ADDIS ABABA UNIVERSITY

COLLEGE OF NATURAL AND COMPUTATIONAL SCIENCES

CENTER FOR FOOD SCIENCE AND NUTRITION

Evaluating quality deterioration of used frying vegetable oils and improving the quality using adsorbent treatment

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RESEARCH THESIS APPROVAL

This is to certify that the thesis prepared by Zehara Nuru entitled: Evaluating quality deterioration of used frying vegetable oils and improving the quality using adsorbent treatment and submitted in partial fulfillment of requirements for the degree of Master of Science in Food Science and Nutrition complies with the regulations of the university and meets the accepted standards with respect to originality and quality.

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ABSTRACT

Frying is the most commonly used cooking method in food preparation. Continuously frying food items at high temperature will result in frying oil and fried food quality deterioration. in this study as an alternative option the effects of adsorbents (betonite, ash, magnesium oxide, silica gel, and bleaching earth) to improve the quality of used frying vegetable oils (Palm and Niger seed oil) were evaluated. Accordingly, each adsorbent was mixed with 20 hours fried oils (15% w/v) at 150 ^{o}C and stirred together for 30 min. The oil was recovered through centrifugation at 4200 rpm for 15 min. Then, the physico-chemical characteristics of the fried and adsorbent treated oils were investigated on both oil types.

The chemical quality parameters of palm oil increased after the prolonged frying (i.e. acid value (AV) (0.42 to 1.40) mg KOH/gm oil, free fatty acid (FFA) % (0.20 to 0.64) %, and peroxide value (PV) (1.99 to 11.00 mEq oxygen/gm of oil)). Similarly, in the 20 hrs fried niger seed oil increased values of (AV (2.24 to 8.31) mg KOH/gm, FFA % (1.13 to 4.17), PV (1.00 to 13.97) mEq oxygen/gm of oil) were found.

In both fried palm and niger seed oils, magnesium oxide (MgO) treatment gave the highest improvement on the physical quality parameters. Treatment of the fried PO with 15% (w/v) (ash, bentonite, bleaching earth, silca gel and MgO) reduced the FFA% by (55, 45, 35, 65 and 61) % (silca gel > MgO > ash > bentonite > bleaching earth) respectively. Similarly, treatment of the used fried NO with the same adsorbents improved the FFA% by (61, 66, 56, 61 and 73) % respectively. The PV of the fried PO was also reduced by (55, 37, 9, 28 and 64) % respectively (MgO > ash > bentonite > silca gel > bleaching earth). Upon the same treatment the PV of the used NO was improved by (57, 43, 21, 50 and 64) % respectively. The recovery of PO after ash, bentonite, bleaching earth, silca gel, MgO treatment was (75, 88, 85, 70, 40) % respectively. Meanwhile with the same treatments of the fried NO, the oil recovery was (80, 88, 85, 70 and 40) % respectively. Based on both physical and chemical quality improvement effectiveness ash and MgO were selected for further objectives of the study (i.e. effect of concentration and synergism by the two adsorbents).

To determine the minimum proportion of the selected adsorbents that will improve the quality of the used oil, (2.5, 5.0, 7.5, 12.5) % (w/v) of ash and MgO were used in both fried PO and NO. Treatments with 12.5% and 15.0% of ash improved the AV and FFA% of fried PO to the recommended acceptable range for human consumption. Treatments with (2.5, 5.0, 7.5, 10.0, 12.5 and 15.0) % of ash reduced the AV of fried NO gradient-wise by (26, 39, 46, 53, 53 and 60) % respectively ($p < 0.05$).

Key words: used frying oil, Plam oil, Niger seed oil, adsorbents, Magnesium oxide, ash,

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ACRONYMS

- AV-Acid Value
- DFF-Deep Fat Frying
- FDA-Food and Drug Administration
- FFA-Free Fatty Acid
- IV-Iodine Value
- mEq-mili equivalent
- MgO- Magnesium Oxide
- NI - No Improvement
- NVDP- Non-Volatile Decomposition Products
- PV-Peroxide Value
- R.I-Refractive Index
- S.G-Specific Gravity
- SE-Standard Error
- SPSS-Software Package for Statistical Analysis
- VDP -Volatile Decomposition Products
- VISCO-Viscosity

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1. INTRODUCTION

1.1. Background of the study

Deep-fat frying is one of the oldest and most popular food preparation methods (Serjouie et al., 2010). Its popularity among consumers arises from the desirable flavor, color and crispy texture of deep-fat fried foods (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 high temperature of 150 to 190 ^{o}C (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. However, in the presence of oxygen, moisture, trace elements and free radicals, physicochemical reactions such as thermo oxidation, hydrolysis, polymerization, isomerization or cyclization take place at high temperatures of the frying process. This will lead to decomposition of frying oil and formation of monomeric, polymeric oxidative products (Andrikopoulos et al., 2002). These oxidized products of fatty acids give off-flavours and odour to the frying medium and fried foods (Lin et al., 2001).

The reactions in deep fat frying depend on factors such as replenishment with fresh oil, frying conditions, original quality of oil, food materials, type of fryer, type and concentration of antioxidants and oxygen concentration (Arroyo et al., 1992). Other factors such as frying temperature, quantity of frying, initial content of free fatty acids, polyvalent metals and unsaturated fatty acid content of the oil also affect the oxidative stability and overall quality of oil during the process (Melton et al., 1994). In general, deep-fat frying increases foaming, color, viscosity, density, amount of polymeric and polar compounds and the free fatty acid content of frying oils.

