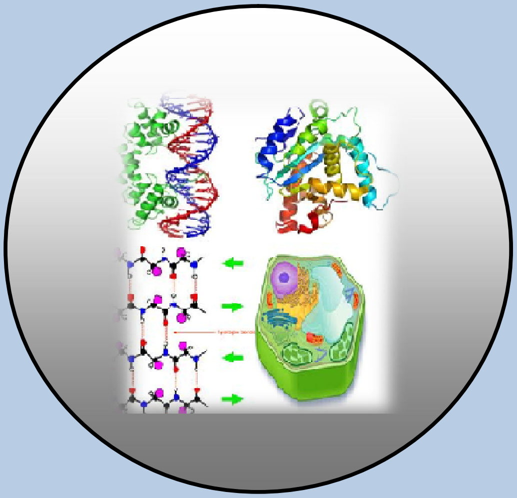
Maximize the Benefit from Date Pits for Production Activated Carbon and using it for Removing Peroxides from Fried Oils

By

Amany M. M. Basuny and Shaker M. Arafat

ISSN 0970-4973 (Print)
ISSN 2319-3077 (Online/Electronic)



J. Biol. Chem. Research
Volume 31 (1) 2014 Pages No. 81-98

Journal of Biological and Chemical Research
(An International Journal of Life Sciences and Chemistry)

Published by Society for Advancement of Sciences®

J. Biol. Chem. Research. Vol. 31, No. 1: 81-98 (2014)
(An International Journal of Life Sciences and Chemistry)
Ms 30/2/132/2013, All rights reserved
ISSN 0970-4973 (Print)
ISSN 2319-3077 (Online/Electronic)

Dr. Shaker Arafat
http:// www.jbcr.in
jbiolchemres@gmail.com
info@jbcr.in

RESEARCH PAPER

Received: 19/10/2013 Revised: 19/12/2013 Accepted: 06/01/2013

Maximize the Benefit from Date Pits for Production Activated Carbon and using it for Removing Peroxides from Fried Oils

Amany M. M. Basuny* and Shaker M. Arafat**

*Food Science and Nutrition Department, Faculty of Agricultural Science and Foods, King Faisal University, Saudi Arabia

**Oils and Fats Research Department, Food Technology Research Institute, Agricultural Research Center, Giza, Egypt.

ABSTRACT

The present study was aimed at improving the quality of fried sunflower oil. Synthetic (Magnesol XL) natural (agriculture wastes of date industry) were used to absorb the oxidation products of fried sunflower oil. The mineral (Si, Mg, Ca, Fe, Al, Mn, and Cu) of the aforementioned substances were determined. The physico-chemical properties of non-fried, fried and fried-treated sunflower oil were determined. The frying process was carried out at 180ºC ± 5ºC for 16h, 4h heating per day for four consecutive days. The fried sunflower oil was treated with synthetic, natural and activated carbon of date pits at level 2%. A set of nutritional experiments was conducted in which rats administrated standard diets were containing non-fried, fried and fried–treated oils with adsorbent materials. The safety limits of the fried-treated oils were determined by measuring the activities of alanine aminotransferase (ALT), aspartate aminotransferase (AST) and alkaline phosphatatse (AP), and levels of total lipids, total cholesterol, HDL-cholesterol and LDL-cholesterol of rat sera. The results indicated that Magnesol XL, diatomaceous earth and activated carbon of date pits contained Si + Mg + Si + Mn + Ca and Si +Mg + Ca as the basic metals, respectively. Frying of sunflower oil led to significant increase in physico-chemical properties. Treatments of fried sunflower oil with the aforementioned substances greatly improve the quality of fried oil. Also, the results highlight the potential effect of Magnesol XL, diatomaceous earth and activated carbon of date pits in improved rat liver (AST, ALT and AP) and levels of sera constituents were similar to those of rats given non-fried oils.

Key words: Activated Carbon, Date Pits, Adsorbent Materials, Frying Process and Biological Evaluation.

Published by Society for Advancement of Science®

INTRODUCTION

Oils are quite susceptible to oxidation during deep-fat frying process. Generally, there are two basic oxidation reactions during oil frying, that is, the primary reaction which produces hydroperoxides and the secondary oxidation where the hydroperoxides decompose to produce smaller organic compounds such as aldehydes, alcohols, ketones, acids, etc. Nutritional experiments were performed to envisage the effect of oil oxidation products on rat health. For instance, methyl linoleate hydroperoxides orally administered to mice caused necrosis, fatty degeneration and congestion in tissues (Paik *et al.,* 1976 & Wang *et al.,* 2013)
Methyl linoleate hydroperoxides inhibited lipase, succinate dehydrogenase and thiokinase activities, and also hemolyse red blood cells (Yoshioka *et al.,* 1974). In addition, secondary oil oxidation products have stronger toxic effects than hydroperoxides (Buck, 1981). These reports indicate the necessity to remove peroxides from deteriorated fried oils. It is of interest to note that frying leads to darkening, thickening, foaming and smoking of the oil (Farag & El-Anany, 2006; Farag *et al.,* 2007). There are various methods that can be used to remove these products such as treatment with acid solution of ferrous sulphate (Farag & Basuny, 2002), filtration through special membranes (Mulflur & Munson, 1987; Subramanian *et al.,* 2000) and by using different adsorbent materials (Lin *et al.,* 1999; Farag & El-Anany, 2006). By these methods, the treated oils can be used again in deep-fat frying process. Saudi Arabia is among the cultivation countries and there are many agricultural wastes such as wheat hull, rice hull and barley hull, etc. which can be used in different industrial processes. Dates of date palm tree (*Phoenix dactylifera* L.) are popular among the population of the Middle Eastern Countries. The fruit is composed of a fleshy pericarp and seed which constitutes between 10 % and 15 % of date fruit weight (Hussein *et al.,* 1998). The date seeds considered a waste product of many date processing plants producing pitted dates, date syrup and date confectionery. At present, seeds are used mainly for animal feeds in the cattle, sheep, and camel and poultry industries. With world production of dates reaching 9 million tons in 2007, from this approximately 960 thousand tones of date seeds are produced (FAO. 2010). Thus, utilization of such waste is very important to date cultivation and to increase the income to this sector (Al-Farsi *et al.,* 2008). Chemical and nutritional constituents of date seeds were reported by (Basuny & Al-Marzooq, 2010; Ardekani *et al.,* 2010, El-Rayes; 2009 and Mobarak 2009). Most current literature was limited to proximate and mineral composition. Beyond compositional analysis, there is work of (Al-Farsi *et al.,* 2007) who researched the functional properties of date seeds. Their reported composition was 3.10-7.10% moisture, 2.30-6.40 % protein, 5.00-13.20 fat, 0.90-1.80 % ash and 22.50-80.20 % dietary fiber. Also seeds contain high levels of phenolics (3102-4430 mg Gallic acid 1100 gm) (Ardekani *et al.,* 2010 & Basuny *et al.,* 2012. It is well known that adsorbents such as activated carbon, silica and acid clay are widely used by vegetable oil processes to remove components such as free fatty acids, peroxides, carotenoides and phospholipids (Yates & Caldwell, 1993; Lin *et al.,* 2001). Activated carbon of the agricultural plant wastes can be considered as good adsorbents to get rid of the oxidation products of oil . Activated carbon has undoubtedly been the most popular and widely used adsorbent in wastewater treatment

throughout the world. Charcoal, the forerunner of modern activated carbon has been recognized as the oldest adsorbent known in wastewater treatment.

