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NUTRITIONAL EVALUATION, CHEMICAL COMPOSITION AND ANTIOXIDANT ACTIVITY OF SOME FOOD PROCESSING WASTES

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ABSTRACT

This study was carried out to evaluate the chemical composition, nutritional value, bioactive compounds, antioxidant activity and inhibition of lipid peroxidation in linoleic acid system for some food processing wastes and its extracts which were, the peels of pomegranate (*Punica granatum* L.), two varieties of Egyptian orange (Baladi and Navel) (*Citrus sinensis*) and pea pod (*Pisum sativum*). By using gradient aqueous ethanol (80, 70 and 50% *V/V*), twelve extracts of the tested wastes were obtained. Total phenolic contents were measured using Folin-Ciocalteu reagent. While, total antioxidant capacity of the extracts was estimated by two different methods including: DPPH (1, 1-diphenyl-2-picrylhydrazyl radical and β-carotene/linoleic bleaching test. The most important results obtained showed that the highest ($P \leq 0.05$) content of total protein, crude fiber and minerals were found in pea pod. On the other hand, the highest content of total phenolic compounds detected by HPLC was found in pomegranate peel (5497.67 mg/100 g dried peels). While, the highest content of total flavonoids was found in navel and baladi orange peel (39071.09 and 10191.52 mg/kg dried peels, respectively). In addition, results showed that the highest content of ascorbic acid was found in baladi and navel orange peel (64.49 and 54.04 mg/100g dry matter; respectively). The present study indicated that the largest amount of total phenolic content which leads to more effective radical scavenging effect was found in ethanolic extracts (80%) of pomegranate peel (259.38 mg GAE/g extract). Furthermore, percentage of inhibit lipid peroxidation for the different extracts were between 22.46 to 96.84%. The current results suggest that it should be directed to incorporate powders and extracts of pomegranate peel, orange peel and pea pod into the food processing and preservation technology to improve their nutritional quality and to prolong the shelf-life of these food products.

Keywords: Pomegranate peel, baladi orange peel, navel orange peel, pea pod, chemical composition, vitamins, phenolic compounds, antioxidant activity.

INTRODUCTION

Synthetic antioxidants generally used in food products are BHT, BHA and TBHQ. Recent literature revealed that synthetic antioxidant are toxic and may possess potential health risks, which include cancer. In the last few years, an increased attention has been focused on the industrial wastes, especially those containing residual phenols from the plant raw material used (Ibrahium, 2010).

The growing demand for natural antioxidants observed in food and cosmetic industries forces the search for new sources of these compounds. Numerous scientific investigations point at consecutive rich sources of antioxidants, especially among fruit and vegetable wastes (Duda-Chodak and Tarko, 2007).

The search for cheap and abundant sources of natural antioxidants is attracting worldwide interest and scientific research. Much research is needed in order to select raw materials (Yasoubi *et al.*, 2007). Therefore, selection of sources of

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natural antioxidant such as food processing wastes and add them in food industry decrease the lipid oxidation, extend its shelf-life and prevent any harmful effect on human.

Fruit and vegetable wastes, which are formed in great amounts during industrial processing, represent a serious problem, as they exert an influence on environment and need to be managed and/or utilized. On the other hand, they are very rich in bioactive components, which are considered to have a beneficial effect on health. For the last decade, efforts have been made to improve methods and ways of re-using fruit and vegetable wastes. The important purpose is the valorization of the antioxidants and other biocomponents in by-products from fruit and vegetable industries (Duda-Chodak and Tarko, 2007).

Peels of fruits and vegetables are wastes of the juice industry and the saved vegetables but a proper utilization of these waste products could lead to an important new source of natural antioxidant and thereby limiting the problem of disposal. The industrial transformation of vegetables and fruits generates large quantities of by-products rich in bioactive compounds that may well be suitable for other purposes (Viuda-Martos *et al.,* 2009).

In 2013, 106260 tons of pomegranate fruit were produced in Egypt. The orange is an important commercial fruit in Egypt with a total production of 2855022 tons in 2013. While, total production of peas was 190146 tons (Agricultural Statistics, 2014).

The processing of pomegranate fruits produces 46% peels, 14% seeds and 40% juice with by-products representing more than 50% of total weight (Suryawanshi *et al.,* 2009). It has been reported that the pomegranate by-products contains a substantial amount of polyphenols. Pomegranate peels contain 249.4 mg/g of phenolic compounds as compared to only 24.4 mg/g phenolic compounds found in the pulp of pomegranates (Rudra *et al.,* 2015).

The peel which represents roughly half of the fruit mass, contains the highest concentrations of flavonoids in the citrus fruit (Manthley and Grohmann, 2001). Citrus peel, remaining after juice extraction, is the primary waste fraction amounting to almost 50% of the fruit mass (Rudra *et al.,* 2015).

Hegazy and Ibrahium (2012) stated that orange constitutes about 60% of the total citrus world production. In 2008, 3.23 million tons of citrus fruit were produced in Egypt, contained 2.14 million tons of orange. A large portion of this production is addressed to the industrial extraction of citrus juice which leads to huge amounts of residues, including peel and segment membranes. Peels represent about 50% of total weight of the fruits and remain as the primary by product. If not processed further, it becomes waste produce odour, soil pollution, harborage for insects and can give rise to serious environmental pollution (Mandalari *et al.,* 2006).

Citrus by-products, if utilized fully, could be major sources of phenolic compounds. The peels, in particular, are an abundant source of natural flavonoids, and contain higher amount of phenolics compared to the edible portions. It has been reported that the contents of total phenolics in peels of lemons, oranges, and grapefruit were 15% higher than those in the peeled fruits (Rudra *et al.,* 2015).

The presence of bioactive compounds in pea pod is equal to that present in pea cotyledon which indicates that pea pod can also be consumed. The results demonstrate that pea pod and pea cotyledon contain almost equal amounts of antioxidants, indicating that pea pods can also be consumed (Haymanti *et al.,* 2014). Peas waste represent approx 40% of total weight of the fruits and remain as the primary by product (Rudra *et al.,* 2015).

