, the ultrasound-assisted enrichment resulted in supplementation of the oil with several polyphenolic metabolites occurring in WOP (termed as “enriched”), while the same profile was obtained for the oil enriched by applying the stirred-tank mode (data not shown). Based on original standards (where available) and analytical data from previous studies [44], the compounds detected were tentatively identified as ferulic acid (1), hesperidin (2), didymin (3), sinensetin (4), nobiletin (5), and dimethylnobiletin (6).



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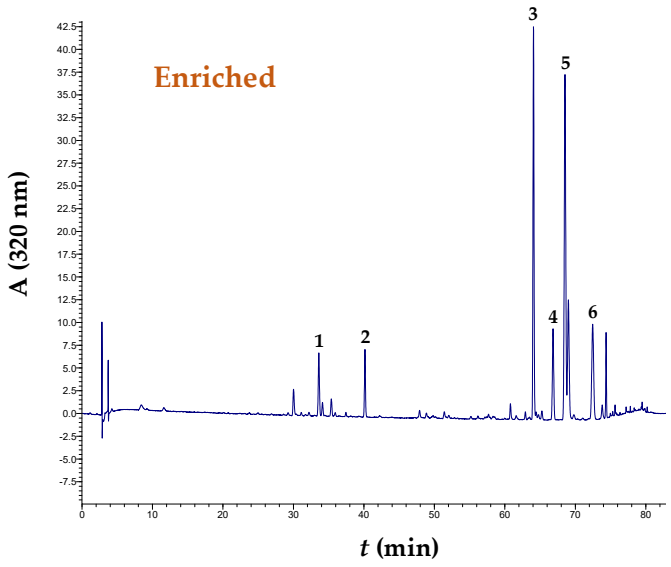

Figure 6. Representative HPLC traces showing the polyphenolic profile of neat corn oil (control) and corn oil enriched with WOP using the stirred-tank mode (25 °C, 24 h). Chromatograms were obtained at 320 nm. Peak assignment: 1, ferulic acid; 2, naringenin; 3, didymin; 4, sinensetin; 5, nobiletin; 6, demethylnobiletin.

Quantitative examination was also carried out to ascertain the degree of incorporation of these compounds into the oil. The results obtained demonstrated that for all compounds detected, a more advanced enrichment was achieved by the stirred-tank mode, whereas the ultrasound-assisted process was significantly less efficacious (Table 3). The most abundant polyphenol was nobiletin, and its content in the corn oil enriched with the stirred-tank mode was 40% higher than the content in the ultrasound-assisted sample.

Table 3. Polyphenolic composition of corn oil samples enriched with the ultrasonication and the stirred-tank mode. Results are given as means of at least two different experiments ± standard deviation. .

#	Compound	Yield (mg kg^{-1} oil)	
		Ultrasonication	Stirred-tank
1	Ferulic acid	1.08±0.06	3.03±0.09
2	Hesperidin	2.31±0.11	19.54±1.01
3	Didymin	12.28±0.82	24.06±1.09
4	Sinensetin	5.78±0.24	9.63±0.73
5	Nobiletin	20.94±1.52	35.05±2.20
6	Demethylnobiletin	12.14±0.85	17.83±0.79
	Total	54.52	109.15

Likewise, didymin, which was the second most abundant constituent, had 49% higher content, while the greatest difference (88%) was found for hesperidin. Overall, the stirred-tank enrichment mode afforded corn oil with 50% higher polyphenol content compared to the one enriched using ultrasonication. This finding contrasted the results obtained by determining the total polyphenol content, suggesting that the Folin-Ciocalteu assay might be misleading in such a case. This outcome is of particular importance and should be taken into consideration in future studies.

The findings of this study are in agreement with previous ones, which demonstrated that olive oil enrichment with oregano polyphenols was more effective when performed with stirring-assisted mixing rather than ultrasonication [45]. In another study on the enrichment of oils such as olive, sunflower and soya oil, using olive leaf powder, it was shown that ultrasonication was more effective

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than conventional stirring. However, in this case too, compounds including hydroxytyrosol, luteolin and apigenin had higher content in samples enriched by applying stirring compared to ultrasonication [46]. In a following examination, although the ultrasound-assisted enrichment of olive oil with olive leaf polyphenols showed over than 50% higher efficiency compared to conventional stirred-tank process, the ultrasound-treated oil was virtually richer only in oleuropein but not in tyrosol and hydroxytyrosol [47]. Considering these findings, it could be argued that the level of enrichment may depend on factors such as the type of oil [48], the polyphenolic composition of the plant material used for the enrichment, and the mode of enrichment. Thus, based on the evidence emerged by the investigations mentioned above, and as also revealed by the data generated by this study, conventional stirred-tank mode might in some cases be more advantageous compared to ultrasonication, in supplying oils with polyphenolic compounds.

