Original Research Article

Peels of Lemon and Orange as Value-Added Ingredients: Chemical and Antioxidant Properties

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ABSTRACT

The present work aimed to evaluate some chemical and antioxidant properties of lemon and orange peels (primary byproducts discarded as waste) to identify their potential use as value-added functional ingredients. Ethanolic or methanolic extracts of the dried peels (microwave or air oven drying methods) were conducted. Proximate chemical composition, vitamin C, phenolic, flavonoids contents, also radical scavenging activities (DPPH), Trolox equivalent antiradical capacity (ABTS) and β-carotene assays for antioxidant activity were determined. All analyzed samples showed that citrus peels are cheap and good source for natural bioactive compounds with high contents and have good antioxidant activities.

Keywords
Citrus byproducts, Lemon peels, Orange peels, Antioxidant properties, Phenolic compounds.

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Introduction

Citrus is a universal term for plants belonging to family Rutaceae (Ladaniya, 2008) which considered as an important fruit around world and one-third of the crop is processed (Jiang et al., 2014). This family has rich phytochemicals sources of many bioactive compounds which are responsible for antioxidant and many other biological activities (Fejzić and Ćavar, 2014).

Citrus byproducts are promising sources of bioactive ingredients and of valuable technological and nutritional properties.

These byproducts can be used as ingredients and food additives (Marín et al., 2002; Puuppinen-Pimia et al., 2002; O'Shea et al., 2012) in food industry for their cheap valuable component (Galanakis (2012). Peels are generated as the primary citrus byproducts represent about 50-65% of fruit weight during processing. These byproducts discarded and considered as a huge load to the environment (Mandalari et al., 2006; Nayak et al., 2015; Wang et al., 2008; Ramful et al., 2011).
Orange and lemon peels are common byproducts (wastes) produce from processing food and juice extraction industry. Lemon peels were applied for pectin and flavonoids (narirutin) production. Orange peels were also employed for recovery of flavonoids e.g. hesperidin, essential oils, and carotenoids. In Egypt and many Mediterranean countries, a major quantity of the citrus peels does not process. Some efforts were made to use these residues as livestock feed (Ghasemi et al., 2009; Kim et al., 2004; Masmoudi et al., 2008; Chedea et al., 2010; Di Mauro et al., 1999; Farhat et al., 2011; Bampidis, and Robinson, 2006).

Natural products present in citrus peels e.g. sugars, flavonoids, carotenoids, folic acid, vitamin C, pectin and essential oils present are very useful for food industry and human health. Also, citrus peels are good source of phenolic compounds can be extracted and employed as natural antioxidants to prevent oxidation of some foods or may be utilized in designing functional foods (Patil et al., 2009; Albishi et al., 2013). Citrus peels described as rich source of unique phenolic compounds to citrus, especially the characteristic flavanone glycosides (mainly naringin, hesperidin, narirutin, and neo hesperidin). Huge amounts of flavanones and many polymethoxylated flavones which are very rare in other plants are contained in citrus peels (Bocco et al. 1998; Swapna and Bhaskar 2013). The antioxidant character of phenolics is due to their ability to donate an electron or hydrogen from phenolic hydroxyl groups. Phenoxyl radical resultant tends to be poorly reactive because of electron delocalization in the aromatic ring, and therefore reactive radical is replaced by other one of limited activity (Li et al., 2006 ; Shahidi and Naczak 2004 ; Topčagić 2009). β-carotene is a strongly red–orange pigment found in orange peels also their phenolic content has their contributions for quality attributes with color, bitterness, antioxidant and flavor (Delia - Gabriela Dumbravă et. al. 2010 ; Kumar et al., 2014 ; Legua et al., 2014). β-carotene showed a nature strong antioxidant for avoiding and treatment of many diseases (Cooper et al., 1999).

Antioxidants are a heterogeneous category of molecules which can safely interact with free radicals and stop the chain reaction before are damaged. Antioxidant capacity of food can use as an indicator of the beneficial effects on human health (Prior and Wu 2013). Antioxidants e.g., flavonoids, phenolic acids, vitamin C, vitamin E and tannins have different biological properties, such as anti-carcinogenic, anti-atherosclerotic effects, reduce coronary diseases and contribute to the maintenance of the gut health by modulation of microbial balance and these properties improve the quality and value of food & anti-aging (Lucia et al., 2008; Kondo et al., 2002; Tuberoso et al., 2013; Liu 2004; Cai et al., 2004; Ke et al., 2015).