The present study aimed to evaluate the chemical composition, nutritional value, bioactive compounds for some food processing wastes. Furthermore, the purpose of this study was also to evaluate the effect of using aqueous ethanol (80, 70 and 50% ethanol *V/V*) on the extraction efficiency of total phenols from the tested wastes. In addition, their effect on the yield percentage, antioxidant activity and inhibition of lipid peroxidation for the produced extracts was investigated. The used wastes were pomegranate, orange either baladi or navel peels and pea pods.

MATERIALS AND METHODS

Materials

Pomegranate fruit *(Punica granatum* L.*)*, two varieties of Egyptian orange fruit (Baladi and Navel) (*Citrus sinensis*) and pea (*Pisum sativum*) were obtained from local market, Zagazig City, Sharkia Governorate, Egypt.

Chemicals and Reagents

All chemical and reagents used in the analytical method (Analytical grade) were purchased from Sigma Chemical Company (St. Louis, Mo, USA) and El- Gamhouria Trading Chemicals and Drugs Company, Egypt.

Standard phenolic compounds of gallic acid, pyrogallol, 4-Amino-benzoic, 3-OH-Tyrosol, protocatechuic, chlorogenic, epi-catechin, catechin, catechol, caffeine, P-OH-benzoic, caffeic, vanillic, P-coumaric, ferulic, iso-ferulic, reversetrol, ellagic acid, e- vanillic, α-coumaric, benzoic, (3,4,5 methoxy cinnamic), coumarin, salicylic and cinnamic were imported from Koch light Laboratories, Ltd. England. Standard flavonoid compounds of luteolin, Naringin, Rutin, Hesperidin, Rosmarinic, Quercetrin, Quercetin, Hispertin, Kampferol, Apigenin and 7-OH-Flavone were imported from Koch light Laboratories, Ltd. England. Standard vitamins of A, D, E, K, C, B_1, B_2, B_3, B_6 and B_9 were imported from Koch light Laboratories, Ltd. England.

Preparation of Extracts

The plant materials were washed by distilled water then peeled. Fresh peels were cut into small pieces with a sharp knife for easy drying and directly dried in a hot - air oven at 40˚C until complete drying (About 48 hr.). The dried samples were ground to a fine powder by laboratory blender. Extracts were prepared by the method of Sultana *et al.* (2008) with some modifications. The material that passed through 80-mesh sieve was used for extraction purposes. Powdered material (10 g) for each sample was extracted with 100 ml of aqueous (80%, 70% and 50%) ethanol by using a magnetic stirrer at room temperature overnight. The extracts were separated from the residues by filtering through Whatman No.1 filter paper. The residues were re-extracted twice with the same solvent under the same conditions and extracts were pooled. After that all of the combined extracts were concentrated by using rotary evaporator under vacuum at 45˚C to obtain the crude extracts. The dry extracts were weighed to calculate the yield and stored in a refrigerator at -18˚C, until used for further analyses.

Analytical Methods

Determination of chemical composition and minerals

Moisture, crude protein, fat, ash and crude fiber contents of food processing wastes powders were determined according to the procedures of the AOAC (2012). Total carbohydrates were calculated in all samples by subtraction as follows: (%) Carbohydrates= 100- the sum of (crude protein (%) + fat (%) + ash (%) + crude fiber (%). Metal elements of food processing wastes powders were measured according to the method of the AOAC (2000), using Atomic Absorption Spectrophotometer (Perkin Elmer, Model 3300, Germany).

Fractionation of phenolic and flavonoid compounds using HPLC

A high performance liquid chromatography system equipped with a variable wave length detector (Agilant technologies, Germany) 1200 Series. Also the HPLC was equipped with auto sampler, Quaternary pump degasser and column compartment set at 35ºC. Analyses were performed on a C18 reverse phase (BDS 5 µm, Labio, Czech Republic) packed stainless-steel column (4×250mm, i.d.). To determine phenolic acids and flavonoids, samples were prepared according to the method described by Goupy *et al.* (1999) and Mattila *et al.* (2000). After samples preparation (1-3 ml) was collected from previous step in a vials for injection into HPLC. HPLC method started with linear gradient at flow rate of 1.0ml/min with mobile phase of water/acetic acid (98:2, *V/V*, solvent A) and methanol/acetonitrile (50:50, *V/V*, solvent B), starting with 5% B and increasing B to levels of 30% at 25 min, 40% at 35 min, 52% at 40 min, 70% at 50 min, 100% at 55 min. The initial conditions were re-established by 5 min wash in both solvents. All chromatograms were plotted at 280 nm to estimate phenolic acids and at 330

nm for flavonoids. All components were identified and quantified by comparison of peak areas with external standards (Schieber *et al.*, 2001). This assay was conducting in (Food Chemistry Lab., Food Technology Research Institute, ARC, Egypt).

Determination of vitamins using HPLC

Vitamins A (Retinol), D (Calciferol), E (αTocopherol) and K (phylloquinone) of food processing wastes powders were estimated according to the method mentioned by (Plozza *et al.,* 2012). Vitamins C (Ascorbic acid), B_1 (Thiamine), B_2 (Riboflavin), B_3 (Nicotinic acid), B_6 (Pyridoxine), B_9 (Folic acid) of food processing wastes powders were determined according to the method described in the AOAC (2000) using High Performance Liquid Chromatography (Agilant technologies, Germany) 1200 series. For the calculation, concentration of external standard and peak area for external standard and sample are used. This assay was conducting in (Food Chemistry Lab., Agricultural Research Center, Egypt).

Determination of total phenolic content (TPC)

The Folin–Ciocalteu method was used for the determination of the total phenolics. In brief, an aliquot (1 ml) of the appropriate diluted extracts was added to a 10 ml volumetric flask, containing 5 ml of distilled water. Then, 0.5 ml of Folin-Ciocalteu reagent was added and the contents were mixed. After 3 min, 1.5 ml Na_2CO_3 solution of concentration 5 g/l was added and made up to a total volume of 10 ml with distilled water. After keeping the samples at 50˚C (water bath) for 16 min in sealed flasks and subsequent cooling, their absorbances were measured at 765 nm against distilled water as the blank. A calibration curve was constructed using gallic acid standard solutions. The concentration of total phenolics is expressed as the gallic acid equivalent (GAE) per 1 g of extract. All samples were prepared in triplicate (Ivanova *et al.,* 2010). The results were calculated according to the following equation :

$$y = 5.67x - 0.0905$$
$$R^2 = 0.9761$$

Where y is the absorbance and *x* is the concentration (mg GAE g^{-1} extract). R^2 = Correlation coefficient.

