

Phenolics in Potato Peels: Extraction and Utilization as Natural Antioxidants

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Abstract: The total phenolics content of potato peel extracts of five different solvents (water, ethanol, hexane, methanol and acetone) and two solvent extraction methods (Solvent and ultrasound-assisted) were studied. The content of total phenolics in the extracts was determined spectrometrically according to the Folin-Ciocalteu procedure and calculated as gallic acid equivalents. Antioxidant activity of methanolic extracts was determined by using the Oven (63°C) and Rancimat (90,120,150°C) methods on refined soybean oil and compared with the effects of synthetic antioxidants (BHA, BHT and TBHQ). Peroxide values and 2-thiobarbituric acid values were used to assess lipid peroxidation. The greatest amount of extract was obtained with water but the greatest amounts of phenolic acids resulted when potato peels was extracted with methanol. Using ultrasound improved the total phenolic compounds of the potato peel extract. After 16 days storage at 63°C, 5.00g of soybean oil containing either the methanolic extract (800, 1600 ppm) or BHA (200 ppm) and BHT (200 ppm) reached peroxide values (PV) of 37.35, 24.65, 33.20 and 28.88 meq/kg respectively. Also the Rancimat method revealed that TBHQ was the best antioxidant but potato peel extract was as good as BHA and BHT.

Key words: Potato extracts • Lipid peroxidation • Ultrasound • Phenolics • Soybean oil

INTRODUCTION

Oil oxidation is a free radical chain process leading to the deterioration of oil and lipid containing materials [1, 2]. In foods, these reactions can lead to rancidity, loss of nutritional value from the destruction of vitamins (A, D and E) and essential fatty acids and the possible formation of toxic compounds and colored products.

Oxidation reactions may involve highly reactive molecules called free radicals. Free radicals are molecules that have lost an electron and try to replace it by reacting with other molecules. This causes the substance to break down. In our bodies, this break down may be a primary cause of Cancer. However, addition of some suitable antioxidant in fats and oils retard the oxidation process [3]. The action of antioxidant depends on its participation in a series of reactions involving radicals [4]. In order to overcome the stability problems of oils and fats, synthetic antioxidants, such as butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT) and ter-butyl

hydroquinone (TBHQ) have been used as food additives. But, recent reports revealed that these compounds may be implicated in many health risks, including cancer and carcinogenesis [5, 6].

Phenolic compounds are the main class of natural antioxidants [7, 8, 9]. Therefore as sources of natural antioxidants much attention is being paid to plants and other organisms. Thus interest in natural antioxidant, especially of plant origin, has greatly increased in recent years [10]. The antioxidant activities of chamomile (*Matricaria Chamomilla L.*) and olive waste cake extracts have previously been studied [11, 12].

Potato peel contains phenolic acids. The largest part consist of chlorogenic acid (CGA). Other phenolics, gallic acid (GAC), caffeic acid (CFA) and protocatechuic acid (PCA), are present in potato peel in low amounts [13]. Identification and quantification of CGA and other phenolic acids in most potato cultivars by HPLC have been reported [14-17]. According to the last studies the antioxidant activity and total phenolics are different between potato cultivars.

Our objectives were to (1) Study the extraction of phenolics from Ramus potato peel using solvent and ultrasound-assisted methods. (2) Extract natural antioxidant from potato peels using different solvents. (3) Evaluate the antioxidant activity and total phenolics in the Ramus potato peel. (4) Compare its antioxidant activity with commercially available antioxidants.

MATERIALS AND METHODS

Reagents: Refined, bleached and deodorized soybean oil was obtained from a local refinery.

Potato tubers (Ramus variety) were obtained from the Faridan of Iran. Tubers were washed, peeled and then the peels were dried and then ground to give 40-mesh size powder. Synthetic antioxidants, namely butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT) and tertiary butylhydroquinone (TBHQ) were purchased from Danisco Co. All chemicals and solvents were of analytical grade and obtained from Merk Chemical Co.

