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IMPROVING OILS STABILITY DURING DEEP-FAT FRYING USING NATURAL ANTIOXIDANTS EXTRACTED FROM AGRO-INDUSTRIAL BY-PRODUCTS

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ABSTRACT: ***The present study was carried out to evalute the possibility of extraction of some natural antioxidative (phenolic compounds) from agro-industrial by-products (mango seed kernel, mango peel, onion skin and black rice bran) . The extracted phenolic compounds were tested as natural antioxidants using mixure of refined Sunflower 75% and soybean 25% oils after deep frying (170-180°C) of potato for 25 hours compare with synthetic antioxidants; Tetra butyled hydroxyl quinone (TBHQ) . The results indicated that methanolic extract gave the highest extract yield compared to the other solvent. Methanol exhibited the highest extraction ability for phenolic compound (6.54,5.40, 5.10 and 6.80 mg/gdw), for mango seed kernel, mango peel, onion skin and black rice bran extracts, respectively and also showed the strongest antioxidant activity of black rice bran extract activity owing to its high content of phenolic compounds. HPLC analysis for the total polyphenols extracted from agro-industrial by-products indicated Ferulic, p-coumaric and Caffeic acids were the major phenolic compounds presented and identified in black rice bran (164.3, 32.1, and 25.4 mg/100g, respectively); while Salicylic, Chtechin and Protocatechuic acids were the major phenolic compounds presented and identified in Mango seed kernel (60.7, 51.7 and 46.1 mg/100g respectively). peroxide value of blend oils without additives (control) was increased significantly (P ≤ 0.05) after 5 days of storage at 60° C meanwhile slowed increase was detected in samples with 200 ppm TBHQ and 400 ppm phenolic compounds extracted from agro-industrial by-products . Peroxide and TBA values of the frying blend oils increased significantly (P ≤ 0.05) with increasing frying time. Black rice bran extract was more effective as antioxidant than those of the other studied agro-industrial by-products at 400 ppm and TBHQ at 200 ppm.***

Key words: ***Mango seed kernel, mango peel, onion skin, black rice bran, phenolic compounds; antioxidant activity, oxidative stability.***

INTRODUCTION

Deep frying is widely used for the preparation of many types of foods. The high temperatures reached during food frying lead to a complex series of reactions that resulted in hydrolysis, oxidation and polymerization of oil. (Gertz *et al.,* 2000). Lipid oxidation is the main deterioration process that occurs during thermal processing of vegetable oils containing poly unsaturated lipid molecules. Additionally, certain oxidation products are potentially toxic at relatively low concentrations (El Anany, 2007). The addition of antioxidants is considered as one of the methods of increasing shelf life of lipids and lipid-containing foods. Synthetic antioxidant, such as butylated hydroxyl anisole (BHA) and butylated hydroxyl - toluene (BHT), have restricted use in foods as these synthetic antioxidants are suspected to be carcinogenic (Hou 2003 and Jayaprakasha *et al.,* 2001). Due to these safety concerns, there is an increasing trend among food scientists to replace

these synthetic antioxidants with natural ones, which, in general, are supposed to be safer (Yanishlieva and Marinova, 2001). Antioxidants (natural and synthetic) play a significant role in retarding lipid oxidation reactions in food products. The main classes of natural antioxidant compounds in nature are flavonoids and phenolic acids in free or complexes forms. These compounds have been identified and quantified in several fruits and vegetables, and show a high correlation with antioxidant activity (Einbond *et al.,* 2004). Dried mango peel and kernel products can improve the nutritional, functional and sensory properties, and oxidative stability of oil/oil rich product (Abdalla *et al.,* 2007b). Mango peel is rich in pectin, cellulose, hemicellulose, lipids, protein, polyphenols and carotenoids with excellent antioxidant and functional properties (Ajila *et al.,* 2007). Mango peel and kernel contain various classes of polyphenols, carotenoids, and vitamins with different health-promoting properties, mainly antioxidant activity (Manthey and Perkins-Veazie, 2009). Mango kernels are rich sources of gallic acid, ellagic acid, ferulic acid, cinnamic acids, tanins, vanillin, coumarin, and mangiferrin, all having potential to act as a source of natural antioxidants (Abdalla *et al.,* 2007a).