DPPH radical-scavenging activity assay

The electron donation ability of the obtained extracts was measured by bleaching of the purple coloured solution of DPPH according to the method of Hanato *et al.* (1988). One hundred µl of each extract (10mg extract/10 ml solvent) was added to 3 ml of 0.1 mM DPPH dissolved in ethanol (80%, 70% and 50%) according to the solvent used for extraction. After incubation period of 30, 60 and 120 min at room temperature, the absorbance was determined against a control at 517 nm (Gulcin *et al.,* 2004). Percentage of antioxidant activity of free radical DPPH was calculated as follow:

$$\text{Antioxidant activity (\%)} = [(A_{control} - A_{sample}) / A_{control}] \times 100$$

Where $A_{control}$ is the absorbance of the control reaction and A_{sample} is the absorbance in the presence of plant extract. BHT and α-tocopherol were used as a positive control. Samples were analyzed in triplicate.

β-Carotene / linoleic acid bleaching (βCB) assay

The ability of extracts and synthetic antioxidants to prevent the bleaching of β-carotene was assessed as described by Keyvan *et al.* (2007). In brief, 0.2 mg of β-carotene in 1 ml of chloroform, 20 mg of linoleic acid and 200 mg of Tween 20 were placed in a round-bottom flask. After removal of the chloroform, 50 ml of distilled water were added and the resulting mixture was stirred vigorously. Aliquots (3 ml) of the emulsion were transferred to tubes containing extract or synthetic antioxidant. Immediately after mixing 0.5 ml of extract solution (10 mg extract / 10 ml solvent), an aliquot from each tube was transferred to a cuvette and the absorbance at 470 nm was recorded (Abs^0). The remaining samples were placed in a water bath at 50˚C for 120 min, then the absorbance at 470 nm was recorded (Abs^{120}). A control without added extract was also analysed. Antioxidant activity was calculated as follows:

Antioxidant activity (inhibition %) =

$$[1 - (Abs^0_{sample} - Abs^{120}_{sample}) / (Abs^0_{control} - Abs^{120}_{control})] \times 100$$

Where Abs^{0}_{sample} is the absorbance of sample at 0-time, Abs^{120}_{sample} is the absorbance of sample after 120 min, $Abs^{0}_{control}$ is the absorbance of control at 0-time and $Abs^{120}_{control}$ is the absorbance of control after 120 min.

Statistical Analyses

Experiments were conducted in triplicates, the obtained data were expressed as Mean ± SD. Statistical analyses of data were performed using SPSS softwere (17.0 for windows) and were analyzed by one-way ANOVA test. Significant differences between means were determined using Duncan's multiple range tests (Duncan, 1955). The significance level was $P \leq 0.05$.

RESULTS AND DISCUSSION

Chemical Composition of Food Processing Wastes

The gross chemical components; *i.e.* moisture, crude fat, crude protein, ash, crude fibers and carbohydrate contents of food processing wastes powders are represented in Table 1.

As shown in Table 1 the moisture content of pomegranate peel, pea pod, baladi orange peel and navel orange peel was found to be13.04, 11.43, 9.35 and 9.84%, respectively. In addition, crude fat, crude protein, ash, crude fibers and carbohydrates contents for pomegranate fruits peel powder were 1.56, 3.95, 7.34, 14.92 and 72.23%, versus, 1.34, 17.33, 6.61, 20.12 and 54.60% for pea pod powder, on dry weight basis, respectively. While, crude fat, crude protein, ash, crude fibers and carbohydrates contents for baladi orange fruits peel powder were 1.74, 6.39,3.92,12.46 and 75.49%,versus, 2.02, 5.69, 3.81, 12.17 and 76.31% for navel orange fruits peel powder, on dry weight basis; respectively. Thereupon, the pomegranate fruits peel powder is considered a good source of crude fibers, ash and carbohydrates. While, pea pod powder is considered a good source of crude fiber, crude protein, ash and carbohydrates. While, baladi orange fruits peel powder and navel orange fruits peel powder are considered a good source of crude fiber, crude protein and carbohydrates. These results are within the range reported by Magda *et al.* (2008), Al-Saadi *et al.* (2009), Rowayshed *et al.* (2013), Sharoba *et al.* (2013), Sayed (2014) and Rehman *et al.* (2015).

Minerals Content of Food Processing Wastes

From the obtained data in Table 2, it could be observed that the food processing wastes powders under study contained all tested minerals at adequate concentration and the predominant minerals were found to be Ca, Na and Mg. In addition, the food processing wastes powders under study contained a suitable content of Fe, Zn and Mn. Therefore, they are considered a good source of macro and micro elements and they should be used in food fortification. Presence of higher amounts of all necessary mineral contents in pea pod indicates that pea pod may find their place in human diet according to Zia-Ul-Haq *et al.* (2012). These results are within the range reported by Kushwaha *et al.* (2013), Rachel *et al.* (2013) and Rowayshed *et al.* (2013).