3.4. Effect on Oxidative Resilience

The oils enriched with WOP polyphenols using either mode (stirred-tank, ultrasonication) were subjected to a simulated long-term stability trial, by maintaining samples at 65 °C for a period of 46 days [19, 49, 50]. Along with the enriched oils, non-enriched samples with and without BHT addition (200 mg kg^{-1}) were also assayed to detect any effect of ultrasonication on oil oxidative stability. Oil resilience against oxidative deterioration was assessed by monitoring the onset of peroxide value (PV), which is a measure of primary oxidation products accumulation, and *p*-anisidine value (*p*-AV), which represents formation of secondary lipid oxidation products. Such an approach would provide an integrated picture of the effect of enrichment on the stabilization of corn oil.

It can be seen in Figure 7 that the control sample (neat oil) exhibited the most abrupt increase in PV, which, at the end of the trial, mounted up to 62.3 mmol H_2O_2 kg^{-1} oil. An almost identical course was also displayed by the ultrasound-assisted enriched corn oil, which had a PV level of 62.2 mmol H_2O_2 kg^{-1} oil. On the other hand, the ultrasonicated oil showed consistently lower PV levels throughout the whole examination period, reaching a final value of 32.7 mmol H_2O_2 kg^{-1} oil, which was equal to that found for the ultrasonicated oil sample with BHT. The sample enriched with WOP using the stirred-tank mode had higher PV level compared to both control and the ultrasound-assisted enriched sample, up to the 30th day of trial, but thereafter the progression of PV onset was slower, resulting in 32% lower PV value compared to control. This behavior manifested that the corn oil enrichment with the stirred-tank mode was far more effective in providing protection against rancidity development.

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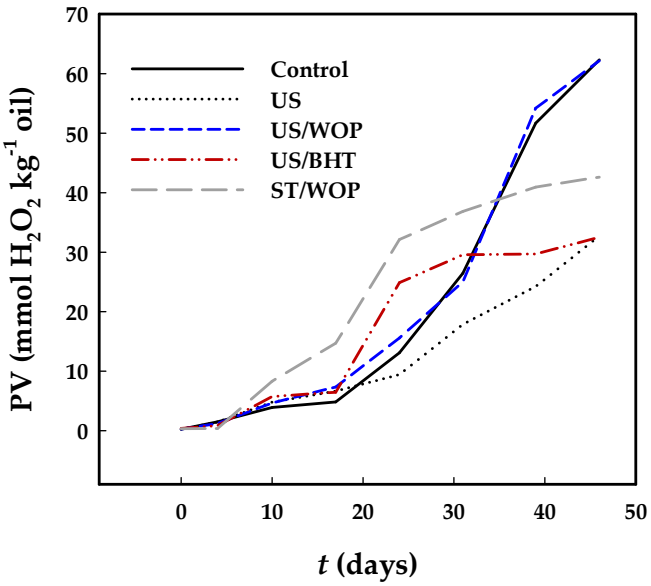

Figure 7. Course of peroxide value (PV) onset during incubation of corn oil samples at 60 °C. Assignments: Control, no enrichment (neat oil); US, ultrasonicated neat oil; US/WOP, oil enriched using the ultrasonication mode; US/BHT, ultrasonicated oil containing 200 mg BHT kg^{-1}; ST/WOP, oil enriched using the stirred-tank mode. .

The investigation of the onset of *p*-AV confirmed that the control sample and the sample enriched with WOP using ultrasonication had roughly the same behavior (Figure 8). This finding strongly suggested that the ultrasound-assisted enrichment conferred practically no resilience against oxidation. By contrast, the oil sample enriched using the stirring-assisted mode exhibited 27% lower *p*-AV at the end of the trial. Furthermore, once again the ultrasonicated oil sample that contained BHT was the most resilient. Another finding of interest was also the fact that the non-enriched oil sample that underwent ultrasonication displayed significantly increased resistance to oxidation, and at the end of the trial it had 29% lower *p*-AV compared to control. Based on these data, it was first concluded that the ultrasound-assisted enrichment had virtually no impact on corn oil stabilization against rancidity. Taking into account both PV and *p*-AV, the corn oil sample enriched using the ultrasonication mode showed no differentiation with the control, either in the onset or the final value of both indices. This fact indicated that the level of enrichment was not sufficient to provide shielding against oxidation.

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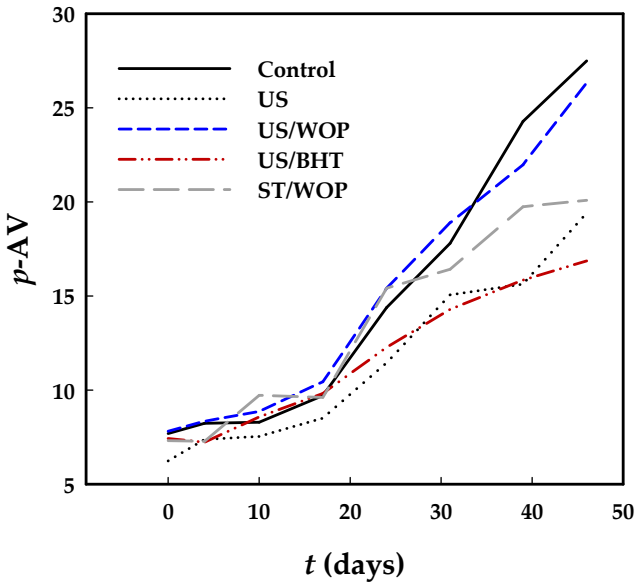