In recent years, the consumption of onion has increased due to its flavor and health benefits. These beneficial properties seem to strongly relate to the high content of sulfur compounds and flavonoids. Because of their activity as antioxidants and anticarcinogens, their effects on lipid metabolism and the cardiovascular system, and their antibiotic effects were put under investigation (Griffiths *et al.,* 2002). The flavonoids present in the onion consist of anthocyanins (cyanidin and peonin) and mainly flavonols (quercetin, kaempferol, isorhamnetin, and their glycosides). The onion skin has a high content of free and glycosidically bonded quercetin (2-10% w/w) and oxidized quercetin derivatives such as minor flavonols and phenolic compounds (Hala, S. Sayed, *et al.,* 2014). Rice, being one of the most produced and consumed cereals in the world, has an important role in the relation between the diet and health. Several compounds with antioxidant activity have been identified in rice, including phenolic compounds, tocopherols, tocotrienols and ɤ-oryzanol (Iqbal *et al.,* 2005). The phenolic compounds are mainly associated with the pericarp in rice, hence, the milling process reduces the concentration of these compounds in the grain. Besides, grains with darker pericarp colour, such as red and black rice, contain higher amounts of polyphenols (Walter and Marchesan, 2011). In addition, the concentration of total phenolics in the grain has been positively associated with the antioxidant activity, with potential beneficial effects on health, such as reduction of oxidative stress, aid in the prevention of cancer, in the blood lipids control and related diseases, which may help in the prevention of cardiovascular problems, and in the prevention of the complications of diabetes (Yawadio *et al.,* 2007). The present study was under taken to evaluate the efficiency of natural antioxidants extracted from agro-industrial by-products (mango seed kernel, mango peel, onion skin and black rice bran) as a new sources of natural antioxidants during frying process of oil Blends in a comparison with TBHQ as synthetic antioxidant.

MATERIALS AND METHODS

Materials:

Market-ripe mangoes *(Magnifera indica L.)* zebda variety and red onion *(Allium cepa L.)* were purchased from local market, Kafer El-Sheikh , Egypt , Season 2016.

Black rice bran *(Oryza sativa L.)* was obtained from the Rice Research and

Training Center (RRTC) , Sakha , Kafer El-Sheikh , Egypt , Season 2016 and stored in deep freezing at -20ºC until further use. Commercial antioxidant; Tetra butyled hydroxyl quinone (TBHQ), 1,1-diphenyl -2 –picrylhydrazyl (DPPH) , Folin- ciocalteau reagents and solvents were purchased from Sigma-Aldrich Co. (St. Louis, Mo., U.S.A.) and Blend it oils (mixed of refined Sunflower 75% and soybean 25% oils) antioxidant free were obtained from Tanta Company for Oils and Soap, Tanta, Egypt, (2016).

Methods:

Preparation of samples:

A-Preparation of mango peels and kernels:

Fruits were sorted for maturity and defects, followed by well washing. Peel and kernel stones were removed manually using stainless steel knives. The stones were opened to get kernels. Mango peel were cut into thin strips whereas the kernels were cut cross-section wise into thin thick slices. Mango peel and kernel pieces were spread in single layer and dried at 50º C and finely ground into powdery form .

B-Preparation of onion skin powder (OSP):

Onion skin powder (OSP) was prepared according to the method described by Gawlik-Dziki *et al.* (2013) as follows: the dried onion skin was separated and washed twice with deionized water and dried in an oven at 50°C. Once dried, the samples were powdered using a laboratory mill and then sieved (60 mesh). and stored in deep freeze at -20ºC until further use.

Extraction of natural antioxidants from agro-industrial by-products:

The prepared ground materials (10 g) of each sample were soaked in 100 ml of each solvent (Ethanol, Acetone, Ethyl acetate and Methanol) over night in a shaker at room temperature according to Mohdaly *et al*. (2010). The extracts were filtrated through Whatman No.1 filter paper. The residues were re-extracted three time under the same conditions. The combined filtrates were evaporated under vacuum in a rotary evaporator below 40ºC. The extracts obtained after evaporation of organic solvents were weighted to determine the extract yield and stored at -20° C until further analysis.

Gross chemical composition of agro-industrial by-products:

Moisture, Crude fat, Crude protein, and ash content were determined according to the methods of A.O.A.C. (2005). Total carbohydrates were determined by difference.

Determination of total phenolic compounds:

Total phenolic compounds of the extracts were determined spectrophotometrically using Folin-ciocalteau reagent according to the method described by Bonoli *et al.* (2004) and used to estimate the phenolics-acid content using a standard curve prepared using tannic acid.

Determination of DPPH· radical scavenging capacity:

The 1,1-diphenyl - 2- picrylhydrazyl (DPPH) assay was based on the method of Lee *et al*. (2003) .

Identification of phenolic compounds by HPLC:

Phenolic compounds of agro-industrial by-products samples were extracted according to the method outlined by Evangelisti *et al.* (1997).

Antioxidant activity testing:

Extracted phenolic compounds from agro-industrial by-products samples were tested as Antioxidant by the determination of peroxide value (POV) during incubation of blend oil at 60ºC for 7 days as described by Matthous, (2002).