The products of thermal oxidation and polymerization upon deep-fat frying are nonvolatile compounds, hydro peroxides and cyclic peroxides (Hidayatullah et al., 2007). The hydrolysis reaction and heat treatment will result increased level of free fatty acid in the oil. The degradation of the frying oil can reduce the quality of the fried food products and ultimately can cause adverse effects to human health Yilmaz and Bulu (2012). So far applied methods to improve the quality of used frying oils include, replenishing with fresh oil, blending different oils to increase oxidative stability and treatment with adsorbents. Among these methods treatment with adsorbents seems cost effective and easily applicable. There are many adsorbent materials, which have been studied for the purposes of improving the quality of used frying oils. Hidayatullah et al. (2007) reported that activated charcoal and magnesium oxide could improve fried *Silybum marianum* oil. Similarly, Okiel et al. (2011) indicated that bentonite had the effect of adsorbing organic pollutants. Similarly, the combination of Hubersorb 600, Magnesol and Britesorb reduced the amount of free fatty acids, total polar material and improved the color of used-frying oil (Lin et al., 1999). Yilmaz and Bulu (2012) reported that mixed adsorbents of natural zeolite, lime and diatomaceous earth effectively improved viscosity, turbidity, free fatty acid content, peroxide value, conjugated dienes and the total polar materials of used oil.

As it can be noticed in major cities in Ethiopia, the consumption of deep-fat fried foods (potato chips, sambussa etc) is increasing. Based on the interview conducted with street food vendors in Addis Ababa, it is noticed that the oil for frying is used over and over again on daily basis. Yet, in the evaluation of the used-frying oils' quality and treating them for quality improvement has not been investigated as per our literature review. Therefore, this study aimed to evaluate the physico-chemical composition of used-frying oils, considering the widely utilized frying oils (palm and niger seed oils) in making street fried foods (i.e. based on interview conducted in Addis Ababa in major street food sites through an interview).

1.2. Statement of the problem

During deep-fat frying of food items at high temperature, physicochemical reactions such as thermoxidation, hydrolysis, polymerization, isomerization or cyclization will proceed. These reactions will lead to decomposition of the frying oil and formation of monomeric, polymeric oxidative products. The oxidized products will deteriorate the physical (viscosity, color, taste etc) and chemical (acid value, peroxide value, etc.) qualities of the oil. Replenishment of frying oils with new oil at each frying cycle and blending the oil with oxidative resistance oils (like sesame oil) will improve the oil quality. However, these methods are not cost effective. As an alternative option treating used frying oils using adsorbents was investigated well. For instance, Yilmaz and Bulut (2012) have studied frying oil refreshing capacity using adsorbent mixtures. However, this study has a limitation of using limited types of adsorbents (diatomaceous earth, natural zeolite and lime). Similarly, Wonglamom and Rakariyatham (2014) have evaluated the effect of two-step adsorbent treatment in improving the quality of used vegetable oils. Yet in this study the authors applied commercially available only two types of adsorbents (bentonite and activated carbon). Both bentonite and activated carbon are hydrophobic adsorbents, which will make their conclusion partial. Also, the used vegetable oil is collected from street vendors, which lacks scientific figures to base the frying process. Siasakul (2005) has also investigated improvement of used-frying oils with only three types of adsorbents (bentonite, activated carbon and celite).

Similar with the other part of the world, in Ethiopia consumption of street deep fat fried foods is increasing as per our interview. Though consumption of fried foods increased in Ethiopia, to our knowledge there is no study on the used frying oils quality and methods to improve it. Therefore, this study aimed to evaluate the physico-chemical composition of used-frying oils which are commonly utilized in making deep fat fried products in Addis Ababa. Also, based on the research gaps of the above mentioned studies and others, the effects of various adsorbents (i.e. both hydrophobic (bentonite, ash) and hydrophilic (magnesium oxide, silica gel, bleaching earth) to improve the quality of the used-frying oils was evaluated. Then, the two most effective adsorbents were selected and their minimum amount with the highest quality improvement was investigated. Finally, synergetic effects of selected adsorbents on the quality improvement of the used oils were evaluated. The frying process in this study was simulated in our laboratory. Hence, frying time, temperature and amount of substrate (food item) were controlled.

1.3. Objectives

1.3.1. General objective

To evaluate the effects of different adsorbents on quality improvement of used-frying vegetable oils, after investigating its quality deterioration.

1.3.2. Specific objectives

- To evaluate the quality degradation of vegetable oils upon deep-fat frying
- To investigate the effects of different adsorbents on improving quality of used-frying vegetable oils
- To determine minimum amount of the adsorbents that can be applied to improve the used-frying oils quality
- To evaluate the synergetic effects of selected adsorbents on quality improvement of used-frying vegetable oils

2. LITERATURE REVIEW

2.1. Oilseeds processing in Ethiopia

Several oil seeds grown in Ethiopia including sesame, soybean, niger seed, cotton seed, linseed, rapeseed (Fig 1). Some of the oil crops like sesame are one of the leading export items for the nation. With this regard, Ethiopia has a large number of local small-scale vegetable oil processing industries. Since the majority of the oil seeds are becoming export commodities, raw material scarcity is becoming a problem for the local oil processors. Hence, the country is importing edible vegetable oils from abroad, palm oil taking the major share. The estimated actual domestic production of edible oil ranges between (5,000- 8,000) tons annually for the medium and large-scale enterprises. This production is less than half of the full capacity, because of different reasons among which raw material scarcity being the major obstacle (Wijnands et al., 2009).

Taking into account that the small-scale local producers have a market share of two-third, the total available production is between (15,000 -24,000) tons annually. Ethiopia imported (15,000 - 160,000) tons of edible oil between (2001-2008) and in the years before around (10,000 - 20,000) tons. This makes the import rate 15 times higher than the domestic production in the past five years. This resulted in an available amount of edible oil of less than 0.5 Kg per capita in 2000 to around 2.0 Kg per capita in 2009. The increased import amount suggests a potentially large domestic market, in which palm and soybean oil being the major imported oils (Wijnands et al., 2009).