Yield of Extracts of Food Processing Wastes

The different polarity of solvent employed in the extraction had strong association to the yield and antioxidant activity of the natural plant extract (Moure *et al.,* 2001). However, the choice of determining the best solvent extraction properties had a lot to consider. The selection must consider each element of assorted structure and composition of the matrix and complex behavior of each matrix-solvent system which particularly hard to predicted (Al-Farsi and Lee, 2008). In addition, the increased or decreased of extraction yields were depended on the solvent polarity of extraction (Fernández-Agullóa *et al.,* 2013). The gross percentage yield of peels extracts from the tested wastes are depicted in Table 3, The yield of extracts from different food processing wastes powders using aqueous (80%) ethanol, aqueous (70%) ethanol and aqueous (50%) ethanol varied from 53.00 to 27.70%. Extract of aqueous (50%) ethanol from each the wastes (pomegranate peel, pea pod, baladi orange peel and navel orange peel) showed high extract yield (53.00, 39.55, 29.78 and 34.64%; respectively). In the present

Table 1. Chemical composition of food processing wastes powders

Component (%)*	PPP	PP*P	BOPP	NOPP
Moisture	13.04±0.81[a]	11.43±0.15[b]	9.35±0.53[c]	9.84±0.55[c]
Total fat	1.56±0.12[c]	1.34±0.12[d]	1.74±0.02[b]	2.02±0.09[a]
Total Protein	3.95±0.20[d]	17.33±0.48[a]	6.39±0.17[b]	5.69±0.34[c]
Total Ash	7.34±0.39[a]	6.61±0.26[b]	3.92±0.36[c]	3.81±0.38[c]
Crude fiber	14.92±0.18[b]	20.12±1.87[a]	12.46±0.36[c]	12.17±0.27[c]
Total carbohydrates	72.23±0.51[b]	54.60±1.74[c]	75.49±0.21[a]	76.31±0.55[a]

[a-d] Means within a raw with different superscript are significantly different (P≤0.05). The obtained results represented the mean of triplicate determinations result. Values are expressed as mean± SD. PPP: Pomegranate peel powder, PP*P: Pea pod powder, BOPP: Baladi orange peel powder and NOPP: Navel orange peel powder. *: on dry weight basis.

Table 2. Mineral content of food processing wastes powders (mg/100g)

Mineral	PPP	PP*P	BOPP	NOPP
Calcium (Ca)	341.89±10.29[d]	1037.99±23.58[a]	625.31±19.34[b]	553.88±14.97[c]
Sodium (Na)	189.86±7.18[b]	315.39±11.94[a]	147.70±6.32[c]	131.20±4.56[d]
Magnesium (Mg)	168.78±6.82[b]	808.64±17.71[a]	141.95±4.74[c]	146.87±5.60[c]
Iron (Fe)	6.38±0.14[c]	31.41±0.25[a]	10.15±0.18[b]	5.49±0.11[d]
Zinc (Zn)	0.73±0.02[c]	2.64±0.08[a]	0.87±0.03[b]	0.58±0.04[d]
Manganese (Mn)	0.68±0.03[b]	1.90±0.05[a]	0.60±0.02[c]	0.55±0.01[c]

[a-d] Means within a raw with different superscript are significantly different (P≤0.05). The obtained results represented the mean of triplicate determinations result. Values are expressed as mean± SD. PPP: Pomegranate peel powder, PP*P: Pea pod powder, BOPP: Baladi orange peel powder and NOPP: Navel orange peel powder.

Table 3. Yield of extracts of various food processing wastes powders (g/100g dry matter)

Food processing waste	Yield of extract
Pomegranate peels extract (80%)	48.39±0.40
Pomegranate peels extract (70%)	52.40±0.83
Pomegranate peels extract (50%)	53.00±1.29
Pea pod extract (80%)	34.08±0.23
Pea pod extract (70%)	35.89±1.26
Pea pod extract (50%)	39.55±0.61
Baladi orange peels extract (80%)	27.70±0.26
Baladi orange peels extract (70%)	28.68±0.11
Baladi orange peels extract (50%)	29.78±0.13
Navel orange peels extract (80%)	33.24±0.89
Navel orange peels extract (70%)	33.81±1.61
Navel orange peels extract (50%)	34.64±1.16

The obtained results represented the mean of triplicate determinations result. Values are expressed as mean± SD. (80%): By using aqueous (80%) ethanol, (70%): By using aqueous (70%) ethanol and (50%): By using aqueous (50%) ethanol.

study, water was not used for extraction of phenolic compounds because previous studies suggested that water was not very efficient in extraction of phenolic compounds (Prasad *et al.*, 2009). It is assumed that wastes contained antioxidant compounds which are more soluble in aqueous ethanol as against the pure ethanol. The ability of different ethanol percentage in water on crude extraction yield from Arabian jasmine dried leaves followed the order: 50% ethanol > 75% ethanol > 100% ethanol (Poonpaiboonpipat *et al.*, 2011). The ability of different solvents to extract antioxidant components from almond shells followed the order: 80% ethanol > 80% methanol > 100% ethanol >100% methanol (Sarwar *et al.*, 2012). These results are in a good agreement with those reported by Hegazy and Ibrahium (2012), Hadrich *et al.* (2014) and Abdel-Mohsen (2015).

Individualize and Identified the Bioactive Compounds in Food Processing Wastes

The differences in content of bioactive compounds could be due to many reasons such as the condition of the peels, extraction temperature used, extraction system employed, method of analysis, concentration of the solvent, variety and the climatic conditions (Li *et al.*, 2006). Phenolic and flavonoid compounds as well as vitamins content in pomegranate peel, pea pod, baladi orange peel and navel orange peel as determined by HPLC analysis are shown in Tables 4, 5 and 6.

Phenolic Compounds

Data represented in Table 4 show the phenolic compounds in dried pomegranate peel, dried pea pod, dried baladi orange peel and dried navel orange peel. Twenty-five compounds were monitored from ninety-three compounds by HPLC. The estimated total phenolic compounds for pomegranate peel, pea pod, baladi orange peel and navel orange peel were 5497.67, 121.43, 484.11 and 1209.72 mg/100g dried peels, respectively. Dried pomegranate peels showed higher value than dried navel orange peels for total monitored compounds, followed by dried baladi orange peels and dried pea pods. Pyrogallol compound in dried pomegranate peels has the highest value (3642.70 mg/100g dried peels) followed by Ellagic acid, E-vanillic, Chlorogenic, Gallic acid, Caffeine and Catechol (573.33, 340.30, 329.02, 196.10, 87.40 and 73.02 mg/100g dried peels, respectively). E-vanillic compound in dried pea pods has the highest value (30.52 mg/100g dried peels) followed by Salicylic, Protocatechuic, Benzoic, Ellagic acid, Catachin and P-OH-benzoic (13.11, 11.16, 9.42, 8.41, 7.79 and 7.45 mg/100g dried peels, respectively). Dried navel orange peels had higher value of Iso-ferulic, E-vanillic, Gallic acid, Chlorogenic, Ellagic acid, P-coumaric and Salicylic (209.59, 153.89, 116.54, 114.28, 105.00, 93.10 and 84.10 mg/100g dried peels; respectively) than there in dried baladi orange peels (56.06, 96.63, 91.60, 82.61, 25.16, 30.75 and 16.85 mg/100g dried peels, respectively). Vanillic was not detected in dried pomegranate peel. 3-OH-Tyrosol was not detected in dried baladi orange peel. Epi-catechin was not detected in all food processing wastes under study. These results are within the range reported by Ramadan *et al.* (2009), Zulkifli *et al.* (2012), Rowayshed *et al.* (2013) and Abdel-Mohsen (2015).

