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Exploration of Fruit Peels as a Natural Antioxidants for Edible Oil Rancidity Reduction

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ABSTRACT

Present investigations deal with the study of natural antioxidant potential in rancidity reduction of edible oil. Although in India, various enriched and fortified oil brands are available, rancidity of the oil is still unresolved challenge. Negative side effect of synthetic Antioxidant is a reason to study natural antioxidant as a safer alternative to decline free radical in the body. (Sen *et al*., 2010). The main objective behind this study is to enhance oxidative stability of sunflower oil (SFO) and soybean oil (SBO). Pomegranate Peel Extract (PPE) and Orange peel Extract (OPE) being a potential antioxidant source is incorporated in the blended edible oil, Sunflower and Soybean oil (70:30 proportion). As per the available literature studies the 1 gm and 2 gm PPE peel powder and OPE powder was decided to use for present investigation. Hence 1 gm and 2 gm peel powder of both the fruits was added in 30ml of blended oil. Hydroxytoluene BHT 200 ppm was used as standard in this study. The oil samples were and stored in clear amber colored glass bottles. Blend oil was used as negative control sample), Blend oil with 200 PPM BHT was used as positive control. Each 30ml of the ready sample was sited in a hermetic dark brown glass bottle and bottles were stored at a room temperature for four months. After each month changes in rancidity was evaluated by determining Free fatty acid value,(FFA) peroxidase value (PV) and Iodine value.(IV).The obtained resulted underlined the potential of OPE and PPE in the edible oil rancidity reduction and hence can be proposed for its application in edible oil to avoid rancidity.

INTRODUCTION

Present investigations deal with the study of natural antioxidant potential in rancidity reduction of edible oil. Although in India, various enriched and fortified oil brands are available, rancidity of the oil is still unresolved challenge. Negative side effect of synthetic Antioxidant is a reason to study natural antioxidant as a safer alternative to decline free radical in the body (Sen *et al*., 2010). In general, natural antioxidants are found in fruits, vegetables, seeds, herbs, spices, and herbal plants. Utilization of these antioxidants especially from the fruit waste would be the cost effective method of mitigating the oxidative rancidity of oils. Natural antioxidants application for reduction of rancidity is also widely experimented idea (Othón-Díaz *et al.,* 2023). Next level of thought process based on utilization of fruit peels (natural herbs) antioxidant potentials has also rightly linked to advance the research on cost effective natural antioxidant source to deal with oil rancidity challenge (Kumar *et al.,* 2015) Due to their high antioxidant properties, pomegranate (*Punica granatum* L.) peels and Orange Peels have been investigated as potential sources of antioxidants. Few research have examined the use of food wastes to stabilize edible oils, despite the fact that these by-products have substantial antioxidant activity. Peels are the amusing foundations of phenolic compounds with antioxidant activities. The goal of the current study was to assess the antioxidant efficiency of Pomegranate peel Extract (PPE) and Orange Peel Extract (OPE) as natural antioxidants for enlightening the oxidative stability of refined bleached deodorized (RBD) sunflower and soybean oils. (Islam M. A.I *et al.,* 2018). Sunflower oil and soybean oil are the most popular types of edible oil used for

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cooking in Indian households, according to a poll done in April 2022. (Kanimozhi S, 2023) hence focused for study in present investigation.

MATERIALS AND METHODOLOGY

Materials

Ingredients

RBD Sunflower oil and Soyabean oil of Saffola band, were procured from local market near Loni kalbhor , Pomegranate peel extract of Citokain brand was purchased from Pune city market .30 ml of amber color glass bottles were also purchased from local market.