Antioxidant property is connected with the ability of phenolic compounds to scavenge free radicals, break radical chain reactions and chelate metals (Nayak et al., 2015). The total antioxidant capacity of plant extracts is influenced by their chemical composition and antioxidant content. Antioxidants are greatly used as food additives to support degradation of foods and to improve their shelf life by preventing lipid per-oxidation as well protect oxidative damage (Kumaran and Karunakaran 2006). Therefore, natural antioxidants are needed for use in foods or medicinal materials and replace synthetic derivatives (Ramesh et al., 2011). The antioxidant activity gives the ability of a bioactive compound to maintain cell structure and function by effectively clearing free radicals, inhibiting lipid
peroxidation reactions and preventing other oxidative damage (Bravo, 1998). Accordingly, citrus peels have been studied because they contain numerous biologically active compounds including natural antioxidants compounds (Hayat et al., 2009). The antioxidant activity of orange flesh and peel extract containing compounds with different polarities, up to the knowledge, has not been reported. In addition, antioxidants may respond to different radical or oxidant sources in a different manner. Consequently, no single assay can accurately reflect all of the radical sources and antioxidants present in a mixed or complex system due to multiple reaction characteristics, mechanisms, and phase localizations which are usually involved (Prior et al., 2005)

Since the citrus peels contain many valuable substances (natural products and bioactive phenolic compounds) can be changed into raw materials for intermediate food ingredients or as ingredients for value-added new products with health benefits. Also, peels are considered as natural byproducts that can work as an outstanding low-cost antioxidant source. The present study objectives were intended to investigate some chemical properties e.g.: proximate composition, vitamin C, total phenols and total flavonoids contents as well to evaluate the antioxidant activities of the lemon and orange peels using DPPH, ABTS and β-carotene assays for detect potential use as value-added ingredients.

Materials and Methods

Materials

Plant materials

Ripened and freshly harvested Citrus lemon (Baladi) (Citrus aurantiifolia, Rutaceae) fruits and navelat navel orange (Citrus sinensis, Rutaceae) fruits were purchased from an Egyptian local market.

Chemicals

Chemicals, solvents, standards and reagents were purchased from Sigma Chemical Co. (St. Louis, Mo, USA). All other chemicals used were of analytical grade.

Methods

Lemon and Orange Peel samples preparation

Lemon and orange fruits were washed by running tap water, peeled and their edible portions were carefully separated. The obtained fresh citrus peels were cut into small pieces before the drying processes.

Drying Methods

Each of fresh lemon or orange peel pieces was divided separately into two parts and each part was dried using the following two methods:

Air Oven-Drying

The fresh citrus peels pieces were dried in an air oven (Shellab-Model 1350FX.-Made in USA) at 40 ± 2°C for ~ 48 h.

Microwave-Drying

A programmable domestic microwave oven (type Samsung, 77 QH 400148, MF 2015, with a maximum output of 1500W at 2450 MHz) was used for drying the fresh lemon or orange peel pieces samples for 6 min.

The two (lemon or orange) dried citrus peels were ground to a fine powder using a mechanical laboratory grinder and passed through a 24-mesh sieve, then packaged in
polyethylene bags and stored at 4±1°C until required for use.

**Ethanol and Methanol extraction**

Ethanol and methanol solvents were applied for bioactive compounds extraction to determine and compare antioxidant activity of the tested citrus peel samples. Dried powder peels (10g) and (4g) of each lemon or orange sample was extracted with 100ml of ethanol(70%) and 80 ml of methanol (80%) respectively at room temperature and several agitations with sonication using the ultrasonic device (200 W, 59 kHz, Shanghai Kudos) for 60 min at room temperature. Both extracts were centrifuged (5000 rpm for 30 min at room temperature). Then the extracts were filtered using filter paper Whatman No.4 according to (Jo et al., 2003) and (Xu, G. et al., 2008 with some modification).

**Analytical Methods**

**Proximate Chemical Composition**

Moisture, ash, protein fat (ether extract) and crude fiber contents were determined in accordance with standard AOAC methods (AOAC 2005). Each analysis was carried out in triplicate.

**Determination of Vitamin C content**

The 2,6-dichloroindophenol titrimetric method (Ramful et al., 2010) was used to determine the vitamin C content of citrus peel extract. The tested peel sample(s) was blended with metaphosphoric acid -acetic acid solutions. After filtration and dilution, the diluted solutions were titrated against standard indophenols solutions. Results are expressed in mg ascorbic acid/g dry weight.