Flavonoid Compounds

Data represented in Table 5 show the flavonoid compounds in dried pomegranate peel, dried pea pod, dried baladi orange peel and dried navel orange peel. Eleven compounds were monitored from ninety-three compounds by HPLC. The estimated total flavonoid compounds for pomegranate peel, pea pod, baladi orange peel and navel orange peel were (1050.05, 1181.16, 10191.52 and 39071.09 mg/kg dried peels; respectively). Dried navel orange peels showed higher value than dried baladi orange peels for total monitored compounds, followed by dried pea pods and dried pomegranate peels. Hesperidin compound in dried navel orange peels, dried baladi orange peels and dried pea pods has the highest values (31856.59, 8080.45 and 838.08 mg/kg dried peels, respectively). Rosmarinic compound in dried pomegranate peels has the highest value (461.27 mg/kg dried peels). Dried pomegranate peels had higher values of Rosmarinic, Naringin, Rutin, Kampferol and Hispertin (461.27, 394.61, 98.27, 63.72 and 23.90 mg/kg dried peels; respectively) than those found in dried pea pods (200.29, 14.04, ND, 5.09 and 14.79 mg/kg dried peels, respectively). Dried pea pods had higher values

Table 4. Phenolic compounds in food processing wastes powders

Phenolic compound	Concentration of phenolic compound (mg/100g dried peels)			
	PPP	PP*P	BOPP	NOPP
Gallic acid	196.10	2.23	91.60	116.54
Pyrogallol	3642.70	6.23	7.83	42.01
4-Amino-benzoic	3.56	0.12	0.72	0.62
3-OH -Tyrosol	16.74	3.82	ND	4.75
Protocatechuic	45.31	11.16	3.06	26.51
Chlorogenic	329.02	2.71	82.61	114.28
Epi-catechin	ND	ND	ND	ND
Catechin	41.26	7.79	10.19	45.53
Catechol	73.02	ND	4.17	26.16
Caffeine	87.40	1.59	1.84	6.83
P-OH-benzoic	27.15	7.45	1.40	10.66
Caffeic	14.05	5.54	4.49	5.15
Vanillic	ND	0.51	1.08	11.05
P-coumaric	16.92	1.13	30.75	93.10
Ferulic	18.71	1.47	1.14	12.47
Iso-ferulic	13.93	0.83	56.06	209.59
Reversetrol	1.88	1.84	2.74	23.78
Ellagic acid	573.33	8.41	25.16	105.00
E-vanillic	340.30	30.52	96.63	153.89
α-coumaric	10.73	2.12	7.25	37.91
Benzoic	32.63	9.42	21.12	34.37
(3,4,5 methoxy cinnamic)	2.38	1.55	5.72	6.89
Coumarin	2.16	0.56	9.29	32.84
Salicylic	6.97	13.11	16.85	84.10
Cinnamic	1.42	1.32	2.41	5.69
Total	5497.67	121.43	484.11	1209.72

PPP: Pomegranate peel powder, PP*P: Pea pod powder, BOPP: Baladi orange peel powder and NOPP: Navel orange peel powder. ND: Not detected.

Table 5. Flavonoid compounds in food processing wastes powders

Flavonoid compound	Concentration of flavonoid compound (mg/kg dried peels)			
	PPP	PP*P	BOPP	NOPP
Luteolin	ND	38.90	412.97	556.21
Naringin	394.61	14.04	48.71	317.80
Rutin	98.27	ND	ND	ND
Hesperidin	ND	838.08	8080.45	31856.59
Rosmarinic	461.27	200.29	1130.46	3780.10
Quercetrin	ND	18.75	149.61	167.13
Quercetin	4.39	32.70	41.56	193.78
Hispertin	23.90	14.79	241.65	2108.02
Kampferol	63.72	5.09	58.44	29.82
Apigenin	3.85	18.32	27.44	43.55
7-OH-Flavone	0.04	0.20	0.23	18.09
Total	1050.05	1181.16	10191.52	39071.09

PPP: Pomegranate peel powder, PP*P: Pea pod powder, BOPP: Baladi orange peel powder and NOPP: Navel orange peel powder. ND: Not detected.

of Hesperidin, Luteolin, Quercetin, Quercetrin, Apigenin and 7- OH- Flavone (838.08, 38.90, 32.70, 18.75, 18.32 and 0.20 mg/kg dried peels; respectively) than those in dried pomegranate peels (ND, ND, 4.39, ND, 3.85 and 0.04 mg/kg dried peels; respectively). Dried navel orange peels had higher values of Hesperidin, Rosmarinic, Hispertin, Luteolin, Naringin, Quercetin, Quercetrin, Apigenin and 7- OH-Flavone (31856.59, 3780.10, 2108.02, 556.21, 317.80, 193.78, 167.13, 43.55 and 18.09 mg/kg dried peels; respectively) than those in dried baladi orange peels (8080.45, 1130.46, 241.65, 412.97, 48.71, 41.56, 149.61, 27.44 and 0.23 mg/kg dried peels; respectively). Dried baladi orange peels had higher value of Kampferol (58.44 mg/kg dried peels) than that in dried navel orange peels (29.82 mg/kg dried peels). The major flavonoid was Hesperidin followed by Rosmarinic acid in locust bean and orange peel albedo (Osheba *et al.*, 2013). These results are nearly similar with those obtained by Sultana *et al.* (2008), Tumbas *et al.* (2010), Zhou *et al.* (2011), Seo *et al.* (2011) and Zulkifli *et al.* (2012).

Vitamins Content of Food Processing Wastes

The vitamins; including B_1 (Thiamine), B_2 (Riboflavin), B_3 (Nicotinic acid), B_6 (Pyridoxine), B_9 (Folic acid), C (Ascorbic acid), A (Retinol), D (Calciferol), E (α-tochoferol) and K (Phylloquinone) were determined, the obtained results were recorded in Table 6. All oxygen-consuming organisms are used antioxidant such as vitamin C, E, A, and phenolic to protect their possible damage to biological molecules (Jacob, 1995).

Data represented in Table 6 show the vitamins content in dried pomegranate peel, dried pea pod, dried baladi orange peel and dried navel orange peel. pomegranate peel contained adequate content of vitamins (retinol, calciferol, αTocopherol, ascorbic acid, thiamine**,** riboflavin**,** nicotinic acid**,** pyridoxine and folic acid) at the level of 0.219, 0.020, 0.099, 15.70, 0.546, 0.191, 0.054, 0.105 and 0.025 mg/100g dry matter, versus 0.181, 0.052, 0.057, 28.12, 0.179, 0.065, 0.072, 0.237 and 0.073 mg/100g dry matter for pea pod, respectively. Baladi orange peel contained

Table 6. Vitamins content of food processing wastes powders (mg/100g dry matter)

Vitamins	PPP	PP*P	BOPP	NOPP
A (Retinol)	0.219	0.181	0.249	0.190
D (Calciferol)	0.020	0.052	0.051	0.026
E (αTocopherol)	0.099	0.057	0.062	0.039
K (phylloquinone) µg/100g	35.47	17.14	0.321	0.209
C (Ascorbic acid)	15.70	28.12	64.49	54.04
B_1 (Thiamine)	0.546	0.179	0.014	0.078
B_2 (Riboflavin)	0.191	0.065	0.037	0.012
B_3 (Nicotinic acid)	0.054	0.072	0.021	0.008
B_6 (Pyridoxine)	0.105	0.237	0.042	0.020
B_9 (Folic acid)	0.025	0.073	0.013	0.028

PPP: Pomegranate peel powder, PP*P: Pea pod powder, BOPP: Baladi orange peel powder and NOPP: Navel orange peel powder.

adequate content of vitamins mentioned previously at the level of 0.249, 0.051, 0.062, 64.49, 0.014, 0.037, 0.021, 0.042 and 0.013 mg/100g dry matter, versus 0.190, 0.026, 0.039, 54.04, 0.078, 0.012, 0.008, 0.020 and 0.028 mg/100g dry matter for navel orange peel, respectively, phylloquinone content at the level of 35.47, 17.14, 0.321 and 0.209 µg/100g dry matter; respectively. The determined vitamins naturally occurred in food processing waste are considered one of the most important phytochemicals having the antioxidant, antimicrobial, chemo preventive cancer properties and good standpoint in human nutrition (Huxley and Neil, 2003). From the above discussion, it could be observed that food processing wastes under study are considered a good source of the determined vitamins. These vitamins work both or synergistically to prevent or delay oxidative reaction that lead to degenerative disease (Elliot, 1999). There are studies on citrus fruits evaluated the ascorbic acid content of the peels (polar fraction) and found values in the range of 0.823 to 1.780 mg of ascorbic acid equivalent to g^{-1} extract. The difference may be due to method used in this study. Pomegranate contain small amount of vitamin B complex (Bhowmik *et al.,* 2013). Green pea is rich source of vitamins A and C (Kumar, 2015). These results are nearly similar with those obtained by Nehra and Sharma (2012), Rowayshed *et al.* (2013) and Barros *et al.* (2014).

Total Phenolic Content (TPC)

Data in Table 7 show that aqueous ethanol extract (80% ethanol) of pomegranate peel showed the highest total phenolic content (259.38 mg gallic acid/g extract), followed by aqueous ethanol extract (50% ethanol) of pomegranate peel (247.71mg gallic acid/g extract). While, the lowest value was ethanolic extract (50%) of pea pod (4.78 mg gallic acid/g extract). Ethanolic extract (80%) from each waste (pomegranate peel, pea pod, baladi orange peel and navel orange peel) showed highest total phenolic content (259.38, 7.94, 167.15 and 168.74 mg gallic acid/g extract, respectively). The extracts with the highest total phenol contents were obtained with aqueous (80%) ethanol, followed by aqueous (50%) ethanol, then aqueous (70%) ethanol in pomegranate peel, baladi orange peel and navel orange peel. While, the extracts with the highest total phenol contents were obtained with aqueous (80%) ethanol, followed by aqueous (70%) ethanol, then aqueous (50%) ethanol in pea pod. The highest value from the total phenolic contents

Table 7. Total phenolic content (TPC) of aqueous ethanol extracts at different concentrations expressed as mg gallic acid equivalent (GAE) per g extract

Sample	Concentration (mg gallic acid / g extract)		
	Ethanolic extracts (80%)	Ethanolic extracts (70%)	Ethanolic extracts (50%)
PPE	259.38±0.54	241.98±0.70	247.71±0.85
PP*E	7.94±0.23	5.39±0.44	4.78±0.13
BOPE	167.15±1.72	150.33±1.09	155.66±0.93
NOPE	168.74±0.40	153.12±0.97	156.76±1.32

The results obtained from the assay were expressed as means as standard deviation of triplicate analyses. PPE: Pomegranate peel extract, PP*E: Pea pod extract, BOPE: Baladi orange peel extract and NOPE: Navel orange peel extract.

in the ethanolic extract (80%) of food processing wastes were attributed to the effectiveness of solvent before extraction to keep the bioactive compounds. The total phenolic contents obtained by ethanolic 80% concentration extract was higher than total phenolic contents obtained by ethanolic 100% concentration extract (Sarwar *et al.*, 2012). The extracts with the highest total phenols content were obtained with 100% ethanol followed by 50% ethanol and 75% ethanol in Betula alba. While, the extracts with the highest total phenols content were obtained with 100% ethanol followed by 75% ethanol and 50% ethanol in Convolvulus arvensis (Nurul *et al.*, 2013). These results are in agreement with the results reported by Hegazy and Ibrahium (2012); Singh and Immanuel (2014) and El-Houfi (2015).