Figure 8. Course of *p*-anisidine value (*p*-AV) onset during incubation of corn oil samples at 60 °C. Assignments: Control, no enrichment (neat oil); US, ultrasonicated neat oil; US/WOP, oil enriched using the ultrasonication mode; US/BHT, ultrasonicated oil containing 200 mg BHT kg^{-1}; ST/WOP, oil enriched using the stirred-tank mode. .

It is known that ultrasonication might in some cases be deleterious to oil quality, causing the formation of off-flavor compounds [51, 52] and accelerating oxidative oil deterioration [53, 54]. However, such an effect did not seem to have occurred, since the oil sample that underwent ultrasonication, along with the one that contained BHT, were the most stable. Therefore, ultrasound-induced oxidation should be rather ruled out; to the contrary, ultrasonication was shown to be particularly effective in stabilizing neat corn oil, and this is a finding that merits further investigation. Most probably, ultrasonication caused degassing of oil, thus eliminating oxygen. This might be a possible reason for the exceptional stability observed for the ultrasonicated oil. In such a case, BHT addition had a rather negligible effect, as witnessed by the onset and final level of both PV and *p*-AV for the corresponding sample.

The oil sample enriched using the stirred tank mode was proven to have the highest polyphenol content and it also displayed significantly higher resilience against oxidation compared to both the control sample and the one enriched using ultrasonication. This outcome strongly suggested that the level of polyphenols entrained from WOP into the oil, which in was in total 109.15 mg GAE kg^{-1} oil, sufficed to provide a considerable protection against rancidity. A previous study on the use of WOP or WOP extracts for stabilizing corn oil showcased the potency of WOP, compared to several other agri-food waste extracts [55]. Similar evidence emerged from an examination on sunflower oil stabilization using WOP extracts [56]. Furthermore, a recent examination also evidenced that corn, sunflower and soybean oils may exhibit increased stability upon addition of polyphenol-containing triacetin extracts of WOP [19]. However, in the study presented herein it was for the first time demonstrated that a total WOP polyphenol level of about 100 mg kg^{-1} oil, was far more effective than 200 mg BHT kg^{-1} oil. Such an outcome might indicate that the mode of enrichment implemented could fortify corn oil with the kind and amount of polyphenols adequate for providing a strong protection against the development of oxidative rancidity.

At this point it should be emphasized that from a high number of agri-food processing by-products tested as natural antioxidant additives in oils and fat-containing foods, only WOP contain highly lipophilic flavonoids, such as the polymethoxylated flavones [57], which possess strong antiradical potency [58]. Furthermore, these compounds have been claimed to express other beneficial biological properties, such as anti-carcinogenic activity and cardiovascular effect [59].

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Thus, WOP may be regarded as a highly suitable source of polyphenolic constituents that could effectively stabilize edible oils, but also lend them with biologically active ingredients. The value of WOP as a source of oil antioxidants has also been exemplified by previous examinations, which demonstrated that the addition of WOP extracts in sunflower oil [56, 60], and soybean oil [60], at levels higher than 1,200 mg kg^{-1}, enhanced oil stability. Considering that these levels were far higher than the enrichment level achieved in this study (almost 109 mg kg^{-1} oil), it could be safely argued that through the methodology proposed herein, corn oil, and presumably other seed oils, could be effectively fortified with WOP polyphenols to reinforce their oxidative stability. Since this stability was proven to be higher than that attained with the widely used synthetic BHT, then WOP would be an ideal candidate for producing highly potent oil antioxidants.

5. Conclusions

From the examinations carried out in this study, it was shown that corn oil may be very effectively enriched in polyphenols, using dried waste orange peels and stirring at ambient temperature. The attempt to perform enrichment using ultrasonication was significantly less effective, as demonstrated by detailed chromatographic analyses. The enriched corn oil sample was shown to contain mainly polymethoxylated flavones, which represent the most lipophilic fraction of orange peel polyphenols. The enrichment resulted in significant protection of corn oil against oxidative rancidity, a fact that manifested the value of waste orange peels as a pool of natural antioxidants. It was also worth mentioning that high stability of neat corn oil was also observed after short ultrasonication, and this finding merits profounder study. The current investigation showcased the exploitation of an industrial food waste, orange peels, to produce stable oils, fortified with functional compounds (polymethylated flavonoids). The prospect arising from such an approach may enable the applicability of novel biorefinery concepts, since the methodology proposed is green, without the use of volatile solvents, straight-forward and of low cost. The development of similar processes may pave the way for the production of safer foods with increased functionality, contributing at the same time to establishing sustainable frames for biowaste harnessing, and consolidating bioeconomy policies.

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