RECOVERY OF FRIED SUNFLOWER OIL BY USING SUGAR CANE INDUSTRY WASTE AND HOT WATER

Rehab Farouk Mohammed Ali[1], El Anany Ayman Mohammed*[2]
[1]Department of Biochemistry, Faculty of Agriculture, Cairo University , 12613, Giza, Egypt .
[2]Special Food & Nutrition Department, Food Technology Research Institute,
Agricultural Research Center , Giza , Egypt
*E-mail: ayman_anaany@yahoo.com

Abstract
The main goal of the current investigation was to use sugar cane bagasse ash (SCBA) and to compare its adsorption efficiency with Magnesol XL as synthetic adsorbents to regenerate the quality of fried sunflower oil. In addition, to evaluate the effect of water washing process on the quality of fried and fried – treated sunflower oil. The metal patterns of sugar cane bagasse ash and Magnesol XL were determined. Some physical and chemical properties non-fried, fried and fried–treated, sunflower oil were determined. Sunflower oil sample was heated at 180 °C $\pm$ 5 °C, then frozen French fries potato were fried every 30 min. during a continuous period of 20 h. Oil samples were taken every 4 h. The filter aids were added individually to the fried oil at levels 1, 2 and 3 % (w / v), then mechanically stirred for 60 min at 105 ºC. The results indicate that all the filter aids under study were characterized by high levels of Si and variable levels of other minerals. The highest level of Si was recorded for sugar cane bagasse ash (SCBA) was 76.79 wt. %. Frying process caused significant (P$\leq$0.05) increases in physico-chemical properties of fried sunflower oil. The treatments of fried oil with different levels of SCBA and Magnesol XL caused significant (P$\leq$0.05) increase in the quality of fried-treated oil, however the soap content of fried – treated oil was increased also, therefore, the effects of water washing process on the quality of fried and fried – treated sunflower oil was evaluated. The values of soap and polar after water washing process were about 4.62 and 7.27 times as low as that for fried sunflower oil treated with 3 % sugar cane bagasse ash (SCBA).

Keywords: sugarcane, industrial waste, frying , ash, adsorbent , quality and water washing.

1. INTRODUCTION

Deep-fat/oil frying is extensively used in food processing both industrially and at home, and fried potato products are one of its largest applications. Deep-fat frying is one of the oldest and most popular food preparation methods. As reported by Garayo and Moreira (2002), the economy of commercial deep fat frying has been estimated to be $6 billion year[-1] in the United States and at least twice that amount for the rest of the world. Fried foods have a desirable flavor, color and crispy texture, which make deep-fat fried foods very popular with consumers (Boskou et al., 2006). Deep-fat frying is a process of immersing food in hot oil with a contact among oil, air and food at a high temperature of 150 to 190℃ (Yamsaengsung and Moreira, 2002). The simultaneous heat and mass transfer of oil, food and air during deep-fat frying produces

the desirable quality of fried foods. In the presence of oxygen, moisture, trace elements and free radicals, physiochemical reactions such as thermoxidation, hydrolysis, polymerization, isomerization or cyclization take place at the high temperatures of the frying process, thus leading to the decomposition of frying oil and formation of monomeric, polymeric, primary and secondary oxidative compounds, thereby affecting the quality of oil and fried product (Andrikopoulos et al., 2002). The oxidized products of fatty acids give off-flavors and odors (hydrolytic rancidity) to the frying medium and fried foods (Lin et al., 2001; Remero et al., 2007; Farag and El-Anany, 2007). Several studies reported that using vegetable oils in prolonged frying processes may be a principle or strong reason for inducing or forming mutagenic or carcinogenic diets (Hamilton et al., 1997; Coultate, 2002; Gouveia De Souza et al., 2004;

Pavia & Gordon, 2005; Khalil et al., 2009). The mutagenicity/ carcinogenicity of such diets may be due to the fact that the repeatedly used vegetable oils in frying processes undergo degradation by oxidative reactions that lead to form lipid peroxidation (Nagao et al., 1997; Lampe, 1999; Raloff, 1999). High intakes of diets containing lipid peroxidation component may be associated with the generation of free radicals (Schut et al., 1997; Lampe, 1999; Coultate, 2002; Guardiola et al., 2008). In this respect, methyl linoleate hydroperoxides orally administered to mice caused necrosis, fatty degeneration and congestion in tissues (Paik et al., 1976). 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). For example, 4-hydroxy-trans-2- nonenal is a strong toxic compound in oxidized fats and oils in heated cooking oil (Seppanen and Csallany, 2004). These reports indicate the necessity to remove peroxides and these toxic compounds from deteriorated fried oils. In this respect, there are various methods that can be used to remove these products such as filtration through special membranes (Mulflur &Munson, 1987; Subramanian et al., 2000) and by using different adsorbent materials including both natural and synthetic adsorbents. Usually, active forms of carbon, calcium, silica, alumina, and magnesia are major constituents of such products (Yates and Caldwell, 1992, 1993; Lin et al., 1999; Farag and El-Anany, 2006; El-Anany & Rehab,Ali, 2008 and Farag et al., 2009). By these methods, the treated oils can be used again in deep-fat frying process. Many reports have been appeared on the production of low cost adsorbents using cheaper and readily available materials (Babel and Kurniawan, 2003, and El Nemr et al., 2008). In this regard, Sugar cane is one of the most common raw materials used in sugar and ethanol production. Sugarcane is one of the major crops grown in over 110 countries and its total production is over 1500 million tons (Deepchand, 1986). After the extraction of all economical sugar from sugarcane, about 40-45% fibrous residue (FAO, 2006, Partha and Sivasubramanian, 2006 and Rasul et al., 1999) is obtained, which is reused in the same industry as fuel in boilers for heat generation leaving behind 8 -10 % ash as waste (Payá et. al., 2002), known as sugarcane bagasse ash (SCBA). The SCBA contains high amounts of un-burnt matter, silicon, aluminum and calcium oxides (Deepchand, 1986). The high polyunsaturated fatty acids (PUFA) content in oil are highly susceptible to oxidative reactions. Therefore, appropriate processing conditions should be used to eliminate or reduce impurities such as phospholipids, gums, metals, free fatty acids (FFA), oxidation products (peroxides, aldehydes and ketones) and pigments, in order to ensure the best oil quality. The impurities are eliminated through degumming (Farr, 2000); the principal method of degumming employed in the United States is a batch treatment of the oil with 1 to 3% of water, based on oil volume (Carr, 1978). The mixture is agitated for 30-60 min at 70-80 C. The hydrated phosphatides and gums can be separated from the oil by settling, filtering or centrifuging. (Brekke, 1980; Erickson, 1995). The water washing process removes about 90% of the soap content in the refined oil; the remainder of the soap is removed in the bleaching process (Mounts and Khym, 1980).