**Determination of Total Phenolics Content**

The Folin – Ciocalteu assay, adapted from (Singleton and Rossi 1965) was used for the determination of total phenolics present in the citrus peel extracts. Distilled water (3.5 mL) was added to 0.25 mL of diluted extract, followed by 0.25 mL of Folin – Ciocalteu reagent. A blank was prepared using 0.25 mL of 80% methanol instead of citrus peel extract. After 3 min, 1 mL of 20% sodium carbonate was added. Tube contents were vortexed then incubated for 40 min in a water-bath set at 40 °C. The absorbance of the blue coloration formed was read at 685 nm against the blank standard. Total phenolics were calculated with respect to gallic acid standard curve (concentration range: 0–12μgmL⁻¹). Results were expressed in μg of gallic acid g⁻¹ fresh weight of plant material.

**Determination of Total Flavonoids Content**

Colorimetric aluminum chloride method was used for flavonoids determination according to the methods described by (Ebrahimzadeh et al., 2008) with some modifications. 0.5 ml solution of each sample extract was separately mixed with 1.5 ml methanol, 0.1 ml of 10% aluminum chloride, 0.1 ml of 1 M potassium acetate and 2.8 ml distilled water then left at room temperature for 30 min. The absorbance of the reaction mixture was measured at 415 nm with a double beam Perkin Elmer UV/Visible Spectrophotometer. Total flavonoid contents were calculated as quercetin from a calibration curve, which prepared by preparing quercetin solutions at concentrations 12.5 to 100 mg ml⁻¹ in methanol.

**Antioxidant Activity Determinations**

**Radical Scavenging Activity (DPPH)**

The effect of citrus peels extracts on 1,1-diphenyl-2-picrylhydrazyl (DPPH) free radical was estimated in order to assess the antioxidant capacity according to the
procedure described by (Yi, Z. et al 2008) with some modifications. An aliquot of 400μl of sample solution was mixed with 800 μl of methanolic solution of DPPH (0.2 mM). The reaction mixture was incubated for 30 min in the darkness at room temperature. The absorbance of the resulting solution was measured at 517 nm with spectrophotometer. For the control, the assay was conducted in the same manner but ethanol was used instead of sample solution. DPPH scavenging capacity of the tested samples was measured as a decrease in the absorbance and was calculated by using the following equation:

\[ \text{Scavenging activity (\%)} = \frac{A_c - A_s}{A_c} \times 100 \]

Where \( A_c \) and \( A_s \) are the absorbance's at 517 nm of the control and sample, respectively.

**Trolox Equivalent Antioxidant Capacity (ABTS)**

The ABTS free radical assay reported by (Re et al. 1999) was based on the ability of antioxidants to reduce with \( ABTS^+ \) (blue/green) to generate \( ABTS^2^- \) (colorless). The ABTS radical cation solution was produced by reacting 7mM ABTS [2, 2’-azinobis (3-ethylbenzo-thiazoline-6-sulfonic acid) diammomium salt] and 2.45mM \( K_2S_2O_8 \) at a ratio 2:1 (v/v); the mixture was then allowed to stand in the dark at room temperature for 12–16 h before use.

This solution was adjusted with absolute ethanol to \( \text{Abs} = 0.7 \pm 0.02 \) at 734 nm. For the analysis, 990 μL of diluted radical solution was mixed with 10 μL of sample, ethanol or standard in plastic cuvettes. The absorbance was read instantly at 734 nm. The results are expressed in μmol Trolox per gm fresh weight sample.

\[ \% \text{ABTS}^+ \text{inhibition} = \frac{A_{\text{blank}} - A_{\text{sample}}}{A_{\text{blank}}} \times 100 \]

Where, \( A_{\text{blank}} \) = the absorbance value of ethanol, and \( A_{\text{sample}} \) = the absorbance of the sample

**β-carotene bleaching test**

A modified method described by (Koleva et al. 2002) was employed. β-carotene (2 mg) was dissolved in 20 mL chloroform. Then, 4 mL of this solution were added to linoleic acid (40 mg) and Tween 40 (400 mg). Chloroform was evaporated under vacuum at 40°C and 100 mL of oxygenated ultra-pure water was added then the emulsion was vigorously shaken. The emulsion (3 mL) was added to a tube containing 0.2 mL of different concentrations of citrus peels extract. The absorbance was immediately measured at 470 nm and the test emulsion was incubated in a water bath at 50°C for 120 min, when the absorbance was measured again. In the negative control, the extract was substituted with an equal volume of methanol. The antioxidant activity (\%) was evaluated in terms of the bleaching of the β-carotene using the following formula:

\[ \% \text{Inhibition} = \frac{A_t - A_c}{C_0 - A_c} \times 100 \]

Where \( A_t \) and \( A_c \) are the absorbance values measured for the test sample and control, respectively, after incubation for 120 min, and \( C_0 \) is the absorbance values for the control measured at zero time during the incubation. The results are expressed as IC\(_{50}\) values (mg/mL), the concentration required to cause a 50% β-carotene bleaching inhibition.

**Statistical Analysis**

All the measurements were performed in triplicate and the data are presented as mean ± SD. The obtained data were subjected to
analysis of variance (ANOVA) according to PC-STAT, Version I A Copyright 1985, the university of Georgia, USA.

**Result and Discussion**

**Chemical Analyses**

**Proximate Chemical Composition**

Proximate composition provides a general nutritional value of a food and includes analyses of the moisture, ash, protein, lipid content and crude fiber. Data in Table 1 showed the moisture contents of fresh lemon and orange peels & their samples dried by air oven (hot air) or microwave methods.

Fresh lemon peel sample contained more moisture content (81.23%) than orange sample (74.35%). Fresh citrus peel of Thompson navel, mandarin, and lemon are characterized by high moisture contents as reported by Nesrine et al., (2012). After drying, the air oven lemon and orange peels still have more moisture than microwave dried samples without significant difference in between. As regard to microwave drying, lemon peels showed significant high moisture content compared to orange peels by ~10.24 %. These findings agreed Adewole et al., (2014).

Table 1 revealed also %s of crude protein, fat (ether extract), fiber, and ash of control and both dried peel samples. Fresh lemon peels contained 11.53% crude protein whereas; orange peels had less crude protein by about 38.51%. Also, ether extract of dried lemon peel exhibited higher amount by 15.90% compared with dried orange peels. Total fiber contents of fresh lemon sample were greater than orange peels, i.e. 16.15 vs 11.48 respectively. After drying, lemon peels still have more crude protein, total fiber and ash (Table 1). With respect to ether extract, orange peels had significantly more amounts, reached to 2.44, 2.12% compared to 1.42 and 1.35% in lemon peels dried by the used two methods respectively. Regarding ash content, lemon peels had significantly more %s (5.92, 5.71) compared to (3.51 and 3.33) orange peels dried by microwave or air oven methods, respectively. These results agreed with Janati et al., (2012) and Marian, et al., (2007) for total fiber, ether extract and protein. Also, Lemon peels had higher ashes content than orange (Nesrine et al., 2012).

**Ascorbic Acid Content**

Vitamin C (L-ascorbic acid or simply ascorbate) is a water soluble material. It is major in citrus and rich in the flesh & peel of fruits. It can efficiently scavenge diversity of reactive oxygen species (ROS), as a natural free radical scavenger, and give off semi dehydroascorbic acid, clearing \(^1\)O\(_2\) and reducing sulfur radicals (Amitava and Kimberly, 2014).

Ascorbic acid contents of the investigated lemon and orange peel samples were determined by the 2,6-dichloroindophenol titrimetric method. Their corresponding concentrations of fresh peels were found 127.70±.04 and 166.42±0.1 mg/100g dry weight basis (Table 2). Drying of these citrus peels, either by microwave or air oven greatly reduced the ascorbic acid concentration to ~ less half content of their original values (control). Vitamin C loss in orange peels was of lower % than lemon peels after drying.

For example, its concentration in orange peels is reduced by ~ 47.89 and 47.93% after microwave and air oven drying, respectively. There is no significant difference in ascorbic acid content after drying by the two methods.
A similar trend was observed in lemon peels, although their loss was more than that happened in orange peels. The ascorbic acid loss in lemon peels, as a result of drying were 55.33 and 53.34% when drying was carried out by microwave or hot air (40°C), respectively. No significant difference was observed in ascorbic acid content as a result of the used drying methods. These results agreed with Fernández-López et al., (2004).

Total Phenolic Content

Polyphenolic compounds (as phenolic acids and flavonoids) are important fruit phytochemicals compounds for their antioxidant activities, their chelation of redox-active metal ions, and inactivation of lipid free radical chains and prevention of hydro peroxide conversion into reactive oxyradicals (Cabral de Oliveira et al., 2009). Phenolic content can be used as an indicator of antioxidant capacity and as a preliminary screen for any product when planned to utilize as a natural source of antioxidants in functional foods (Viuda-Martos et al., 2011).