Frying performance:

Frying oil blend 3 kg (sunflower 75% and soybean 25% oils) were heated in a domestic fryer (Model 7122 A, Tefal Super 500 deluxe, France) to 185 + 5ºC. Potato tubers were first washed with tap water then manually peeled, cut into 5.0 x 0.7 x 0.7 cm pieces using mechanical cutter (type chef, La Minerva, Italy) and submerged in tap water until frying. After draining off excess water, 200 g of them were placed in a wire basket and deep fried in the tested Blend oils as follows:

1- Blend Oil without any antioxidant treatment.
2- 2- Blend Oil treating with (200 ppm) Tetra butyled hydroxyl quinone (TBHQ).
3- Blend Oil treating with (400 ppm) of Methanolic extract from mango seed kernel.
4- Blend Oil treating with (400 ppm) of Methanolic extract from mango peel.
5- Blend Oil treating with (400 ppm) of Methanolic extract from onion skin.
6- Blend Oil treating with (400 ppm) of Methanolic extract from black rice bran. As described by Mostafa, (2013) with some modified. The frying process was daily repeated for five hours. The heating frying cycle was continued for five days. At the end of each frying period, the oil was filtered through muslin to remove the remaining fried particles, allowed to cool overnight at room temperature. Two hundred ml of the filtered oils were taken and preserved in dark glass bottles with stoppers in a refrigerator until analyzed.

Peroxide value (PV): was determined by potassium iodide method according to Leonard *et al*. (1987).

Iodine value: Iodine value was determined via titration by sodium thiosulfate according to the method described in A.O.A.C, (2005).

Thiobarbituric acid (TBA): values were determined according to Sidwell *et al.* (1990). The concentration of malonaldehyde in oil samples were calculated from standard curve. Absorbance was read at 532 nm against distilled water.

Statistical analysis:

Most of the received data were analyzed statistically using the analysis of variance and the means were further tested using the least significant difference test (LSD) as outlined by Steell and Torrie (1980).

RESULTS AND DISCUSSION

Gross chemical composition of agro-industrial by-products (g/100g dry weight).

The chemical composition of agro-industrial by-products (mango seed kernel, mango peel, onion skin and black rice bran) were determined and the results are recorded in Table (1). The moisture content of agro-industrial by-products were ranged from (5.24 to 12.66%). However, black rice bran contain the highest content of crud protein which was (16.11%) followed by mango seed kernel which recorded (7.33%) while the lowest value of crud protein was (2.67%) for onion skin.

Apparent also from the same table that, Crude Fat contents were 9.89% in Mango seed kernel, 1.48% in Mango peel, 1.03% in Onion skin and 16.95% in black rice bran. Furthermore, agro-industrial by-products contain 1.89 to 7.71% ash content, and 59.23 to 90.20% total carbohydrate. These results are in line with Ajila *et al*. (2010); Hala, S. Sayed *et al*. (2014); Nordin *et al*. (2014); El-Faham, *et al*. (2016); El-hassaneen, *et al*. (2016); Elizabeth *et al*. (2017) and Gumte, *et al.,* (2018).

Table (1): Gross chemical composition of agro-industrial by-products (g/100g on dry weight basis).

Samples	Moisture	Crude protein	Crude Fat	Ash	carbohydrates
Mango seed kernel	5.94^{c}	7.33^{b}	9.89^{b}	1.89^{d}	80.89^{c}
Mango peel	12.66^{a}	5.50^{c}	1.48^{c}	3.15^{c}	89.87^{b}
Onion skin	5.24^{d}	2.67^{d}	1.03^{d}	6.10^{b}	90.20^{a}
black rice bran	8.56^{b}	16.11^{a}	16.95^{a}	7.71^{a}	59.23^{d}
LSD	**	**	**	**	**

*** Each value is an average of three determinations.**

+ Values followed by the same letter in Colum are not significantly different at P ≤ 0.05.

***= Significant; **= high Significant; NS= No Significant.**

Effect of solvent type on the extraction yield of agro –industrial by-products (Yield g /100 g of dry weight).

Choice of solvent plays a vital role in the extraction of phytochemicals. Earlier studies reported the use of polar solvents for effective extraction of phenolic compounds (QD *et al.*, 2014). Antioxidant compound extracted from agro-industrial by-products (mango seed kernel, mango peel, onion skin and black rice bran) using different solvents (ethanol, acetone, ethyl acetate and methanol) were showed in Table (2). It was observed that methanol extracts of black rice bran had the highest amount of extract yields (23.89g ⁄ 100g), while the lowest extract yields recorded for onion skin (7.30 g ⁄ 100g) with aceton. Furthermore, The extraction yield increase in order: Acetone < Ethyl acetate < ethanol < methanol.

