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REFINING OF HIGH-FREE FATTY ACID OLIVE OIL

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ABSTRACT

The objective of the present work was to improve the quality of high-free fatty acid olive (HFFAO) oil. Normal silica gel (SG) adsorbent was used by applying filtration and stirring techniques. On the other side, chemical treatments with alkali using NaOH and $Ca(OH)_2$ were conducted to neutralize the acidity of HFFAO. Untreated and treated HFFAO oil samples were stored under accelerated conditions for 30 days. The progress of oxidation at 60°C was followed by measuring the formation of oxidative products [peroxide value (PV) and *p*-anisidine value (AnV)], total phenolic compounds (TPC) and recording radical scavenging activity (RSA) toward 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical. The results indicated that SG and alkali treatments were effective in reducing the acidity of HFFAO oil. Generally, alkali treatments reduced the acid value of HFFAO oil, while treatments with SG induced variable degrees of improvements in HFFAO oil acidity. Alkali treatments resulted in increasing the PV levels to 35 and 28 meq peroxide kg^{-1} oil for HFFAO treated with soda and lime, respectively. The corresponding improvement in the PV reduction (%) for HFFAO oil using SG was in the range of 10.5% to 47.3%.Treatments with SG or alkali resulted in reduction of AnV, whereas filtration with SG had a remarkable effect on AnV. Levels of TPC were reduced (*ca.* 70%) with alkali treatments, while treatments with SG also resulted in reduction (ca. 22-48%) in the TPC levels. Antiradical properties of HFFAO oils were compared using stable DPPH free radicals. After 60 min incubation with DPPH, 78% of DPPH radicals were quenched by control sample, while HFFAO oils treated with SG or alkali were able to quench from 48 to 56%. During autoxidation experiments the same trends of results was noted for both control and treated oils.

Keywords: High free fatty acid olive oil (HFFAO), silica gel (SG), alkali treatment, acidity, oxidation, phenolic compounds.

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INTRODUCTION

In the global economy, the production of oils and fats plays an important role. Commercial sources of edible oils and fats include oilseeds, fruit pulp, animals, and fish. Oilseeds are the major source for the production of edible oils, wherein the total world production of major oilseeds in 2004 was 380.3 million metric tons (www.soystats.com). Whatever the source, crude oil must be separated from other seed materials and refined to remove free fatty acids (FFA) and other impurities that impact on flavor, odor, and appearance. The deacidification process significantly influences the economics of vegetable oil production. The purpose of deacidification in the conventional chemical process is to remove non-glyceride impurities consisting of FFA- that contribute to bitter and soapy flavor in food- as well as significant quantities of mucilaginous substances, phospholipids and color pigments (Young *et al.*, 1994). Conventional approaches to refining include degumming, dewaxing, alkali refining, bleaching, and deodorization, are best used with low-FFA oils. Pretreatment with alkali prior to membrane filtration resulted in a very high reduction (*ca.* 90%) of FFA in the processed oils (Sen Gupta 1985 and Pioch *et al.*, 1998). These approaches, however, lead to high refining loss when applied to high-FFA oils. Therefore, several authors have proposed physical refining for high-FFA oils (Tandy *et al.*, 1984; Kim *et al.*, 1985; Cvengros, 1995 and De and Bhattacharyya, 1998). This process removes FFA along with odoriferous compounds by purging saturated steam through the oil at a high temperature under high vacuum. Physical refining, however, results in large quantities of distilled fatty acids with concomitant reduction in the quantity of the original oil, especially if the oil being processed is high in FFA content. Alternative approaches have been proposed to reduce neutral oil loss during physical refining. Liquid–liquid extraction with polar solvents (e.g., azeotropic isopropanol) is a better process for extracting FFA along with color and peroxide bodies. Treating frying oil with a mixture of gel-derived alumina and activated clay or magnesium silicate had a significant reduction in the amount of fatty acids, aldehydes, ketones and odour- and colour-forming compounds (Bhattacharyya *et al.*, 1987). Lin *et al.* (1999) used combinations of

four commonly used filter aids (Britesorb, Hubersorb, Frypowder and Magnesol) to recover the used frying oils, wherein the levels of FFA were reduced by 82.6–87.6%.