Data in Table 3 & Fig 1 illustrated that total phenolics (TPC) amount varied greatly and ranged in fresh to orange peel dried samples extracted with ethanol or methanol from 5255.02 ±24.04 to 1410.73 ±5.91 mg Gallic acid/ 100gm sample dry weight. The total phenolics content of orange peel extracted with ethanol was significantly higher (p < 0.05) than in methanol extract. No significant differences (p > 0.05) were observed in the phenolic levels of the two dried orange peels extracted with methanol. An opposite pattern was observed in dried orange peels extracted with ethanol compared to control samples. Meanwhile, ethanol extract exhibited higher phenolic content than lemon peel extracted with methanol and dried by microwave. On the contrary, a significant difference was found between TPC contents of air dried lemon peel and microwave dried samples. Additionally, a presence of significant differences in the TPC content was noticed between all lemon peels extracted with ethanol. The noticed differences in the TPC may be related to nature and characteristics of the varieties of citrus fruit. The differences in the values of TPCS for various citrus peels types may be affected by environmental conditions, the degree of fruit ripening and genetic factors (Ladaniya, 2008). TPC of fresh peels are higher than the recovery from dried samples because the water in fresh plant cells can help phenols extraction.

The reduction of phenolic compounds recovered from dried peels may be due to water evaporation and components in the cells (e.g., membranes and organelles) may hold together in the water absence and probably the extraction with solvent become more difficult. Moreover, if the citrus peel is dried before extraction, the recovery is much lower than using the fresh materials (Li et al., 2006). The increase in drying temperature lead to a decrease in total polyphenols content after re-dissolution (Karsheva et al., 2013).

Therefore, these reasons may explain present study results (Table 3). Worthy to note, that extraction of polyphenols from plant material is affected by the solubility of the polyphenols in the extraction solvent. Furthermore, solvent polarity plays a key role in increasing the extract contents (Naczk and Shahidi 2006). Also, Methanol and ethanol were better than the acetone at extracting phenolic compounds owing to their higher polarity and good solubility for phenolic components as indicated by Wieland et al., (2006).
Total Flavonoids content

Citrus peels are rich source of natural flavonoids. Also, phenolic and flavonoid compounds of citrus have high antioxidant activity. Flavonoids possess a broad spectrum of chemical and biological activities including radical scavenging properties. Such properties are especially evident for flavonols (Kamran, *et al.*, 2009; Hayat *et al.*, 2010; El–Seedi *et al.*, 2012).

Total flavonoids content (TFC) of the investigated citrus peels is revealed in Table 4. Generally, TFC of the tested peel samples, extracted with methanol, were higher than those extracted with ethanol. Contents of the fresh orange peel samples, extracted with methanol, was 506.82 ±0.97; meanwhile, the orange peel samples dried by microwave or air oven reduced to 309±0.32 and 365.40±0.16 QE/100g (db) respectively. TFC content of dried peels with air oven was higher than microwave dried samples. Also, the same trend was noticed in the case of ethanolic extract. These findings varied from methanol extracts results for orange peel either fresh or dried samples which contained more (TFC) than ethanol extracts (Hegazy and Ibrahium 2012).

With regard to TFC content, data in Table 4 indicated that the lemon peel dried by air oven and extracted with methanol had the highest (P< 0.05) content (469.08 ±0.42 mg quercetin equivalent / 100g db), followed by microwave dried and control samples with values 442.79 ±0.42 and 430.58 ±0.77mg /100g db respectively. It was noticed also that TFC in the methanolic extract of lemon peels was higher than its corresponding ethanolic extract. Considering flavonoids, lemon gave the highest concentrations, which is agreed with reports available in literature.

Antioxidant Properties

Host of antioxidant phytophenolics found in citrus. Polyphenolic compounds (phenolic acids and flavonoids) are mainly responsible for fruits antioxidant activity. Total antioxidant capacity of food was measured using numerous methods. Different antioxidants may work through different mechanisms according to generation of different radicals and/or target molecules vary in their chemistry and in the way end points of these assays were measured. No single method can evaluate total antioxidant activity of foods. Two or more methods should always be employed to evaluate the total antioxidative effects of vegetables (Pellegrini, *et al.*, 2003; Nuutila *et al.*, 2003). The antioxidant activity of peel extract might be due to the reduction of superoxide anion, inactivation of free radicals, or complexion with metal ions or their combination (Karoui and Marzouk, 2013). Two complementary test systems: carotene–linoleic acid and DPPH were applied by Moulehi *et al.*, (2012) for evaluating the antioxidant capacities.

In the current work, the antioxidant activity of lemon and orange peels extracted with ethanol or methanol was evaluated using a range of antioxidant tests, including the Radical scavenging activities (DPPH), Trolox equivalent antiradical capacity (ABTS) and β-carotene.

Radical Scavenging Activities (DPPH)

Free radicals are harmful byproducts generated during normal cellular metabolism and can initiate oxidative damage. Antioxidants are playing a considerable role against free radicals. The DPPH free-radical is considered as simple and very fast method for determining antioxidant activity. It can only be dissolved in organic media,
especially in ethanol, which is an important limitation when interpreting the role of hydrophilic antioxidants. DPPH is a stable organic free radical with an absorption band around 515-528 nm which usually used as a reagent to measure free radical scavenging activity of antioxidants. It is sensitive sufficient to detect active ingredients at low concentrations and widely used for screening antiradical activities of fruit and vegetable juices or extracts (Molyneux, 2004; Yi, et al., 2008).

Table 5 and Fig. 2 revealed that antioxidant activity determination by DPPH in fresh orange peel extracted with methanol or ethanol, were 99.79±0.95 and 98.76±0.36 % respectively. The DPPH % activity of the microwave dried orange peel extracted with methanol or ethanol were higher than air oven dried orange peel extracts. No significant differences were found between methanolic and ethanolic orange peel extracts results. Concerning lemon peel samples dried by air oven and extracted with methanol, the DPPH % was found lower than of lemon peel dried by microwave and fresh lemon peel samples as they realized 50.93 ±0.01, 56.69 ±0.02, and 79.37 ±0.25 % respectively. Regarding ethanol extract, the microwave dried lemon peel was higher than the dried air oven peels and of lower % of fresh lemon peel. Noticeably, there are significant differences in the results of dried air oven lemon peel samples in cases of the two used extract solvents. The solvent plays a necessary role in extraction of the plant constituents. Methanol and ethanol are the highest polar amongst the solvents. Therefore, they include high yield of phenolic compounds and highest antioxidant activity (% DPHH scavenging activity) if compared to other solvents extracts (Hegazy and Ibrahim 2012). Casquete et al., (2015) determined the antioxidant capacity of lemon, lime, mandarin and orange peel using (DPPH and ABTS). Regarding DPPH in control samples of lemon, lime, mandarin and orange peel was 80.93, 53.11, 69.02 and 102.39 mg Trolox /100 g of peel extracts, respectively. The different levels obtained from these assays may indicate a relative difference in the ability of antioxidant compounds in the extracts to quench aqueous peroxyl radicals (Thaipong et al., 2006).

**Trolox Equivalent Antiradical Capacity (ABTS)**

The ABTS test is commonly applied to determine antioxidant activity in plants. It is based on the ability of antioxidants to scavenge the long-life radical cation ABTS+ (Martinez et al., 2012). This ABTS method is generally indicated for evaluating the antioxidant activity of hydrophilic compounds (Rufino et al., 2010).

Table 6 revealed data for Trolox equivalent antiradical capacity (ABTS) for the antioxidant activity of the peel samples extracted with methanol or ethanol. From the obtained data fresh orange peel, extracted with methanol, was of higher ATBS capacity than the dried orange peel extracted by microwave or air oven samples (1.09 ±0.05, 0.68 ±0.01 and 0.66 ± 0.01 mM Trolox equivalent respectively. Nearly, there are no significant difference between microwave or air oven dried orange peel extracted with methanol. Meanwhile, significant differences were noticed between the air oven dried orange peel samples dried by microwave or air oven the obtained ABTS capacity were nearly of similar values either for methanol or ethanol extracts with no significant differences.
Table 1 Proximate chemical composition of orange and lemon peels as affected by air oven and microwave drying methods (db)

<table>
<thead>
<tr>
<th>Components</th>
<th>Orange peel samples</th>
<th>Lemon peel samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Control (Fresh)</td>
<td>Microwave Drying</td>
</tr>
<tr>
<td>*Moisture</td>
<td>74.35±0.2a</td>
<td>8.51±0.01c</td>
</tr>
<tr>
<td>Protein</td>
<td>7.09±0.01a</td>
<td>6.44±0.02b</td>
</tr>
<tr>
<td>Ether-extract</td>
<td>2.75±0.01a</td>
<td>2.44 ±0.05b</td>
</tr>
<tr>
<td>Fiber</td>
<td>11.48±0.01a</td>
<td>10.40±0.01b</td>
</tr>
<tr>
<td>Ash</td>
<td>4.21±0.08a</td>
<td>3.33 ±0.10c</td>
</tr>
</tbody>
</table>

(db) = dry weight basis. * = wet weight basis. Results are presented as means for triplicate analyses ± standard deviation (SD). Means within row with different letters are significantly different (P < 0.05).