Ultrasonic Extraction: The ultrasound assisted extraction procedure was used for the extraction of potato peel with different solvents (methanol, ethanol, hexane, acetone and water). Thus 20 ml of solvent were added to 1 g of powdered peels, the mixture was sonicated in an ultrasonic bath for 15 min. The extract was filtered through wathman No.42 filter paper for removal of peel particles and then centrifuged at $3000 \times g$ for 10 min at 5°C and stored in a refrigerator [18].

Solvent Extraction: 10 g of ground peels were extracted by mixing using a magnetic stirrer, with 200 ml of methanol at room temperature over night. The extract was filtered through wathman No.42 filter paper and the residue was re-extracted under the same conditions. The combined filtered was evaporated in a rotary evaporator below 40°C . Then centrifuged at $3000 \times g$ for 10 min at 5°C and stored in a refrigerator [18].

Determination of Total Phenolics: The concentration of phenolics in the extracts was determined by the method of Singh *et al.* [19] and results were expressed as gallic acid equivalents per gramme dry weight of sample (GAE/gdw). Five milligrams of each dried potato peel extract was dissolved in a 10 ml mixture of methanol and water (6:4 v/v). Samples (0.2 ml) were mixed with 1.0 ml of 10-fold-diluted Folin-Ciocalteu reagent and 0.8 ml of 7.5% sodium carbonate solution; after standing for 30 min at room temperature, the absorbance was measured at 765 nm

using a UNICAM 8620 UV-Vis spectrophotometer. The estimation of phenolic compounds in the extracts was carried out in triplicate and the results were averaged.

Antioxidant Activity Assay: Potato peel extract was added to soybean oil (Refined soybean oil, free of additives) at levels of 200, 800, 1600 and 2400 ppm. Synthetic antioxidants (BHA, BHT and TBHQ), at levels of 200 ppm were used for comparison. A control sample was prepared under the same condition, without adding any antioxidant.

Oven Test Method: The oven test method at 63°C was used to check stability. Oxidation was periodically assessed by the measurement of peroxide value and thiobarbituric acid value, according to the AOCS method [20]. All the experiments were carried out in triplicate and the results were averaged.

Rancimat Method: Oxidative stability was also evaluated by the Rancimat method (Metrohm Rancimat 749). Samples of extracts dissolved in soy bean oil at a concentration range from 200 to 2400 ppm were heated at 90, 120 and 150°C . BHA, BHT and TBHQ were added to soy bean oil, giving a final concentration of 200 ppm and tested at the same conditions. A continuous air stream (20 L h^{-1}) at ambient condition was passed through the heated samples and the volatile compounds were absorbed in a conductivity cell. The conductivity was monitored continuously until a sudden rise signified the end of the induction period [21].

Statistical Analysis: Experimental data was analysed using analysis of variance (ANOVA) and significant differences among means from triplicate analyses at ($P < 0.05$) were determined by Duncan's multiple range test (DMRT) using the SPSS System (SPSS).

RESULTS AND DISCUSSION

Extraction: Table 1 shows the percentage yield of potato peel extract obtained after ultrasound ground potato peels with different solvents; i.e. methanol, ethanol, hexane, acetone and water and refluxing ground potato peels with methanol. The maximum amount of potato peels extract (11.2 %) was obtained with water followed by methanol (7.9 %) and ethanol (5.6 %). Higher percentage yield were obtained with an increase in polarity of the solvents. It seems the changes in the extraction conditions can effect on the results. There was no

Table 1: Percent yield of potato peels extract obtained with different solvents

| Extraction methods-solvent | Potato peels extract yield (%) |
|----------------------------|--------------------------------|
| Methanol | 8.03±0.03b |
| Ultrasonic-water | 11.20±0.01c |
| Ultrasonic-methanol | 7.90±0.04b |
| Ultrasonic-ethanol | 5.65±0.08d |
| Ultrasonic-acetone | 2.88±0.04e |
| Ultrasonic-hexane | 1.00±0.01f |