These results are similar with that obtained by Sultana *et al.* (2007) who reported that, rice bran had the highest yield of antioxidant than rice hull. Furthermore, The polarity of the solvent and of the different phenolic compounds affect extraction efficiency and the activity of the obtained extracts (Gonzalez and Gonzalez 2010). Generaly, highly hydroxylated aglycone forms of phenolic compounds are soluble in alcohols such as methanol or ethanol and their mixtures with water (Lafka *et al.,* 2007).

Table (2): Effect of using different solvents on yield extracted from agro –industrial by-products (g /100 g of dry weight).

Extraction solvent	(extracted Yields g/100 g of dry weight)			
	mango seed kernel	mango peel	Onion skin	black rice bran
Ethanol	20.75^{b}	16.84^{a}	10.73^{b}	22.82^{b}
Acetone	16.45^{d}	7.78^{c}	7.30^{d}	16.82^{d}
Ethyl acetate	18.74^{c}	9.98 ^{b}	8.65^{c}	20.86^{c}
Methanol	22.65^{a}	16.90 ^{a}	13.40^{a}	23.89^{a}
LSD	**	**	**	**

*** Each value is an average of three determinations.**

+ Values followed by the same letter in Colum are not significantly different at P ≤ 0.05.

***= Significant; **= high Significant; NS= No Significant.**

Effect of solvents type on total polyphenol extracted from agro-industrial by-products.

Total polyphenols extracted from (mango seed kernel, mango peel, onion skin and black rice bran) are given in Table (3). The data indicate that methanol was the best solvent for extracting polyphenols from the studied agro-industrial by-products. High, amounts of extracted polyphenolic compounds by methanol from black rice bran, mango seed kernel, mango peel and onion skin, were 6.80, 6.54, 5.40 and 5.10 mg tannic / g dw, respectively, comparing with other solvents. These results are similar with that obtained by Su *et al.* (2007) They revealed that, methanol and ethanol were better ($P < 0.05$) than the ethyl acetate and acetone for extracting phenolic compounds owing to their higher polarity and good solubility for phenolic components from plant materials. On the other hand, the data in the same table showed that, black rice bran contained highest amounts of polyphenolic compounds with all using solvents comparing with other agro-industrial by-products. These results are agreement with the results obtained by Kim *et al.,* (2010); Araba *et al.* (2011); Abdel *et al.* (2012); Hala, S. Sayed *et al.* (2014); Abbasi *et al.* (2015); Pitchaporn, and Sirithon, (2016); Viera, *et al*. (2017); Azza M. Abdel-Aty, *et al.* (2018) and Salem *et al.* (2018).

Antioxidant activity of methanol extracts from agro-industrial by-products.

The free redical scavenging of the extracts of agro-industrial by-products were evaluated using the DPPH method and the results were presented in Table (4) The results showed that, antioxidant activity of TBHQ was higher than all extracts at different level. In addition, The DPPH radical scavenging of mango seed kernel, mango peel, onion skin, black rice bran and TBHQ at concentration of 400 ppm were 80.30, 78.10 ,78.19 ,82.90 and 97.20%. The varied radical scavenging activity of the extracts depended on the amount of total phenolic in each agro-industrial by-products This difference might be due to the interspecies variation. These findings are in close agreement with previous findings of Ajila *et al.* (2010); Yao *et al.* (2010); Hala, S. Sayed, *et al.* (2014); El-Faham, *et al.* (2016); Pitchaporn, and Sirithon (2016).

Table (3): Effect of using different solvents on total polyphenol contents extracted from agro-industrial by-products.

Extraction solvent	Total polyphenols (mg Tannic acid/g of dry weight)			
	mango seed	mango peel	Onion skin	black rice bran
Ethanol	6.18^{b}	4.91^{b}	4.63^{b}	6.38^{b}
Ethyl acetate	4.40^{c}	3.70^{c}	2.80^{c}	5.30^{c}
Acetone	3.30^{d}	3.00^{d}	2.30^{d}	3.90^{d}
Methanol	6.54^{a}	5.40^{a}	5.10^{a}	6.80^{a}
LSD	**	**	**	**

* Each value is an average of three determinations.

+ Values followed by the same letter in Colum are not significantly different at $P \leq 0.05$.

*= Significant; **= high Significant; NS= No Significant.

Table (4): Antioxidant activity assays of crude methanol extracts of agro-industrial by-products by DPPH .