Table 2 Effect of air oven and microwave drying methods on Ascorbic acid content (mg/100g db) of orange and lemon peels

<table>
<thead>
<tr>
<th>Peel Samples</th>
<th>Control Fresh</th>
<th>Microwave-Drying</th>
<th>Air oven-Drying</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orange</td>
<td>127.70±0.04a</td>
<td>66.55±0.006b</td>
<td>66.50±0.05b</td>
</tr>
<tr>
<td>Lemon</td>
<td>166.42±0.01a</td>
<td>77.67±0.05b</td>
<td>77.64±64.01b</td>
</tr>
</tbody>
</table>

(db) = Dry weight basis. Results are presented as means for triplicate analyses ± standard deviation (SD). Means within row with different letters are significantly different (P < 0.05).

Table 3 Total phenolic content (mg Gallic acid/100g sample) of dried citrus peel extracted by methanol or ethanol (db)

<table>
<thead>
<tr>
<th>Peel Samples</th>
<th>Extract solvents</th>
<th>Control (Fresh)</th>
<th>Microwave-Drying</th>
<th>Air oven-Drying</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orange peel</td>
<td>Methanol</td>
<td>2619.39±12.72a</td>
<td>1535.94±1.61b</td>
<td>1410.73±5.91b</td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td>5255.02±24.04a</td>
<td>3026.34±6.26b</td>
<td>2453.75±9.72c</td>
</tr>
<tr>
<td>Lemon peel</td>
<td>Methanol</td>
<td>1353.88±2.54a</td>
<td>1323.31±8.53a</td>
<td>1180.78±4.60b</td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td>3251.53±76.67a</td>
<td>2632.81±7.09b</td>
<td>2504.40±7.26c</td>
</tr>
</tbody>
</table>

(db) = dry weight basis. Results are presented as means for triplicate analyses ± standard deviation (SD). Means within row with different letters are significantly different (P < 0.05).
Table 4: Total flavonoids content (mg QE/100g sample) of dried citrus peel extracted by methanol or ethanol (db)

<table>
<thead>
<tr>
<th>Peel samples</th>
<th>Extract solvents</th>
<th>Control (Fresh)</th>
<th>Microwave-Drying</th>
<th>Air oven-Drying</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orange</td>
<td>Methanol</td>
<td>506.82±0.97</td>
<td>309.69±0.32</td>
<td>365.40±0.16</td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td>376.87 ±1.96</td>
<td>241.20 ±0.25</td>
<td>273.82 ±0.13</td>
</tr>
<tr>
<td>Lemon</td>
<td>Methanol</td>
<td>430.58±0.77</td>
<td>424.79±0.42</td>
<td>469.08±0.42</td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td>316.05±0.62</td>
<td>317.41±1.22</td>
<td>390.75 ±0.68</td>
</tr>
</tbody>
</table>

*db= dry weight basis. Results are presented as means for triplicate analyses ± standard deviation (SD). Means within row with different letters are significantly different (*P* < 0.05).

Table 5: Radical scavenging activities% (DPPH) of dried citrus peel extracted by methanol or ethanol (db)

<table>
<thead>
<tr>
<th>Peel sample</th>
<th>Extract solvents</th>
<th>Control (Fresh)</th>
<th>Microwave-Drying</th>
<th>Air oven-Drying</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orange</td>
<td>Methanol</td>
<td>99.79 ±0.95</td>
<td>69.83±0.04</td>
<td>56.29 ±0.30</td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td>98.76 ±0.36</td>
<td>68.85 ±0.25</td>
<td>53.83 ±0.04</td>
</tr>
<tr>
<td>Lemon</td>
<td>Methanol</td>
<td>79.37 ±0.25</td>
<td>56.69 ±0.02</td>
<td>50.93 ±0.01</td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td>65.56 ±0.59</td>
<td>56.01± 0.11</td>
<td>52.64 ±0.03</td>
</tr>
</tbody>
</table>

*db= dry weight basis. Results are presented as means for triplicate analyses ± standard deviation (SD). Means within row with different letters are significantly different (*P* < 0.05).