Activated carbon is produced by a process consisting of raw material dehydration and carbonization followed by activation. The product obtained is known as activated carbon and generally has a very porous structure with a large surface area ranging from 600 to 2000m2/g . Activated carbon (AC) is an amorphous form of carbon that is specially treated to produce a highly developed internal pore structure and a large surface area, thus, producing reasonably cheap and excellent adsorbent (Derbyshire *et al.,* 19955). There is a multitude of industrial applications of AC including decolorization, purification and deodorization of vegetable oils and fats, sugar refining and other food industries. Pollution control and wastewater treatment are growing areas of use to combat environmental pollution .

Large quantities of dates' stones which can be obtained from more than million metric tons of dates produced annually in Saudi Arabia (Alhamed, 2002) justify the use of dates' stones as a raw material production of AC. Knowing that dates' stone account for about 10% of fruit weight it can be easily shown that about 150000 metric tons of dates' stones are available annually. A reasonable fraction of this quantity can be reclaimed easily from dates' processing plants and can be used for production of AC. Therefore, the objective of this study is to explore the effect of preparation conditions on the yield and quality of AC produced from dates' stones. Different methods for production of active carbon (Zinc chloride, phosphoric acid, will be used in this study since little attention has been paid for this activator in literature. The optimum conditions for AC production will be evaluated based on the determination of various adsorption parameters (e.g. unit capacity, maximum capacity, and percentage removal) using aldehydes, alcohols, ketones, acids methylene as adsorbents from deep fried edible oils (Sekirifa *et al.,* 2013). The main goal of the current investigation was to use activated carbon of date pits and to compare its adsorbent efficiency with Magnesol XL as synthetic adsorbents and diatomaceous earth as natural adsorbents to regenerate the quality of fried sunflower oil. Also, study the effect of the regenerated sunflower oil on rat liver function such as the determination of alanine amino transferase, aspartate aminotransferase and alkaline phosphate activities and serum contents of total lipids, total cholesterol, high and low-density lipoproteins.

MATERIAL AND METHODS

Source of Sunflower oil

Refined sunflower oil was obtained from Areej Vegetable Oil & Derivatives Co. Riyadh, Saudi Arabia. Acid and peroxide values of the oil were 0.1 mg of KOH per gram of oil and 0.45 active oxygen peroxides per kilogram of oil, respectively.

Table 1. Mineral pattern of Magnesol XL, diatomaceous earth and activated carbon of date pits.

Mineral (ppm)	Magnesol XL	Diatomaceous earth	Activated carbon of date pits
Si	345.00±3.50	322.00±3.00	316.30±3.41
Mg	290.00±2.50	100.12±1.51	250.30±2.81
Ca	155.00±1.90	284.00±2.81	233.19±1.90
Fe	9.01±0.60	18.30±0.92	22.16±0.71
Al	7.20±0.30	9.03±0.10	5.51±0.62
Mn	500.00±5.501	490.00±4.52	292.00±2.11

Cu	**8.90±0.41**	**60.33±1.09**	**25.16±1.00**

The data (values ± SE) are the mean values of three measurements for the same sample.

Source of date pits

The pits of Khalas variety was obtained from Dates Packaging Factory in Al-Hasa Region, Saudi Arabia and collected at the tamer stage (fruit ripeness).

Source of Magnesol XL and diatomaceous earth clay

Magnesol XL (hydrous, white, amorphous and odourless) obtained from Magnesol Products Division (Reagent Chemical and Research, Inc., Houston, Tx, USA). Diatomaceous earth clay (white, amorphous and odourless) was obtained from Qasr El-Sagha Deposit (Fayoum Governorate, Egypt).

Preparation of activated carbon

Pit was first washed thoroughly with water to remove all foreign materials, mud and sticky sweet remnants of dates, then; they were speared in one layer over plastic sheets and left to dry in doors. Washed-clean whole dates pits was dried in a drying oven at 110ºC to facilitate crushing and grinding in a grinder (Perten, model LM 3310, USA) to a particle size of 180µm, placed in a crucible, carbonized in air in a muffle furnace (5000, Thermolyne, Iowa, USA) at 550ºC for 12 hr and then cooled to room temperature in a desiccator and stored in glass screw-capped bottles (AOAC, 2005).

Elemental analysis

The elemental analysis of (Si, Mg, Ca, Fe, Al, Mn, and Cu) of various materials (date pits, Magnesol XL and Diatomaceous earth clay) were carried out at the SCS-CNRS Laboratory using micro analytic devices ensuring a precision of ± 0.3% for the major components (> 10%). A LECO analyzer (model SC 144) was used for determination.

Frying process

A known amount (c. 2 kg) of refined sunflower oil was placed in a stainless steel pan fryer (60 cm diameter X 30 cm height) and heated at 180ºC ± 5ºC. Then, potato chips (2mm thickness) previously soaked in NaCl solution (10%, w/v) were fried. The frying process was repeated for four consecutive days for 4 hr every day. Hence, the total continuous frying period was 16 hr. The oil samples were left to cool down and then stored at -5ºC for further analysis.

Adsorption process

Each adsorbent (2%, w/v) based on the weight of the oil was added to frying oil after heating, stirred for 15 min, vacuum filtered through whatman filter paper No. 1 the filtrate was stored in a sealed vessel at 4ºC after flushing with nitrogen.

Quality assurance tests for non-fried, fried and fried-treated sunflower oil

Refractive index, acid value and peroxide value were determined according to A.O.A.C (2005). Smoke point refers to the temperature at which the oil sample begins to smoke and is recorded as outlined by Nielsen (1998). A Lovibond Tintometer apparatus (The Tintometer Ltd., Salisbury, England) was applied to measure the colour of non-fried, fried and fried – treated sunflower oil samples. The yellow glass slides were fixed at 35 and the intensity of red glass was assigned through matching with the oil samples (Nielsen, 1988). Brookfield LV viscometer Model TC-500 (Brookfield Engineering Laboratories Stoughton, MA, USA) was used to measure the viscosity of the oil samples at 30ºC according to the method described by Saguy *et al.,* 1996). Thiobarbituric acid (TBA) value, oxidized fatty acid and polymer contents for the sunflower oil samples were determined according to the methods of Sidwell *at al.,* (1954), Billek *et al.,* (1978) and Wu & Nawar (1986), respectively.

Polar components in sunflower oil samples were measured by column chromatography according to the method described by Waltking & Wessel (1981). An aliquot of the sunflower oil samples (0.1 ml) was dissolved in methanol (3 ml), vortexed and the absorbances at 232 and 268nm were recorded for conjugated dienes and trienes, respectively as mentioned by Kates (1972).

Animals and diets

A total of 50 male adult rats (Sprague Dawley strain) with an average weight of 90-100 gm were purchased from the animal house of the Faculty of Veterinary Medicine, King Faisal University. The rats were randomly divided into five groups according to the oil type (non-fried oil, fried oil and fried-treated oil with 2% Magnesol XL, diatomaceous earth and activated carbon of date pits), each group of ten rats. The rats were housed in plastic cages and fed on standard diet (oil 15%, casein 16.11%, vitamin mixture 1%; mineral mixture 4%, fiber 1% and starch 62.82%) and water was available *ad libitum* for 17 days as an adaptation period.

Table 2. Sera enzymes activities of rats fed on non-fried, fried and fried-treated sunflower oil with various adsorbent materials.

Experimental period	Non-fried oil	Fried oil	Fried-treated oil		
			Magnesol XL (2%)	Diatomaceous earth (2%)	Activated carbon of date pits (2%)
Alanine aminotransferase (IUL^{-1})					
0	12.00±1.50	12.00±1.50	12.00±1.50	12.00±1.50	12.00±1.50
2	12.02±1.30	13.32±2.00	12.11±1.17	11.85±1.90	12.10±2.00
4	12.13±1.95	15.60±2.30	11.98±1.75	12.09±2.00	11.93±1.83
6	11.99±1.80	17.20±3.00	12.05±1.80	11.90±1.73	12.09±2.11
8	12.10±1.72	19.32±3.13	12.01±2.00	12.04±1.93	12.00±1.95
Aspartate aminotransferase (IUL^{-1})					
0	11.90±1.45	11.90±1.45	11.90±1.45	11.90±1.45	11.90±1.45
2	11.95±1.53	12.80±2.00	11.87±1.50	11.95±1.63	11.88±1.43
4	11.93±1.61	14.50±2.50	11.95±1.61	12.03±1.91	12.01±2.00
6	12.00±1.90	16.90±3.00	12.03±2.00	12.00±2.01	11.98±2.03
8	11.87±1.66	19.30±3.80	11.98±2.00	11.90±1.88	12.09±1.01
Alkaline phosphatase (IUL^{-1})					
0	66.01±3.50	66.01±3.50	66.01±3.50	66.01±3.50	66.01±3.50
2	66.09±3.46	69.00±3.80	66.13±3.65	66.12±3.65	66.19±3.62
4	66.81±3.64	73.00±4.50	65.90±3.41	66.00±3.14	65.13±3.00
6	66.28±3.41	78.00±5.03	66.30±3.61	65.85±3.59	66.00±3.41
8	66.11±3.32	81.00±6.12	66.00±3.05	66.32±3.91	66.30±3.23

The data (values ± SE) are the mean values of three measurements for the same sample.

Blood sample

Blood samples were taken at the start of the experiment and at 2, 4, 6, and 8 weeks after administration of the tested diets.

The blood samples were obtained from the orbital venous plexus by means of capillary tube (1-1.5 ml from each rat). The blood of ten rats in each group was placed in a centrifuge tube. Sera were obtained by centrifugation at 1100 x g for 20 min and kept frozen until analysis.

Serum analysis

The methods of Bergmeyer and Harder (1986) and Belfied and Goldberg (1971) were used for the determination of ALT (EC 2.6.1.2), AST (EC 2.6.1.1) and AP (EC 3.1.3.1) activities, respectively. Total lipids, total cholesterol, HDL-C and LDL-C were estimated as outlined by Fryings and Dunn (1970), Roeschlau *et al.,* (1974) and Assmann (1979), respectively.

Statistical analysis

The data of the present work were subjected to analysis of variance, and the least significant difference (LSD) test was used to compare the mean values of the studied parameters using SPSS program package.

RESULTS AND DISCUSSION

Elemental analysis of various adsorbents

Table 1 shows the mineral content of Magnesol XL (synthetic filter aid), diatomaceous earth (natural filter aid) and date pits activated carbon (agricultural plant wastes). All the filter aids can be distinguished by their metal pattern. For instance, date pits activated carbon contained the highest level of Cu as great as that in Magnesol XL and diatomaceous earth, respectively. The highest level of Si was recorded for Magnesol XL followed by diatomaceous earth and date pits activated carbon. Generally, the basic metals for Magnesol XL, diatomaceous and date pits activated carbon were Si + Mg + Mn, Si + Mn + Ca and Si + Mg + Ca, respectively.

Quality of starting sunflower oil

Figure 1-12 show some physico-chemical properties of starting sunflower oil. In general, the values of the physical and chemical constants for sunflower oil quality under study (refractive index, smoke point, color, viscosity, acid value, peroxide, TBA value, Conjugated dienes and trienes, polar content, polymer content and oxidized fatty acids) were similar to those published in many works (Farag *et al.,* 2009 & Bhattacharya *et al.,* 2008) and indicate that the fresh sunflower oil used was of good quality.

Quality loss of fried sunflower oil

The changes in quality parameters of sunflower oil during intermittent frying are shown in Figures 1-12. It is worth noting that sunflower oil was heated at 180ºC ± 5ºC for 4h each day and this process was reported for four consecutive days. Oil samples were taken at the end of each day and kept at – 5ºC until analysis. Refractive index is a good diagnostic parameter for the degree of oil unsaturation and this value increased by increasing the number of conjugated double bonds in the oil. The data in Figure 1 show that there were slight increases in the refractive index of sunflower oil during the various frying times. The intermitted frying of sunflower oil led to a gradual and significant decrease in the smoke point values (Figure 2). The color of fried sunflower oil samples collected at different period was measured on a fixed yellow glass slide (35) and variable red glass slides. The color of sunflower oil changed from clear yellow to dark brown especially during the last days of the frying process. The dark color patterns were significantly different from each heating period correlated with hours of deep fat frying process (Figure 3).

The viscosity of sunflower oil (Figure 4) was gradually and significantly increased during the frying process. It is worth mentioning that the viscosity at the end of the frying process was about 4.00 times as high as that in the oil at the beginning of the experiment.

Table 3. Effect of non-fried, fried and fried-treated sunflower oil with various adsorbent materials on total lipids, total cholesterol, high density lipoprotein cholesterol and low-density lipoprotein cholesterol levels of rat serum.

Experimental period	Non-fried oil	Fried oil	Fried-treated oil		
			Magnesol XL (2%)	Diatomaceous earth (2%)	Activated carbon of date pits (2%)
Total lipids ($mgdL^{-1}$)					
0	290.00±4.50	290.00±4.50	290.00±4.50	290.00±4.50	290.00±4.50
2	291.00±4.11	290.50±4.56	291.00±4.61	289.09±4.13	290.13±4.19
4	298.90±4.09	291.03±4.66	291.33±4.71	290.33±4.71	289.70±4.19
6	298.99±4.20	290.90±4.70	290.31±4.00	289.50±4.81	289.66±4.20
8	290.00±4.13	291.90±5.01	290..00±4.01	290.21±4.00	290.11±4.00
Total cholesterol ($mgdL^{-1}$)					
0	160.00±1.13	160.00±1.13	160.00±1.13	160.00±1.13	160.00±1.13
2	160.19±1.11	165.00±1.62	160.33±1.53	160.55±1.50	160.81±1.33
4	161.20±1.32	172.30±1.70	160.56±1.90	161.14±1.56	161.01±1.72
6	161.50±1.35	179.81±1.85	161.90±2.01	161.00±1.71	160.85±1.90
8	160.95±1.45	188.50±1.55	160.83±1.86	160.87±1.53	160.05±1.83
High density lipoprotein cholesterol ($mgdL^{-1}$)					
0	101.01±0.95	101.01±0.95	101.01±0.95	101.01±0.95	101.01±0.95
2	10153.±0.87	101.83±1.01	100.98±0.85	101.00±0.90	100.90±0.93
4	101.67±0.98	100.85±0.75	101.03±0.90	101.19±0.85	101.97±0.94
6	102.00±1.00	101.90±1.00	100.88±0.85	102.03±1.00	102.00±1.09
8	100.90±0.90	102.00±1.03	102.13±1.03	101.81±1.01	101.80±1.13
Low density lipoprotein cholesterol ($mgdL^{-1}$)					
0	45.00±0.33	45.00±0.33	45.00±0.33	45.00±0.33	45.00±0.33
2	45.09±0.39	45.13±0.41	45.00±0.39	45.19±0.41	45.50±0.40
4	45.90±0.51	44.91±0.31	45.41±0.45	46.11±0.61	45.90±0.55
6	45.30±0.42	45.31±0.51	46.14±0.61	45.90±0.53	44.31±0.62
8	46.00±0.63	46.20±0.60	45.82±0.38	46.13±0.61	45.81±0.65

The data (values ± SE) are the mean values of three measurements for the same sample.

The acid values of sunflower oil increased significantly during frying and were strongly correlated with the heating time (Figure 5). Hydroperoxides are the primary products of lipid oxidation. Therefore, the determination of peroxides can be used as an oxidation index for the primary stages of oxidation of sunflower oil. The data in Figure 6 show that the peroxide value of sunflower oil gradually increased with the frying time and become unacceptable after the second day of frying.

It is well know that carbonyl compounds are formed as part of secondary oxidation products from the decomposition of hydroperoxides during frying. The carbonyl compounds react with TBA reagent to produce TBA derivatives that have high absorbance at 535nm. The TBA values of sunflower oil (Figure 7) increased slowly at the early stages of frying and become more after the second day of frying. The conjugated dienes and trienes in the oil system absorb at 232 and 268nm, respectively. The data in Figures 8 and 9 shows that the frying process caused positional rearrangement of the double bonds in sunflower oil and consequently a part of the non-conjugated system was converted to conjugated dienes and trienes double bonds. It is well known that the thermal degradation products is polar in nature and a value of 27% of the total polar materials has been established as the maximum limit for frying oils (Firestone *et al.,* 1991). The polar content of sunflower oil under study was gradually increased during intermittent frying and there were significant differences in the contents of the polar compound at any of the measured frying times polar (Figure 10). The frying process caused gradual and significant increases in the formation of polymer materials (Figure 11). The oil quality control regulations (IUPAC, 1987) indicate that the polymer levels must not exceed 10%. Accordingly, the fried sunflower oil has to be discarded after 2 days and should not be used for human nutrition. Fresh sunflower oil had no oxidized fatty acids at the beginning of the experiment. During the frying process, the levels of oxidized fatty acids of sunflower oil were gradually and significantly increased with frying time (Figure 12).

Effect of adsorbent materials and fried sunflower oil quality

Fried sunflower oil had a refractive index of 1.4707 at 25ºC. The treatment with Magnesol XL at 2% level caused significant decreases in the refractive index values. The same finding was achieved when fried sunflower oil was separately treated with diatomaceous earth and activated carbon of date pits (Figure 1). The fried sunflower oil had a smoke point of 205.00ºC. The treatment of fried sunflower oil with Magnesol XL at the 2% level induced a significant lowering effect on the smoke point. These findings were also recorded for the treatment of fried sunflower oil with diatomaceous earth and activated carbon of date pits (Figure 2). The color of fried sunflower oil was 35 yellow and 18.00 red. The treatment with Magnesol XL at the 2% level caused a significant decrease of the red-colored glasses. The same finding was achieved when fried sunflower oil was separately treated with diatomaceous earth and activated carbon of date pits (Figure 3). The viscosity of fried sunflower oil at 180ºC for 4 h was 65.00 centipoises. Treatment with Magnesol XL remarkably lowered the viscosity of fried sunflower oil. The treatment with diatomaceous earth and activated carbon of date pits had the same effect on the viscosity of fried sunflower oil (Figure 4). The results demonstrate that the treatment of fried sunflower oil with Magnesol XL at the 2% level led to significant reduction in the levels of free fatty acids. The data for fried sunflower oil samples treated with diatomaceous and activated carbon of date pits was in accordance with the results of Magnesol XL treatments (Figures). Similar results were achieved by (Sulaiman *et al.,* 2011) that used activated carbon from wastes in regeneration of frying oils. The peroxide value of fried sunflower oil was 36.30. The treatment with Magnesol XL resulted in a significant decrease of the peroxide value of fried sunflower oil. The efficiency of various adsorbent materials in lowering the peroxide value of the fried sunflower oil was approximately the same (Figure 6).

In general, the adsorbent materials can be used effectively to lower the peroxide value of fried or oxidized oils. Fried sunflower oil had a TBA value of 1.33. Treated with Magnesol XL significantly decreased the amount of TBA-reacting substances. Treatments with other adsorbent materials induced the same effect on the levels of secondary oxidation products (Figure 7). The levels of conjugated dienes and trienes of fried sunflower oil were 1.85 and 1.09 as determined by the absorption at 232 and 268nm, respectively. The treatment of fried sunflower oil with Magnesol XL, diatomaceous earth and activated carbon of date pits at the 2% level significantly decreased the contents of conjugated dienes and trienes. These results indicate that these adsorbent materials had nearly the same capacity for adsorption of conjugated dienes and trienes present in fried sunflower oil (Figures 8 & 9). Treatment with Magnesol XL significantly lowered the polar content, which agreed well the oil quality regulations (IUPAC, 1987). Treatment with other adsorbent materials significantly decreased and had nearly the same effect in reducing the level of polar compounds (Figure 10). The results indicated that the fried sunflower oil heated 180ºC for 16 h had 7.80% polymers. The treatment of fried sunflower oil with different adsorbent materials at the 2% level induced a significant decrease in the polymer contents (Figure 11). The results illustrate that the treatment of fried sunflower oil with Magnesol XL significantly lowered the oxidized fatty acid levels. The data for fried sunflower oil samples treated with diatomaceous earth and activated carbon of date pits were in accordance with the results of Magnesol XL treatments (Figure 12). Overall, the data suggest that the adsorbent materials under study possess useful scavenging properties; they remove the oxidation products from the fried sunflower oil and the regenerated oil may by re-utilize in the date industry. In addition, the activated carbon of date pits had different levels of minerals. Generally, the present work provides information on improving the quality of fried sunflower oil using Magnesol XL, diatomaceous earth and activated carbon of date pits at 2% level. The potential for using Magnesol XL as adsorbent material to remove the oxidation products from frying oils is restricted by its irritant effect of skin and eyes. The natural adsorbent material (diatomaceous earth) and activated carbon of date pits do not exhibit any harmful effects on humans and possess nearly the same adsorbing effects in removing oil oxidation products. In addition, they are cheap and are useful for regenerating the quality of fried oils.

Influence of fried and fried-treated sunflower oil with the different adsorbent materials on rat health

A set of nutritional experiments was performed to elucidate the effect of non-fried, fried and fried-treated oils with different synthetic and natural materials at the 2% level on rat liver function and sera contents were taken as a guide to evaluate the safety of the fried and fried-treated sunflower oil.

Activity of rat sera enzymes

Table 2 shows some sera enzyme activities of rats fed non-fried sunflower oil. There were slight and non significant increases in the activities of these enzymes (ALT, AST and AP) during the whole experiment (8 weeks) the administration of fried sunflower oil caused gradual and significant increase in rat sera enzyme activities starting from the second week and towards the end of the experimental period.

The data for the administration of fried-treated sunflower oil indicate that the activities of ALT, AST and AP enzymes paralleled the non-fried sunflower oil. This means that adsorbent materials under study removed the oil oxidation products, which are produced during oil frying and caused an increase in enzyme activities. These results highlight the potential effect of the adsorbent materials in removing oil oxidation products.

Total lipids

Table 3 indicates the changes in total lipid contents of rats' administrated non-fried, fried and fried-treated sunflower oil. All samples caused gradual and non-significant increases in the levels of total starting from the second week from commencement and towards the end of the experiment.

Total cholesterol content

Table 3 shows the serum cholesterol contents of rats fed on non-fried, fried and fried-treated sunflower oil treated with Magnesol XL, diatomaceous earth and activated carbon of date pits at the 2% level. The results indicate very little increase in the total cholesterol due to administration of non-fried sunflower oil during the whole experiment. On the other hand, the sera total cholesterol content for rats fed a diet containing fried sunflower oil induced a gradual and significant increase in total cholesterol throughout the entire nutritional experiment. The administration of fried-treated sunflower oil with various adsorbent materials caused a non-significant increase in the total cholesterol level and paralleled the results of non-fried sunflower oil.

Low-density lipoprotein cholesterol content

The results (Table 3) demonstrates that there are non-significant changes in the sera levels of LDL-C for rats fed on various samples of sunflower oil (non-fried, fried and fried-treated).

High –density lipoprotein cholesterol content

Table 3 shows the sera levels of HDL-C of rats fed on non-fried, fried and fried-treated sunflower oil. The results demonstrate that these samples of sunflower oil did not cause any significant changes in HDL-C level. The oil oxidation products can safety is removed by natural adsorbent materials (diatomaceous earth and activated carbon of date pits). Magnesol XL is a synthetic adsorbent material used for adsorption of metal ions, polymers, polar compounds and free and oxidized fatty acids. However, this material induces irritant effects on the eyes and skin of the handler.

Consequently, natural adsorbent materials have to be used instead of Magnesol XL since these substances possess the same scavenging properties on the oil oxidation products.

CONCLUSION

The data of the present study demonstrate that filtration treatment with activated carbon date pits regenerated the quality of fried sunflower oil and possess higher adsorbing effects than the natural adsorbent material (diatomaceous earth) and synthetic adsorbent material (Magnesol XL) in removing oil oxidation products. In addition a date pit is cheap and useful for regenerating the quality of fried oil.

ACKNOWLEDGEMENTS

Extent my sincere thanks and appreciation to the deanship of Scientific Research, King Faisal University on full support for this research project No. 140030.

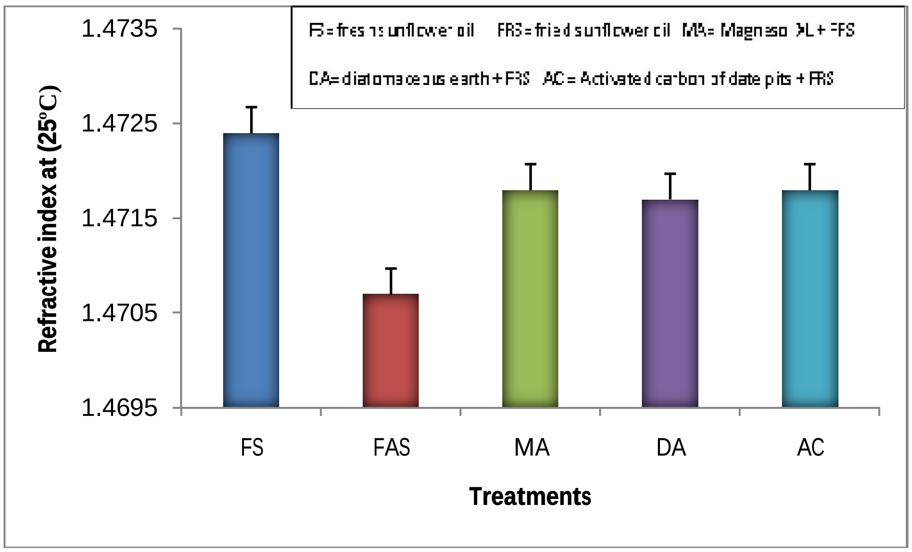


Figure 1. Changes in refractive index of non fried, fried and fried-treated sunflower oil with different adsorbent materials.

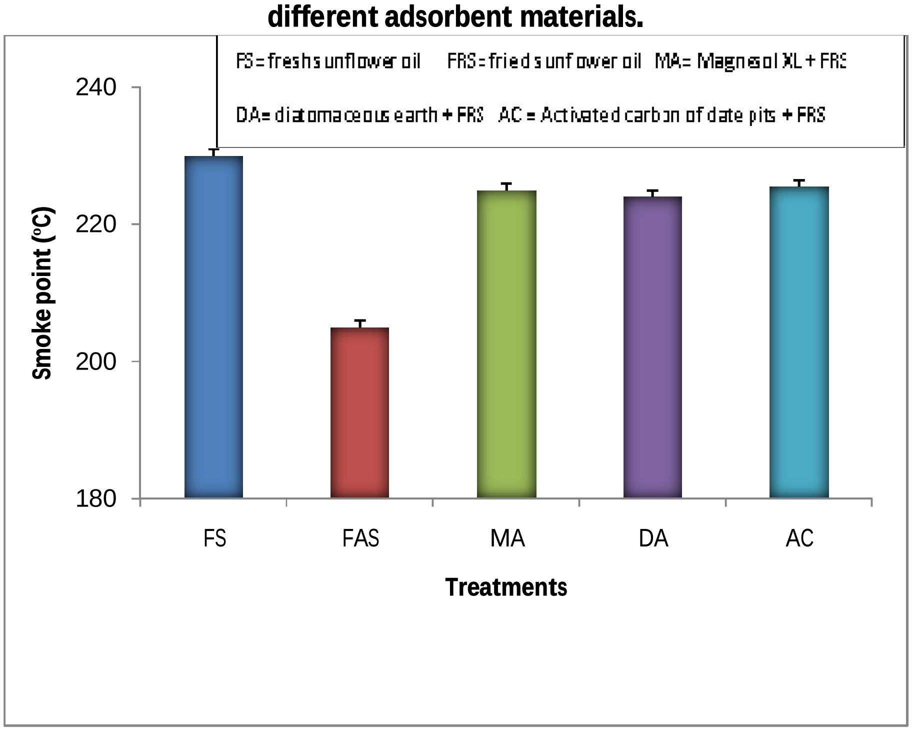


Figure 2. Changes in smoke point of non fried, fried and fried-treated sunflower oil with different adsorbent materials.

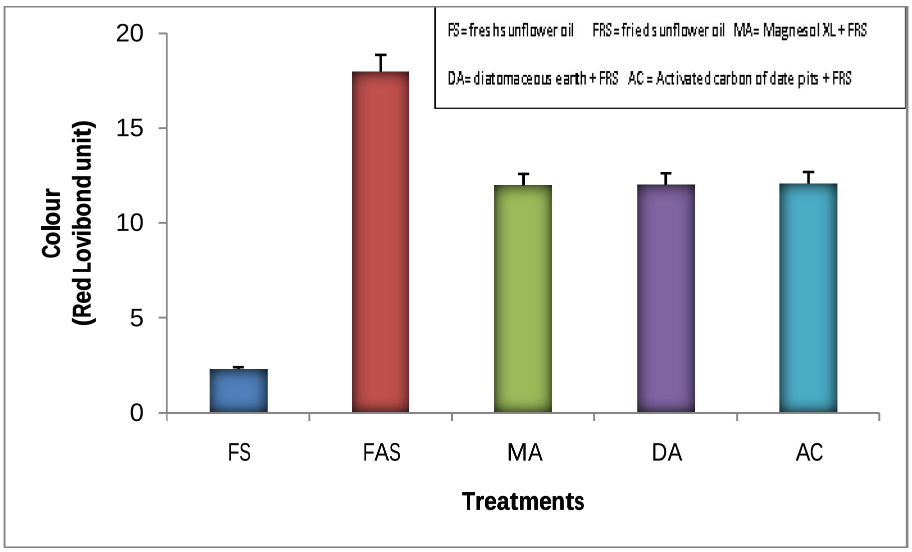


Figure 3. Changes in colour of non fried, fried and fried-treated sunflower oil with different adsorbent materials.

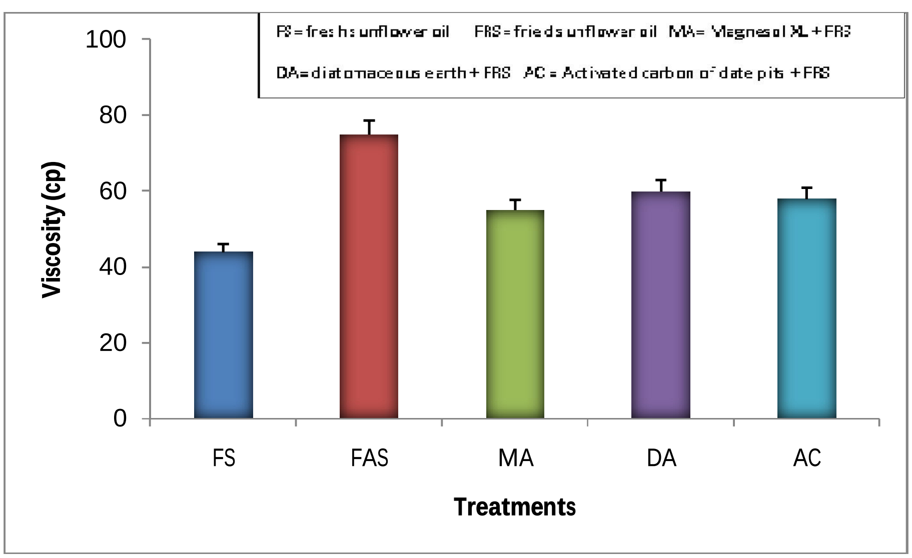


Figure 4. Changes in viscosity of non fried, fried and fried-treated sunflower oil with different adsorbent materials.

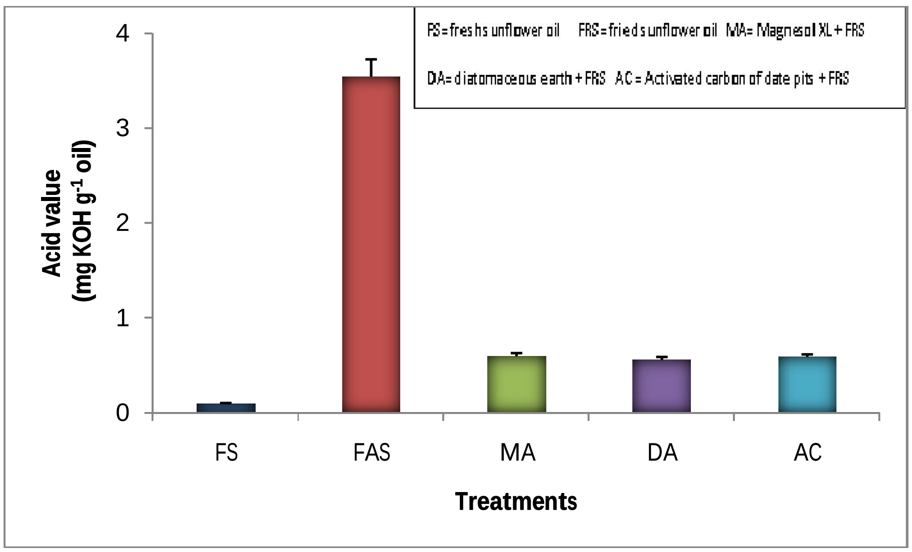


Figure 5. Changes in acid value of non fried, fried and fried-treated sunflower oil with different adsorbent materials.

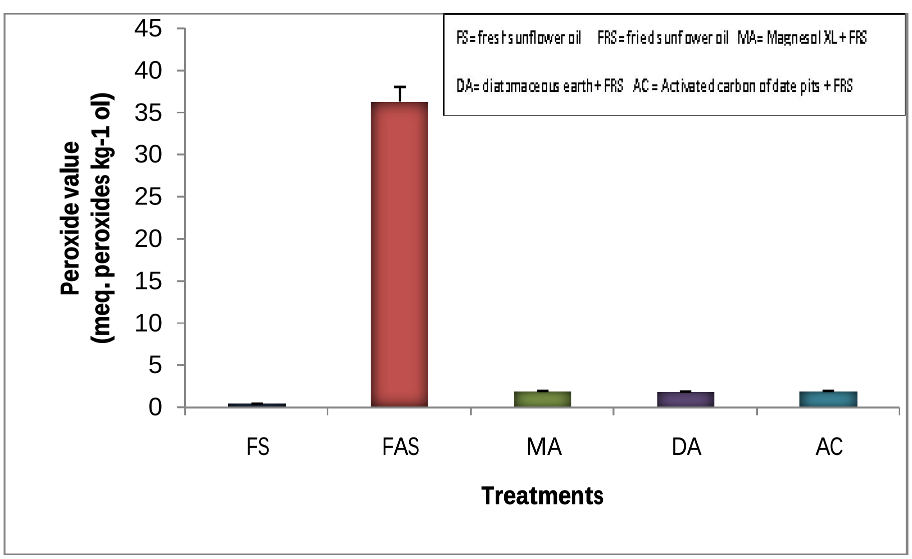


Figure 6. Changes in peroxide value of non fried, fried and fried-treated sunflower oil with different adsorbent materials.

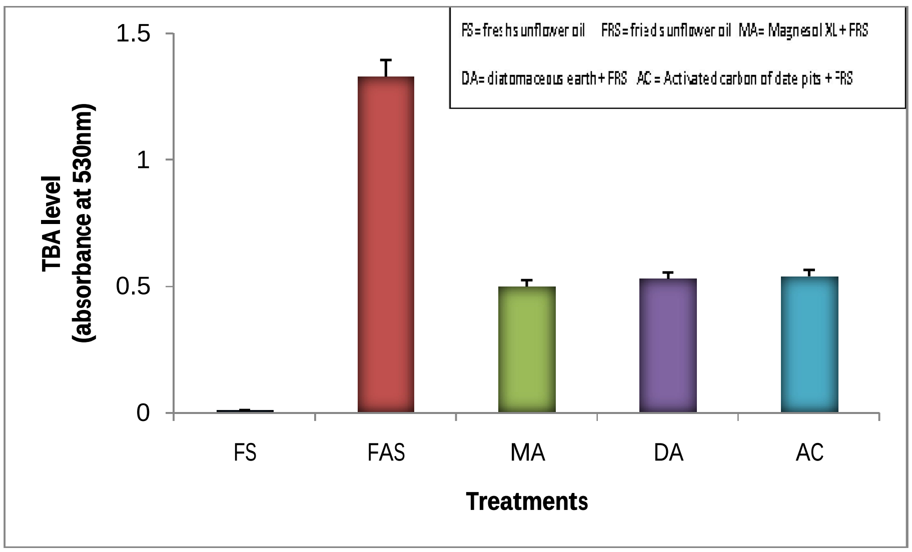


Figure 7. Changes in TBA level of non fried, fried and fried-treated sunflower oil with different adsorbent materials.

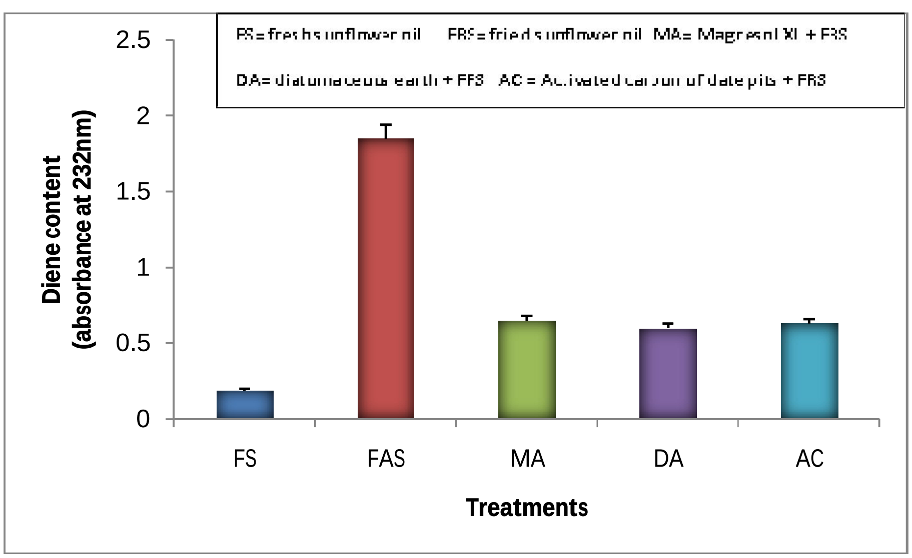


Figure 8. Changes in diene content of non fried, fried and fried-treated sunflower oil with different adsorbent materials.

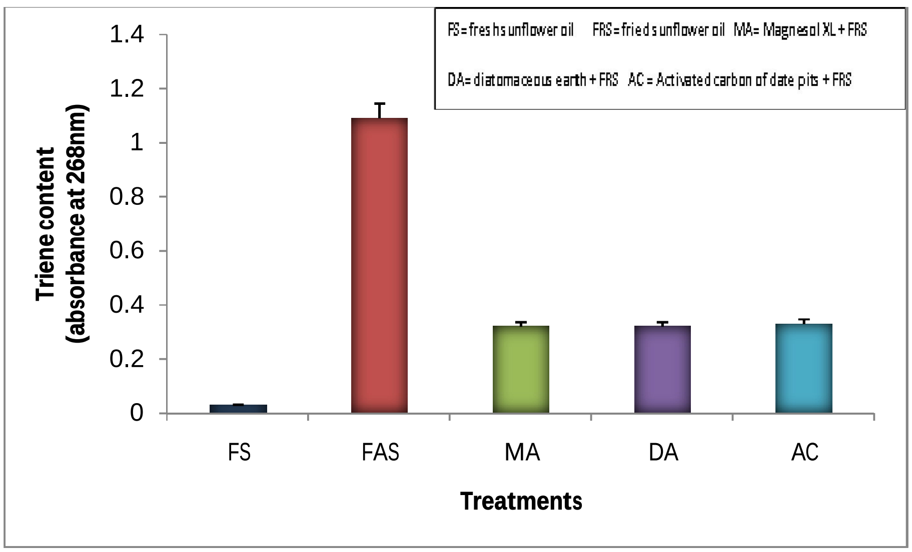


Figure 9. Changes in triene content of non fried, fried and fried-treated sunflower oil with different adsorbent materials.

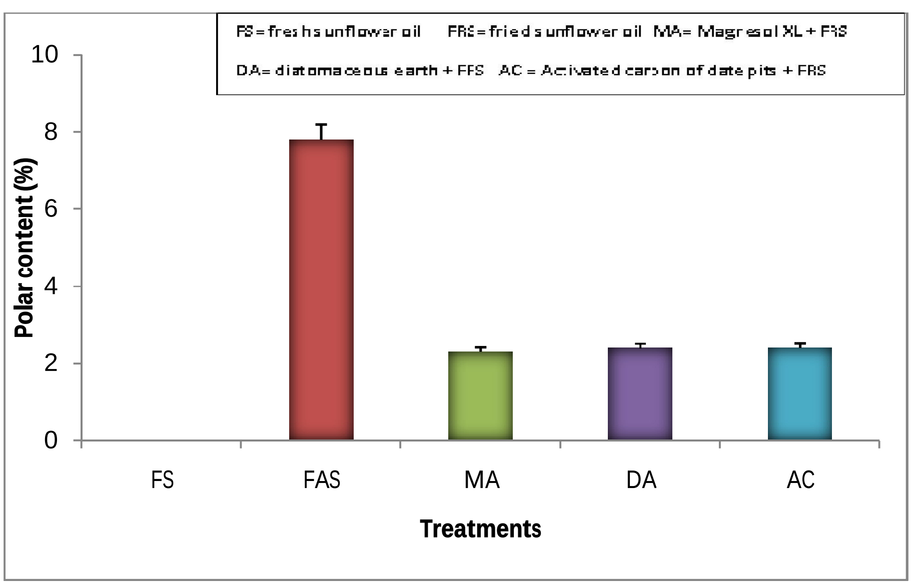


Figure 10. Changes in polar content of non fried, fried and fried-treated sunflower oil with different adsorbent materials.

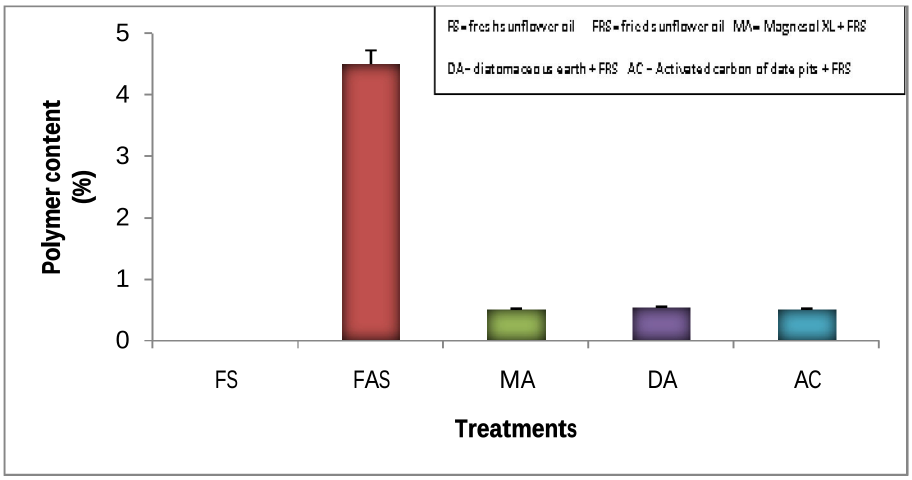


Figure 11. Changes in polymer content of non fried, fried and fried-treated sunflower oil with different adsorbent materials.

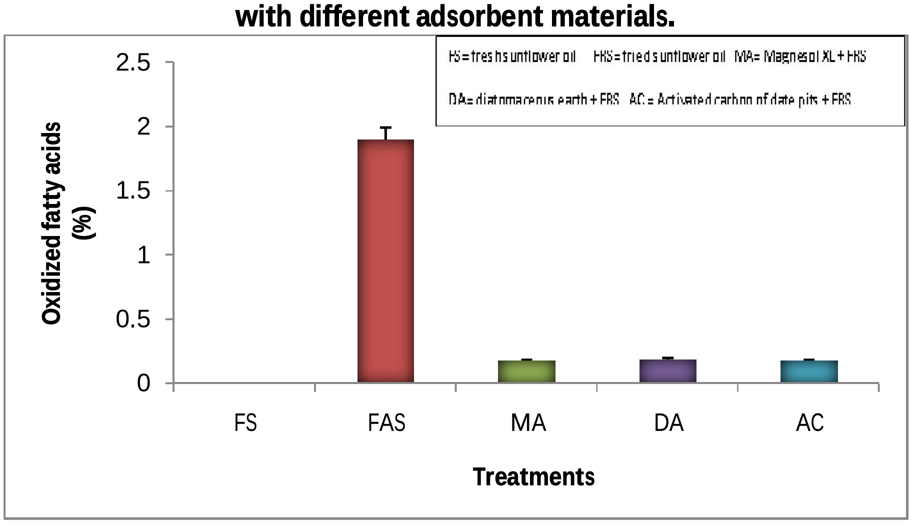


Figure 12. Changes in oxidized fatty acids of non fried, fried and fried-treated sunflower oil with different adsorbent materials.

REFERENCES

Al-Farsi, M., Alasalvar, C., Al-Abid, M., Al-Shoaily, K., Al-Amry, M. and Al-Rawahy, F. 2007. Compositional and functional characteristics of dates, syrups and their by-products. Food Chemistry. 104: 943-947.

Alhamed, Y. A. 2002. “Preparation and characterization of activated carbon from dates stones”, The 6th Saudi Engineering Conference, King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia. Proceedings, Volume 2, Chemical Engineering, pp: 461 – 472, 14– 17 December (2002).

Alhamed, Y. A. 2006. Activated Carbon from Dates' Stone by ZnCl2 Activation JKAU: Eng. Sci. 17 (2), 75–100.

AOAC 2005. Official Methods of Association of Agricultural Chemicals,18th edn. Washington, DC: AOAC.

Ardekani, M. R., Khanavi, M., Hajimahmoodi, M., Jahangiri, M. and Hadjiakhoondi, A. 2010. Comparison of antioxidant activity and total phenol contents of some date seed varieties from Iran. Iranian Journal of Pharmaceutical Research, 9: 141-146.

Assmann, G. 1979. Cholesterol determination in high density lipoproteins separated by three different methods. The Internist, 20, 559–604.

Basuny, A. M. and Al-Marzooq, A. M. 2010. Production of mayonnaise from date pits oil. Banat's Journal of Biotechnology, 2: 3-8.

Basuny, A. M., Shaker, M. Arafat, and Abeer, A. Kinawy. 2012. Antioxidant activities of date pits in a model meat system,International of Food Resrarch Journal, 19; 223-227.

Belfield, A. and Goldberg, D. M. 1971. A colorimetric method for determination of alkaline phosphatase in serum. *Enzyme*, 12, 561– 565

Bergmeyer, H. U. and Harder, M. 1986. A colorimetric method of determination of serum glutamic oxaloacetic and pyruvic tranasminase. *Clinical Biochemistry*, 24, 28–34.

Bhattacharya, A. B., Saijilata, M. G., Tiwari, R. S. and Singhal, R. S. 2008. Regeneration of thermally polymerized frying oils with adsorbents. *Food Chemistry*, 110: 562-570.

Billek, G., Guhr, G. and Waibl, J. 1978. Quality assessment of used frying fats: a comparison of four methods. *Journal of the American Oil Chemical Society*, 55, 778–783.

Buck, D. F. 1981. Antioxidants in soy oil. *Journal of the American Oil Chemical Society*, 58: 275–278.

Derbyshire, F, Jagtoyen, M. and Thwaites, M., 1995. Activated Carbons-Production and Applications, in: *J. W. Patrick*, (Edit.), Porosity in Carbon, Halsted Press, New York

El-Rayes, D. A. 2009. Characterization of three date palm cultivars based on RAPD finger prints and fruit chemical composition. *Environmental & Arid Land Agriculture Science*, 20: 3-20.

FAO 2010. Statistical databases. http://faostat.fao.org Accessed June 2010.

Farag, R. S. and Basuny, A. M. 2002. New method for improving the quality of peroxidized oils. *Advances in Food Sciences*, 24, 50–54.

Farag, R. S. and El-Anany, A. M. 2006. Improving the quality of fried oils by using different filter aids. *Journal of the Science of Food and Agriculture*, 86, 2228–2240.

Farag, R. S., Ebtesam, A. M. and Amany, B. M. M. 2007. Use crude olive leaf juice as a natural antioxidant for the stability of sunflower oil during heating. *International Journal of Food Science and Technology*, 42, 107–115

Farag, R. S., Basuny, A. M., Aafat, S. M. and Arafa, S. A. 2009. Use of some agricultural waste hull ashes for the regeneration of fried sunflower oil. Intr. *J. Food Sci. & Tech*. 44: 1850-1856.

Firestane, D., Stier, F. R. and Blumenthal, M. M. 1991. Regulation of frying fats and oils. *Food Technology*, 45: 90-94

Frings, C. C. and Dunn, R. T. 1970. Colorimetric method for determination of total sera lipids based on the sulphophovanillin reaction. *Am. J. Clin. Pathol*. 53: 89-91.

Hussein, A. S., Alhadrami, G. A. and Khalil, Y. H. 1998. The use of dates and dates pits in broiler starter and finisher diets. *Bioresource Technology*, 66: 219-223.

IUPAC. 1987. Standard Methods for the Analysis of Oil, Fats and Derivatives, 7th edn (edited by C. Paquot & A. Hautfenne). Oxiford, UK: Blackwell Publishing.

Lin, S., Khoh, C. C. and Reynolds, A. S. 2001. Recovery of used frying oils with adsorbent combinations; Refrying and frequent oil replenishment. *Food Res. Intr*. 34: 159-166.

Lin, S., Akoh, C. C. and Reynilds, A. E. 1999. Recovery of used frying oils with adsorbent combinations: refrying and frequent oil replenishment. *Food Research International*, 34, 159–166.

Mobarak, S. A. 2009. Antioxidant properties of date palm (Phoenix dactylifera L.) cultivars. Ph.D. Colorado State University.

Nielsen, S.S. 1998. Food Analysis, 2nd edn. Pp. 222–223. Gaithersburg, *Maryland*: Aspen Inc.

Paik, T. H., Hoshino, T. and Kaneda, T. 1976. Histopathological studies on mice administered autooxidized oils (acute toxicity). *Journal of the Japan Society of Food and Nutrition*, 59, 85–94.

Roechlau, P., Bernt, E. and Gruber, W. L. 1974. Kinetics of the cholesterol sulfuric acid reaction: a fast kinetic method for serum cholesterol. *Clinical Chemists and Clinical Biochemistry*, 12, 403–408.

Sekirifa, M. L., Hadj-Mahammed, M., Pallier, S., Baammeur, L., Richard, D. and Al-Dujaili, A. H. 2013. Preparation and characterization of an activated carbon from a date stones variety by physical activation with carbon dioxide. *Journal Analytical & Applied Pyrolysis*, 99: 155-160.

Sidwell, G. G., Harold, S., Milado, B. and Mitchell, J. H. 1954. The use of thiobarbituric acid as a measure of fat oxidation. *Journal of the American Oil Chemical Society*, 63, 1363–1367.

Subramanian, K. E., Nandini, P. M. and Sheola, A. G. G. 2000. Membrane processing of used frying oil. *Journal of the American Oil Chemical Society*, 77, 323–328

Sulaiman, A., Hassan, N. and Abbas, F. 2011. Using activated carbon from waste date-pits as an adsorbent for transformer oil regeneration. *Sustainable Technology*, 10: 69-72.

Waltking, A. E. and Wessels, H. 1981. Chromatographic separation of polar and nonpolar components of frying oils. *Journal of the Association of Official Analytical Chemistry*, 64, 1329–1330.

Wang, F., Jiang, L., Zhu, X. and Hou, J. 2013. Effects of frying on polar material and free fatty acids in soybean oils. *Int. J. Food Sci. & Tech*. 48: 110-117.

Wu, P. F. and Nawar, W. W.1986. A technique for monitoring the quality of used frying oils. *Journal of the American Oil Chemical Society*, 63, 1363–1367.

Yates, R. A. and Calsdwell, J. D. 1993. Regeneration of oils used for deep-frying: a comparison of active filter aids. *J. Am. Oil Chem. Soc*. 70: 507-511.

Yoshioka, M., Tachibana, K. and Kaneda, T. 1974. Studies on the toxicity of the auto oxidized oils. IV. Impairment of metabolic functions induced by auto oxidized methyl linoleate. *Journal of the Japan Oil Chemical Society*, 23, 327–331.

Corresponding author: Dr. Amany M. M. Basuny, Food Science and Nutrition Department, Faculty of Agricultural Science and Foods, King Faisal University, Saudi Arabia.
Email: dramany_basuny@yahoo.com dr_shakerarafat@yahoo.com