The main goal of the current investigation was to use sugar cane bagasse ash (SCBA) and to compare its adsorption efficiency with Magnesol XL as synthetic adsorbents to regenerate the quality of fried sunflower oil. In addition, to evaluate the effect of water washing process on the quality of fried and fried – treated sunflower oil.

2. MATERIAL AND METHODS

Sunflower oil
Refined sunflower oil (25 Kg) was obtained from Sila edible oil Co. S. A. E., Kom Osheim, El-Fayoum governorate, Egypt. The oil peroxide and acid values were 0.40 (meq/kg oil) and 0.10 (mg KOH/g oil), respectively.

Sugar cane bagasse (SCB)
Sugar cane bagasse (SCB) was obtained from Hawamdiah sugar refinery company, El-Hawamdiah, Egypt.

Magnesol XL:
Magnesol XL (Hydrous, white, amorphous, and odorless synthetic magnesium silicate) was obtained from Magnesol Product Division, Reagent Chemical and Research, Inc. Houston, Texas, USA.

Chemicals
All chemicals were used in the current study were obtained from Sigma Chemical Company (England, London Ltd., Pools).

Preparation of Sugar cane bagasse ash (SCBA).
Sugar cane bagasse (SCB) was first washed thoroughly with distilled water to remove the dust particles, then dried in an oven at 100 °C for 72 h. The dried product was ground in a grinder (Perten, USA) to a particle size of about 190 nm, placed in a crucible, carbonised in air in a muffle furnace (Furnace 5000; Thermolyne, Iowa, USA) at $650^{\circ}C$ for 12 h and then cooled to room temperature in a desiccator and stored in glass screw-capped bottles.

Determination of metals
The metal contents (Si, Ca, Fe, Al, Mg, K and Na) of various filter aids were determined using a Perkin-Elmer Model 3300 atomic absorption spectrophotometer (The Perkin-Elmer Corporation, Norwalk, USA) after digestion with fluoro-boric acid according to the procedure given by Bernas (1968). As follows: A known weight of the ground sample (ca 50 mg) was placed in a teflon vessel of the acid digestion bomb. Aqua regia (mixture of HNO_3 (1 part) and concentrated HCl (3 parts), 0.5 ml) followed by HF (3 ml, 48%) were added to the sample. The contents of digestion bomb were heated at 110 °C for 40 min. After cooling, the contents of the bomb were quantitatively transferred into a 100 ml polyethylene beaker, with deionised water (5 ml). Boric acid (2.8 g) and deionized water (5 ml) were added to

dissolve any precipitate. This solution was quantitatively transferred to a 100 ml polyethylene volumetric flask, completed to the mark with deionised water and used for the metal determination. A blank was conducted simultaneously using all reagents except the filter aid.

Frying Process
Sunflower oil (25 kg) was placed in a stainless steel pan of electric fryer (45 cm depth x 52 cm length x 40 cm width, Frymaster L.L.C., Shreveport, Louisiana, U.S.A) and heated at 180°C ± 5°C. Then 500 g of frozen French fries potato were fried every 20 min. Oil samples were taken every 4 h and the continuous frying period was 20 h. The oil samples were left to cool down then stored at – 18°C for physico-chemical analysis and filtration process.

Filtration Process
The filter aids were added individually to the fried oil at levels 1, 2 and 3 % (w/v), then mechanically stirred for 60 min at 105 ºC. The slurry was vacuum filtered through a Whatman No 41 filter paper (Whatman International Ltd, Maidstone, UK). Vacuum filtration facilitated flow of oil through the filter paper. The untreated fried sunflower oil was vacuum filtered through a Whatman No 41 filter paper.

Water washing process
Oil sample was heated at 70°C and hot water 80–85 °C was added (1/1 v/v). The mixture was mixed for 15 minutes with the aid of a glass rod, and then left at room temperature for cooling. The upper oil phase was separated by centrifugation at 10,000 × g for 20 min. The centrifuged oil was left in contact (stirred) with the anhydrous Sodium sulfate for ca. 5 min, then vacuum filtered through a Whatman No 41 filter paper.

