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Study the Effect of Heating Process on Nutritional, Phytochemical and Antioxidant Activity of Mandarin Peel: Implication for Waste Management

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Abstract

The aim of present study was to explore nutritional value of mandarin peel (waste product) and utilize it in feed or an alternative to synthetic supplements as it is a powerful source of vitamin C and polyphenolic contents. Mandarin peels were dried by placing them at three different heating systems (Sun, vacuum oven and microwave drying) and extraction was carried out using four different solvent systems (methanol, ethanol, acetone and aqueous). Present results showed that mandarin peels retain best nutritional quality on electric oven drying followed by sun drying and microwave drying systems. A significant amount of ascorbic acid was found as sun drying (18.34 mg) > electrical oven drying (17.49 mg) > microwave oven drying (15.22 mg) per 100 g of sample. Highest antioxidant activity of mandarin peels was observed in ethanolic extraction of electrical oven drying (89.38±0.7%). Maximum value of total phenolics content (TPC) was present in electrical oven dried (189±0.9 mg gallic acid equivalent /100 g) and sun dried sample (171.1±0.9 mg gallic acid equivalent/100 g) of ethanolic extraction. Total Flavonoid content (TFC) was present highly in ethanolic extraction of sun dried sample (376.55±0.7 mg quercetin equivalent/100 g).

Keywords: Mandarin peels waste; Sundrying; Microwave drying; Polyphenols; Quercetin; Antioxidant activity.

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1. Introduction

Plant products such as fruits and vegetables are a proven source of both natural diet and drugs for a long period of time to maintain human health [1]. These days, scientific community is searching for natural remedies and treatments so as to avoid the hazardous effects of synthetic drugs and antioxidants like butylated hydroxyltoluene (BHT) and butylated hydroxylanisole (BHA). Vitamin C rich fruits like citrus fruits act as significant source of antioxidants and play an important role to maintain and enhance the immunity of body [2]. Citrus is an important cashfruit crop of Pakistan grown on a large scale about 170, 000 ha of land in Pakistan, comprising about 30 % of the area under all fruit orchards

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[3]. It is the 4th most important commodity of Pakistan after rice, alcohol and wheat [4]. The major citrus variety grown in Punjab is "Kinnow mandarin," a cross between King (*C. nobilis* Lour) and willow mandarin (*C. deliciosa* Tenoras). Mandarin is second most important group of citrus plants in world with highest climatic adaptation among the cultivated citrus. It is covering 80 % of the total citrus growing area [5]. In Pakistan, Kinnow is grown under totally natural conditions to achieve thesuperior taste, flavor, aroma of the fruit, to preserve its qualityand nutrition [6]. Its fruit yield was 2294.5 thousand tons in 2008 in Pakistan. Fair amounts of vitamins A & B also reside in kinnow mandarin. Besides this they are source of minerals (calcium, phosphorus, iron). It is rich in vitamin C which is required for maintenance of healthy skin, gums and blood vessels. It functions in collagen formation, absorption of inorganic iron, reduction of plasma cholesterol level, inhibition of nitrosamine formation, and reaction with singlet oxygen and other free radicals (antioxidant) [7]. Consumption of fast food (junk food) has reached to a very high level in our present-day society. Such foods i.e. fried foods, also the alcohol, beverages, tobacco, cola drinks, pesticides and air pollutants are the major cause of production of free radicals (reactive oxygen) in human body through oxidation. When such radicals are produced in large amount, the human body fails to balance and neutralize the effects of these free radicals and there creates an "imbalance"which is called as "oxidative stress", so as an antioxidant, vitamin C is considered good for immune system thus reportedly reduce the risk of arteriosclerosis, cardiovascular diseases and some forms of cancer. The antioxidants present in kinnow mandarins deactivate the free radicals and prevent cellular damage, reduce the bad cholesterol and support good cholesterol [8]. Citrus fruits are majorly consumed by people in their natural form as well as in processed form. Jam is one of the best example of such processed foods. Jam prepared from whole mandarin fruit is very tasty, conserved the typical fruit flavor, poly phenols and antioxidants at significant level [9]. The juice of kinnow is very refreshing, delicious and soothing. After the citrus juice is being extracted from these fruits, there remains a huge amount of by-products which we call as waste materials, mainly consisting of peels, seeds, rag (membranes and cores) [10]. These waste materials are already being used as feed of livestock. Such feed given to livestock gives two advantages such as low cost and a purely natural feed containing great variety of micronutrients and minerals free of any synthetic hormones and antibiotics [11]. Skin benefits of mandarin oranges include glowing skin, improved skin tone, lower the wrinkles on skin and wound healing [12, 13]. In mandarin juice industry, the primary waste material collected is fruit peel [14]. Citrus peel has many potential uses which should be investigated determining their functional properties like pectin flavonoids, carotenoids, limonin and polymethoxyflyons [15]. The present research was conducted with an aim to explore the effect of heating, used for drying of mandarin peels, on its nutritional quality, phytochemicals and antioxidant properties so as to get knowledge about best method of heating and utilize a waste product in a fruitful way (could be as an alternative to synthetic supplement).