DPPH Free Radical Scavenging Activity

The effect of antioxidants on DPPH radical-scavenging is thought to be due to their hydrogen-donating ability, DPPH$^{\bullet}$ is a stable free radical and accepts an electron or hydrogen radical to become a stable molecule (Gulcin *et al.*, 2004). Free radicals involved in the process of lipid peroxidation are considered to play a major role in numerous chronic pathologies such as cancer and cardiovascular diseases (Dorman *et al.*, 2003). DPPH$^{\bullet}$ is considered to be a model of a stable lipophilic radical. A chain reaction of lipophilic radicals is initiated by lipid autooxidation. Antioxidants react with DPPH$^{\bullet}$, reducing the number of DPPH$^{\bullet}$ free radicals to the number of their available hydroxyl groups. Therefore, the absorption at 517 nm is proportional to the amount of residual DPPH$^{\bullet}$ (Juan *et al.*, 2005). The results of DPPH radical-scavenging activities of various food processing wastes extracts are represented in Table 8. The results clearly indicated that all extracts exhibited antioxidant activity. The extracts that contained high amount of total phenolic content showed relatively high antioxidant activity. It has been proven that the antioxidant activity of plant extracts is mainly ascribable to the concentration of phenolic compounds in the plant (Heim *et al.*, 2002). The extracts antioxidant activity with aqueous ethanol at different concentrations varied from 95.62 to 16.72% after 120 min. The antioxidant activity of pomegranate peel extracts were stronger than baladi orange peel extracts in scavenging activity against DPPH radicals followed by navel orange peel extracts and minimum scavenging activity against DPPH radicals was found in pea pod extracts. The highest antioxidant activity was observed with aqueous ethanol extracts (80% ethanol, 50% ethanol and 70% ethanol) of pomegranate peel, with respective values 95.62%, 94.13% and 92.08%, followed by aqueous ethanol extracts (80% ethanol, 50% ethanol and 70% ethanol) of baladi orange peel, with respective values 76.39%,75.02 % and 73.80 %. Aqueous ethanol extracts (80% ethanol, 50% ethanol and 70%

Table 8. DPPH free radical scavenging activity (%) of aqueous ethanol extracts at different concentrations

Sample	Zero time	30 minute	60 minute	120 minute
PPE 80%	95.40±0.84	95.45±0.06	96.25±0.12	95.62±0.66
PPE 70%	92.68±0.24	92.89±0.42	91.62±0.06	92.08±0.96
PPE 50%	95.02±0.78	94.81±0.95	93.91±0.42	94.13±0.36
PP*E 80%	18.78±1.02	18.80±1.07	19.13±0.94	19.29±0.93
PP*E 70%	16.24±0.30	16.43±0.24	16.56±0.19	16.72±0.27
PP*E 50%	16.91±0.44	17.22±0.34	17.29±0.35	17.35±0.32
BOPE 80%	71.89±0.41	74.24±0.41	75.56±0.35	76.39±0.28
BOPE 70%	69.73±0.13	70.91±0.28	73.16±0.14	73.80±0.07
BOPE 50%	70.62±0.42	72.18±0.27	74.44±0.28	75.02±0.42
NOPE 80%	64.76±0.25	64.55±0.18	63.79±0.06	63.53±0.06
NOPE 70%	56.55±0.18	56.17±0.13	56.29±0.06	56.21±0.30
NOPE 50%	58.63±0.24	59.14±0.12	58.85±0.18	58.46±0.25
BHT	93.11±0.60	92.64±0.06	92.55±0.54	91.40±0.72
α-tocopherol	92.98±0.18	93.32±0.30	92.47±0.06	90.72±0.84

The obtained results represented the mean of triplicate determinations result. Values are expressed as mean± SD. PPE 80%: Pomegranate peel extract using aqueous (80%) ethanol, PPE 70%: Pomegranate peel extract using aqueous (70%) ethanol, PPE 50%: Pomegranate peel extract using aqueous (50%) ethanol, PP*E 80%: Pea pod extract using aqueous (80%) ethanol, PP*E 70%: Pea pod extract using aqueous (70%) ethanol, PP*E 50%: Pea pod extract using aqueous (50%) ethanol, BOPE 80%: Baladi orange peel extract using aqueous (80%) ethanol, BOPE 70%: Baladi orange peel extract using aqueous (70%) ethanol, BOPE 50%: Baladi orange peel extract using aqueous (50%) ethanol, NOPE 80%: Navel orange peel extract using aqueous (80%) ethanol, NOPE 70%: Navel orange peel extract using aqueous (70%) ethanol and NOPE 50%: Navel orange peel extract using aqueous (50%) ethanol.

ethanol) of navel orange peel has respective values 63.53%, 58.46% and 56.21%, followed by aqueous ethanol extracts (80% ethanol, 50% ethanol and 70% ethanol) of pea pod, with respective values 19.29%, 17.35% and 16.72%, after 120 min. The results of the DPPH$^{\bullet}$ free radical scavenging assay suggest to capability of the extracts to scavenge different free radicals in different systems, indicating that they may be useful therapeutic agents for treating radical-related pathological damage. These results are similar with those obtained by Abd El-Aal and Halaweish (2010) as well as Singh and Immanuel (2014).