Samples	DPPH Scavenging (%)			
	100 (ppm)	200 (ppm)	300 (ppm)	400 (ppm)
TBHQ	81.20[a]	87.50[a]	93.60[a]	97.20[a]
mango seed	42.20[c]	60.01[d]	72.30[d]	80.30[c]
mango peel	40.60[d]	60.00[d]	70.90[e]	78.10[d]
Onion skin	41.90[c]	61.50[c]	73. 50[c]	78.19[d]
black rice bran	46.90 [b]	64.30 [b]	74.60 [b]	82.90[b]
LSD	**	**	**	**

Each value is an average of three determinations.

Values followed by the same letter in columns are not significantly different at P<0.05.

*= Significant; **= high Significant; NS= No Significant.

Identification of polyphenolic compound of agro-industrial by-products methanol extracts.

The aforementioned set of experiments relevant to the antioxidant efficiency of the total polyphenols extracts of agro-industrial by-products (mango seed kernel, mango peel, onion skin and black rice bran) and demonstrated that the total polyphenols compounds possessed remarkable antioxidant activity. Therefore, it is quite necessary to characterize the phenolic compounds of total polyphenols extracts. High performance liquid chromatography (HPLC) was used for the qualitative and quantitative determination of total polyphenols. Table (5) indicated that, Salicylic, Chtechin and Protocatechuic acids (60.7, 51.7 and 46.1 mg/100g respectively) were the major phenolic compounds presented and identified in Mango seed kernel. In addition, Salicylic, EL lagalic and mangifern acids (74.9, 47.3, and 42.7 mg/100g respectively) were the major phenolic compounds presented and identified in Mango peel. while, Benzoic, Caffeic and Catechol acids (46.8, 40.1, and 39.4 mg/100g respectively) were the major phenolic compounds presented and identified in Onion skein. Ferulic, p-coumaric and Caffeic acids (164.3, 32.1, and 25.4 mg/100g respectively) were the major phenolic compounds presented and identified in black rice bran These result agree with Salem *et al.* (2018).

Antioxidant activity of phenolic compounds:

Effect of antioxidant activity for phenolic compounds extracted from agro-industrial by-products on blend oils (mixture with sunflour and soyabean oils) is shown in Table (6). The effect of various concentrations of phenolic compounds extracted from agro-industrial by-products and TBHQ at 200 ppm as antioxidant on the development of peroxide value of blended oils during 5 days of storage at 60^{o}C. It is evident from these results that, a continuous increase in peroxide value of blend oil with the increasing of storage times for all the samples.

Peroxide value of blend oil without additives (control) was increased rapidly after 5 days and slowly increased in samples with 200 ppm TBHQ and 400 ppm phenolic compounds extracted from agro-industrial by-products, as the concentration of antioxidant increased the inhibitory effect on peroxide value increased. However after 5 days of storage at 60C, peroxide value were 9.23, 8.91 and 8.68; 9.36, 9.00 and 8.75: 9.47,9.09 and 8.86 and9.27, 8.92 and 8.66

meq/kg-1 for blend oil treated with 100, 200 and 400 ppm of phenolic compound extracted from, Mango seed kernel, mango peel; onion skin and black rice bran respectively. Whereas, the corresponding value were 19.10 and 9.22 meq/kg-1 at (control) without additives and 200 ppm concentration of TBHQ respectively. On the other hand, concentration of 400 ppm of phenolic compounds extracted from agro-industrial by-products had the same effective for retarding development of peroxide value than using 200 ppm TBHQ. Therefore, adding natural phenolic compounds extracted from agro-industrial by-products either using 200 or 400 ppm as antioxidant with blend oil were more effective for decreasing the development of blend oils oxidation than using 100 ppm as antioxidant. Our results may be due to the antioxidant activity of phenolic compounds is mainly due to their redox properties, which can play an important role in adsorbing and neutralizing free radicals, quenching singlet triplet oxygen, or decomposing peroxides (Zheng and Wang 2001).

Effect of using methanolic extracts from agro-industrial by-products on peroxide value (PV) of blend oil:

The data presented in Table (7) illustrate that, peroxide value (PV) of blend oil was increased by increasing the frying hours. On the other hand, PV for oils treated by mango seed kernel, mango peel, onion skin, black rice bran phenolic extracts at 400 ppm concentration, TBHQ at 200 ppm concentration and control were increased to 19.20, 19.40, 19.80, 19.00, 20.10 and 26.00 meq/kg oil after 25 hours of frying, respectively.

Table (5): Identification of polyphenolic compounds of mango seed kernel, mango peel, onion skein and black rice bran (mg/100g).