Care must be taken in the selection of filter aids because some of these substances can affect the potential stability of the fats (Yates *et al.*, 1993). Clay minerals having these properties are able to adsorb particular amount of trace metals, to reduce the components giving color and chlorophyll, to remove soap and phosphates and to have the effect of reducing FFA to a certain extent (Rossi *et al.*, 2003). Sepiolite, represented by Si_{12} Mg_8O_{30} $(OH)_4$ $(H_2O)_4$ $8H_2O$ which belongs to the group of silicate, is widely used to remove undesired components from household and industrial wastewaters and in various industrial manufacturing processes, it has not been previously tested for the purification of edible oils, such as olive, cotton, soybean, sunflower oils (Ugurlu and Kula, 2007). Degumming, neutralization, bleaching, and deodorization are typical refining steps of vegetable oil processing. The highly desirable tocopherols are reduced during soybean oil refining, and this removal reduces oxidative stability and nutritional value of the refined oil when compared with the crude oil (Jung *et al.*, 1989). Tocopherols are more volatile than the neutral triacylglycerides and can be removed with the high temperature and high vacuum of deodorization. Short exposure of the oil to heating is desirable to reduce this loss.

Virgin olive oil, which is obtained using only mechanical systems, is a foodstuff that is consumed in its crude (unrefined) form. However, a great proportion of the olive oil that is produced must be refined to render it edible. Virgin olive oil is consumed unrefined, although a great proportion of the olive oil produced has to be refined to render it edible. Refining treatments are needed to remove or reduce the content of minor substances that may affect oil quality, such as phospholipids, FFA, pigments, peroxides, traces of metals, herbicides, and volatile components. Phenolic compounds are among the substances eliminated during the different refining steps (Krishna *et al.*, 2001).

At present, three types of olive oils are intended for refining: lampante olive oil, olive pomace oil, and second centrifugation olive oil. Lampante olive oil is obtained from fruits by mechanical means, but it has undesirable organoleptic or chemical characteristics that make it unfit for consumption.

Likewise, the olive paste obtained during the dual-phase centrifugation system used for olive oil extraction is stored for months and subjected to chemical extraction with hexane to produce the traditional olive-pomace oil (Ruiz-Méndez and Dobarganes, 1999), or it can also undergo a new second centrifugation to yield a second centrifugation olive oil (Alba *et al.*, 1996). Olive-residue oil has a high percentage of FFA, ranging from 5 to 60% by weight (Nefzaoui, 1991). The elimination of FFA is the most important refining operation. Several methods to remove FFA have been developed to enhance the value of degraded vegetable oils, for example, physical refining based on distillation and chemical refining with soda (sodium hydroxide). Distillation is an effective method to neutralize vegetable oils with high acidity, but this operation is also energy intensive. Moreover, heating oils to high temperature under reduced pressure generates secondary reactions that alter their physicochemical characteristics and organoleptic properties (Cecchi, 1998).

Due to the increase in oil price and the environmental concerns about pollution coming from the incineration of certain agricultural hull wastes, the present study was carried out to improve the quality of HFFAO oil and to assess the feasibility of deacidification of the HFFAO oil using inorganic normal silica gel (SG) regeneration agent by applying filtering and stirring techniques. The efficacy of the aforementioned regeneration agent was compared and their mode of action is discussed. In addition, the objective of this study was to examine changes in qualities of HFFAO oil and treated HFFAO oil during storage under accelerated oxidation conditions. Quality assurance methods were conducted to evaluate the quality of the refined oils.

MATERIALS AND METHODS

Sources of Olive Oil and Adsorbant

Lampante high free fatty acid olive (HFFAO) oil was obtained from El-Salheya olive oil company (El-Salhya City, Sharkia Governorate, Egypt). The peroxide value of the oil was 19 meq peroxide kg^{-1} oil, and the acid value was 3 mg KOH g^{-1} oil, respectively. Silica gel (60-120 mesh) was purchased from BDH Chemicals Ltd (Poole, UK). All

solvents and reagents from various suppliers were of the highest purity needed for each application and used without further purification.

Treatment of HFFAO Oil with SG

Filtration

Silica gel was activated by heating at 120 °C for 2 h. Glass chromatographic column (50 cm × 10 cm) was filled with activated SG and HFFAO oil samples dissolved in hexane (5 g oil: 1 mL hexane) were filtered through SG. This process was repeated three times using two ratios of SG to HFFAO (1:2 and 1:3, w/w).

Stirring

Silica gel (SG) was added individually to the HFFAO oil then mechanically stirred on magnetic stirrer for 120 min at 25 °C then filtered through Whatman No. 1 filter paper. This process was repeated three times using two ratios of SG to HFFAO (1:2 and 1:3, w/w). The untreated HFFAO oil was also filtered through Whatman No. 1 filter paper.

Chemical Treatments (Neutralization) of HFFAO Oil Using NaOH and Ca $(OH)_2$

Alkali treatments using NaOH and Ca $(OH)_2$ were conducted to neutralize and modify the acidity of HFFAO. Neutralization with soda (NaOH) and lime Ca $(OH)_2$ was carried out as follow. One gram of sodium hydroxide or lime was dissolved in 1 mL distilled water then the mixture was added to 150 g olive oil and stirred for 30 min. Hexane (15 mL) was added and the mixture was stirred for 30 min. The mixture was centrifuged at 3500 rpm for 30 min and hexane was evaporated and the oil was used for further analyses.

Oxidation Experiments

Samples of HFFAO and untreated HFFAO oils were placed individually in a series of transparent glass bottles having a volume 20 mL each. The bottles were completely filled with oil and sealed. No headspace was left in the bottles. The oxidation reaction was accelerated in a forced-draft air oven T6 (Heraeus Instruments GmbH; Hanau, Germany) set at 60 ± 2 °C for up to 0, 7, 14 and 30 days. Immediately after storage period, oil samples were withdrawn for triplicate analyses.

Anaiytica! Procedures

The progress of the oxidative deterioration of the oils during storage was followed by measuring the following parameters.

Acid value

A known weight of oil sample (~ 2g) was dissolved in neutralised alcohol (50 mL) and titrated with KOH (0.1 mol L−1) according to AOAC (2000).

Peroxide value and p-anisidine value

A known weight of oil sample (~ 2g) was dissolved in 30mL chloroform:acetic acid (3:2, v/v) then 1mL freshly prepared saturated KI solution was added and the mixture vortexed for exactly 1 min. Distilled water (30mL) and starch solution (0.5 mL, 1%) were added and the liberated iodine was titrated with sodium thiosulfate (0.1 mol L^{-1}) according to AOAC (2000). *p*-Anisidine value (AnV) was measured according to the official methods of the American Oil Chemists' Society (2000, Cd 18-90).

Total phenolics

Aliquots of oil (2 g) were dissolved in *n*-hexane (5 mL) and mixed with 10 mL methanol-water (80:20, v/v) in a glass tube for two min in a vortex. After centrifugation at 3000 rpm for 10 min, the hydroalcoholic extracts were separated from the lipid phase by using Pasteur pipet then combined and concentrated *in vacuo* at 35°C until a syrup consistency was reached. The lipidic residue was redissolved in 10 mL methanol-water (80:20, v/v) and the extraction was repeated twice. Hydroalcoholic extracts were redissolved in acetonitrile (15 mL) and the mixture was washed with *n*-hexane three times (15 mL each). Purified phenols in acetonitrile were concentrated *in vacuo* at 30°C then dissolved in methanol for further analysis. Aliquots (0.2 mL) of phenolic extracts were evaporated to dryness under nitrogen. The residue was redissolved in 0.2 mL water and diluted (1:30) Folin-Ciocalteu's phenol reagent (1 mL) was added. After 3 min, 7.5% sodium carbonate (0.8 mL) was added. After a further 30 min, the absorbance was measured at 765 nm using UV-260 visible recording spectrophotometer (Shimadzu, Kyoto, Japan). Caffeic acid was used for the calibration and the results of triplicate analyses are expressed as parts per million of caffeic acid.

Radical scavenging activity (RSA) toward DPPH radical (Spectrophotometric assay)

Antiradical action of oil samples were examined by reduction of

DPPH in toluene according to Ramadan *et al.* (2006). Toluenic solution of DPPH radicals was freshly prepared at a concentration of 10^{-4} M. The radical, in the absence of antioxidant compounds, was stable for more than 2 h of normal kinetic assay. For evaluation, 10 mg of oils (in 100 µL toluene) was mixed with 390 µL toluenic solution of DPPH radicals and the mixture was vortexed for 20 s at ambient temperature. Against a blank of pure toluene without DPPH, the decrease in absorption at 515 nm was measured in 1-cm quartz cells after 60 min of mixing using UV-260 visible recording spectrophotometer (Shimadzu, Kyoto, Japan). RSA toward DPPH radicals was estimated from the differences in absorbance of toluenic DPPH solution with or without sample (control) and the inhibition percent was calculated from the following equation:

% inhibition = [(absorbance of control–absorbance of test sample)/ absorbance of control] x 100.

All results presented are mean values of at least three experiments, wherein no statistically significant difference ($P > 0.05$) was found among the experiments.

RESULTS AND DISCUSSION

Impact of Different De-Acidification Treatments on the Acid Value (Av) of HFFAO Oil

The most versatile fat chemical characteristics for the determination of olive oil quality are: acid value, peroxide value, anisidin value and phenolics content. It has been reported that humidity of the environment has been reported to be a factor affecting hydrolysis of oils (Omar *et al.*, 2003). The initial values of HFFAO oil were, acid value (3 mg KOH g^{-1} oil), peroxide value (19 meq peroxide kg^{-1} oil), anisidin value (20), wherein the total phenolics level (0.43 mg/kg as caffeic acid equivalent). These findings indicate that the HFFAO oil was characterized by high level of acidity.

Acidic changes taking place in the experiments conducted with silica gel (SG) were investigated. FFA removal profile with SG as well as alkali treatments are plotted in Fig. 1. Generally, alkali treatments with soda or lime reduced the acid value of HFFAO oil. On the other side, treatments with SG induced variable degrees of improvements in HFFAO oil quality.

Filtration technique through SG achieved more FFA removal than stirring technique. As seen in the figure, at zero time, maximum FFA removal observed with SG filtration technique (about 57.6%) when the ratio 2:1 was applied. On the contrary, nearly 21.6% FFA removal was achieved with SG stirring technique when the ratio 3:1 was applied.

During storage for 30 days under accelerated oxidation conditions at 60°C the same levels of reducing acid values of stored samples were recorded. The results demonstrated that the treatment of HFFAO oil with alkali [NaOH or Ca $(OH)_2$] greatly lowered the free fatty acid levels. The effects of filtration and stirring using SG was nearly the same during the experiment.

Impact of Different De-Acidification Treatments on the Peroxide Value (PV) of HFFAO Oil

Peroxides and hydroperoxides, the primary oxidation products, decompose to form aldehydes, ketones, acids, alcohols, hydrocarbons and other compounds.

These substances formed during thermal oxidation of oils. The products of oil degradation as defined by International Union of Pure and Applied Chemistry (IUPAC, 1987) are polar materials. The polar fraction of used oil is composed of free fatty acids, monoglycerides, oxidized triglycerides and oligomeric triglycerides. In this study, silica gel was used as an attempt to improve the quality of high free fatty acid olive oil. All treatments and regeneration adsorbents used in the present work caused an improvement in stored and treated HFFAO oil quality comparable to that of fresh oil.

The initial peroxide value of HFFAO oil was 19 meq peroxide kg^{-1} oil. Alkali treatments with soda or lime did not improve the quality of HFFAO oil in the terms of PV but resulted in increasing the PV levels to 35 and 28 meq peroxide kg^{-1} oil for HFFAO oil treated with soda and lime, respectively (Fig. 2). The corresponding improvement in the PV reduction (%) for HFFAO oil using SG of 60–120 mesh was in the range of 10.5% to 47.3%. These results demonstrated that the adsorbing efficiency of normal SG with small particle size (60–120 mesh) permitted high adsorbing capacity and very good in scavenging the peroxides of HFFAO

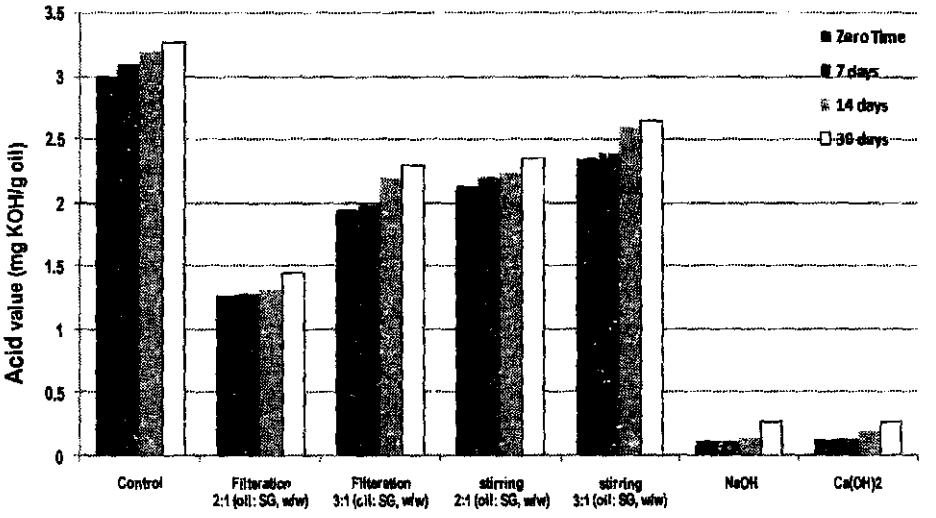


Fig. 1. Changes in acidity (AV) of untreated HFFAO and treated HFFAO oils as affected by SG and alkali treatments during oven test

