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Optimization of antioxidants extraction from peanut skin to prevent oxidative processes during soybean oil storage

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ABSTRACT

The aim of this study was to determine the antioxidant efficacy of peanut skin extracts (PSE) to prevent the oxidative processes of soybean oil during storage and to compare the results with those obtained after using a positive control with butylated hydroxytoluene (BHT) under accelerated oxidation conditions (16 d at 60 °C). Progress in lipid oxidation of soybean oil was followed by chemical indices (peroxide value, *p*-anisidine value, and conjugated dienes) at the end of the storage. A second goal was to achieve the optimal conditions for the extraction of antioxidant molecules from peanut skin using response surface methodology. At level of 750 mg/kg of PSE, primary and secondary oxidation inhibition was equivalent to the obtained with BHT, hence our results revealed PSE as an effective antioxidant for the stabilization of soybean oil. The best conditions for the recovery of antioxidant compounds were dependent on the variables measured but, in general, concentration of ethanol (73.9%) and temperature of 66.5 °C maximized the responses and the recovery of activities was not significantly influenced by extracting time.

1. Introduction

Oxidative processes in food during storage lead to the degradation of proteins and lipids that could affect the deterioration in flavour, colour, texture and nutritional food value (Lorenzo, González-Rodríguez, Sánchez, Amado, & Franco, 2013). Therefore, a great interest has been shown by both food retailers and consumers to improve food products' quality through preventing lipid oxidation processes (Pateiro, Lorenzo, Amado, & Franco, 2014). For instance, one useful strategy to reduce food deterioration is based on the utilization of synthetic antioxidants, but their use is restricted due to possible toxicity effects (Babbar, Oberoi, Uppal, & Patil, 2011).

Therefore, there has been increasing interest in alternative antioxidants from natural sources (Putnik, Kovačević, Penić, & Dragović-Uzelac, 2015; Putnik, Kovačević, Penić, Fegeš, & Dragović-Uzelac, 2016) which gradually provided impetus to eliminate synthetic preservatives in food (Barba, Galanakis, Esteve, Frigola, & Vorobiev, 2015). The food industry is actively exploring new solutions to reduce oxidative rancidity and increase the shelf-life of products in response to the recent consumers' demand for natural products. Recent studies have reported about the use of natural plant extracts (eg. extracts from grape seeds or leaves from chestnut and green tea) (Lorenzo, Sineiro, Amado, & Franco, 2014; Lorenzo et al., 2013; Pateiro et al., 2014) in several meat products. However, the results are not always better than those obtained with synthetic antioxidants. Thus, over the last years, the antioxidant potential of many plant extracts and food by-products from different origin has been investigated (Barba, Zhu, Koubaa,

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Sant'Ana, & Orlien, 2016; Koubaa et al., 2017).

Specifically, the use of residual biomass as a source of antioxidant compounds can be an attractive and viable alternative because it will reduce disposal costs and adds value to the by-product (Putnik, Kovačević, Jambrak, et al., 2017; Putnik, Kovačević, Ježek, et al., 2017; Puértolas, Koubaa, & Barba, 2016). Peanuts are an important crop in many parts of the world, the world's peanut production totalling 43 million tonnes a year (FAO, 2014). Peanut by-produce represents 3% of the total weight of the fruit, which is mainly composed of peanut skin (PS) (testae or seed coat) of a peanut seed from the blanching process of peanut kernels (Hathorn & Sanders, 2012).

Recent studies have confirmed that peanut skin extracts (PSE) contain many natural polyphenols such as phenolic acids, flavonols and tocopherols (Francisco & Resurreccion, 2012). Moreover, previous works have reported PSE antioxidant activity in food products such as dry-cured sausages (Larrauri et al., 2013), sheep patties (Munekata, Fernandes, de Melo, Trindade, & Lorenzo, 2016), vegetable oils (Nepote, Grosso, & Guzman, 2002) and honey roasted peanuts (Nepote, Mestrallet, & Grosso, 2004).

The food industry goal to produce antioxidants from wastes and by-products have to depend on developing an efficient, economically viable and environmentally respectful extraction process (Putnik, Kovačević, Ježek, et al., 2017; Putnik, Kovačević, Radojčin, & Dragović-Uzelac, 2017). To obtain these objectives, operational conditions for extraction have to determined in order to maximize both phenolic yields and antioxidant activities of the extracts (Putnik, Bursać Kovačević, & Dragović-Uzelac, 2016). To determine the optimal extraction conditions from PS at a laboratory scale, thinking towards a further development at industry level, the best methodology is based on response surface methodology (Wardhani, Vázquez, & Pandiella, 2010). The purpose of this work was to optimise the extraction conditions of antioxidant compounds from PSE, using ethanol-water mixtures and to assess its possibilities to reduce soybean oil oxidation as an alternative to commercial synthetic antioxidants.