Chemicals: All the chemicals required for the experimentation were purchased from Lobo chemicals.Pune.
Packaging material: Packaging materials such as, 30 ml of amber color glass bottles, LDPE (Low Density Polyethylene) Pouches required to store the developed product were sourced from the local market Pune

Methodology

1. Preparation of Oil blend and experiment design

In order to dissolve the pomegranate peel and orange peel crude extracts in abs ethanol for proper dispersion in to sunflower and soybean oils., the 1 gm and 2 gm weighed proportion of both peels were dissolved in to the 5 ml abs ethanol and added to preheated (50°C) RBD sunflower and soybeanoil of (70:30) Proportion. After adding peel powder, oil samples were agitated for 30 min at 50°C for dispersion. Negative control (without antioxidant addition) and Positive control (with BHT in the limit 200PPM)) were set to obtained meaningful results. Each 30ml of the all the prepared sample, negative and positive control bottles containing 30 ml sample was placed in an airtightdark brown glass bottle. Storage study was carried out at Room Temperature for 24 days and were periodically analyzed at different intervals.

Independent variable setup

Table: 1 Experimental set up to determine the peel extract effect in comparison with std synthetic antioxidant.

Concentration of peel powder	Antioxidants			
	Negative control (30mlof oil)	Positive control (30ml of oil)	Pomegranate peel extract (30ml of oil)	Orange peel extract (30 mlof oil)
1gm	_	1gm	1gm	1gm
2gm	_	2gm	2gm	2gm

2. Determination of Free fatty acid content

To determine the Free fatty acid value, 10gm of oil sample was weighed and Dissolved in hot 100ml of neutralized ethanol and titrated using 0.1 N KOH using phenolphthalein as an indicator. Shook vigorously during titration, titrated until pale pink color last longing for 10sec appears. . (S.K. Thimmaiah, 2004) FFA % = ml of alkali × N of alkali × 56.1/ wt. of sample (g).The free fatty acid of the sample was determined using titration method.

2. Determination of Peroxide Value

In 250 mL stoppered conicalflask 10 gm (±10 mg) sample was weighed and 30 mL acetic acid chloroform solvent mixture was added and spin to dissolve. Using Mohr's pipette 0.5 mL saturated potassium iodide solution was added to the conical flask. Mixture was incubated for one minute in dark with infrequent shaking, and 30 mL of water was added gradually which is further titrated with 0.1 N sodium thiosulphate solution with strong shaking until yellow colour is nearly vanished. About 0.5 mL starch solution was added as indicator and continued titration by vigorously shaking to release chloroform layer until blue color disappeared. (S.K. Thimmaiah, 2004) Peroxide value expressed as mill equivalent of peroxide oxygen per kg sample (meq/kg) byusing formula:

Peroxide value = Titre × N × 1000 / wt. of sample

3. Determination of Iodine Value

0.2 gm. of oil dissolved in 10ml of carbon tetra chloride. The flask was rotated gently to mix the content thoroughly. Then 20 ml of 10% Potassium iodide solution was diluted by adding 200 ml of water. The titration was carried out with standard thio- sulphate solution using starch as an indicator. To calculate iodine number. The blank without oil was used to obtained blank value.(S.K. Thimmaiah, 2004)

Iodine value = 12.69(BS) N/WWhere,
B = ml of standard sodium thiosulphate solution requisite for the blank

S = ml of standard sodium thiosulphate solution requisite for the Sample
N = Normality of the standard sodium thiosulphate solution
W = Weight in g of the sample

4.RESULT AND DISCUSSION

4.1 Effect of peel extract on free fatty acid content of edible oil

Table: 4.1 Free fatty acid value (%) in blended oil of Sunflower and soybean (70:30) proportion

Samples	Free fatty acid value (%)				
	Initial	1st month	2ND month	3rd. month	4the month
Negative Control	0.3	0.37	0.4	0.47	0.5
Positive control (BHT 200ppm)	0.29	0.34	0.37	0.4	0.43
PPE 1gm	0.29	0.33	0.35	0.37	0.39
OPE1gm	0.29	0.34	0.36	0.38	0.4
PPE2gm	0.28	0.3	0.32	0.34	0.34
OPE2gm	0.29	0.33	0.34	0.35	0.36
SE±	0.0064	0.003	0.006	0.02	0.006
CD%5	NS	0.011	0.02	NS	0/021