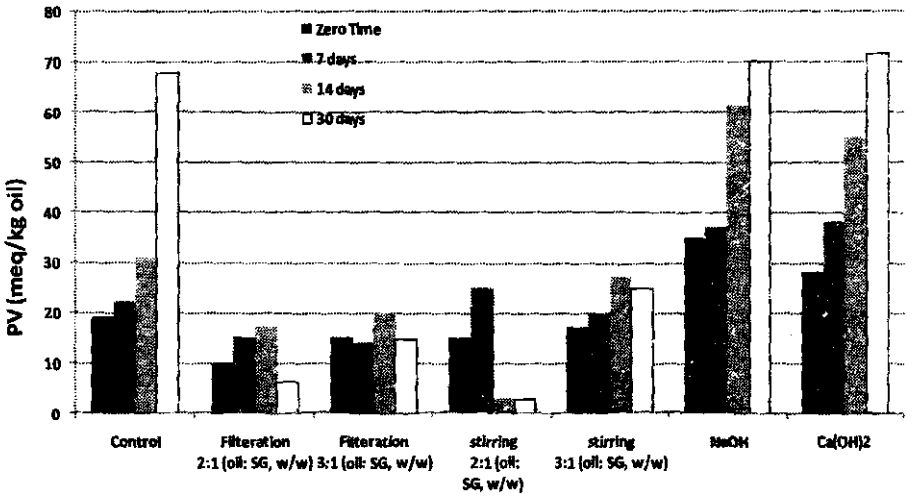


Fig. 2. Changes in the PV levels of untreated HFFAO and treated HFFAO oils as affected by SG and alkali treatments during oven test

oil. Yates *et al.* (1997) added silicates in powdered form and subsequently removed by filtration in order to regenerate the quality of used oils. In this respect, Kalapathy and Proctor (2000) prepared sodium silicate films from rice hull ash silica and mentioned that free fatty acids content gradually decreased with treatment time for all films.

The PV for the treated oils were progressively increased during storage under accelerated oxidation conditions. However, after 7 and 14 days of storage, the PV levels were increased gradually in all treated samples. PV were reduced after 30 days of storage in the samples treated with SG and this finding could be due to the volatilization of some peroxides under accelerated oxidation conditions. The efficiency of various SG:oil ratios (1:2 and 1:3, w/w) on lowering the PV of HFFAO oil was approximately the same at a certain level.

Impact of Different De-Acidification Treatments on the *P*-anisidine Value (AnV) of HFFAO Oil

The *p*-anisidine value (AnV), which measures the unsaturated aldehydes (principally 2-alkenals and 2,4-dienals) in oils, was determined by reacting *p*-anisidine with the oil in *iso*-octane and the resultant color was measured at 350 nm. The initial AnV for HFFAO oil was 20 and it could be noted that treatments with SG or alkali resulted in reduction of An (Fig. 3). In addition, filtration with SG was more active in reduction of AnV than stirring technique.

During autoxidation at 60°C in the dark (Fig. 3), treated HFFAO oils were more stable than the control oil. Here again, SG with high polarity led to a higher adsorbing capacity in removing the secondary oxidation products of HFFAO oil. However, at the end of oxidation experiment the AnV levels in treated HFFAO oils (except of oil treated with lime) were higher than control oil. Moreover, after 14 days of storage, the AnV for HFFAO oils treated by stirring with SG (3:1) reached 40 which was higher than AnV of untreaded sample at the end of oxidation experiment (Fig. 3). The results demonstrated that all treated HFFAO oils had a potent oxidative stability (OS) higher than control oil. Meanwhile, treatment with SG and alkali caused reduction in both peroxide and *p*-anisidine levels during incubation intervals for 30 days at 60°C.

Impact of Different De-Acidification Treatments on the Total Phenolic Compounds (TPC) of HFFAO Oil

Figure 4 shows the impact of different treatments on the TPC of HFFAO oils during oxidation storage.

The initial TPC in HFFAO oil was 43 mg/kg oil and the levels of TPC were highly reduced (*ca.* 70%) with alkali treatments (soda and lime). Treatments with SG also resulted in relative reduction (ca. 22-48%) in the TPC levels. During oxidation at 60°C (Fig. 4), all samples showed a gradual decrease in TPC levels, wherein the levels of TPC in SG treated HFFAO oils were higher than alkali treated oils. After 30 days of storage, the lowest level of TPC was recoded for HFFAO oils treated by stirring with SG (2:1). During oxidation at 60°C (Fig. 4), all samples showed a gradual decrease, wherein SG treated HFFAO oils were more stable than alkali treated oils. The total polyphenol content of olive oil determined colorimetrically is reduced almost to zero with refining (Vázquez *et al.*, 1973). Nergiz (1993) reported that a residual amount of total polyphenols and *o*-diphenols can be found in refined olive oils.

Impact of Different De-Acidification Treatments on the Radical Scavenging Activity (RSA) of HFFAO Oil

Interest has increased in the past few years in the free radical theory of disease causation, particularly in vascular diseases and certain forms of cancer. These developments have led to the investigation on dietary agents, the antioxidant nutrients (mainly vitamins A, C, and E), in a possible prophylactic, even curative, role in the disease process. Closely related to this probable benefit of natural antioxidants is their role in controlling free radicals as they may lead to pathological effects such as vascular diseases and cancer. A free radical is defined as any chemical species that has one or more unpaired electrons. This often results in very reactive compounds. Oxidation is a natural and needed reaction in metabolism. Highly reactive hydroxyl radicals, •OH, results. These can attack DNA, protein and polyunsaturated fatty acids residues of membrane phospholipids, among others. With the latter, a peroxyl radical is formed. Antioxidants quench this radical. If the supply of antioxidants is inadequate, a chain reaction takes place that may lead

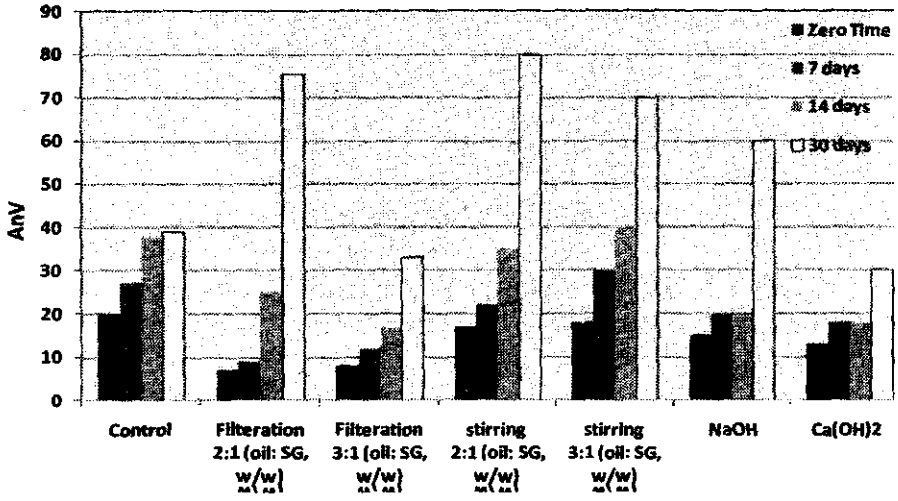


Fig. 3. Changes in the AnV levels of untreated HFFAO and treated HFFAO oils as affected by SG and alkali treatments during oven test

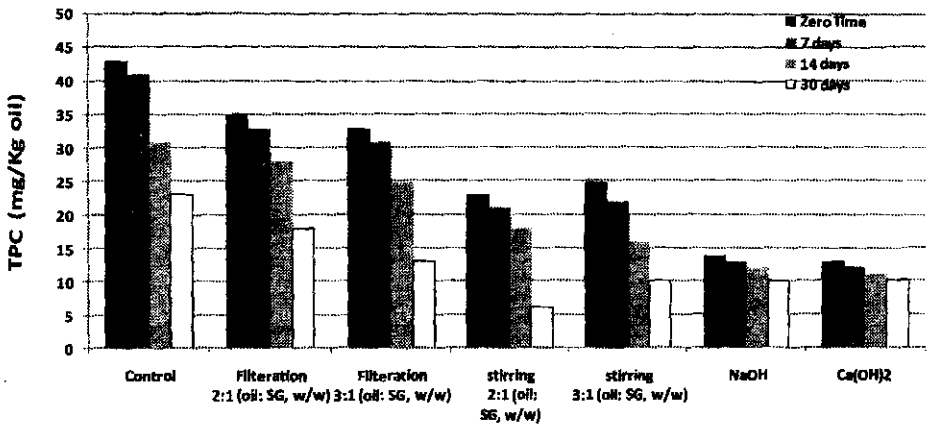


Fig. 4. Changes in the amounts of TPC for untreated HFFAO and treated HFFAO oils as affected by SG and alkali treatments during oven test

to damaged tissue. The evidence in the literature begins to make an overwhelming case for the existence of a relationship between high blood levels of antioxidant nutrients and a lowered incidence of disease.