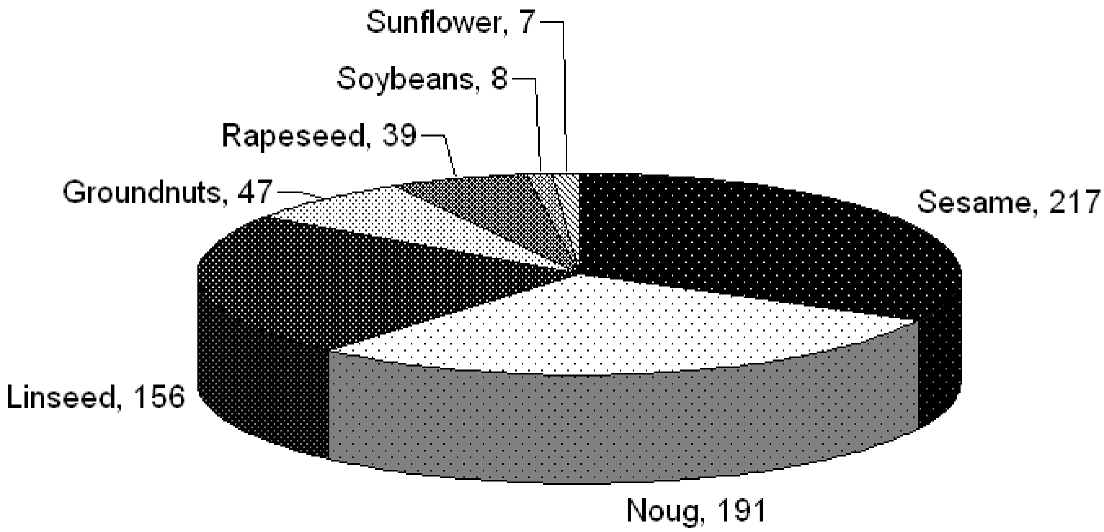


Figure 1 Ethiopian oilseeds production in tons in the year 2008/2009 (2001 E.C)

Source: (Wijnands et al., 2009)

According to CSA, 2013 Oil crops accounted for 6.7% of areas covered by grain crops (818 thousands hectares) and 3.1% of production volume of grain crops (726 tons) in Ethiopia. Niger, sesame and linseed covered 2.5% (about 304 thousand hectares), 1.95% (about 240 thousand hectares) and 1% (about 128 thousand hectares) of the grain crop area and 0.92% (about 212 tons), 0.78% (about 181tons) and 0.53% (about 122 tons) of the grain production, respectively .

2.2. Characteristics of vegetable oils

Oils and fats are macronutrients for humans, who need to consume about 20 to 25 Kg per capita per year, as recommended by the World Health Organization (WHO). For good health, one needs a balanced diet, including oils and fats that supply energy and essential fatty acids. There are many sources of oils and fats, but vegetable oils including soybean oil, palm oil, sunflower oil, and rapeseed oil contribute 60% to 70% of the world's oil production (Ong and Goh, 2002). Vegetable oils have the triacylglycerol or triglyceride basic structure as shown below in Figure 2. The difference between different vegetable oils lie in the types of fatty acids (RCOOH) attached to the glycerol backbone in positions 1st, 2nd, and 3rd.

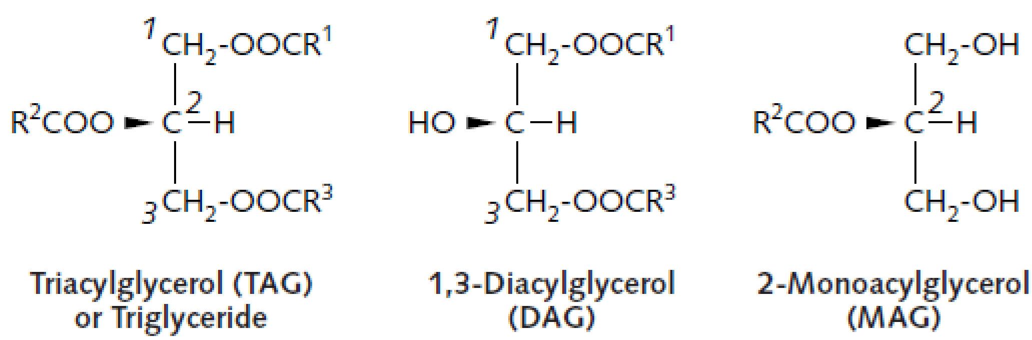


Figure 2 Basic structure of a triglyceride molecule

In general, fats and oils are classified as saturated, monounsaturated, and polyunsaturated based on the unsaturation of the fatty acids it is composed of dominantly (Ong and Goh, 2002).

The following are well-known facts about vegetable oils:

- Fatty acids from vegetable oils are mainly unsaturated at the 2nd positions of the glyceride structure. Some vegetable oils like cocoa butter and palm oil can be considered highly structured (solid at room temperature), having the 2nd position fatty acids mainly unsaturated and the 1st, 3rd position-fatty acids saturated.

- In contrast with animal fats, vegetable oils and fats, are cholesterol-free (Ong and Goh, 2002).

2.2.1. Quality of vegetable oils

The quality of vegetable oils is dependent on their resistance to two major chemical reactions:

a) Hydrolysis

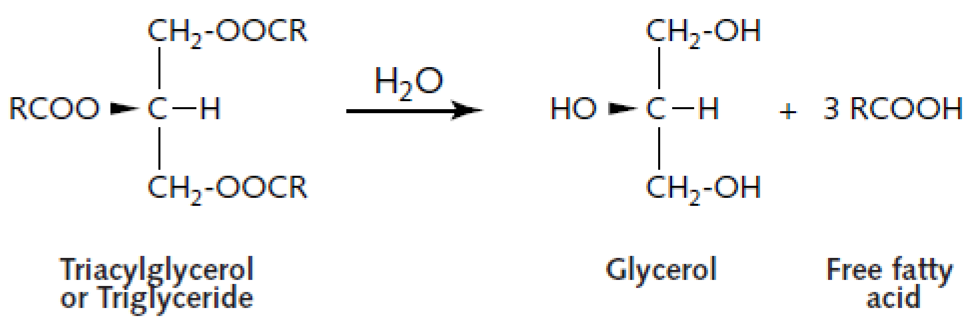


Figure 3 Hydrolysis reaction of oils

Hydrolysis reaction occurs slowly in the presence of water but is catalyzed by lipase enzymes as well as acid (Fig 3) (Ong and Goh, 2002).