PPE: Pomegranate peel extract, BHT: Butylated Hydroxyl Toluene, OPE: Orange peel extract
All the values are average of three readings ±sign indicates standard error

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*Standard ANNOVA is triplicate of three values, NS: non-significant

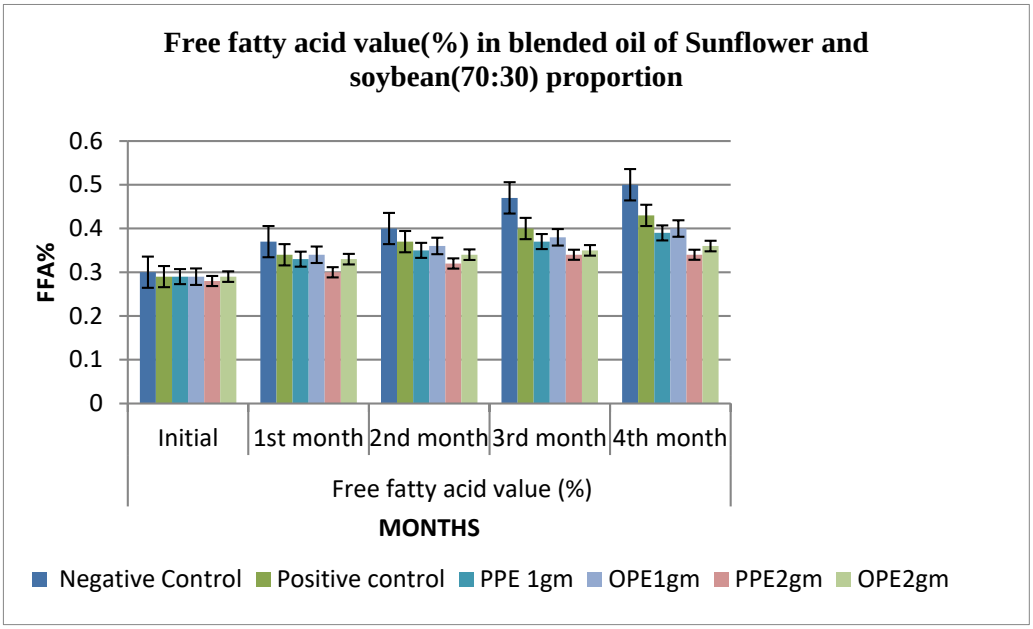

Fig: 4.1 Free fatty acid value (%) in blended oil of Sunflower and soybean (70:30) proportion
OPE: Orange peel extract, PPE: pomegranate peel extract

One of the most important factors regulating lipid oxidation is the degree of unsaturation of its fatty acids. At various rates, air exposure oxidizes fats, oils, and lipid-containing foods, resulting in sensory and nutritional degradation. Natural compounds with varied chemical structures that exhibit antioxidant activity may also have an effect on the oxidative rate. Lipid hydrolysis is another type of lipid alteration that results in the formation of free fatty acids (FFA) via chemical or enzymatic activity (Dyer *et al.*, 1959). Unsaturated fatty acids have lesser stability than saturated fatty acids. As a result, they're more prone to rancidity. Rancidity is the oxidation of lipids caused by hydration (water), oxidation (oxygen), metallic atoms, or microbes (Wójcicki *et al.*, 2015). Rancidity frequently produces an unusual aroma and/or taste. The current study sought to assess the antioxidant efficiency of fruit peel powder as natural antioxidants for comforting the oxidative stability of refined bleached deodorized (RBD) sunflower and soybean oils. The degree of oil breakdown is determined by the free fatty acid concentration. FFA is produced by the hydrolysis of triglycerides in oil and is considered a primary indicator of oil rancidity. Table 4.2 shows the extent of FFA changes in sunflower and soybean oils kept with PPE, OPE, and BHT. A steady rise in FFA content was notified during storage of sunflower oil at room temperature for 4 months. Initially, the FFA concentration of the oil without antioxidant (control) was 0.3%. After 4 months of storage, the FFA content was 0.5%. According to table 4.2 the negative control sample had a 0.67% rise in free fatty acid level. Following the addition of the synthetic antioxidants listed in Table 4.2. From obtained results the potential of BHT in rancidity reduction is quite confirmed .The initial FFA percentage of synthetic antioxidant-containing oil was 0.29%, and after 4 months of storage, the FFA content was 0.43%. The percentage increase in FFA content of positive control sample was 0.48%. A similar investigation was conducted on the oxidative stability of edible oils using pomegranate and orange peel extracts. The researchers' major goal was to improve the oxidative stability of soybean oil (SBO) and sunflower oil (SFO). Pomegranate and Baladi