2. Materials and Methods

Kinnow mandarins were collected from local market of Lahore and were peeled off. These peels were then dried in three different places till a crispy form obtained for grind milling; sun drying (for three days), microwave drying (at 100 PW for 20 min) and electric oven drying (at 50 ºC for 48 h).

2.1. *Proximateanalysis*

Moisture, total ash, protein, fat and crude fiber content of the citrus fruit peel were analyzed according to AOAC [16]. Carbohydrate content was determined by difference method:
Total carbohydrates (% dry weight) = {100- moisture (%) – protein content (% dry weight) – crude fat (% dry weight) – total ash (% dry weight)}.

2.2. *Extraction of peels*

Two g peel was extracted with 25 mL of acetone in a stoppered flask with occasional shaking for 24 h at room temperature. Extract was filtered and filtrate was evaporated in pre-weighed china dish. Dried sample was dissolved within alcohol/dimethl sulfoxide (DMSO) as required [17]. Same procedure was followed for methanol, ethanol and aqueous extraction, respectively and stored in ambered colored bottles at 4 °C in refrigerator. These solutions will be used in further study for preliminary phytochemical screening to quantify the various phyto-constituents present in them.

2.3. *Estimation of ascorbic acid*

Ascorbic acid (AA) content in dried mandarin peels was determined according to the colorimetric method of Bajaj and kaur [18]. The reduction of ammonium molybdate with L ascorbic acid in the presence of sulphuric acid and solution of metaphosphoric acid-acetic acid results the development of molybedenum blue complex. Absorbance of the colored product was taken at 760 nm and expressed in terms of mg ascorbic acid/100 g of dry extract.

2.4. *Determination of total phenolic content*

Total phenolic content was determined by Folin Ciocalteu reagent method [17]. Appropriate amount of sample was taken along with Folin Ciocalteu, 20% sodium carbonate and made volume up to 25 mL. After that reaction mixture was covered with paraffin and let to stand for 15 min and its absorbance was measured at 765 nm. Gallic acid was used as a standard and the result was expressed as milligram of Gallic acid equivalents (GAE). Same procedure was followed for acetone, ethanol, methanol and aqueous dilutions separately.

2.5. *Determination of total flavonoid content*

Total flavonoid content was estimated through colorimetric method [17]. Appropriate amount of sample as well as methanol, 10% aluminum chloride, 1.0 M potassium acetate were added in 25 mL volumetric flask and then incubated for 30 min. Absorbance was measured at 415 nm against blank through spectrophotometer. Quercetin was used as a reference and total flavonoid content was measured in milligram of Quercetin equivalents (mg QE/100 g).

2.6. *Determination of antioxidant activity*

Antioxidant capacity of dried peels subjected to various heating conditions was quantified through DPPH (α,α-diphenyl-β-picrylhydrazyl) assay [17]. A range of test tubes containing 3 mL of 0.004% DPPH (Alfa Aesar, Germany) were taken and at concentration of 0.1mg/mL of each dried extract were added in appropriate amount (100 μL) separately. Incubated for 30 min under dark. Absorbance was measured at 517 nm by using UV-spectrophotometer and then calculates percentage (%) scavenging activity of DPPH according to following formula:

$$\text{Antioxidant Activity (\%)} = \{(OD_{blank} - OD_{sample})/OD_{blank}\} \times 100$$

2.7. *Statistical analysis*

All data are presented as mean ±SD. Data of at least three independent experiments were taken as mean value. Graph pad Prism-5 [19] was used to perform two ways Analysis of Variance (ANOVA) to see the significant difference among results. Results exhibiting probability value of <0.05 were considered to be statistically significant.