b) oxidation

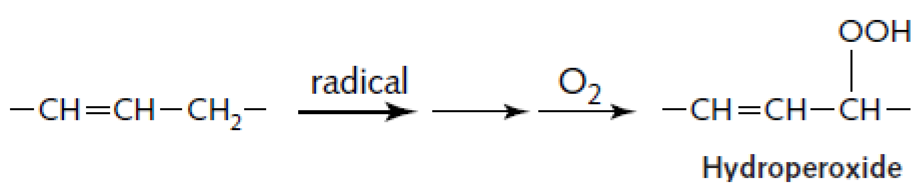


Figure 4 Oxidation reaction of fatty acids

Oxidation is mediated by initiating free radicals to produce more radicals from fat molecules, which then readily combine with oxygen, to give hydro peroxy radicals and then hydro peroxides (Fig 4). In the presence of photosensitizes di-radical oxygen can be transformed into singlet state, $^1O_2$; which is excited state of oxygen and more reactive. The oxidized products usually proceed to generate more radicals, which will cause the destruction of more oil molecules (Fig 5) (Ong and Goh, 2002).

For example:

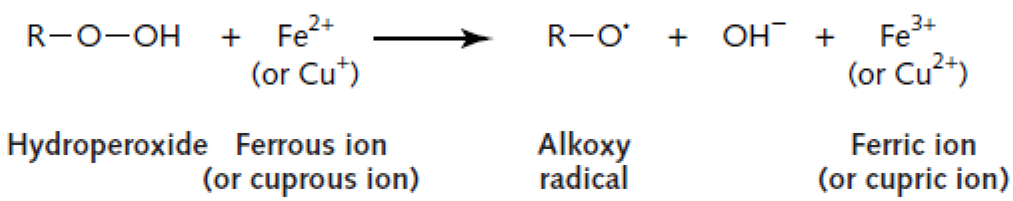


Figure 5 Reaction between hydroperoxides and metal ions

Breakdown products of oxidation cause rancid odors, and its consumption is highly suspected to cause undesirable biochemical reactions in human beings. The role of fats in health and nutrition and its quality should be evaluated in the context of its digestion, absorption, and metabolism. Triacylglycerols with long-chain fatty acids are mainly hydrolyzed by the pancreatic lipase to 2-monoacylglycerols and free fatty acids from 1st and 3rd positions of the triglycerides. The ease/difficulty of absorption of these components will affect their subsequent metabolism and finally their role (Ong and Goh, 2002; Willis et al., 1998). With this regard, the formation of reactive oxygen initiated compounds upon oxidation of oils will lead to consequences of non-communicable diseases including cancer. Therefore, oxidative stability of vegetable oils is an important factor in the formulation and processing of foods.

2.2.2. Technical performance of vegetable oils

Quality must also be considered in the performance of the oil during processing. For example, during frying at 180°C, polyunsaturated fatty acids will undergo extensive oxidation, giving rise to oxidized products and dimeric/oligomeric compounds. Similarly, biological oxidation of polyunsaturated molecules leads to reactive free oxy-radicals, which are harmful to human cells and genetic material. Although the polyunsaturated oil can be stabilized by hydrogenation to produce more saturated material, partial hydrogenation inevitably produces *trans* fatty acids, which have been reported to cause undesirable effects (i.e. raising the “bad” low-density-lipoprotein (LDL) cholesterol and lowering the “good” high-density lipoprotein (HDL) cholesterol. Both effects being considered harmful to the heart in the long term. Therefore, an oil with high oxidative stability, such as palm oil, which does not require hydrogenation in the majority of applications, would be the preferred over other vegetable oils considering processes like deep-fat frying (Ong and Goh, 2002).

2.3. Frying oils

Deep-fat frying is one of the oldest and most popular food preparation methods (Serjourie et al., 2010). Its popularity among consumers arises from the desirable flavor, color and crispy texture of deep-fat fried foods (Boskou et al., 2006). It is a process of immersing food in hot oil with a contact among oil, air, and food at a high temperature of 150 ˚C to 190 ˚C. The simultaneous heat and mass transfer of oil, food, and air during deep-fat frying produces the desirable and unique quality of fried foods. In this process the frying oil acts as a heat transfer medium and contributes to the texture and flavor of fried foods. Frying temperature and time, type of frying oil, presence of antioxidants, and the type of fryer affect reactions like hydrolysis, oxidation, and polymerization of the oil during frying. If uncontrolled these reactions will affect the flavor of the oil and the fried food negatively (Ong and Goh, 2002).

As a major medium of reaction quality of frying oils is detrimental for the quality of fried foods. Oil stability is primarily determined by its fatty acid composition. The higher the concentration of unsaturated fatty acids, especially polyunsaturated fatty acids (i.e. linoleic, linolenic, eicospentanoic, docosahexanoic acids, etc) the more unstable the oil will become upon frying (Fatemi and Hammond, 1980). Due to this fact the oil industry uses hydrogenation as a means of increasing the stability of oils rich in polyunsaturated fatty acids (FDA, 1980) such as soybean and canola oils.

In Ethiopia most consumed deep fat fried foods include potatoe chips, sambusa, fried biscuits (koker, pasty) etc. As per our interview conducted with Addis Ababa's street food vendors, the consumption of street fried products is increasing. Commonly used frying oils worldwide are corn oil, sesame oil and palm oil (FDA, 1980). According to the information that we gathered from street food venders in Addis Ababa, the commonly used frying oil is palm oil. However, when palm oil is in shortage, niger seed oil is widely used. Hence, in this study both palm oil and niger seed oil were used representing highly saturated and unsaturated oil types respectively. Accordingly, the basic physico-chemical characteristics of palm and niger seed oils are discussed below.