Quality assurance tests
These tests were conducted on fresh, fried and fried- treated oil samples.
Physical properties

Refractive index

Refractive index of the oil was determined according to the A.O.A.C. method (2000) using Abbe - refractometer (NYRL - 3 - Poland).
Colour Lovibond tintometer (Tintometer Limited Solstice Park, Amesbury, UK) was used to measure the colour of the oil samples under investigation, the yellow glass filter was fixed at 30 and the intensity of red glass colour was measured according to the A.O.A.C. method (2000).

Viscosity

Brookfield LV viscometer Model TC-500 (Brookfield Engineering Laboratories Stoughton, MA, USA) was used to measure the viscosity of the oil samples at 30 °C. according to the method described by Saguy et al. (1996).

Chemical properties

Acid value

Acid value was determined according the A.O.A.C. method (2000) as follows. A Known weight (2 g) of the oil was dissolved in a neutral ethyl alcohol (30 ml). The mixture was boiled on a water bath for 2min and then titrated with potassium hydroxide solution (0.1N).

Peroxide value

The peroxide value was determined according to A.O.A.C method (2000) A known weight of the oil sample (2.5 g) was dissolved in a mixture consisted of glacial acetic acid: chloroform (30 ml, 3 : 2, v/v) then freshly prepared saturated potassium iodide solution (1 ml) was added. Distilled water (30 ml) was added then titrated slowly with sodium thiosulphate solution (0.1N).

Thiobarbituric acid value (TBA)

The method of Sidwell et al. (1954) was conducted to determine the TBA value as follows. A known weight of oil (3g) was dissolved in a carbon tetrachloride (10ml) followed by the addition of TBA reagent (10ml, 0.67% TBA in 50% acetic acid). The mixture was transferred to a separatory funnel and the aqueous layer was drawn into a test tube and immersed in a boiling water bath for 30 min. The absorbance of the developed pink colour was then recorded at 532nm against a blank reagent.

Insoluble polymer content

The insoluble polymers were determined according to the method outlined by Wu and Nawer (1986) as follows. One gram of oil was added to methanol (125 ml) containing 1% H_2SO_4. The mixture was boiled under a reflux condenser for 2 h and cooled to room temperature. The methanol insoluble were filtered and washed with methanol until no sulphuric acid remained. The washed insoluble polymers were dissolved in petroleum ether (25 ml) and transferred to a pre - weighed flask. The solvent was then evaporated under a stream of nitrogen and the flask was again weighed.

UV spectroscopic indices

An aliquot of the sunflower oil samples (0.1 mL) was dissolved in methanol (3 mL), vortexed and the absorbances at 232 and 288 nm were recorded for conjugated dienes and trienes, respectively as mentioned by Kates (1972)

Total polar compounds (TPC) content

Polar components in sunflower oil samples were measured by column chromatography according to the method described by Waltking & Wessels (1981).

Statistical analysis

Data were statistically analyzed in completely randomized design in factorial arrangement according to the procedures outlined by Gomez and Gomez 1986 and the treatments means were compared by least significant differences (L.S.D) and Duncan multiple range using SPSS program package.

3. RESULTS AND DISCUSSION

Mineral patterns of synthetic and natural filter aids:

Table 1 shows the mineral content of Magnesol XL (synthetic filter aid) and sugar cane bagasse ash (SCBA), sugar cane industry waste). All the filter aids under study were characterized by high levels of Si and variable levels of other minerals. The highest level of Si was recorded for sugar cane bagasse ash (SCBA) was 76.79 wt. % followed by Magnesol XL was 70.92 wt. %. Sugar cane bagasse ash (SCBA) had also other minerals were Al_2O_3, CuO, Fe_2O_3, CaO, K_2O, MgO , and Na_2O (1.87 wt.%, 0.58, wt.% 0.48, 5.81 wt.%, 2.42 wt.% 2.37 and 0.15 wt.%, respectively). Magnesol XL had the highest level of Mg was 17.78 wt. % however it was free from Cu and K . Several authors studied the mineral contents of various natural and synthetic filter aids. For instance, Jacobson (1967) mentioned that the major constituents of filter aids (natural and synthetic adsorbents) were carbon, calcium, silicon, alumina and magnesia. Farag and El-Anany, 2006 determined the minerals in Magnesol XL to be Si (34.75%), Mg (27.33%), Ca (4.36%), Na (1.92%) and Fe (1.09%). Also, Ajay Goyal et al., 2007, Frı´as et al ., 2007 and Samsudin et al., 2009 determined the minerals of sugar cane bagasse ash (SCBA). Their analysis indicated that sugar cane bagasse ash (SCBA) contained Si (from 50.36 to 74.79 %), Al (from 1.78% to 4.38%), Fe (from 0.45% to 2.25%), Na (from 0.15- to 2.05%), K (from 0.52% to 3.10%) an Ti (0.02%).

Table 1. Mineral pattern of Magnesol XL and sugar cane bagasse ash (SCBA)

adsorbent	SiO2 (%)	CuO (%)	Fe2O3 (%)	CaO (%)	K2O (%)	MgO (%)	Na2O (%)
Magnesol XL	70.92b ±1.58	0.00b ± 0.00	0.25b ±0.03	6.00b ±0.50	0.00b ±0.00	17.78a ±1.60	4.55a ±0.35
(SCBA)	76.79a ±1.99	0.58a ± 0.08	0.38a ±0.07	8.98a ±0.40	2.37a ±0.22	7.45b ±1.30	3.21b ±0.26
LSD at 0.05=	4.07	0.12	0.12	1.02	0.35	3.30	0.69

Quality of fresh and fried sunflower oil.

Refractive index
Refractive index is a good diagnostic parameter for the degree of oil unsaturation and this value increased by increasing number of conjugated double bonds in the oil. The data in table 2 show that frying process led to gradual increases in the refractive index. It is well known that frying process caused conversion some of the non-conjugated double bonds into conjugated ones. This case led to an increase in the refractive index. This increase in refractive index became significant ($P \leq 0.05$) after 16 and 20 h of frying process.

Colour
Colour of oil is one of the most eminent physical properties which attract the consumer appellant. In general this property affects the colour of fried food .The colour of fresh and fried oil samples was measured at the fixed yellow glass slide(35) and variable red glass slides. The colour of fresh sunflower oil was clear yellow, its value was 2.43. Frying caused gradual and significant ($P \leq 0.05$) increase of colour value. Colour darkening is a complicated process involving interaction with fatty acids, dimers, polymers and other minor compounds present in the oil (Xu et al.,1999).
The value of colour of fried sunflower oil at the end of frying process was about 4.69 times as high as that of fresh sunflower oil. The colour of sunflower oil changed from clear yellow to dark brown especially during the last days of the frying process.
The dark colour patterns were significantly different from each heating period and correlated with hours of deep fat frying process (Farag et al., 2009a, b ; El-Anany and Ali, Rehab, 2010).

Table 2. Changes in some physico-chemical properties of sunflower oil during frying (180°C ± 5°C)

Physico-chemical properties	Frying period (h)						
	0	4	8	12	16	20	LSD at 0.05=
Refractive index	1.4724e 0.00035±	1.4734d ±0.0004	1.4748c ±0.0005	1.4770b ±0.0003	1.4820a ±0.0007	1.4825a ±0.0005	0.000868
Viscosity (centipoises)	38.12e ±0.69	43.42d ±1.09	47.68c ±1.31	48.74c ±1.21	52.33b ±0.98	63.52a ±1.45	2.042
Color (Red slide)	2.43 e ±0.64	3.50d ±0.50	6.46c ±0.25	8.79b ±0.34	10.68a ±0.30	11.40a ±0.35	0.749
Acid value (mg KOH g^{-1}oil)	0.10f ±0.03	0.26e ±0.05	0.42d ±0.07	0.54c ±0.07	0.711b ±0.04	0.88a ±0.04	0.10
Peroxide value (meq.Peroxides/Kg oil)	0.40f ±0.09	2.05e ±0.30	4.90d ±0.06	7.46 c ±0.36	10.58b ±0.44	8.42a ±0.42	0.56
TBA value(absorbance at 530 nm)	0.00 ±0.00	0.11 ±0.025	0.25 ±0.050	0.28 ±0.03	0.43 ±0.025	0.49 ±0.051	0.06
Polymer content (%)	0.00e ±0.00	0.29c ±0.04	0.48c ±0.08	0.84b ±0.09	0.93b ±0.14	1.28a ±0.25	0.228
Conjugated dienes (absorbance at 234nm)	0.09f ±0.005	0.12e ±0.02	0.17d ±0.01	0.22c ±0.01	0.27b ±0.01	0.34a ±0.02	0.026
Conjucated trienes (absorbance at 268nm)	0.03e ±0.01	0.07d ±0.01	0.09cd ±0.01	0.12bc ±0.02	0.14b ±0.02	0.17a ±0.01	0.029
Polar content (%)	0.06f ±0.03	0.85e ±0.22	2.65d ±0.41	5.51c ±0.42	7.92b ±0.56	12.56a ±0.80	0.84
Soap (ppm)	0.00e ±0.00	0.11e ±0.02	0.42d ±0.07	0.65c ±0.15	1.42b ±0.2	4.10a ±0.18	0.23

Viscosity

Viscosity is one of the most important parameters required to determine the quality and stability of food system. Table 2 shows the changes in viscosity of fresh and fried sunflower oil. Viscosity of non-fried oil at the beginning of the frying experiment was 38.12 centipoises, however the viscosity value of fried sunflower oil was about 1.66 times as high as that in fresh oil. The increase of viscosity may due to the formation of high molecular weight polymer compounds leading to the higher the degree of deterioration (Gray, 1978 ; Abdulkarim et al., 2007). These polymer compounds led to increase the viscosity values of fried oil.

Acid value

Determination of FFA appears to be the method favored by many operations for quality control evaluation of used frying oil (Stevenson, 1984). Free fatty acids in the fryer oil could be considered as a valid oil quality indicator, where the free fatty acids are allowed

to go up to >0.5% in the fryer (Gupta, 2005; Abdulkarim et al., 2007).Data presented in Table (2) show that the acid values of fried sunflower oil were gradually and significantly (P≤0.05) increased with increasing the period of frying. The acid value of fried sunflower oil at the end of frying process (20 h) was 0.88, and this value was about 8.8 times as high as that in non- fried sunflower oil . Free fatty acids (FFA) are formed during oil hydrolysis and during deep – fat frying process (Wu and Nawar, 1986). As a result of this, the amount of FFA was increased by almost 9 times (Orthoefer et al ., 1996).

Peroxide value (PV)

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 oil oxidation. Data presented in Table 2 show that peroxide values of fried sunflower oil were gradually and significantly (P≤0.05) increased during the first hours of frying time and then decreased after

20 h of frying period. The increase in the PV during frying process indicates a decrease of unsaturated fatty acid due to oxidation. However, peroxides are unstable compounds particularly under high temperature conditions; therefore the peroxides decompose to form carbonyl and aldehydic compounds causing the decease in peroxide value (Perkins, 1967; Shahidi and Wanasundara, 2002).

The amount of hydroperoxides that were formed at the   end of the frying process was more than 27.1 times as high as that at the beginning of the frying process. Frying process caused forming a molecule of hydroperoxide and releasing peroxy radical (Gupta, 2005).

TBA values

Table 2 shows the changes in the TBA values of fresh and fried sunflower oil. Frying process led to a gradual and significant (P≤0.05) increases in the TBA values (absorbance at 535 nm) and this value was more than 49 times that in fresh sunflower oil at the end of frying period. This finding clearly indicates that the strong effect of the frying period on the formation of secondary oxidation products that were formed during frying process and could be explained by the fact that the   primary oxidation compounds (i.e. hydroperoxides) are very unstable and decompose into a series of aldehydes, ketones, hydrocarbons, alcohols, and many more reaction products as the oil oxidation process continues. These carbonyl compounds react with TBA reagent to produce TBA derivatives that have a high absorbance at 535 nm. (Przybylski and Eskin, 1995).

UV spectroscopic indices

Data presented in Table 2 show the changes in the content of each conjugated dienes and trienes in fresh and fried sunflower oil. These data show that fresh sunflower oil had low levels of conjugated diene and trienes were 0.09 and 0.03, respectively. Frying process led to increase the values of conjugated diene and trienes, this increase was gradually and significantly with increasing frying period. The fried sunflower oil at the end of frying period had significantly (P≤0.05) the highest levels of

conjugated diene and trienes were 0.34 and 0.17, respectively. Frying process at 180 ° ± 5ºC caused positional rearrangement in sunflower oil double bonds and part of the non-conjugated system was converted to conjugated diene and triene double bonds (Farag et al., 2009a, b; El-Anany and Ali, Rehab, 2010).

Polymer Content

Polymer content is one of quality indicator of the validation of fried oil. The oil quality control regulations (IUPAC, 1987) indicate that the polymer levels must not exceed 1.5%. Data presented in Table 2 show that non fried sunflower oil did not contain polymers, whereas frying process caused gradual and significant (P≤0.05) increase in the level of polymer materials this increase was gradually and significantly with increasing frying period. Fried sunflower oil at the end of frying process (20 h) had significantly (P≤0.05) the highest levels of polymer materials was 1.28 % . It is well known that the polymer content increases as the oxidative rancidity of oil exposed to frying temperatures proceeds (Yoon et al., 1985).

The increase in polymer content is due to the formation of higher molecular weight substances by polymerization occurring at elevated frying temperature (Peled et al., 1975).

Total Polar Compounds TPC

Determination of TPC is mainly carried out as the most accurate method for assessing the degree of frying oil degradation (Blumenthal, 1996). The concentration level of polar compounds is a good indicator of the overall quality of frying oils, providing critical information about the total amount of newly formed compounds having higher polarity than triacylglycerols. Many European countries such as Spain, Portugal, France, Germany, Belgium, Switzerland, Italy and the Netherlands have established regulatory limits for TPC in frying oils (Blumenthal, 1996).

Most of these countries have considered a limit of 25% TPC.   The changes in the TPC content of fresh and fried sunflower oil are shown in Table 2. Fresh sunflower oil had low level of

total polar materials was 0.06 % and this low level indicate that fresh oil was of good quality. However, frying process caused significant increase in the level of polar materials. The polar content of sunflower oil 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 (Table 2).The TPC content of fried sunflower oil at the end of frying process was about 209.3 times as high as that of fresh sunflower oil. Thermal oxidation degradation products are polar in nature (Orthoefer et al., 1996).

Soap Content
Table 2 shows the soap content of fresh and fried sunflower oil. Fresh sunflower oil did not contain soap materials. However, the frying process caused gradual and significant ($P \leq 0.05$) increases in the formation of soap content. Fried sunflower oil at the end of frying period had 4.10 ppm of soap materials.
This amount of soap materials was probably due to the interaction of some food components with oil during frying process, the metals, naturally present in the food, can form soap by reacting with the free fatty acids in the oil. Soap, thus formed in the oil, can produce an oil/water solution in the fryer and promote hydrolysis in the oil. (Blumenthal and Stockler, 1986 ; Gupta, 2005).

Effect of filter aids on the quality of fried sunflower oil.
Although some adsorbent suppliers and researches recommended between 0.1 to 2.0 % for single adsorbent (Brook, 1991). Therefore, we decided to evaluate the efficiency 1- 3 % concentration of each adsorbent. Table 3 shows the changes in some physico-chemical properties of fried- treated sunflower oil. Fried sunflower oil had a refractive index of 1.4825 at 25 °C. This decrease was gradually and significantly increased with increasing the adsorbent concentration. The treatment with

different levels of Magnesol XL and sugar cane bagasse ash (SCBA) caused a significant ($P \leq 0.05$) decreases in the values of the refractive index.
The treatment with 2 and 3 % of SCBA had significantly ($P \leq 0.05$) the highest efficiency in removing some of some unsaturated compounds resulted from frying at 180 °C ± 5 °C for 20 hr. In addition, the treatment with 1% SCBA as well as 2 and 3 % of Magnesol XL induced non-significant effect between them on the refractive index of sunflower oil. The viscosity of fried sunflower oil at 180 _C for 20 h was 63.52 centipoises. Formation of polymers during frying is mainly responsible for the changes in the viscosity of the oil (Paul and Mittal, 1997)
The treatment of fried sunflower oil with filter aids at different levels induced a significant lowering effect on the viscosity. It is worth noting that the value of viscosity was dependent upon the level of adsorbent, the higher level caused the higher lowering effect on the value of viscosity.
The efficiency of SCBA at level 3 % was significantly ($P \leq 0.05$) the highest in reduction the viscosity of fried sunflower oil. The efficiency of SCBA at level 2 % in lowering the viscosity of fried sunflower oil was significantly ($P \leq 0.05$) the same as that of Magnesol XL at levels 2 and 3 %. The reduction in viscosity indicates that polymers, which are the high molecular weight fraction of the degradation products, are reduced in the oil (Subramanian et al., 2000). The value of intensity of red glasses of fried sunflower oil was 11.40. Oxidation products, polymerization products and carbonization products, are responsible for the red color (Paul and Mittal, 1997).
Treatment with various levels of adsorbents caused significant ($P \leq 0.05$) decreases of the red–coloured glasses. The values of red–coloured glasses were gradually and significantly ($P \leq 0.05$) decreased with the increasing the level of the adsorbent.

Table 3. Changes of some physico-chemical properties of fried sunflower oil treated with different levels of adsorbents.

Physico-chemical parameters	Fried oil	Fried- treated with						LSD at 0.05=
		Sugar cane bagasse ash (SCBA).			Magnesol XL			
		1 %	2 %	3 %	1 %	2 %	3 %	
Refractive index	1.4825a ±0.0005	1.4742c ±0.0004	1.4729d ±0.0006	1.4727d ±0.0006	1.4770b ±0.0003	1.4741c ±0.0007	1.4740c ±0.0003	0.0009
Viscosity(centipoises)	63.52a ±1.45	48.60b ±1.38	45.23c ±0.87	40.00d ±1.60	47.54b ±0.99	44.40c ±1.70	44.31c ±0.60	2.250
Color (Red slide)	11.40a ±0.35	5.50b ±0.65	3.20c ±0.42	2.70c ±0.61	5.65b ±0.85	3.26c ±0.52	3.21c ±0.24	1.27
Acid value (mg KOH g^{-1}oil)	0.88a ±0.04	0.42b ±0.09	0.17c ±0.01	0.16c ±0.02	0.40b ±0.06	0.20c ±0.1	0.15c ±0.07	0.110
Peroxide value (meq.Peroxides/Kg oil)	8.42a ±0.42	1.92b ±0.14	0.96c ±0.10	0.91c ±0.09	1.99b ±0.26	0.94c ±0.05	0.90c ±0.01	0.60
TBA value (absorbance at 530 nm)	0.49 a ±0.051	0.21b ±0.03	0.15bc ±0.04	0.11c ±0.01	0.23b ±0.055	0.16bc ±0.025	0.10c ±0.005	0.062
Polymer content (%)	1.28a ±0.25	0.45bc ±0.12	0.34bc ±0.10	0.14c ±0.02	0.48b ±0.12	0.33bc ±0.08	0.13c ±0.01	0.21
Conjugated dienes (absorbance at 234 nm)	0.34a ±0.02	0.22b ±0.02	0.15bc ±0.04	0.10c ±0.00	0.20b ±0.06	0.16bc ±0.05	0.10c ±0.00	0.061
Conjucated trienes (absorbance at 268 nm)	0.17a ±0.01	0.11bc ±0.01	0.08cd ±0.006	0.07d ±0.002	0.13b ±0.02	0.09cd ±0.00	0.07d ±0.01	0.026
Polar content (%)	12.56a ±0.80	7.22b ±0.48	5.18d ±0.41	4.62d ±0.32	7.52b ±0.47	6.18c ±0.46	4.24d ±0.36	0.864
Soap (ppm)	4.10c ±0.18	8.36b ±1.03	11.54ab ±1.62	14.55a ±2.13	8.57b ±1.44	11.89ab ±2.05	15.20a ±1.87	2.80

No significant differences (P≥0.05) in the efficiencies of 2 and 3 % SCBA as well as 2 and 3 % of Magnesol XL in reducing the values of red–coloured glasses were observed. The high performance of the mixture (mixture of 2% Pekmez earth (CaCO3 containing special natural white soil), 3% bentonite, 3% magnesium silicate and 92%, by weight) in improving the colour was believed to be based on the ability of magnesium silicate to remove colour bodies as well as bentonite. (Maskan, 2003). The effectiveness of magnesium silicate in colour improvement and removing the colour producing materials was reported by (Lin et al., 2001, Farag and El-Anany, 2006, Farag et al., 2009 and Suseno et al ., 2011).

Table 3 shows that the acid value of fried sunflower oil was 0.88. The treatment with various levels of adsorbents caused significant (P≤0.05) decreases of the values of free fatty acids. The values of acidity were gradually and significantly (P≤0.05) decreased with the increasing the level of the adsorbent. The treatment with SCBA and Magnesol XL at levels 2 and 3 % as had significantly (P≤0.05) the highest efficiencies in reducing the levels of FFA content of fried sunflower oil . The differences between the FFA content of oil treated with 1 % of SCBA and those treated with 1 and 1% of Magnesol XL were insignificant (P≥0.05). The acidity of fried oils was remarkably reduced by treatment with

adsorbents, the FFA values after treatment dropped by 25-50 % (Lin et al., 1999). The treatment of Lemuru (Sardinella lemuru) oil with Magnesol XL at 1, 3 and 5% levels reduced the acid value. Treatment with 1%Magnesol XL resulted in a reduction of the acid value by 46%. The use of 3% Magnesol XL resulted in no further reduction of the acid values (Suseno et al., 2011). The peroxide value of fried sunflower oil was 8.42.The treatment of fried oil with various levels of adsorbent caused gradual and significant (P≤0.05) decrease in peroxide values of fried sunflower oil . Peroxide values were gradually and significantly decreased with the increase of the adsorbent level. The highest reduction was observed in peroxide value in those fried sunflower oil treated with 2 and 3 % of Magnesol XL or SCBA. In the same time , no differences were observed between the efficiency of synthetic adsorbent (Magnesol XL) and natural adsorbent in removing the hydroperoxides resulted from frying at 180 ℃ ± 5 ℃ for 20 hr. The adsorbent treatment with a combination of conditions of 1% Magnesol concentration for 10 minutes, and 3 % Magnesol concentration for 5 minutes reduced PV by 60% and 59.5% respectively, giving the treated fish oil much lower peroxide values (Suseno et al., 2011). The treatment with hull ashes and Magnesol XL at level 2 % resulted in a significant decrease of the peroxide value of fried sunflower oil from 34.50 to 2.0 (Farag et al., 2009). TBA value of fried sunflower oil at the end of frying period (20 h) was 0.49 as determined by the absorption at 530 nm. Generally, the treatment of fried sunflower oil with various levels of adsorbents caused significant (P≤0.05) and gradual decrease in TBA values of fried sunflower oil. The reduction in TBA values was increased with the increasing the adsorbent level. Fried sunflower oil treated with SCBA and Magnesol XL at levels 3 % had significantly (P≤0.05) the lowest amount of secondary oxidation products were 0.11 and 0.10 as determined by the absorption at 530 nm, respectively. The purification process of palm oil with oxidized active carbon at ratio (15:1 w/w) resulted in a

significant decrease of the secondary oxidation products by about 15 %. (Buczek and Chwialkowski, 2008).

The treatment of fried sunflower oil with normal and modified silica gel adsorbents caused a significant decrease of secondary oxidation products by about 70-77 % (Farag et al., 2009). Table 3 demonstrates the polymer content of fried-treated sunflower oil with different concentrations of Magnesol XL and SCBA. Fried sunflower oil at 180 ± 5℃ for 20 hr had 1.28 % polymers. The treatment with different levels of Magnesol XL and SCBA induced significant (P≤0.05) decrease in the polymer content. In this respect the fried sunflower oil had nearly 5.80 and 5.50 times of polymer content as great as that in fried treated sunflower oil with 3 % of SCBA and Magnesol XL respectively. These findings indicate that these filter aids had significantly (P≤0.05) the same efficiency in removing the polymer compounds from the fried sunflower oil. The levels of conjugated dienes and trienes of fried sunflower at the end of frying period were 0.34 and 0.17 as determined by the absorption at 234 and 268 nm, respectively. The treatment of fried sunflower oil with various levels of Magnesol XL and SCBA caused significant (P≤0.05) decrease of the contents of conjugated dienes and trienes. The levels of conjugated dienes and trienes were gradually and significantly (P≤0.05) decreased with the increasing the level of the adsorbent. The values of conjugated dienes and trienes of fried sunflower oil treated with 3 % of SCBA were about 3.4 and 2.4 times as low as in fried sunflower oil without treatment, respectively Fried sunflower oil at the end of frying period (20 h) had a polar content of 12.56 %. Treatment with different levels of Magnesol XL and SCBA induced significant (P≤0.05) decrease in the polar content. The treatment with SCBA at levels 2 and 3 % as well as Magnesol XL at level 3 % had significantly (P≤0.05) the lowest values of the polar content were 5.18, 4.62 and 4.24 %, respectively. These values agreed well with the oil quality regulations (IUPAC, 1987). Fried sunflower oil at the end of frying period (20 h) had a soap

content of 4.10 ppm. Treatment with different levels of Magnesol XL and SCBA induced significant (P≤0.05) increase in the soap content. This increase was gradually and significantly increased with increasing the adsorbent concentration. The soap content of fried sunflower oil treated with 1, 2 and 3 % of SCBA were about 2.03, 2.57 and 3.06 times as high as that in fried sunflower oil without filtration. The results indicate also that the treatment with Magnesol XL had nearly the same effects in increasing the levels of soap content present in fried sunflower oil. As soap formed due to the reaction of FFA with sodium silicate, the majority of it was re leased into the

oil. Further, stirring the oil also would have induced release of the soap into oil (Kalapathy and Proctor, 2000).
The data of the present study demonstrate that filtration treatment with different levels of SCBA regenerated the quality of fried sunflower oil and possess higher adsorbing effects than the synthetic filter aid (Magnesol XL) in removing oil oxidation products. In addition, SCBA is cheap and useful for regenerating the quality of fried oils. Hence, one would recommend to implement SCBA as natural filter aid to improve and regenerate the quality of fried oils.

Table 4. Effect of hot water (80–85 °C) washing process on physico-chemical properties of fried (F1) and fried-treated (F2 &F3) sunflower oil

Physico-chemical parameters	Fried oil (F1)	Fried-treated with 3 % (SCBA). (F2)	Fried-treated with 2 % Magnesol XL (F3)	F1-treated with hot water	F2-treated with hot water	F3-treated with hot water	LSD at 0.05=
Refractive index	1.4825a ±0.0005	1.4727d ±0.0006	1.4741c ±0.0007	1.4800b ±0.0006	1.4720d ±0.0008	1.4730d ±0.0004	0.0010
Viscosity(centipoises)	63.52a ±1.45	40.00d ±1.60	44.40c ±1.70	50.20b ±1.83	39.30d ±0.62	41.00d ±1.00	2.54
Color (Red slide)	11.40a ±0.35	2.70c ±0.61	3.26c ±0.52	5.00b ±0.54	2.50c ±0.30	3.00c ±0.50	0.87
Acid value (mg KOH g^{-1} oil)	0.88a ±0.04	0.16cd ±0.02	0.20c ±0.1	0.42b ±0.07	0.10d ±0.02	0.12d ±0.01	0.06
Peroxide value (meq.Peroxides/Kg oil)	8.42a ±0.42	0.91c ±0.09	0.94c ±0.05	4.21b ±0.53	0.72c ±0.12	0.68c ±0.09	0.50
TBA value (absorbance at 530 nm)	0.49a ±0.051	0.11c ±0.01	0.16c ±0.025	0.30b ±0.08	0.10c ±0.02	0.10c ±0.00	0.074
Polymer content (%)	1.28a ±0.25	0.14c ±0.02	0.33c ±0.08	0.75b ±0.11	0.14c ±0.05	0.16c ±0.08	0.22
Conjugated dienes (absorbance at 234 nm)	0.34a ±0.02	0.10b ±0.00	0.16b ±0.05	0.20b ±0.09	0.10b ±0.03	0.10b ±0.04	0.076
Conjucated trienes (absorbance at 268 nm)	0.17a ±0.01	0.07b ±0.002	0.09b ±0.00	0.15a 0.03	0.00c 0.00	0.00c 0.00	0.022
Polar content (%)	12.56a ±0.80	4.62c ±0.32	6.18b ±0.46	3.50d ±0.64	1.00e ±0.17	1.50e ±0.26	0.877
Soap (ppm)	4.10c ±0.18	14.55a ±2.13	11.89b ±2.05	1.20c ±0.13	2.00c ±0.24	1.50c ±0.20	2.16

Effect of water washing process on the quality of fried- treated sunflower oil.

The abovementioned results showed that treatments of fried sunflower oil with different levels of SCBA and Magnesol XL caused significant increase in the quality of fried-treated oil, however soap content of fried – treated oil was increased also, therefore, the current experiment was performed to evaluate the effect of water washing process on the quality of fried (F1) and fried – treated sunflower oil (Table 4). According to the abovementioned results fried sunflower oil treated with 3 % of SCBA and 2 % of Magnesol XL (F2 and F3, respectively) performed significantly the highest values in removing the fried sunflower oil oxidation products. Therefore, these treatments were selected to evaluate the efficiency of hot water in improving the quality of fried and fried – treated sunflower oil. Water washing process improved the viscosity, colour, acid, peroxide, TBA, polar and soap content values of fried sunflower oil by 21.28, 56.14, 52.27,50.00,38.77, 28.50 and 70.70, respectively. The values of soap and polar after water washing process were significantly ($P \leq 0.05$) lower than those of fried sunflower oil treated with 3 % sugar cane bagasse ash (SCBA). These values were about 4.62 and 7.27 times as low as that for fried sunflower oil treated with 3 % sugar cane bagasse ash (SCBA). These findings were also recorded for water washing treatment of fried sunflower oil treated with 2 % Magnesol XL. Once the oil has been treated with caustic soda, to remove the soap to levels below 5 ppm it is washed with water (two washes with 10% water each). At this point the oil must have levels of phosphorus not greater than 5 ppm and 0.05% FFA (Farr, 2000). The level of soap should be less than 30 ppm after neutralization and less than 1 ppm after the bleaching (Erickson, 1995). Therefore, water washing process leads to remove most of soap and polar products due to its polar nature. This means that water washing process improved the quality of fried-treated (filtrated) sunflower oil.

4. CONCLUSIONS

The data of the present study demonstrate that filtration treatment with different levels of SCBA regenerated the quality of fried sunflower oil and possess higher adsorbing effects than the synthetic filter aid (Magnesol XL) in removing oil oxidation products. In addition, SCBA is cheap and useful for regenerating the quality of fried oils. Hence, one would recommend to implement SCBA as natural filter aid to improve and regenerate the quality of fried oils. The results also indicate that water washing process improved the quality of fried- treated (filtrated) sunflower oil and reduced the levels of soap and polar content by nearly 86 and 78 %, respectively.

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