Phenolic compounds contents	Mango seed kernel	Mango peel	Onion skein	Black rice bran
Gallic acid	23.80	7.4	4.7	0
Ferulic acid	0.35	13.2	2.35	164.3
Chtechin acid	51.7	20.8	5.4	5.0
Protocatechuic acid	46.1	-	13.6	2.3
Cinnammic acid	-	17.6	-	-
mangifern	11.0	42.7	-	-
Benzoic acid	23.0	-	46.8	-
Catechol acid	-	-	39.4	0
Caffien acid	-	11.6	27.1	22.9
EL lagalic acid	6.4	47.3	-	-
p-coumaric Acid	-	-	-	32.1
Vanilic acid	23.6	21.0	3.8	11.6
Caffeic acid	-	8.2	40.1	25.4
Chlorogenic acid	18.5	-	7.9	1.84
Syringic acid	-	-	-	0.91
Salicylic acid	60.7	74.9	17.1	-
Chrysin	-	-	-	0.67

Table (6): Effect of phenolic compounds extracted from agro-industrial by-products and TBHQ as antioxidant on peroxide value of mixture with sunflour and soyabean oils during storage at 60C for 5 days.

Storage time(h) / Concentration	Control	TBHQ	mango seed kernel			mango peel			Onion skin			black rice bran			LSD
	-	200 ppm	100 ppm	200 ppm	400 ppm	100 ppm	200 ppm	400 ppm	100 ppm	200 ppm	400 ppm	100 ppm	200 ppm	400 ppm	
0	0.79^{Ai}	0.79^{Af}	0.79^{Ag}	0.79^{Ag}	0.79^{Ag}	0.79^{Ai}	0.79^{Ag}	0.79^{Ag}	0.79^{Ah}	0.79^{Ag}	0.79^{Ag}	0.79^{Ag}	0.79^{Ag}	0.79^{Ai}	**
12	4.31^{Ag}	2.82^{Ce}	3.03^{Bf}	2.85^{Cf}	2.60^{Ef}	3.13^{Bg}	2.86^{Cf}	2.62^{Df}	3.22^{Bi}	2.97^{Cf}	2.71^{Df}	3.05^{Bf}	2.75^{Cf}	2.54^{Dh}	**
24	6.71^{Af}	3.90^{Be}	3.90^{Be}	3.60^{Ce}	3.41^{Ee}	4.00^{Bf}	3.71^{Ce}	3.52^{De}	4.10^{Bg}	3.80^{Ce}	3.60^{De}	3.89^{Be}	3.64^{Ce}	2.46^{Dg}	**
36	8.59^{Ae}	4.11^{Bc}	4.03^{Be}	3.79^{Ce}	3.68^{Ee}	4.14^{Bf}	3.91^{Ce}	3.76^{De}	4.25^{Bg}	4.00^{Ce}	3.85^{De}	4.04^{Be}	3.82^{Ce}	3.67^{De}	**
48	9.70^{Ae}	4.80Bc	4.62^{Be}	4.39^{Cd}	4.24^{Ed}	4.75^{Be}	4.52^{Cd}	4.35^{Dd}	4.85^{Bf}	4.61^{Cd}	4.44^{Dd}	4.66^{Bd}	4.43^{Cd}	4.27^{Dd}	**
60	10.99^{Ad}	5.10^{Bcd}	5.12^{Bd}	4.76^{Cd}	4.55^{Ed}	5.22^{Be}	4.88^{Cd}	4.68^{Dd}	5.31^{Be}	4.97^{Cd}	4.78^{Dd}	5.13^{Bd}	4.78^{Cd}	4.59^{Dc}	**
72	12.30^{Ac}	5.68^{Bcd}	5.68^{Bc}	5.37^{Cc}	5.28^{Ec}	5.80^{Bd}	5.49^{Ccd}	5.32^{Dc}	5.91^{Bd}	5.60^{Cc}	5.42^{Dc}	5.71^{Bd}	5..8^{Cc}	5.21^{Dc}	**
84	14.10^{Abc}	6.27^{Bc}	6.18^{Bc}	5.89^{Cc}	5.68^{Ec}	6.04^{Bd}	6.00^{Cc}	5.79^{Dc}	6.33^{Bd}	6.09^{Cc}	5.89^{Dc}	6.13^{Bc}	5.91^{Cc}	5.70^{Dc}	**
96	15.50^{Ab}	7.27Bbc	7.31^{Bb}	7.14^{Cb}	6.93Ebc	7.42^{Bc}	7.16^{Cb}	7.02^{Db}	7.50^{Bc}	7.27Cb	7.12^{Db}	7.33^{Bb}	7.09^{Cb}	6.95^{Db}	**
108	17.30^{Aab}	7.92^{Bb}	7.94^{Bb}	7.71^{Cb}	7.53^{Eb}	8.02^{Bb}	7.83^{Cb}	7.62^{Db}	8.10^{Bb}	7.92^{Cb}	7.71^{Db}	7.94^{Bb}	7.76^{Cb}	7.50^{Db}	**
120	19.10^{Aa}	9.22^{Ba}	9.23^{Ba}	8.91^{Ca}	8.68E^{a}	9.36^{Ba}	9.00^{Ca}	8.75^{Da}	9.47^{Ba}	9.09^{Ca}	8.86^{Da}	9.27^{Ba}	8.92^{Ca}	8.66^{Da}	**
LSD	**	**	**	**	**	**	**	**	**	**	**	**	**	**	