orange peel extracts in aqueous ethanol at concentrations of 800 and 1,200 ppm were used as natural antioxidants in contrast to butylated hydroxytoluene (BHT). Their antioxidant activity was measured after 24 days of storage at 65°C (Islam *et al.,* 2018). However, in our study, we employed pomegranate peel and orange peel extract at 1gm and 2gm proportions as a natural antioxidant in per 30 ml of oil, and their antioxidant activity were assessed after 30 days of room temperature storage. The addition of OPE and PPE extract resulted in a considerable decrease in FFA content oil during room temperature storage. It is evident from the results in Table 4.2 that, as the concentration of OPE and PPE increased, the inhibitory effect on FFA content augmented significantly. Initial FFA of oil containing OPE 2gm was 0.29%, After 4 months of storage FFA was 0.36%.the percentage rise in FFA content of OPE 2gm after 4 months of storage was 0.24%. Addition of PPE 2gm extract is more significant than other antioxidant from the result in table. According to the table 4.2 the initial FFA of oil containing PPE 2gm was 0.28%, and after 4 months of storage at room temperature, it was 0.34%. These data clearly show that PPE 2gm added oil samples result in the lowest percent increase in FFA of 0.22%. Because Pomegranate peel phenolic content is associated with antioxidant activity due to their redox characteristics, which permit them to function as reducing agents, hydrogen donors, and singlet oxygen quenchers. Pomegranate peel extract is rich in strong antioxidants the most important phenolic acids are ellagic, gallic, vanillic, caffeic, ferulic, cinnamic, and coumaric acids, as well as a variety of flavonoids (anthocyanins, catechins, and other complex flavonoids) and hydrolysable tannins (Li *et al*., 2016).

4.2 Effect of peel extract on peroxide value of edible oil

Table: 4.2 Peroxide value (meq/kg) in blended oil of Sunflower and soybean (70:30) proportion

Samples	Peroxide value(meq/kg)				
	Initial	1st month	2nd month	3rd month	4th month
Negative Control	5	5.73	6.03	6.23	6.33
Positive control (BHT 200ppm)	5	5.6	5.7	5.9	6
PPE 1gm	5.1	5.3	5.4	5.8	5.6
OPE1gm	5.1	5.5	5.6	5.7	5.8
PPE2gm	5	5.2	5.3	5.5	5.5
OPE2gm	5.1	5.4	5.5	5.7	5.7
SE±	0.11	0.06	0.07	0.10	0.08
CD%5	NS	NS	NS	NS	0.24

PPE: Pomegranate peel extract, BHT: Butylated Hydroxyl Toluene, OPE: Orange peel extract

All the values are average of three readings ±sign indicates standard error

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*Standard ANNOVA is triplicate of three values, NS: non-significant