3. Results and Discussion

3.1. *Determination of nutritional attributes*

Nutritional attributes of mandarin peels were assessed and the results are shown in Fig. 1. In sun dried peel sample, moisture value and ash content of mandarin were determined to be 6.19±0.12% and 4.61±0.07% respectively. Mandarin peel was found to have rich of carbohydrates (79.67±0.91%) followed by crude fat (2.85±0.26%), protein (4.28±0.28%) and crude fiber (1.49±0.04%).In micro wave dried samples, moisture (8.46±0.14%),total ash (4.42±0.07%) protein (4.03±0.03%), crude fat (2.28±0.14%), crude fiber (1.87±0.021%) and carbohydrates (78.04±0.54%) were estimated. In electric oven dried samples, moisture value (4.88±0.14%) and ash content (4.77±0.89%), protein (4.45±0.10%), crude fat (2.54±0.26%), crude fiber (1.49±0.021%) and carbohydrates (80.89±0.46%) were determined. Present results showed that better nutritional quality was attained in electrical oven drying followed by sundrying and microwave drying. Citrus waste with low moisture content will make it good for feed [10]. Perez-cacho *et al*.

reported that mandarin peels contain plenty of carbohydrates as well as soluble and insoluble dietary fibers that play important role in reduction the risk of cancer, many chronic diseases like arthritis, obesity and heart diseases [20]. Present results also showed that mandarin peels are rich in carbohydrates as well as considerable quantity of protein and elemental minerals are present.

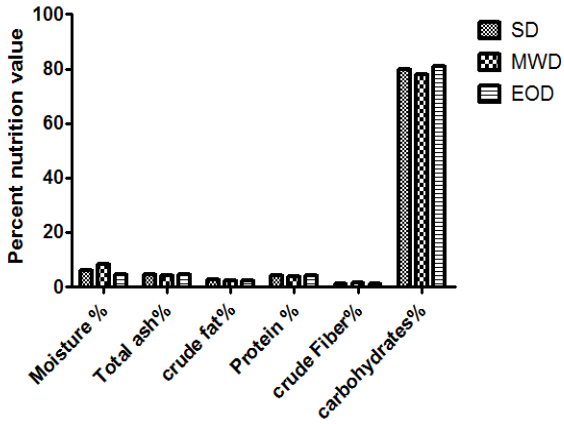

Fig. 1. Proximate analysis of mandarin peels subjected under various heating systems. SD: Sun drying, MWD: Microwave drying, EOD: electrical oven drying.

3.2. *Total ascorbic acid*

Ascorbic acid content of sundried, microwave dried and electrical oven dried peels were found as 18.34 mg, 15.22 mg and 17.49 mg/100 g of prepared samples as shown in Fig. 2. Citrus plants belonging to the family Rutaceae which include fruits such as orange, mandarin, lime, lemon, sour orange and grape fruit rich in ascorbic acid contentas a well-known promising source of multiple beneficial nutrients for human being [21]. In sundried peels and electrical oven dried peels ascorbic acid value is not significantly different from each other but microwave drying considerably reduce the vitamin C value.

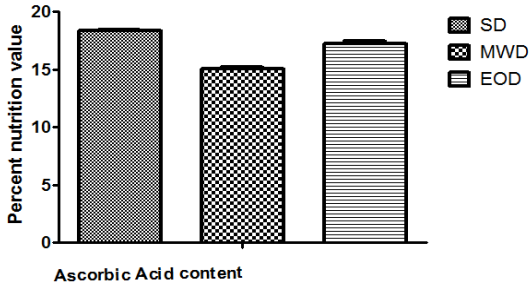

Fig. 2. Ascorbic acid value of mandarin peels subjected under various heating systems. SD: Sun drying, MWD: Microwave drying, EOD: Electrical oven drying. Error bars indicating about standard deviation.

3.3. *Total phenolic content (TPC)*

Total phenolic content of sundried peel extracts was depicted in Fig. 3. The TPC of sundried peel extractswas determined to be 171.1±0.9, 167.30±0.8, 110.18±1.0 and 102.55±0.9 mg GAE/100 g of the extract, from sample extractions of ethanol, methanol, acetone and aqueous, respectively. Total phenolic content of microwave and electric oven dried peel extracts were quantified as 158.54±0.3, 149.54±0.7, 98.05±0.5, 100.85±0.14 and 189±0.9, 176±0.9, 109.4±0.4, 104±0.42 mg GAE/100 g of the extract from solvent extractions of ethanol, methanol, acetone and aqueous, respectively. Presence of good amount of phenolics in fruits and vegetables correlates with its better nutritional quality. Current results showed that ethanolic extraction of electrical oven drying exhibited noteworthy phenolics content. Kour *et al*. reported that kinnow waste has plenty of toal phenolics which are more than the phenolic content present in illichi and grapes waste [21].

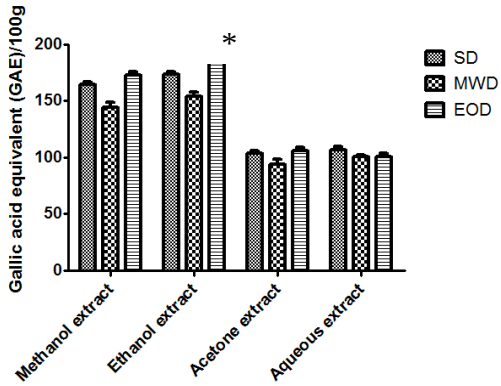

Fig. 3. Total phenolics content of mandarin peels subjected under various heating as well as solvent extraction systems. SD: Sun drying, MWD: Microwave drying, EOD: Electrical oven drying. Error bars indicating about standard deviation. (*) result is statistically significant $P < 0.05$.