Values with different letters (b, c, d, e, f) were significantly different ($P < 0.05$, Duncan's multiple range test). Values expressed are means ± SD of triplicate measurements

Table 2: Total phenolic content extracted from potato peel by different extraction methods and solvents

| Extraction methods-solvent | Phenolic content (µgGAE/gdw) |
|----------------------------|------------------------------|
| Methanol | 522.1±2.14c |
| Ultrasonic-methanol | 593.3±4.02d |
| Ultrasonic-water | 312.2±2.10e |
| Ultrasonic-ethanol | 280.32±5.21f |
| Ultrasonic-acetone | 155.6±4.20g |
| Ultrasonic-hexane | 0.00±0.00h |

Values with different letters (c, d, e, f, g, h) were significantly different ($P < 0.05$, Duncan's multiple range test). Values expressed are means ± SD of triplicate measurements. GAE, gallic acid equivalent

significant difference ($p < 0.05$) in the percentage yields between the extracts of two mentioned methods with methanol.(solvent and ultrasound-assisted solvent methods)

Total Phenolic Content: The concentration of phenolics in the extracts, expressed as µg GAE/g sample, was dependent on the solvent and method used in the extraction, as shown in Table 2. The amount of phenolic compounds in the methanolic extract was highest and total phenolic concentrations in the five solvents were in the order: methanol > water > ethanol > acetone > hexane. Potato peel contains many phenolic compounds, some in free form and some bound. The major phenolic acids in the potato peel extract were identified as chlorogenic acid (CGA), gallic acid (GAC), protocatechuic acid (PCA) and caffeic acid (CFA) [22].

Sonication improved the total phenolic compounds of the methanolic extract of potato peels and shortened the extraction times. Therefore, antioxidant activity of the extract of highest phenolic compounds (methanol) was tested in refined soybean oil at 63, 90, 120 and 150°C.

Effect of Addition of PPE on the Stability of Soybean Oil:

The PPE was used at levels of 200, 800, 1600 and 2400 ppm and synthetic antioxidants (BHA, BHT and TBHQ) were added at 200 ppm, because the latter were pure compounds whereas the former were complex mixtures

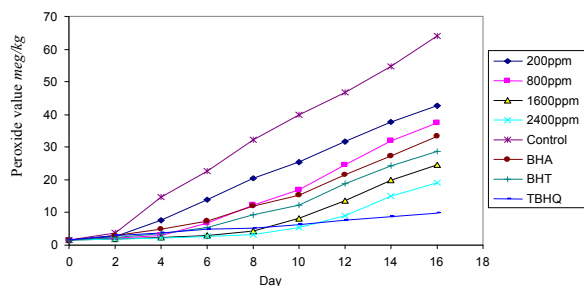


Fig. 1: Effect of potato peel extract (PPE) on soybean oil oxidation expressed as peroxide value formation at 63°C

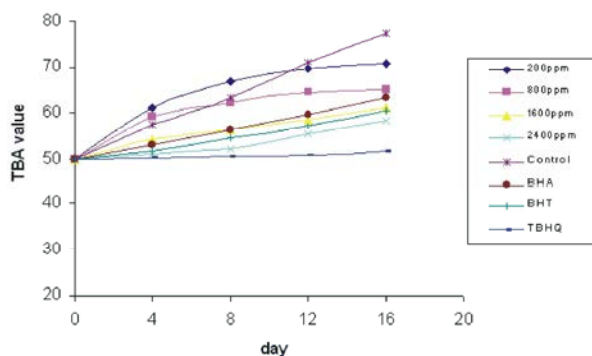


Fig. 2: Changes in the TBA values of soybean oil treated with PPEs during storage at 63°C

with active components being present at low levels. The addition of natural and synthetic antioxidant to soybean oil affected, to different degrees, the peroxide and TBA values during accelerated oxidation at 63°C for 16 days (Fig. 1 and Fig. 2). Peroxide value (PV) measures primary products of lipid oxidation and TBA value measures the formation of secondary oxidation products, mainly malonaldehyde, which may contribute off-flavour to oxidized oil [23]. All samples with PPE level added at 200-2400 ppm were more stable on heating at 63°C than the control, when assessed by the change in peroxide (Fig. 1) and TBA (Fig. 2) values.