2.3.1. Palm Oil

Palm oil, which consists mainly of triglycerides of palmitic acid is semi solid at room temperature. Crude palm oil has a deep orange-red color contributed by high carotene content, 500 to 700 ppm, of which 90% consists of alpha and beta-carotene. Palm oil has a characteristic fatty acid composition, quite different from other commodity oils; it contains almost equal portions of saturated and unsaturated fatty acids. It is unique among vegetable oils because a significant amount of the saturated fatty acids (10 to 16%) are in the *sn*-2 position of its triglycerides. It is also distinguished from other oils by a very high level of palmitic fatty acid (Pantzaris and Ahmad, 2001).

Table 1 Physical and chemical characteristics of palm oil

Parameters	Requirements
Moisture and matter volatile at 105 ^{o}C, % m/m, max.	0.2
Insoluble impurities% m/m, max.	0.05
Soap content% m/m, max.	0.005
Relative density (50^{o}C/ water at 20^{o}C)	0.891 – 0.899
Refractive index 50 ^{o}C	1.454 – 1.456
Melting point ^{o}C, max.	36.7
Saponification value (mg KOH/g oil)	190 – 209
Iodine value (Wij's), min.	45 – 56
Colour, in a 25.4 mm Lovibond cell scale expressed as (Y + 10R), max.	60
Unsaponifiable Matter, g/kg, max.	12
Acid value, mg KOH/g oil, max.	0.6
Peroxide value, milli equivalent peroxide oxygen/Kg oil, max	10
Beta carotenoid (mg/Kg)	500-2000
Total cholesterol (% m/m, max.)	6.7

Source: Compulsory Ethiopian Standard (CES 301:2015)

Palm oil contains nutrients with beneficial health properties. These phytonutrients include carotenoids, vitamin E, sterols, phospholipids, glycolipids, and squalene (Pantzaris and Ahmad, 2001). Palm-based oils are generally proven to have superior frying performance, due to high saturated fatty acid composition (Tarmizi et al., 2014). Stability of palm oil reduces operational cost during frying and retains its quality attributes since significant amount of oil is an integral part of the fried food (Tarmizi et al., 2014). Oil containing higher level of saturated fatty acids is more stable for frying as compared to conventional liquid oils such as soyabean, canola and sunflower oils. However, after prolonged frying even oils with high saturation are liable to oxidation and quality deterioration. In previous studies increased levels of free fatty acid and peroxide values of palm oil after long hours of frying were reported (Gharby et al., 2014). In Table 1, physico-chemical requirements of edible palm oil are listed as per Ethiopian Standard Authority.

As Ethiopia has a broad variety of 17 agro-ecological zones almost any crop including palm tree can grow in the country. Recently, newspapers stated that Ethiopia's leading local investor Sheikh Mohammod Al-Ahmoudi, will develop a large plantation of palm tree in West and Southern Ethiopia on 58,000 hectares together with a Malaysian consultancy. Currently, most Ethiopian imported edible oil that accounts for 80% is palm oil (Wijnands et al., 2009).

According to the information we gathered from street fried food vendors the commonly used frying oil currently in Addis Ababa is plam oil. In average, the vendors will use the palm oil for 20-30 hours of continues frying. As mentioned before like the other frying oils, using palm oil for long hours of frying will lead to quality deterioration of the oil. Hence in this study palm oil is selected as one of the frying oils.

2.3.1.1. Palm oil for frying

For deep-fat frying the conditions are severe, with temperature at about 180 °C under atmospheric oxygen. With these conditions free radical oxidation and hydrolysis reactions will proceed. The nature of the oil will be modified to produce derivatives of the original molecules known as polar compounds. For frying, palm olein is more preferable compared with that of other oils. The stability of palm olein to free radical oxidation is due to its relatively high content of monounsaturated (oleic) and saturated fatty acids. In addition, the presence of natural antioxidants such as tocotrienols in the oil has contributed to its stability. In fact, potato chips have less oil retention when fried in palm olein than when fried in polyunsaturated oils. In general, the performance of polyunsaturated oils such as soybean and sunflower upon frying is very poor (i.e. easily oxidized, isomerized, and polymerized). Thus, palm olein is the preferred choice for industrial frying of potato chips, snacks, instant noodles, etc (Ong and Goh, 2002).

2.3.2. Niger seed oil

In Ethiopia, niger seed provides about 50–60% of the country's edible oil source (Riley and Belayneh, 1989). Whole niger seed contains 4.5 % moisture, 24 % protein, 31% fat, 3.1% ash and 16.9% crude fiber (Bhagya and Sastry, 2003). The oil extracted from niger seed is used for food processing as in frying vegetables, meat and other cereal products. Niger seed exports since 2002 have passed coffee exports to the USA, which accounts for Ethiopia's third export item to USA. United States of America is a major market for Ethiopia's niger seed, which is used as bird seeds. Also niger seed is getting interest in Europe to explore the opportunities for its applications in food products (Wijnands et al., 2009).

Oil from niger seed (*Guizotia abyssinica* Cass.) grown in different regions of Ethiopia are typically high in linoleic acid (54-73%), but with varying levels of oleic (5-27%), palmitic (8-10%) and stearic acids (5.5-8.1%) (Dagne and Jonsson, 1997; Dutta et al., 1994). Palmitoleic, linolenic, arachidic, behenic, and erucic acids account for about 2-3% of the total fatty acids present in the oil. Besides niger seed oil contains other bioactive compounds such as polar lipids (phospholipids) (Ramadan and Orsel, 2003a). Phospholipids are widely distributed in food and anti-oxidant effects have been attributed to them (Ramadan and Orsel, 2003b). In general, the higher the concentration of unsaturated fatty acids (i.e. especially polyunsaturated fatty acids), the more unstable the oil will become upon frying (Fatemi and Hammond, 1980). Hence, upon deep-fat frying, it is likely that niger seed oil will undergo thermal oxidation, hydrolysis, and polymerization reactions due to its fatty acid composition. The general physico-chemical requirements of edible niger seed oil as per Ethiopian Standard Authority are listed in Table 2.