Natural antioxidants, on the other side, allow food processors to produce stable products with clean labels and tout all-natural ingredients. The tests expressing antioxidant potency can be categorized into two groups: assays for radical scavenging ability and assays that test the ability to inhibit lipid oxidation under accelerated conditions. However, the model of scavenging stable free radicals is widely used to evaluate the antioxidant properties in a relatively short time, as compared to other methods. Pervious study on radical scavenging properties of vegetable oils had used different solvents to dissolve the oils and the free radicals. Hence, the results were difficult to compare because the reactions were occurred under different conditions. In contrast, our simple experiment (Ramadan and Mörsel, 2003, 2006 and Ramadan *et al.*, 2006, 2007) has been performed using the same solvent (toluene) to dissolve the fat or oil samples and the free radicals. This allowed us to characterize and compare the RSA of all samples under the same conditions.

Apart from the oxidative stability of vegetable oils and fats depends on the fatty acid composition, the presence of minor fat-soluble bioactives and the initial amount of hydroperoxides. Antiradical properties of HFFAO oil were compared using stable DPPH free radicals. Fig. 5 shows that control sample of HFFAO oil has higher RSA than HFFAO oils treated with SG or alkali. After 1 h incubation, 78% of DPPH radicals were quenched by control sample of HFFAO oil, while HFFAO oils treated with SG or alkali were able to quench from 48 to 56% at the same time of incubation. During autoxidation experiment the same trend of RSA was noted for control and treated oil samples. After 14 and 30 days of storage, the lowest level of DPPH inhibition was recorded for HFFAO oils treated by stirring with SG (2:1).

It could be concluded that treatment of HFFAO oils with SG or alkali resulted in reduction in the levels of polar bioactive antioxidants responsible for antiradical action. It could be said that the RSA of oils can be interpreted as the combined action of different endogenous

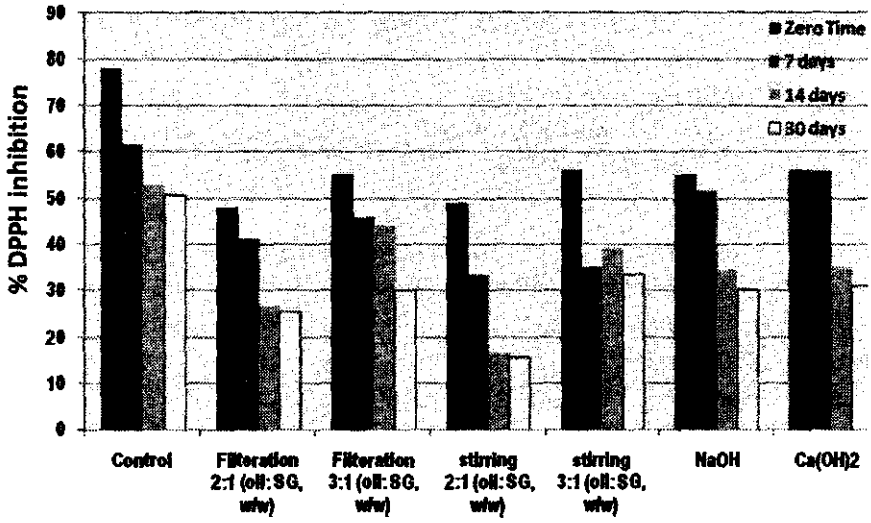


Fig. 5. Changes in RSA of untreated HFFAO and treated HFFAO oils as affected by SG and alkali treatments during oven test

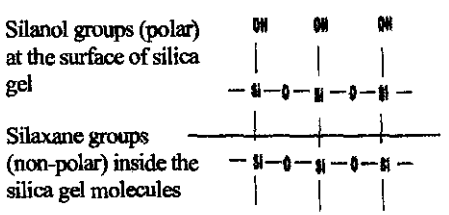
antioxidants. However, when polar fractions, which contain mainly polar lipids and low levels of phenolics, are found in high levels, strong RSA of these components can be expected as well as synergistic activity with primary antioxidants (Ramadan *et al.*, 2006, 2007).

The oil production from oilseeds cannot cope with the high demands of oils especially in the developed countries. In addition, recent target of the developed countries is to produce biofuels from vegetable oils which makes the oil crisis even more worse (Du *et al.*, 2004; Kim *et al.*, 2004). Therefore, any method that extends the useful life of used oils could translate enormous returns for the food services industries. In this respect, several adsorbent agents are used to purify used oils (Lin *et al.*, 1999 and Bheemreddy *et al.*, 2002). Most of these agents, such as clay, magnesium silicate, activated alumina, charcoal, etc., remove one or more of the impurities or colored bodies. In fact, several reports indicated that adsorbents improved the color and viscosity in respect to those of the fresh oil instead of used oil to the extent of fresh oil (Farag and El-Anany, 2006). In addition, these materials reduce the total polar materials and oxidation

products which normally lead to the deterioration of low quality used oil. It is well accepted that during processing partial hydrolysis of the oil takes place and FFA content increases. Another factor that promotes oil hydrolysis is the presence of moisture. As the crude olive oil in this work was dried over anhydrous sodium sulphate, the effect of moisture will be excluded from the discussion.