Extract Capacity to Inhibit Lipid Peroxidation

Data in Table 9 show the effect of pomegranate peel, pea pod, baladi orange peel and navel orange peel extracts on oxidation of β-carotene/ linoleic acid at 50˚C. All extracts were capable of inhibiting the bleaching of β- carotene by scavenging linoleate-derived free radicals. The highest value was (96.84%) for

Table 9. Extract capacity to inhibit lipid peroxidation by β-carotene/linoleic acid bleaching (βCB) assay compared with BHT and α-tocopherol

Sample	Inhibition of lipid peroxidation (%)		
	Ethanolic extracts (80%)	Ethanolic extracts (70%)	Ethanolic extracts (50%)
PPE	96.84±1.05	95.30±0.45	96.15±0.41
PP*E	24.05±0.44	22.46±0.86	22.72±0.38
BOPE	81.62±1.54	78.91±0.56	79.35±0.09
NOPE	70.09±1.53	64.75±0.56	66.06±1.00
BHT	95.45±0.58		
α-tocopherol	94.88±0.64		

The obtained results represented the mean of triplicate determinations result. Values are expressed as mean± SD. PPE: Pomegranate peel extract, PP*E: Pea pod extract, BOPE: Baladi orange peel extract and NOPE: Navel orange peel extract.

ethanolic extract (80%) of pomegranate peel. While, the lowest value was (22.46%) for ethanolic extract (70%) of pea pod. The extracts with the greatest level of inhibition percentage of lipid peroxidation were obtained with pomegranate peel, followed by baladi orange peel, then navel orange peel. On the other hand, the lowest inhibition of lipid peroxidation was obtained by pea pod. Inhibition of lipid peroxidation in this assay based on oxidation of linoleic acid produces hydro-peroxide derived free radicals that attack the chromophore of β-carotene, resulting in bleaching of the reaction emulsion. An extract capable of retarding/ inhibiting the oxidation of β-carotene may be described as a free radical scavenger and primary antioxidant (Liyana-Pathirana and Shahidi, 2006). The ratio of antioxidant activity (% inhibit lipid peroxidation) in β-carotene/ linoleic acid bleaching assay was higher than the ratio of antioxidant activity in DPPH free radical scavenging assay according to (El-Hadary, 2015). These results are nearly similar with those obtained by Sultana *et al.* (2008).

Conclusion

It could be concluded that pea pod could be used as a suitable source of protein, fiber and minerals more than pomegranate and orange peels, and could be incorporated as ingredients in a large variety of food products. Also, it could be concluded that pomegranate peel, orange peel and pea pod contains all of the determined vitamins. Overall, ascorbic acid is the predominant vitamin in food processing wastes under study. Antioxidants were extracted from fruit peels of pomegranate, two varieties of Egyptian oranges (Baladi and Navel) and pea pod. Various extracts showed varying degrees of antioxidant activity. Maximum antioxidant activity was found in pomegranate peel followed by baladi orange peel then navel orange peel while the minimum was found in pea pod. Furthermore, it could be concluded that the obtained extracts using higher-polarity solvents were more yield percentage than those obtained using lower-polarity solvents. Aqueous ethanol (80% ethanol) showed slightly better characteristics than aqueous ethanol (70% and 50% ethanol) as a solvent for phenolic compounds extraction and antioxidant activity. Overall, aqueous ethanol extracts of pomegranate peel and baladi orange peel showed relatively comparable activity to BHT. Therefore, these extracts could be used as preservative ingredients in the food and/or pharmaceutical industries. Also, it can be concluded that pomegranate and orange peels due to its high antioxidant activity and phenolic content may prove to be a better substitute in place of synthetic antioxidants for their role in preventing the auto-oxidation and extending the

shelf life of oils, fats and fatty foods by preventing the peroxide formation. In addition, natural antioxidants are safe and impart health benefit to the consumer.

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التقييم التغذوى والتركيب الكيميائى والنشاط المضاد للأكسدة لبعض مخلفات التصنيع الغذائى

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يعتبر الرمان والبرتقال من أهم محاصيل الفاكهة كما تعتبر البازلاء من أهم محاصيل الخضر ويستهلك كلا منهم على نطاق واسع في جميع أنحاء العالم ويرغبهم قطاع كبير من المستهلكين، كلا من الرمان والبرتقال البلدي والبرتقال أبو سرة والبازلاء من المنتجات الزراعية التي يتخلف عن استهلاكها سواء على النطاق المنزلي أو الصناعي كميات كبيرة من المخلفات تتمثل في القشور، لذلك كان الهدف من هذا البحث هو إلقاء الضوء على مؤشرات القيمة الغذائية والتي تشمل التركيب الكيميائي ومحتوى المعادن والفيتامينات وكذلك مركبات الفينول والفلافونويد لهذه المخلفات لتحقيق القدرة على استخدامها فى تكنولوجيا حفظ وتصنيع الأغذية، تم دراسة الخواص المضادة للأكسدة وكذلك المحتوى الكلى للفينولات الموجودة فى ١٢ مستخلص نباتي للمخلفات سابقة الذكر والتي تم الحصول عليها باستخدام الإيثانول المائي بتركيزات مختلفة (٨٠%، ٧٠%، ٥٠% إيثانول)، تم قياس محتوى الفينولات الكلية باستخدام طريقة فولن؛ كذلك تم تقدير الخواص المضادة للأكسدة لهذه المستخلصات بإستخدام الشقوق الحرة (DPPH) وأيضًا تم استخدام طريقة قصر اللون لمستحلب البيتا كاروتين واللينوليك، وأوضحت النتائج أن هذه المخلفات تحتوى على العديد من المركبات النشطة حيويا وذات محتوى عالى من الكربوهيدرات والألياف، من ناحية أخرى، سجل مخلف قشر البازلاء أعلى محتوى من البروتين والألياف والأملاح المعدنية لذلك يمكن استخدام هذه المخلفات فى تدعيم بعض المنتجات الغذائية، كما أوضحت النتائج أن مستخلص قشر الرمان له أقوى خواص مضادة للأكسدة يليه مستخلص قشر البرتقال البلدى مقارنه بمضادات الأكسدة الصناعية (BHT)، وبالنسبة لمذيب الإستخلاص كان مستخلص الإيثانول المائى (٥٠% إيثانول) أعلى في نسبة الإنتاجية بينما مستخلص الإيثانول المائي (٨٠% إيثانول) كان أعلى في محتوى الفينولات الكلية والخواص المضادة للأكسدة، وبالتالي يمكن استخدام هذه المستخلصات كمضادات أكسده طبيعية في الزيوت والدهون والمنتجات الغذائية الأخرى لإطالة فترة صلاحيتها للإستهلاك الآدمي بالإضافة إلى ذلك هذه المستخلصات الطبيعية تعتبر آمنة وذات فائدة صحية للمستهلك.

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