Each value is an average of three determinations.
Values followed by the same letter in columns ” small letters” and row ” capital letters” are not significantly different at P<0.05.
*= Significant; **= high Significant; NS= No Significant.
TBHQ: tetra butyled hydroxyl quinine.
Control:Blend oil without antioxidants.

Table (7): Effect of polyphenolic extracts and TBHQ on peroxide value (PV) during the deep frying of blend oil.

Treatments / Frying time (hr)	Control	TBHQ (200 ppm)	Antioxidant extracted from agro-industrial by-products at 400 ppm conc.				
			mango seed kernel	Mango peel	Onion skin	black rice bran	
	Peroxide value (meq/kg oil)						
0	5.80^{Af}	5.80 ^{Af}	5.80^{Af}	5.80 ^{Af}	5.80^{Af}	5.80^{Af}	-
5	12.10^{Ae}	8.60^{Be}	8.40 ^{Be}	8.30^{Be}	8.55^{Be}	8.40 ^{Bd}	*
10	15.30^{Ad}	9.40^{Bd}	9.50^{Bd}	9.40^{Bd}	9.80^{Bd}	9.00^{Bc}	*
15	18.10^{Ac}	12.11^{Bc}	11.40^{Cc}	11.70^{Cc}	12.00^{Bc}	11.00^{Dc}	*
20	19.20^{Ab}	16.30$^{B b}$	15.80^{Bb}	15.70$^{B b}$	16.00^{Bb}	15.50 ^{Bb}	*
25	26.00^{Aa}	20.10^{Ba}	19.20 ^{Ba}	19.40 ^{Ba}	19.80^{Ba}	19.00^{Ba}	*
	**	**	**	**	**	**	LSD

Each value is an average of three determinations.
Values followed by the same letter in columns ” small letters” and row ” capital letters” are not significantly different at P<0.05.
***= Significant; **= high Significant; NS= No Significant.**
TBHQ: tetra butyled hydroxyl quinine.
Control: Blend oil without antioxidants.

Black rice bran phenolic extract had the highest activity in increasing the thermal oxidation. These results are consistent with findings of Upadhyay, *et al.* (2017) and Salem *et al.* (2018), who reported that lipid peroxides were significantly reduced by the addition of antioxidants in thermal processed oil.

Effect of using methanolic extracts from agro-industrial by-products on Thiobarbituric acid (TBA) of blend oil:

There are two stages of oil oxidation, i.e., the first stage is the formation of hydro peroxides and the second one is the decomposition of hydroperoxides to produce secondary oxidation products which could be react with TBA reagent to produce coloured compounds (Orthoefer *et al.,* 1996). Thiobarbituric acid (TBA) of fresh and fried blend oil was determined and the results are presented in Table (8). The rates of TBA values were rapidly increased with increasing the frying period compared to control.

Compared to heated control (8.0 mg malonaldhyde/kg oil) for 25 frying hours. All antioxidant extracts and TBHQ decreased the TBA value to 3.20, 3.30, 3.50, 3.0 and 3.60 mg malonaldhyde /kg oil, for mango seed kernel, mango peel, onion skin, black rice bran phenolic extracts at 400 ppm and TBHQ at 200 ppm respectively. Generally, Table (8) also cleared that, black rice bran extract was more effective as antioxidant than those of the other studied by-products and TBHQ. Similar results were obtained by Devi *et al.* (2007) who showed that, the rice bran (RB) extracts were stable at high temperatures and therefore capable of protecting soybean oil against oxidation even at elevated temperatures.

Table (8): Effect of polyphenolic extracts and TBHQ on thiobarbituric acid (T.B.A) during the deep frying of blend oil.