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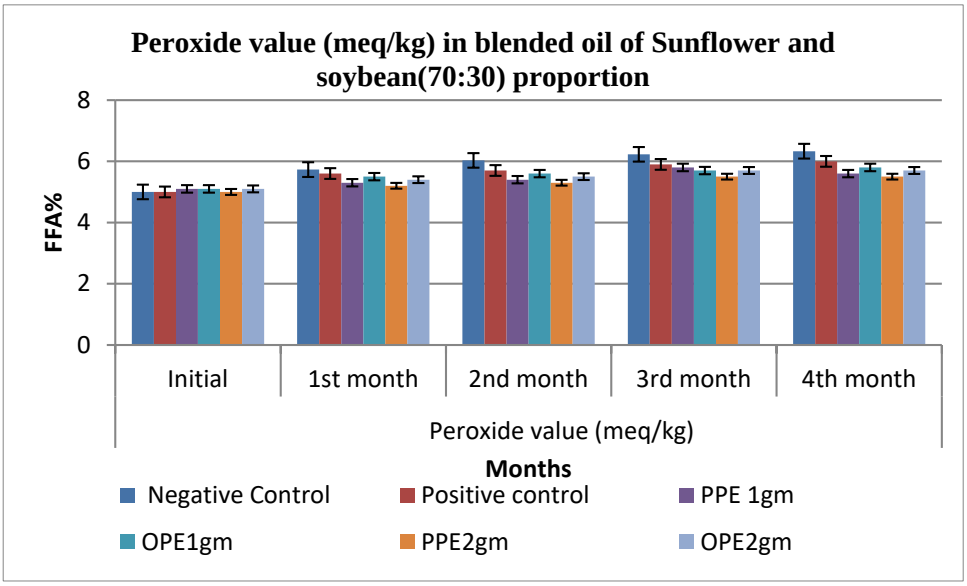

Fig: 4.2 Peroxide value (meq/kg) in blended oil of Sunflower and soybean (70:30) proportion OPE: Orange peel extract, PPE: pomegranate peel extract

The concentration of peroxides and hydro peroxides generated during the early phases of lipid oxidation is measured by PV. PV is a good predictor of oil's principal oxidation products (Wójcicki et al., 2015). In all samples, the PV increased continuously as the storage period increased. The production of hydro peroxides is responsible for the increase in PV. Oils with a high degree of unsaturation are more prone to oxidation than saturated oils (Kaleem *et al.*, 2015) As a result, unpleasant odors and flavors are produced. The PV value is calculated to study the oxidative beginning rancidity of oils. Table 4.3 shows the extent of PV changes in sunflower and soybean oils kept with PPE, OPE, and BHT. A gradual increase in PV content was observed during storage of sunflower oil at room temperature for 4 months. Initially, the PV concentration of the oil without antioxidant (control) was 5 meq/kg After 4 months of storage; the PV content was 6.33meq/kg. According to the obtained results, the negative control sample had a 0.27% rise in peroxide value level. Changes in PV content during oil storage at room temperature following the addition of the synthetic antioxidants listed in Table 4.3 These findings indicate that the addition of BHT slowed the development of rancidity in oil. The initial PV of synthetic antioxidant-containing oil was 5 meq/kg and after 4 months of storage, the PV content was 6 meq/kg. From table 4.3 the percentage increase in PV content of positive control sample was 0.2%. A similar investigation was conducted on the oxidative stability of edible oils using pomegranate and orange peel extracts. The researchers' major goal was to improve the oxidative stability of soybean oil (SBO) and sunflower oil (SFO). Pomegranate and orange peel extracts in aqueous ethanol at concentrations of 800 and 1,200 ppm were used as natural antioxidants in contrast to butylated hydroxytoluene (BHT). Their antioxidant activity was measured after 24 days of storage at 65°C (Islam *et al.*, 2018). However, in our study, we employed pomegranate peel and orange peel extract at 1gm and 2gm proportions as a natural antioxidant in per 30 ml of oil, and their antioxidant activity were assessed after 30 days of room temperature storage. The addition of OPE and PPE extract resulted in a considerable decrease in PV content oil during room temperature storage. It is evident from the results in Table 4.3 that, as the concentration of OPE and PPE increased, the inhibitory effect on PV content increased