The aforementioned data indicated that SG was an effective adsorbing substance in removing secondary oxidation substances from HFFAO oil. Silica gel with 60–120 mesh does not exhibit any harmful effects to the handler and possesses adsorbing efficiency in removing secondary oxidation substances. In addition, the price of normal silica gel is comparable to Magnesol XL and would therefore be useful for regenerating the quality of used oils and high free fatty acid oils (Farag and Basuny, 2009).

According to the chemical structure of silica gel, it exhibits dual functions (polar and non-polar characters). In general, one would say that silica gel with 60–120 mesh had the highest adsorbing capacity than that of all other adsorbing agents except Magnesol XL. In this respect, Kent (2000) mentioned that silica offers the greatest potential for refining the edible oil in industry. It is of interest to note that the silicone atoms of silica gel are joined via oxygen atoms in a giant covalent structure. However, at the surface of the silica gel, the silicone atoms are attached to –OH groups. So, the surface of the silica gel is very polar and the –OH groups can form hydrogen bonds with the secondary oxidation products of used oil as well as van der Waals dispersion forces and dipole- dipole attractions. In fact, the most important features of silica gel are the presence of silanol (Si–OH) groups that are polar and ionisable and siloxane linkage (Si–O–Si) that has a hydrophobic character. The following diagram represents the existence of silanol groups (polar) at the surface while the siloxane groups (non-polar) are located at the interior part of the silica gel molecules.



It is well known that oil secondary oxidation products are mainly polar and some are non-polar substances. As already

mentioned silica gel molecules have polar and non-polar groups which associate with the secondary oxidation products (polar and non-polar molecules) according to the well known basis 'likes dissolve likes'. It could be concluded that silica gel structure allows to great extent improve the quality of olive oil. Normal SG with small particle size permitted high adsorbing capacity and close to that induced with chemical treatments which are used commercially in a large scale to improve oil quality. The experimental results demonstrate that SG is efficient in removing FFA from HFFAO oil, although a relative reduction (ca. 22-48%) in the TPC were induced.

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تكرير زيت الزيتون عالى الحموضة

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عادة ما يستخدم زيت الزيتون دون تكرير إلا أنه فى بعض الأحيان لابد من عمل تكرير لبعض أنواع زيت الزيتون ليكون قابل للاستهلاك. الهدف الأساسى للبحث هو تحسين جودة وخصائص زيت الزيتون عالى المحتوى من الأحماض الدهنية الحرة (عالى الحموضة). عومل زيت الزيتون عالى الحموضة بالسليكا جيل بطريقتين هما الفلترة والتقليب ومن ناحية اخرى تم إجراء المعاملة الكيميائية المعتادة للزيت بهدف تقليل الحموضة بواسطة الصودا الكاوية وهيدروكسيد الكالسيوم. أجريت تجربة تخزين فى الفرن (على درجة حرارة ٦٠ م لمدة ٣٠ يوم) للزيوت المعاملة وزيت الزيتون عالى الحموضة غير المعامل لدراسة سلوك وخصائص الزيوت أثناء التخزين حيث تم تقدير كل من رقم الحامض و رقم البيروكسيد ورقم الانزيدين والمحتوى الكلى للفينولات وأيضاً الفعل المضاد للشقوق الحرة DPPH. أوضحت النتائج أن المعاملة بالسليكا جيل والقلوى أدت إلى تقليل الحموضة بوجه عام، حيث أدت المعاملة بالقلوى إلى تقليل الحموضة بشكل كبير كما اتضح أن الفلترة باستخدام السليكا جيل لها تأثير أكبر فى تقليل الحموضة عن التقليب مع السليكا جيل. أوضحت النتائج أيضا أن رقم البيروكسيد لم يتحسن بالمعاملة بالقلوي إلا أن المعاملة بالسليكا جيل أدت إلى تقليل رقم البيروكسيد. جميع المعاملات بوجه عام أدت إلى تقليل رقم الانزيدين فى العينات أثناء التخزين كما أدت المعاملات إلى تقليل المحتوى الكلى للمركبات الفينولية. أدت المعاملات أيضا إلى تقليل الفعل المضاد للشقوق الحرة نظراً إلى انخفاض مستوى الفينولات فى العينات المعاملة. اتضح من النتائج إمكانية استخدام السليكا جيل على النطاق التجارى فى تحسين خصائص زيت الزيتون عالى الحموضة.