In Ethiopia, majority of the society prefers the taste of crude and/or semi-refined niger seed oil. As per the interview conducted with the street food vendors in Addis Ababa, when there is shortage of palm oil in the market, the street food merchants use niger seed oil. Hence, niger seed oil is selected next to palm oil to simulate the frying process in this study.

Table 2 Physical and chemical characteristics of niger seed oil

Characteristics	Requirements of niger seed oil		
	Crude	Semi refined	Refined
Moisture and volatile matter at 105^{o}C, % m/m, max	0.25	0.2	0.2
Insoluble impurities, % (m/m), max.	1	0.05	0.05
Soap content, % (m/m), max.	-	0.005	0.005
Relative density at 20^{o}C	0.925 – 0.927	0.925 – 0.927	0.925 – 0.927
Refractive index at 40^{o}C	1.4665 – 1.4695	1.466 – 1.470	1.466 – 1.470
Saponification value, mg KOH/g oil	188 – 192	188 – 192	188 – 192
Iodine value, g/100g, min	128 – 134	128 – 134	128 – 134
Colour in a 2.54 cm cell in the Lovibond colour scale (Y+5R)	Characteristic colour of the product	Characteristic colour of the product	8
Unsaponifiable matter, % (m/m), max.	1.5	1	0.8
Acid value and acidity, mg KOH/gm oil, max.	10	0.6	0.6
Peroxide Value, milliequivalents peroxide oxygen/Kg oil, max	-	10	10
Iron, mg/Kg.max.	5	1.5	1.0
Copper, mg/Kg, max.	0.4	0.1	0.1

Sources: Compulsory Ethiopian Standard (CES 20, 2013)

2.4. Health impact of fried oil

Several studies indicate that products generated through oil oxidation can be carcinogenic. Some volatile oxidation products were found to be mutagenic in vapor inhalation during frying (Marquez-Ruiz and Dobarganes, 1996). Lung cancer in women linked to vapour released during fish frying was found in China and Taiwan (Yang et al., 2000; Seow et al., 2000). Food frying in restaurants and institutions may be problematic due to lengthy oil exposure to extreme conditions and the lack of adequate oil replenishment and discarding. For example, a fraction of polar compounds separated from frying oils in restaurants showed mutagenic activity in Ames test in Salmonella. A positive correlation was found with thiobarbituric acid reactive substances (TBARS), formed from fatty acids with three or more double bonds. This fraction contains malondialdehyde (MDA), which was found to be mutagenic in many other studies (Sam and Dina, 2003).

MDA was found to cause skin cancer in rats and created cross-linking with amino groups of DNA solution. The Ames test indicated that MDA is a mutagen causing DNA alterations and reacting mainly with guanine and cytidine by a depletion of this base pair ((Sam and Dina, 2003). MDA can damage proteins and phospholipids by covalent bonding and cross-linking. Rats fed a diet containing MDA suffered from retarded growth, irregular intestinal activities, enlarged liver and kidneys, anaemia and low serum and liver vitamin E (Esterbauer, 1993). Since a considerable amount of oil is absorbed in the product during frying (10–40%), frying in oil that contains mutagens could lead to consumption of foods containing hazardous compounds.

2.5. Deterioration of frying oils

In frying, the food is submerged in oil heated in air, and as such, the oil is exposed to the action of three agents that cause the most drastic changes in structure: (i) Moisture from the foodstuff, giving rise to hydrolytic alteration (ii) Atmospheric oxygen entering the oil from the surface of frying pan, giving rise to oxidative alteration and (iii) High temperature at which the operation takes place, which results in thermal alteration (Lillard, 1983). In general during deep-fat frying the quality of the oil will deteriorate through hydrolytic and oxidative rancidity.

2.5.1. Hydrolytic rancidity

Hydrolysis leads to hydrolytic rancidity and involves hydrothermal hydrolysis of triacylglycerols to free fatty acids and other products. Hydrolysis is the major chemical reaction that takes place during deep-fat frying. Water, which is present as steam, attacks the triglycerides, which are hydrolyzed to free fatty acids, monoacylglycerols, diacylglycerols and glycerol (Roth and Rock, 1972).