3.4. *Total flavonoid content (TFC)*

The results for total flavonoid content of sundried mandarin peels showed that the highest amount of TFC was found in ethanolic extract (376.55±0.7 mg QE/100 g of extract), followed by methanolic extract (264.2±0.3 mg QE/100 g of extract), aqueous extract (239.85±0.5 mg QE/100 g of extract) and acetonic extract (198.55±0.7 mg QE/100 g of extract).Results for total flavonoid content of microwave and electric oven dried peels extracts (ethanolic, methanolic, acetone and aqueous) depicted as 263.85±0.21, 251.65±0.49, 185.5±0.63, 175.8±0.28 and 375.6±0.5, 259±0.21, 187±0.66, 175±0.71 mg QE/100 g of the extract, respectively (Fig. 4). Present study showed that ethanolic extract of sundried peels contain high flavonoid content in comparison to ethanolic extract of electrical oven dried peels.

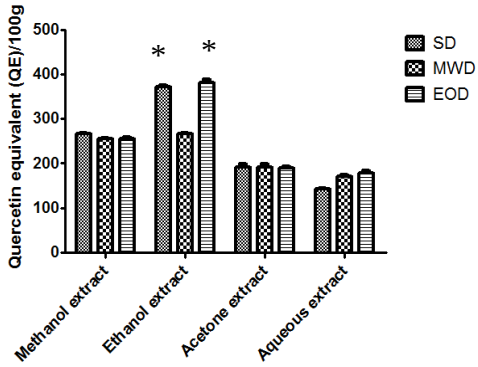

Fig. 4. Total flavonoid content of mandarin peels subjected under various heating as well as solvent extraction systems. SD: Sun drying, MWD: Microwave drying, EOD: Electrical oven drying. Error bars indicating about Standard deviation. (*) result is statistically significant P< 0.05.

3.5. *In Vitro antioxidant activity*

Antioxidant capacity of sundried peel extracts were found in the range of 84.82±0.84% (ethanol) followed by 82.95±0.77% (methanol) then, 79.53±0.84% (acetone) and 83.72±1.18% (aqueous) at 0.1 mg/mL conc. of dried extract (Fig. 5).

Antioxidant activity of microwave dried extracts was determined as 81.03±0.49%, 80.30±0.5%, 79.57±0.3%, 80.96±0.7%, for ethanolic, methanolic, acetone and aqueous extract respectively. Similarly, electric oven dried extracts (ethanol, methanol, acetone and aqueous) subjected to DPPH scavenging activity were showed results as 89.38±0.7%, 86.74±0.9%, 83.54±0.92% and 85.45±0.19%, respectively. Citrus peel and dried orange pulp are by-products from citrus juice production that have natural antioxidant and antimicrobial effect [22].

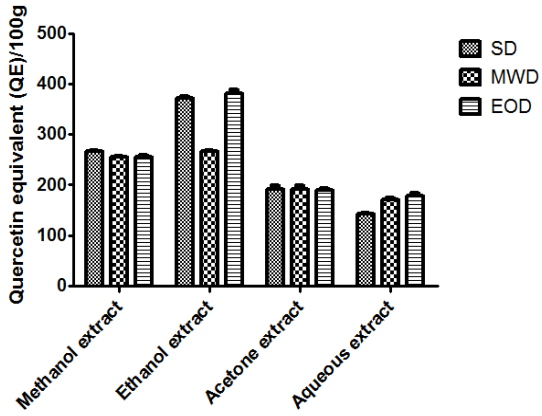

Fig. 5. Antioxidant activity of mandarin peels subjected under various heating as well as solvent extraction systems. SD: Sun drying, MWD: Microwave drying, EOD: Electrical oven drying. Error bars indicating about Standard deviation. (*) result is statistically significant P < 0.05.

4. Conclusion

Among various heating systems used for drying of mandarin peels, electrical oven drying shows the best results regarding nutritional quality maintenance of peels following the sun drying and similarly ethanolic extraction of peel depicted significant phenolic and flavonoid content as well as antioxidant activity as compared to other solvents used for extraction. Mandarin fruit peel waste has better quality due to the presence of associated bioactive compounds (flavonoids and vitamin C) with antioxidant properties, which may provide additional health-promoting benefits and can be used as alternative to synthetic supplements.

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