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considerably. Initial PV of oil containing OPE 2gm was 5.1 me/kg, after 4 months of storage PV was 5.8 meq/kg. The percentage. Rise in FFA content of OPE 2gm after 4 months of storage was 0.12%. Addition of PPE 2gm extract is more significant than other antioxidant from the result in table. According to the table 4.3 the initial PV of oil containing PPE 2gm was 5 meq/kg, and after 4 months of storage at room temperature, it was 5.5 meq/kg. These data clearly show that PPE 2gm added oil samples result in the lowest percent increase in PV of 0.1%. Because Pomegranate peel phenolic content is associated with antioxidant activity due to their redox characteristics, which allow them to operate as reducing agents, hydrogen donors, and singlet oxygen quenchers (Smaoui et al., 2019). Pomegranate peel extract is rich in strong antioxidants the most important phenolic acids are ellagic, Gallic, vanillic, caffeic, ferulic, cinnamic, and coumaric acids, as well as a variety of flavonoids (anthocyanins, catechins, and other complex flavonoids) and hydrolyzable tannins. Free radicals induce oxidative stress by seeking stability by electron pairing with biological macromolecules such as proteins and lipids, and lipid peroxidation occurs. Pomegranate peel extract has a significant amount of phenolic component, which has the capacity to scavenge free radicals during the oxidation process, which is why the hyperoxide generation in the treated oil sample is slowed (Smaoui et al, 2019)

4.3 Effect of peel extract on Iodine value of edible oil

Table: 4.3 Iodine value (gm. iodine/100gm oil) in blended oil of Sunflower and soybean (70:30) proportion.

Samples	Iodine value(gm iodine/100gm oil)				
	Initial	1st month	2nd month	3rd month	4th month
Negative Control	132	134	138	140	142
Positive control (BHT 200ppm)	132	130	124.2	122.4	120.3
PPE 1gm	132	124	122	120	118
OPE1gm	132	126	124	122	120
PPE2gm	132	119	121	119	117
OPE2gm	132	121	123	121	119
SE±	1.5	0.3	0.3	1.3	0.6
CD%5	NS	1.08	1.1	4.2	2.0

PPE: Pomegranate peel extract, BHT: Butylated Hydroxyl Toluene, OPE: Orange peel extract

All the values are average of three readings ±sign indicates standard error

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*Standard ANOVA is triplicate of three values, NS: non-significant

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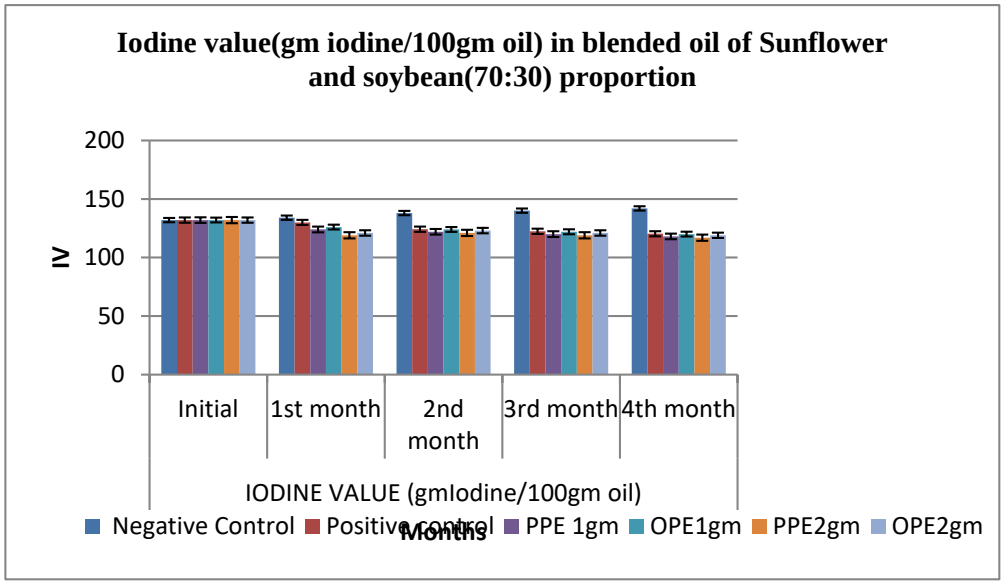

Fig: iodine/100gm oil) in blended oil of Sunflower and soybean (70:30) proportion