2.5.2. Oxidative rancidity

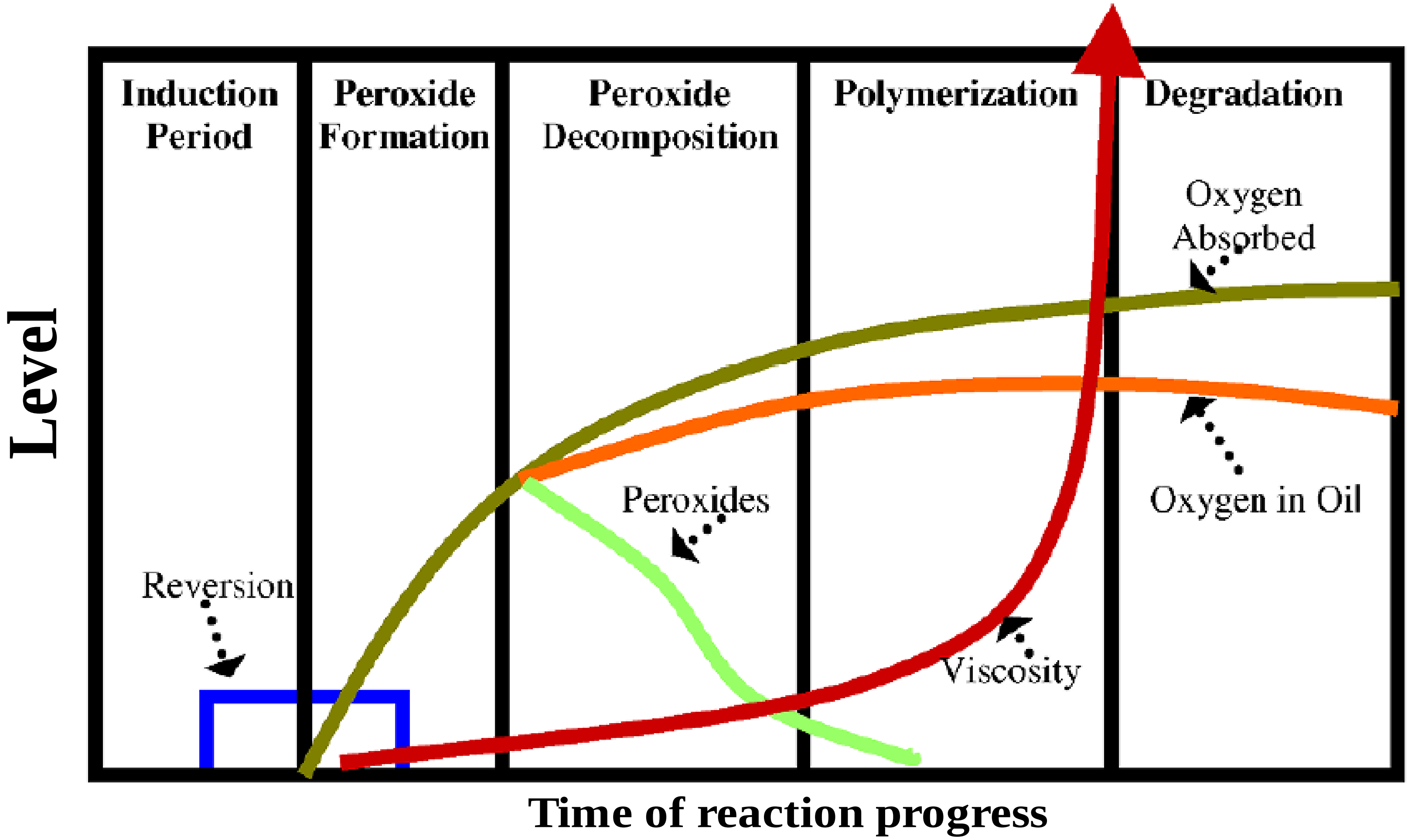
Oxidative rancidity results from more complex lipid oxidation processes. According to Belitz and Grosch (1987), the autoxidation mechanism has several fundamental steps. The oxidation process is essentially a radical-induced chain reaction divided into initiation, propagation, branching and termination steps. Autoxidation is mainly responsible for rancidity in frying oils. The classical route of autoxidation depends on the production of free lipid radicals from triglycerides by their interaction with oxygen. The autoxidation of oils at temperatures less than 80°C has been the subject of extensive investigations (Gunstone and Norris, 1983, Buck, 1981, Labuza, 1971). The reactions and the chemical compounds produced under these conditions have obvious implications with regard to flavors and off-flavors (Nawar and Witchwoot, 1980). Carbonyl compounds formed in lipid oxidation would react with amino acids, especially asparagine, and produce acrylamide and decrease the nutritional value and safety of fried foods (eg. potatoe chips). This process increases the saturation level of the oil, and also produces *trans* fatty acid isomers (deMan, 1993).

The consumption of fats and oils rich in *trans* fatty acids decreases HDL cholesterol levels in human blood serum and increases LDL cholesterol levels (Mensink, 1990). Also, a positive correlation between *trans* fatty acid intake and coronary heart disease in women has been reported (Aramendía et al, 1993). Because of these effects on human metabolism the American Heart Association advices consuming not more than 1% of total calories in the diet from Trans fats (Lichtenstein, 2006).

2.5.3. Thermal oxidation

Various compounds can be formed as a result of thermal oxidation. Oxidation of oil at high temperature differs from oxidation of the same oil at low temperature. Not only are the reactions accelerated at high temperatures, but also quite different reactions take place. This is because the initial oxidation products which are formed at low temperatures are highly unstable to exist more than transiently at high temperatures (Peers et al., 1982 . volatile compounds formed during thermal oxidation like aldehydes, ketones, alcohols, monobasic acids, esters, hydrocarbons, lactones and aromatic compounds (Chen et al., 2013) (Fig 6).

(A)


Induction Period
Peroxide Formation
Peroxide Decomposition
Polymerization
Degradation
Oxygen Absorbed
Oxygen in Oil
Peroxides
Reversion
Viscosity
Level
Time of reaction progress