Treatments / Frying time (hr)	Control	TBHQ (200 ppm)	Antioxidant extracted from agro-industrial by-products at 400 ppm conc.				
			mango seed kernel	Mango peel	Onion skin	black rice bran	
	TBA (mg malonaldhyde/kg oil)						
0	0.70^{Ae}	0.70^{Ad}	0.70^{Ad}	0.70^{Ad}	0.70^{Ad}	0.70^{Ac}	
5	1.87^{Ad}	0.63^{Bd}	0.61^{Bd}	0.61^{Bd}	0.63^{Bd}	0.64^{Bc}	*
10	2.82^{Ac}	0.78^{Bd}	0.71^{Bd}	0.78^{Bd}	0.74^{Bd}	0.73^{Bc}	*
15	3.87^{Ab}	1.64^{Bc}	1.58^{Bc}	1.63^{Bc}	1.64^{Bc}	1.60^{Bb}	*
20	7.85^{Aa}	3.00^{Bb}	2.83^{Bb}	2.90^{Bb}	2.90^{Bb}	2.85^{Ba}	*
25	8.00^{Aa}	3.60^{Ba}	3.20^{Ba}	3.30^{Ba}	3.50^{Ba}	3.00^{Ba}	*
	**	**	**	**	**	**	LSD

Each value is an average of three determinations.

Values followed by the same letter in columns " small letters" and row " capital letters" are not significantly different at P<0.05.

*= Significant; **= high Significant; NS= No Significant.

TBHQ: tetra butyled hydroxyl quinine.

Control Blend oil without antioxidants.

CONCLUSION

From the previous results, it could be concluded that, the antioxidative activity of black rice bran methanolic extracts was greater than those of Mango seed kernel, mango peel and onion skin. The use of methanolic extracted from agro-industrial by-products could be added at levels of 400 ppm to increase the heat stability of oils and in the same time possessed no hazard effect on human being health.

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تحسين ثبات الزيوت أثناء القلي العميق باستخدام مضادات الأكسدة الطبيعية المستخرجة من المنتجات الثانوية الصناعية

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الملخص العربى

أجريت هذه الدراسة بهدف الحصول على بعض المركبات الفينولية المضادة للأكسدة الطبيعية المستخلصة من بعض المنتجات الثانوية للصناعات الزراعية (نواة بذور المانجو ، قشور المانجو ، قشر البصل ونخالة الأرز الأسود) وإمكانية استخدامها كمضادات أكسدة طبيعية بالمقارنة بمضادات الأكسدة الصناعية (رباعى بيوتيل هيدروكس كينون) بإضافتها إلى زيت خليط (زيت عباد الشمس المكرر 75 ٪ - وزيت الصويا 25 ٪) أثناء تحمير البطاطس على فترات بمعدل 5 ساعات يوميا لمدة تصل إلى 25 ساعة.

وقد أظهرت النتائج أن الميثانول كان أفضل مذيب لاستخلاص المواد المضادة للأكسدة .و كانت المركبات الفينولية المستخلصة بواسطة الميثانول اعلى من المذيبات المستخدمة وكانت فى بذور المانجو ، قشور المانجو و قشور البصل ورجيع الكون الأسود هى 6.54 - 5.40 - 5.10 –6.80 ملليجرام لكل جرام على التوالى وبناءا علية تم استخدام الميثانول لاستخلاص المواد المضادة للاكسدة ا للازمة لاستكمال باقى التجارب.

واظهرت النتائج ان المستخلص الميثانولى لرجيع الكون الأسود يملك اعلي نسبه نشاط مضاد للاكسدة مقارنة بالمستخلصات الاخرى بسبب محتواه العالي من المركبات الفينولية.

وبتفريد المركبات الفينولية لمستخلصات المخلفات السابقة الذكر وجد ان احماض Ferulic, p-coumaric and Caffeic acids هى اهم المركبات الفينولية لرجيع الارز الاسود وكانت 164.3 - 32.10 - 25.40 ملليجرام لكل 100جرام على التوالى بينما كانت احماض Salicylic, Chtechin and Protocatechuic acids هى اهم المركبات الفينولية لبذور المانجو وكانت (60.7 - 51.70 - 46.10) ملليجرام كل 100جرام على التوالى.

ازدادت قيمة البيروكسيد لزيت الخليط بدون إضافات (الكنترول) معنويا بعد 5 أيام من التخزين عند 60درجة مئوية فى حين لوحظ معدل زيادة اقل في العينات مع 200 جزء في المليون من TBHQ و 400 جزء في المليون من المركبات الفينولية المستخرجة من المنتجات الثانوية الصناعية .ارتفعت قيم البيروكسيد و TBA لزيت الخليط تدريجياً مع زيادة وقت التحمير بالاضافه لذلك كان مستخلص نخالة الأرز الأسود أكثر فعالية كمضاد للأكسدة من تلك الموجودة في المنتجات الثانوية الأخرى عند 400 جزء في المليون و TBHQ عند 200 جزء في المليون.

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