Table 6: Trolox equivalent antiradical capacity (ABTS) of dried citrus peel extracted by methanol or ethanol (db)

<table>
<thead>
<tr>
<th>Peel sample</th>
<th>Extract solvents</th>
<th>Control (Fresh)</th>
<th>Microwave-Drying</th>
<th>Air oven-Drying</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orange</td>
<td>Methanol</td>
<td>1.09±0.05</td>
<td>0.68 ±0.01</td>
<td>0.66±0.01</td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td>1.14 ±0.04</td>
<td>0.63 ±0.01</td>
<td>0.54 ±0.01</td>
</tr>
<tr>
<td>Lemon</td>
<td>Methanol</td>
<td>0.68 ±0.05</td>
<td>0.43 ±0.01</td>
<td>0.38 ±0.01</td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td>0.86 ±0.01</td>
<td>0.43±0.01</td>
<td>0.42 ±0.02</td>
</tr>
</tbody>
</table>

*db= dry weight basis. Results are presented as means for triplicate analyses ± standard deviation (SD). Means within row with different letters are significantly different (*P* < 0.05)
Table 7 Effect of drying methods on β-carotene (IC50 mg/ml) of citrus peel extracted by methanol or ethanol

<table>
<thead>
<tr>
<th>Peel sample</th>
<th>Extract solvents</th>
<th>Control (Fresh)</th>
<th>Microwave Drying</th>
<th>Air oven-Drying</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orange</td>
<td>Methanol</td>
<td>72.10±0.03&lt;sup&gt;a&lt;/sup&gt;</td>
<td>07.36±0.01&lt;sup&gt;c&lt;/sup&gt;</td>
<td>12.67±0.02&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td>90.57±0.16&lt;sup&gt;a&lt;/sup&gt;</td>
<td>09.46±0.01&lt;sup&gt;c&lt;/sup&gt;</td>
<td>15.93±0.03&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Lemon</td>
<td>Methanol</td>
<td>116.99±0.27&lt;sup&gt;a&lt;/sup&gt;</td>
<td>08.63±0.02&lt;sup&gt;c&lt;/sup&gt;</td>
<td>18.09±0.06&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td>157.34±0.59&lt;sup&gt;a&lt;/sup&gt;</td>
<td>10.22±0.06&lt;sup&gt;c&lt;/sup&gt;</td>
<td>21.89±0.03&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>db</sup>= dry weight basis. Results are presented as means for triplicate analyses ± standard deviation (SD) Means within row with different letters are significantly different (<i>P</i> < 0.05).

Fig. 1 Total phenolic content (mg Gallic acid/100g sample) of citrus peel samples extracted by methanol or ethanol

MO= Methanolic extract of orange peel; EO = Ethanolic extract of orange peel.
ML= Methanolic extract of lemon peel; EL = Ethanolic extract of lemon peel.

Fig. 2 Radical scavenging activities % of dried citrus peel

MO= Methanolic extract of orange peel; EO= Ethanolic extract of orange peel.
ML= Methanolic extract of lemon peel; EL= Ethanolic extract of lemon peel.
The ABTS method, compared with a standard Trolox, measures the relative antioxidant capacity of the sample to scavenge the ABTS\(^+\) radical in the aqueous phase.

The ABTS\(^+\) radical, generated by potassium persulfate, was an excellent tool for determining the antioxidant activity of hydrogen-donating (scavengers of aqueous phase radicals) and the chain breaking antioxidants (scavengers of lipid peroxyl radicals). ABTS\(^+\) assay used to assess a broad variety of substances of antioxidant activity (Leong and Shui, 2002).

**β-Carotene Bleaching Assay**

β-carotene antioxidant capacity for both extracts of fresh orange & lemon peels and their corresponding dried samples is depicted in Table 7. The antioxidant capacity of fresh studied peel samples, extracted by methanol, was lower compared to those extracted by ethanol. It was noticed that β-carotene values of lemon peels in ethanolic or methanolic extracts were higher than orange peel samples. Air oven dried tested peels still have more β-carotene content than microwave dried samples without significant difference in between. β-carotene concentration in methanolic extract of microwave dried orange peel exhibited lower antioxidant capacity than ethanolic extract (7.36±0.005 and 9.46±0.01 mg/ml) compared to lemon peel (8.36±0.02 and 10.22±0.06 mg/ml). The natural β-carotene of orange peel extract showed a better bioavailability than synthetic one (Ghazi 1999). β-carotene is very touchy to free radical mediated oxidation of linoleic acid (Gutierrez et al., 2006). Orange peels polar part revealed high antioxidant potential with the contribution of β-carotene present in high levels (Guimaraes et al., 2010).

Thus, the most orange and lemon peel extracts have good antioxidant activity which agreed Gorinstein et al., (2001). Also, the antioxidant capacities of the navel orange peel and flesh extracts corresponded to phenolic and lycopene compounds present in each fraction might be a good source of antioxidants and probable main mediators of antioxidant activity as reported by Jayaprakasha et al., (2006).

As a general conclusion citrus peels have high contents of natural phenolics, flavonoids, carotenoids and ascorbic acid with significant antioxidant activity which could be recommended as useful value added functional ingredients for food industry.

**References**


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