OPE: Orange peel extract, PPE: pomegranate peel extract

Iodine number is a portion of the degree of oil, fat, or wax unsaturation. It is the quantity of iodine, in gram, that is taken up by 100 gram of the oil (Yildiz et al, 2019). Unsaturated oils because of double or triple bonds reacts with iodine and shows iodine value while saturated oils, fats, and waxes absorb no iodine and so have no iodine value. The greater the iodine value, the oil is more reactive, less stable, softer, and more vulnerable to oxidation and rancidification the oil. Titration is used to quantify the quantity of iodine that remains unreacted when a known excess of iodine, commonly in the form of iodine monochloride, is allowed to react with a known weight of oil. Oils with high iodine levels have a higher concentration of highly unsaturated fatty acids, which are susceptible to quick breakdown events such as autoxidation or polymerization (Ruiz Ruiz *et al.*, 2017)

Table 4.4 shows the extent of IV changes in sunflower and soybean oils kept with PPE, OPE, and BHT. A gradual increase in IV content was observed during storage of sunflower oil at room temperature for 4 months. Initially, the IV concentration of the

4.3 Iodine value (gm. oil without antioxidant (control) was 132gm/100gm oil. After 4 months of storage, the IV content was 142gm/100gm oil. According to Table 4.4, the negative control sample had risen in free IV during storage. Changes in IV content during oil storage at room temperature following the addition of the synthetic antioxidants listed in Table 4.4 These findings indicate that the addition of BHT slowed the development of rancidity in oil. The initial IV of synthetic antioxidant-containing oil was 132gm/100gmoil and after 4 months of storage, the IV content was 120.0gm/100gm oil. From Table 4.4 the percentage decrease in IV content of positive control sample was 0.09%. A similar investigation was conducted on the oxidative stability of edible oils using pomegranate and orange peel extracts by Islam *et al.*, They worked on to improve the oxidative stability of soybean oil (SBO) and sunflower oil (SFO). Pomegranate and orange peel extracts in aqueous ethanol at concentrations of 800 and 1,200 ppm were used as natural antioxidants in place of Butylated hydroxytoluene (BHT). Their antioxidant activity was measured after 24 days of storage at 65°C. However, in our study, we employed pomegranate peel and orange peel extract at 1gm and 2 gm proportions as a natural antioxidant and their antioxidant activity were assessed after 30 days of room temperature storage. The addition of OPE and PPE extract resulted in a

considerable decrease in IV content oil during room temperature storage. From table 4.6 the positive correlation for peel powder and inhibitory inhibitory effect on IV content was obtained. Initial IV of oil containing OPE 2gm was 132gm/100gmoil, After 4 months of storage IV was 117gm/100gmoil. As depicted in table 4.4 the percentage decrease in IV content of OPE 2gm after 4 months of storage was 0.10%. Addition of PPE 2gm extract is more significant than other antioxidant. According to the table 4.4 the initial IV of oil containing PPE 2gm was 132gm/100gmoil, and after 4 months of storage at room temperature, it was 119gm/100gmoil. These data clearly show that PPE 2gm added oil samples result in the lowest percent decrease in IV of 0.13%. Because Pomegranate peel phenolic content is associated with antioxidant activity owing to their redox structures, which allow them to operate as reducing agents, hydrogen donors, and singlet oxygen quenchers. Pomegranate peel extract is rich in strong antioxidants the most important phenolic acids are ellagic, gallic, vanillic, caffeic, ferulic, cinnamic, and coumaric acids, as well as a variety of flavonoids (anthocyanin's, catechins, and other complex flavonoids) and hydrolyzable tannins (Li *et al.*, 2016).

CONCLUSION

The current research showed the efficacy of Pomegranate peel extract and orange peel exact for enhancing the oil stability even at room temperature. It reduces Peroxide value and free fatty acid value of oil sample there is non-significant change in iodine value. These findings have revealed the potential of natural antioxidants obtained from fruit waste as replacer of synthetic antioxidants. Thus the said research explores the low cost natural antioxidants applications in resolving oil rancidity as a cheapest technology to be focused by researchers.

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