Effect of PPE increased with concentration and the antioxidant activity at concentrations of 800 and 1600 ppm were not significantly different ($p < 0.05$) from that of the synthetic antioxidants (BHA and BHT) at levels of 200 ppm but always TBHQ showed higher antioxidant activity than the all levels of PPE concentrations. Similarly, there was no significant difference in peroxide and TBA values when the amount of potato peel extract in soybean oil was increased from 200 ppm to 800 ppm and from 1600 ppm to 2400 ppm. But there was a significant difference in peroxide and TBA values when the amount of potato peel extract in soybean oil was increased from 800 ppm to 1600 ppm.

Table 3: Antioxidant effects of different concentrations of PPE, BHA, BHT and TBHQ, measured by Rancimat, under 90, 120, 150°C temperatures and 20 L h⁻¹ air flow conditions. PF, IT with antioxidant/ ITcontrol

| | 90°C | 120°C | 150°C |
|--------------|-------------------------|-----------|-----------|
| | Induction time (IT) (h) | | |
| Control | 25.70±0.02 | 3.20±0.01 | 0.55±0.00 |
| PPE-200 ppm | 28.48±0.31 | 3.51±0.01 | 0.60±0.00 |
| PPE-800 ppm | 28.71±0.28 | 3.59±0.04 | 0.61±0.00 |
| PPE-1600 ppm | 33.64±0.18 | 3.98±0.07 | 0.62±0.00 |
| PPE-2400 ppm | 36.34±0.22 | 4.28±0.08 | 0.64±0.00 |
| BHA 200 ppm | 28.89±0.05 | 3.65±0.00 | 0.62±0.00 |
| BHT 200 ppm | 29.70±0.12 | 3.71±0.07 | 0.63±0.00 |
| TBHQ 200 ppm | 60.20±0.11 | 6.86±0.04 | 1.01±0.02 |
| | Protection factor (PF) | | |
| PPE-200 ppm | 1.11 | 1.10 | 1.09 |
| PPE-800 ppm | 1.12 | 1.12 | 1.11 |
| PPE-1600 ppm | 1.31 | 1.24 | 1.13 |
| PPE-2400 ppm | 1.41 | 1.33 | 1.16 |
| BHA 200 ppm | 1.12 | 1.14 | 1.13 |
| BHT 200 ppm | 1.15 | 1.16 | 1.14 |
| TBHQ 200 ppm | 2.34 | 2.14 | 1.84 |

Antioxidation Activity Determined by the Rancimat

Method: In Rancimat tests, potato peel extract retarded the oxidation of soy bean oil and increased the induction time of oil peroxidation (Table 3). Longer induction time indicated higher antioxidation activity. Antioxidant activity of the sample decreased in the following order: TBHQ > PPE-2400 ppm > PPE-1600 ppm > BHT > BHA > PPE-800 ppm > PPE-200 ppm > control. The induction times of the samples decreased by the increase of the temperature. Methanol extract at 2400 ppm increased the induction time by 1.4 times compared to control at 90°C.

Phenolic compounds are widely distributed in nature and, according to this paper, potato peel is a natural source of phenolic compounds. Methanol extract was found to have high phenolic contents (522.1-593.3 µg/gdw of sample), so the best method for extraction of phenolic compounds was ultrasonic assisted and solvent extraction with methanol. These results suggest that the PPEs possess antioxidant properties and could be used as alternative natural antioxidants (but after toxicological examination). No single compound can be considered responsible for this stability. This study will provide bases for future studies in this area. It is recommended that other common potato varieties be examined for antioxidant properties.

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