2. Materials and methods

2.1. Raw material

Raw peanuts (Virginia variety) were purchased in a local market. Raw peanuts were manually peeled to eliminate the shell, and the skin was also manually separated from the seed. Skins were collected, grounded, cleaned and placed in polyethylene bags and stored in vacuum conditions until extraction treatment.

A sample of refined soybean oil provided by Aceites Abril (San Cibrao das Viñas, Ourense, Spain) was used to follow the oxidation tests. The composition of the soybean oil according to CODEX Stan 210 normative was acidity (0.04%), peroxide index (<1.2 meq O2/kg), moisture (<0.01%) and impurities (<0.01%). The fatty acid profile in percentage was myristic (0.09), palmitic (10.8), palmitoleic (0.1), stearic (5.1), oleic (19.5), linoleic (48.2), linolenic (4.6), arachidic (0.4), eicosenoic (0.2) behenic (0.6) and lignoceric (0.3).

2.2. Extraction of polyphenolic compounds

2.2.1. Experimental design for antioxidants extraction

The effect of time-processing (t), temperature (T) and ethanol concentration (E) in the extraction of antioxidants from peanut skin was evaluated by a rotatable second order design with 6 experiments in the centre of the experimental domain. The experimental conditions were: t in the range (5–150 min), T in the range (25–90 °C) and E in the range (20–100%). The next equations were used for the codification of the variables: $V_c=(V_n-V_0)/\Delta V_n$ for codification and $V_n = V_0+(\Delta V_n \times V_c)$ for decodification.

Where: V_n = natural value of the variable to codify; V_c = codified value of the variable; V_0 = natural value in the centre of the domain; ΔV_n = increment of V_n for unit of V_c

Table 1 summarizes the codified and natural values for each experimental run. The extractions of antioxidant compounds from peanut samples (0.5 g of peanut skin in each experiment) were performed at a solid to liquid ratio of 1:20 (w/v) in a controlled water bath under high agitation conditions. After the time of extraction defined for each assayed condition, samples were filtrated through Whatman Nº1 filter paper and final extracts (filtrates) were lyophilised for analysis. Then, orthogonal least-squares calculation on factorial design data were used to obtain the empirical equations describing the different antioxidant activities or dependent variables assessed (R) in function of the independent variables (t, T and E):

$$R = b_0 + \sum_{i=1}^{n} b_i X_i + \sum_{\substack{i=1 \\ j>i}}^{n-1} \sum_{j=2}^{n} b_{ij} X_i X_j + \sum_{i=1}^{n} b_{ij} X_i^2 \quad (1)$$

where: R is the antioxidant response; b_0 is the constant coefficient, b_i is the coefficient of linear effect, b_{ij} is the coefficient of interaction effect, b_{ii} the coefficients of quadratic effect, n is the number of variables and X_i and X_j are the independent variables (T, E and t). The Student t-test ($\alpha = 0.05$) was employed to determine the statistical significance of the coefficients. The coefficients of determination (R^2) were employed to establish the goodness-of-fit and the following mean squares ratios from Fisher F test ($\alpha = 0.05$) were calculated to define the model consistency: $F1$ = Model/Total error, being the model acceptable when $F1 \geq F_{den}^{num}$ and $F2$ = (Model + Lack of fitting)/Model, being the model acceptable when $F2 \geq F_{den}^{num}$.

Where: F_{den}^{num} are the theoretical values to $\alpha = 0.05$ with the corresponding degrees of freedom for numerator (num) and denominator (den). A Microsoft Excel spreadsheet was employed for the procedures of numerical fittings, coefficient estimates and statistical evaluations. Inhibition of oil oxidation data were adjusted to the hyperbolic equation by non-linear least-squares method (quasi-Newton), using the Solver complement and 'SolverAid' macro present in a Microsoft Excel spreadsheet.

2.2.2. Total polyphenol quantification

The total phenolic concentration of peanut ethanolic extracts was quantified according to the method of Singleton, Orthofer, and Lamuela-Raventós (1999), using the Folin–Ciocalteu Reagent (FCR) and gallic acid as standard. Results of total phenolics were calculated as weight of gallic acid equivalent per g of freeze dried extract (g GAE/g).

2.2.3. Determination of total flavonoid content

The total flavonoid concentration was quantified based on the protocol of Zhishen, Mengcheng, and Jianming (1999), with slight modifications (Amado, Franco, Sánchez, Zapata, & Vázquez, 2014). Total flavonoid concentration was calculated as weight of catechin equivalent per g of freeze dried extract (g CTE/g).

2.3. Determination of antioxidant capacity

2.3.1. 1,1-Diphenyl-2-picryhydrazyl radical-scavenging capacity

DPPH radical-scavenging capacity was determined according to the protocol reported by Prieto, Curran, Gowen, and Vázquez (2015). The radical-scavenging activity (RSA) was calculated by means of the following expression: