M.Sc. thesis abstract

Some Citrus Peels As A Source of Antioxidants in Different Vegetable Oils and Its Applications in Some Functional Foods

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ABSTRACT

The present study was conducted on the orange peel (OP), mandarin peel (MP) and lemon peel (LP) to evaluate its bioactive compounds and use it in some vegetable oils and some functional foods. The total phenolics content in OP, MP and LP were 818.86, 996.8 and 956.86 mg / 100 g, respectively and total flavonoids content in OP, MP and LP were 476.56, 517.38 and 406.23 mg / 100 g, respectively. Also, the amount of essential oils in OP, MP and LP were 2.4, 1.9 and 0.87 %, respectively. The three citrus peels, OP, MP and LP had a reasonable amount of neutral dietary fiber (NDF) and acid dietary fiber (ADF) (17.85, 21.83 and 12.43 % and 13.52, 10.94 and 11.32 %, respectively). It is clear that the by-product of food processing industries has added value by identifing and isolating of their bioactive compounds. Two analytical methods were used to determine their antioxidant activity 2, 2- diphenyl-1- picrylhydrazyl (DPPH) and ferric reducing antioxidant power (FRAP). IC50 were 6.59, 7.49 and 22.69 mg / ml for OP, MP and LP, respectively. The absorbance of OP, MP and LP in the FRAP method were 0.34, 0.52 and 0.56, respectively. The oxidative stability of palm olein, soybean and sunflower oils containing each of OP, MP and LP and their extracts as novel sources of antioxidants versus butylated hydroxytoluene (BHT) as a synthetic antioxidant were also studied and evaluated by measuring their induction periods (IPs) using the Rancimat method. The ethanolic extracts of the peels were added at two levels; 1000 and 2000 ppm, individually, while the aforementioned whole peels (OP, MP and LP) were added in different quantities according to its extract yield percentage. Moreover, the three citrus peels were added to some functional foods such as cookies and pasta in different concentrations.

Keywords: Orange peels, mandarin peels, lemon peels, bioactive compounds, oxidative stability, functional foods.

By-products of food processing industries have added value by identification and isolation of their bioactive compounds. Consequently, the present study was conducted on the orange peels (OP), mandarin peels (MP) and lemon peels (LP) to achieve the following five goals:

(1) Determination of chemical composition and essential oils of citrus peels.
(2) Investigating bioactive compounds such as phenolics, flavonoids, vitamin C and dietary fibers.
(3) Determination of the antioxidant activity of citrus peels.
(4) Comparing among citrus peels and their ethanolic extract as a source of natural antioxidants in some edible oils to extend its shelf life.
(5) Preparing some functional food products containing citrus peels.

The main results obtained in the present study can be summarized as follows:

A) Chemical composition of orange, mandarin and lemon peels.

1) The moisture content ranged between 70.05 % for LP to 77.82 % for MP, while the moisture content of OP lied in between being 72.33 %.
2) The crude protein content of OP, MP and LP ranged from 4.44 % to 9.91 % on dry weight basis (DW). The OP exhibited significantly ($p \leq 0.05$) the least crude protein content (4.44%), on contrary to LP which possessed significantly ($p \leq 0.05$) the highest content (9.91 %).
3) The LP had significantly ($p \leq 0.05$) the highest crude oil content (12.79 %) and the OP exhibited crude oil content of 8.64 %, while the MP was tailed behind since it had 10.1% crude oil content.
4) The LP possessed significantly ($p \leq 0.05$) the highest ash content (15.13 %), on contrary to MP that had 10.37 % ash content. As for OP, it had ash content being in between the aforementioned two values (10.41%) (DW).

5) A range from 62.17 % to 76.51 % (DW) was figured out for the carbohydrate content for the three types of peels. The OP had significantly ($p \leq 0.05$) the highest content of total carbohydrate (76.51 %) followed by LP (72.9 %) and MP had significantly ($p \leq 0.05$) the least carbohydrate content (62.17%).
6) The MP had significantly ($p \leq 0.05$) the highest total sugars content (33.35 %) and OP exhibited total sugars of 32.82 %, while the LP was tailed behind, since it had 30.7 % total sugars content.
7) The ascorbic acid content of OP, MP and LP ranged from 29.43 to 44.36 mg / 100 g (DW). The LP exhibited significantly ($p \leq 0.05$) the least ascorbic acid content (29.43 mg / 100g), on contrary to MP which possessed significantly ($p \leq 0.05$) the highest content (44.36 mg / 100g), while the ascorbic acid content of OP lied in between (35.27 mg /100 g).

B) Fiber and pectin content in orange, mandarin and lemon peels.

1) Orange peel had significantly ($p \leq 0.05$) the highest crude fiber content (8.73 %), followed by LP (6.51 %), whereas, MP exhibited significantly ($p \leq 0.05$) the lowest crude fiber content (5.48 %).
2) The MP had significantly ($p \leq 0.05$) the highest contents of NDF (21.83 %) and hemicellulose (10.89 %), followed by OP which was 17.85 % NDF and 4.33 % hemicellulose, then LP 12.43 % NDF and 1.11 % hemicellulose. However, OP had significantly ($p \leq 0.05$) the highest contents of ADF (13.52 %) and cellulose (12.4 %), followed by LP being 11.32 % ADF and 10.18 % cellulose, followed by MP which had 10.94 % ADF and 9.87 % cellulose.
3) Lemon peel had significantly ($p \leq 0.05$) the highest content of lignin (1.14 %), followed by OP (1.12 %) and MP (1.07 %).
4) It can be observed that the pectin content for each of MP and LP were comparable (17.72 and 19.04 %, respectively), while OP had significantly ($p \leq 0.05$) the highest content of pectin (25.84 %) as compared with MP and LP.

C) Minerals content of orange, mandarin and lemon peels.

1) The significant ($p \leq 0.05$) high content of calcium was in LP (2185.19 mg /100 g), followed by OP (1147.15 mg / 100 g) and MP (683.2 mg / 100 g).
2) The LP was significantly ($p \leq 0.05$) higher in sodium content (1164 mg /100 g), followed by OP (623 mg / 100 g) and MP (614 mg /100 g). On the other hand, the amount of potassium was higher in OP (7670 mg / 100 g) and MP (6140 mg /100 g) compared to LP (2667 mg / 100 g).
3) Iron, a very important mineral was found in OP in a considerable amount (63.0 mg /100 g), LP (54.9 mg / 100 g) and MP (48.8 mg / 100 g). Magnesium followed the same trend, it was found in OP, MP and LP as follows: (81.0, 69.7 and 92.1 mg / 100 g, respectively)
4) There were trace amounts of copper and manganese in OP (4.0 and 4.5 mg / 100g, respectively) in MP (5.7 and 3.2 mg / 100 g, respectively) and in LP (7.8 and 5.3 mg /100 g, respectively). Also, there was a trace amount of zinc in OP, MP and LP.

D) Essential oils content of orange, mandarin and lemon peels.

The amount of essential oils ranged from 0.87 % in LP to 2.4 % in OP, while the MP lied in between being 1.9 %. The essential oils in OP, MP and LP have been analyzed using GC-MS apparatus to identify different components in the citrus peels. The main components in the essential oil of OP and MP were D-limonene (94.91 % and 77.85 %, respectively), the other main components in OP were β- myrcene (2.96 %), α- pinene (1.17 %) and finally linalool (0.97 %). Furthermore, the other main components in MP were ɣ -terpinene (13.83 %), α-pinene (3.1 %), β-myrcene (2.36 %), β-pinene (1.75 %) and finally α-thujene (1.09 %). In contrast, the main components in LP were α- terpineol (50.64 %), followed by terpinen-4-ol (27.54 %), linalool (7.89 %), Z-citral (7.12 %) and finally trans-caryophyllene (6.81 %), which is mainly different from OP and MP essential oils components.

E) Total phenolic, flavonoid and carotenoid compounds in orange, mandarin and lemon peels.

1) The MP had significantly ($p \leq 0.05$) the highest total phenolics content (996.8 mg / 100 g), while the OP had significantly ($p \leq 0.05$) the least phenolics content (818.86 mg / 100 g) and the LP lied in between being 956.86 mg / 100 g.
2) The MP contained significantly ($p \leq 0.05$) the highest amount of flavonoids (517.38 mg / 100 g), followed by OP and LP (476.56 and 406.23 mg /100 g, respectively).
3) The OP had significantly ($p \leq 0.05$) the highest total carotenoids content (6.66 mg / 100 g), on contrary to LP that possessed the lowest total carotenoids content (1.074 mg /100 g), while MP lied in between being 3.83 mg /100 g.

F) Separation of total phenolic compounds.

The phenolic compounds in OP, MP and LP have been analyzed using HPLC to identify different components in the citrus peels. Ferulic acid, vanillic acid, syringic acid, gallic acid and sinapic acid were found to be the main phenolic compounds in OP (1239.173, 605.878, 463.815, 367.04 and 361.459 µg / g, respectively). Meanwhile, in MP the contents of the latter compounds were 915.606, 446.353, 245.635, 339.988 and 9.089 µg / g, respectively, whereas, in LP apigenin, hesperidin, naringin, sinapic acid and gallic

acid were the main phenolic compounds (1603.230, 1199.429, 334.949, 228.816 and 231.863 µg / g, respectively).

G) Antioxidant activity of orange, mandarin and lemon peel extracts.

1) It was obvious that MP had significantly ($p \leq 0.05$) the highest $DPPH^{\cdot}$ scavenging activity (90.22 %) as compared to each of OP (89.29 %) and LP (88.14 %).
2) Significantly ($p \leq 0.05$) the highest IC_{50} was 22.69 mg / ml for LP, followed by MP (7.49 mg / ml), then OP (6.59 mg / ml).
3) The aforementioned peel extracts can be ordered descendingly in terms of absorbance of the FRAP method as follows: LP (0.56), MP (0.52) and OP (0.34).

H) Oxidative stability of palm olein, soybean and sunflower oils supplemented with orange, mandarin and lemon peels and their extracts.

1) Addition of OPE at 2000 ppm exhibited significantly ($p \leq 0.05$) the highest oxidative stability for palm olein (60 h), soybean (7 h) and sunflower oils (16 h) compared to other additions, followed by the addition of OP at 2000 ppm. Both treatments OPE and OP at 2000 ppm were more powerful than using BHT at 200 ppm and exhibited significantly ($p \leq 0.05$) higher oxidative stability for palm olein and soybean oils, whereas, for sunflower oil, the results were very close for the three treatments. It was obvious, that palm olein oil exhibited significantly ($p \leq 0.05$) the highest oxidative stability (using orange peels and its extracts at both concentrations; (1000 and 2000 ppm) compared to soybean and sunflower oils.
2) Addition of MPE at 2000 ppm exhibited significantly ($p \leq 0.05$) the highest oxidative stability for palm olein (59 h), soybean (7 h) and sunflower oils (14 h) compared to any other addition.
3) Like OP, both treatments of MPE and MP at 2000 ppm were more powerful than using BHT at 200 ppm and exhibited significantly ($p \leq 0.05$) higher oxidative stability for palm olein and soybean oils, whereas for sunflower oil using BHT was more powerful (16 h.) compared to the two other treatments MPE (14 h) and MP (13 h). Moreover, it was obvious, that using palm olein oil exhibited significantly ($p \leq 0.05$) the highest oxidative stability (using mandarin peels and its extracts at both concentrations 1000 and 2000 ppm) compared to sunflower and soybean oils.
4) Addition of LPE at 2000 ppm exhibited significantly ($p \leq 0.05$) the highest oxidative stability for palm olein (45 h), soybean (20 h) and sunflower oils (29 h) compared to other additions. Also, as in OP and MP, both treatments LPE and LP at 2000 ppm were more powerful than using BHT at 200 ppm and exhibited higher oxidative stability for palm olein, soybean oils and sunflower oils.

I) Sensory evaluation of the cookies supplemented with orange, mandarin and lemon peels: -

1) Data of sensory evaluation for cookies revealed significant improvement for the overall acceptability of cookies supplemented with 5, 10 and 15 % of OP being superior to the control. The cookies supplemented with 10 % OP, judged by the panelists was significantly the most acceptable cookies in terms of colour, odour, texture, taste as well as for overall acceptability.
2) Cookies supplemented with MP at the aforementioned three levels were found to be significantly ($p \leq 0.05$) the most acceptable cookies in overall acceptability even though cookies supplemented with 5 % MP was the most acceptable in colour and taste. Meanwhile, the cookies supplemented with 15 % MP was more acceptable only in texture. Notwithstandings cookies supplemented with 5 and 10 % were more acceptable in odour than the cookies supplemented with 15 % as well as the control.
3) Cookies supplemented with 2 % LP were the most acceptable and superior in terms of colour, odour, taste, texture and overall acceptability. However, the cookies supplemented with 4 and 6 % were found to be significantly less acceptable than the control sample.

J) The thickness and the area for the cookies supplemented with orange, mandarin and lemon.

1) Data showed that increasing the supplementation level of OP and MP (5, 10 and 15 %) for cookies resulted in increasing the thickness and area of supplemented cookies compared with the control and increasing the thickness of cookies supplemented with LP at different level (2, 4 and 6 %) compared with the control. The thickness ranged from 10.4 for the control to 11.31 for the cookies supplemented with 5 % MP and 11.32 for the cookies supplemented with 2 % LP.
2) The point of interest is that the supplementation of cookies with the three types of peels investigated here (OP, MP and LP) resulted in an elevation of the thickness of the cookies at 5 % for OP and MP as well as at 2 % for LP followed by a decrease in the thickness by increasing the concentrations to 10 % and 15 % for OP as well as MP.

Consequently, the incorporation of these peels in cookies structure leads to improve the texture of cookies.

K) Sensory evaluation of the pasta supplemented with orange, mandarin and lemon peels.

1) It was obvious that pasta supplemented with 5 % OP were significantly ($p \leq 0.05$) the most acceptable in terms of appearance, colour, odour, taste, tenderness and stickiness as compared with the control and the other two supplemented pasta. Although, appearance, colour, odour, taste, tenderness and stickiness for

pasta control was significantly ($p \leq 0.05$) superior as compared to other supplemented pasta with 10 and 15% OP.

2) Pasta supplemented with 5% MP was significantly higher in colour, odour, taste, tenderness and stickiness compared to other treatments. Meanwhile, pasta supplemented with 5 and 10 % MP possessed the same preference in appearance. Although, pasta control exhibited significantly ($p \leq 0.05$) the higher acceptability in terms of tenderness, stickiness, taste, odour, colour and appearance than the pasta supplemented with 10 and 15% MP.
3) Pasta supplemented with 5 % LP was more acceptable than the two other concentrations (10 and 15 %) regarding stickiness, tenderness, taste, odour, colour and appearance. Even though pasta control was significantly ($p \leq 0.05$) the most acceptable in terms of taste, colour, odour, tenderness, stickiness and appearance.

L) The weight and volume of cooked pasta supplemented with orange, mandarin and lemon peels

Data showed that increasing of pasta supplementation level (5, 10 and 15 %) with OP, MP and LP resulted in increasing the weight percentage and the residue retained in cooking water as compared with the control.

In conclusion, the present study explored the significance of utilizing orange, mandarin and lemon peels as a good source of pivotal bioactive compounds. On the other hand, the aforementioned peels are rich sources for potent antioxidants and dietary fiber, along with numerous mineral elements. It was obvious that in general, orange and mandarin peels were favourite than lemon peels in pasta, while the three types of peels (OP, MP and LP) understudy could be used as supplements for cookies. So, utilization of these peels as supplements for food products or as antioxidants to elongate the shelf life of oils will be quite beneficial from economic, environmental, sustainable and functional points of view.

RECOMMENDATIONS

1- The Ministry of Agriculture as well as the Ministry of Environment must contribute more effort and raise awareness for the sustainability of utilizing the industries wastes instead of throwing it.
2- The Non-government organization should play a big role in society for declaring and learning people the importance of fruit peels.
3- Different industries should use citrus peels and its extracts as effective natural antioxidants in different products, especially oils and fats, instead of using synthetic antioxidants, also, such peels can be added to cookies and pasta to enhance its organoleptic characteristics as well as its nutritional values.