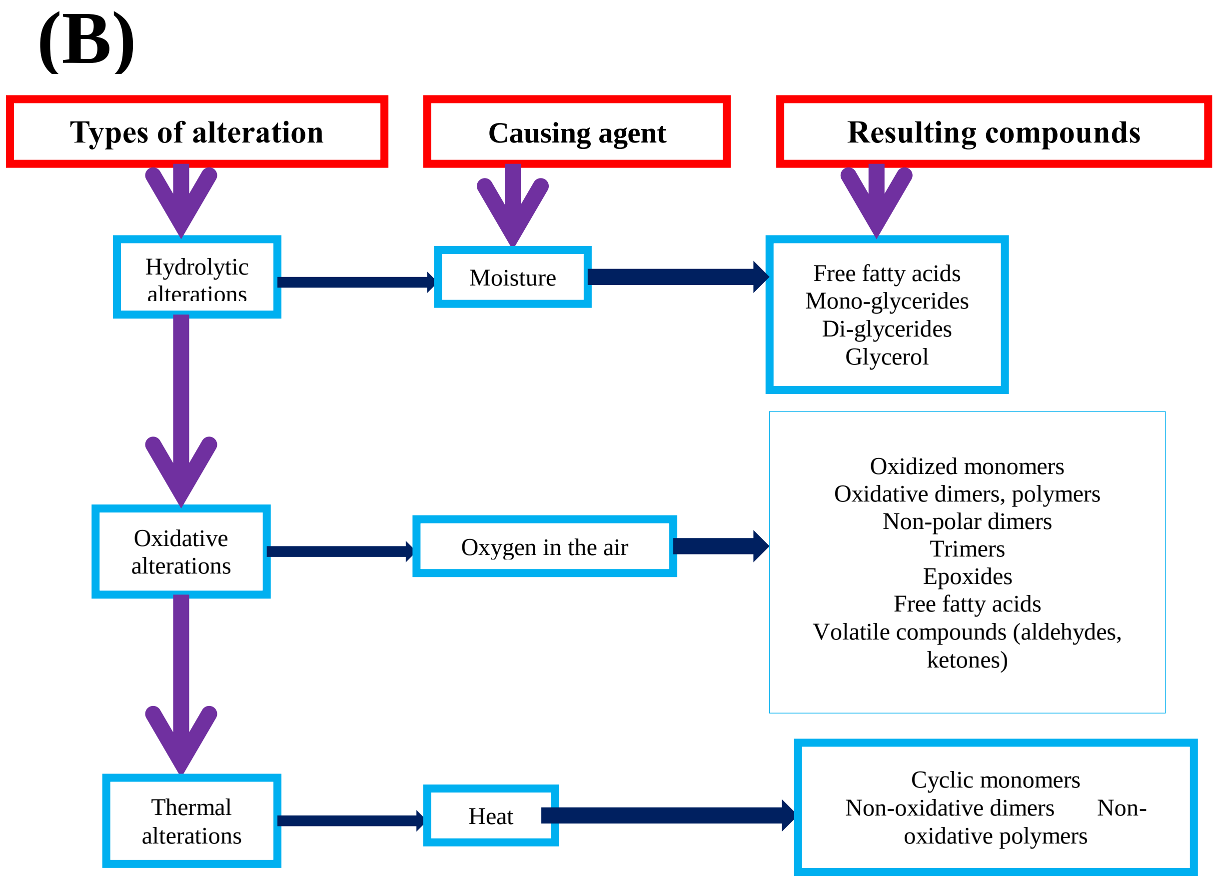


Figure 6 Stages of oil quality degradation (A), types of alterations, causing agents and resulting compounds (B) of fat during Deep-Fat-Frying (Adopted from Perkins, 1967)

2.6. Common methods to improve used-frying vegetable oils quality

2.6.1. Replenishment with fresh oil

High ratio of fresh oil to total oil provides better frying oil quality (Paul and Mittal, 1997). Frequent replenishment of fresh oil during frying decreases the formation of polar compounds, diacylglycerols and free fatty acids and increases the frying life and quality of oils (Romero et al., 1998). -Muniz et al. (1993a) reported that replenishment with fresh oil improved the quality of frying oil after the 30th frying. Frequent turnover of oil caused more oxidative reaction than hydrolytic reaction during deep-fat frying of potatoes (Cuesta et al., 1993). A recommended daily turnover is 15% to 25% of the capacity of the fryer, and the high turnover can decrease the use of antifoaming agent such as silicones (Stevenson et al., 1984).

2.6.2. Blending the frying oil with oxidative stable oils

Frying oils can be blended with oxidative stable oils to derive protective advantage against oxidation (Tiwari et al., 2014). Over all blended oils have better physico-chemical properties and stability against oxidation during deep-fat frying (Serjouie et al., 2010).

2.6.3. Treatments of used frying oils using adsorbents

There are many adsorbent materials, which have been studied for the purposes of improving used frying vegetable oils quality. Adsorption is a sorption procedure, in which certain components of a fluid phase, called solute are selective conveyed to insoluble rigid particles deferred in vessel or packed in a column. Sorption is a general term includes selective transfer to the surface or/and into a bulk of a solid or liquid. In the process, the sorbed solute are referred to as sorbate and the sorbing agent is sorbent. Adsorbents are very porous materials that contain many miniscule internal pores.(Siasakul, 2005).

A. Adsorption mechanism

The process of Adsorption classified as either physical or chemical. The dominant mechanism depends in the adsorbent and the adsorbate(s).

a) Physical adsorption

when London-van der Waals forces bind the adsorbing molecule to the solid substrate; these intermolecular forces are the same ones that bond molecules to the surface of a liquid this is called Physical adsorption. It follows that heats of adsorption are comparable in magnitude to latent heats (10 to 70 KJ/mole). Species that are physically adsorbed to a solid can be released by applying heat (much the same as a liquid can be readily volatilized by heating); the process is reversible. An increase in temperature causes a decrease in adsorption efficiency and capacity. (Siasakul, 2005)

b) Chemical adsorption

Chemical adsorption occurs when covalent or ionic bonds are formed between the adsorbing molecular and the solid substrate. This bonding leads to a change in the chemical form of the adsorbed compounds, and is therefore not reversible. An example of a chemical adsorption process is the formation of CO2 gas adsorbs to a carbon substrate. Chemical adsorptions are much greater than for physical adsorption by chemical adsorption. Thus, more heat is liberated. For many applications the adsorbent is chemically impregnated with a substance that encourages chemical reactions with particular adsorbents. During chemical adsorption, higher temperatures can improve the performance of the adsorbents. (Siasakul, 2005)

Typical requirements for commercial adsorbents to effectively remove unwanted physico-chemical materials from oils include:-

- High porosity, high internal surface
- High adsorption efficiency in a wide range of concentration
- Good balance between macro-pores (for fast internal transport) and micro-pores (for large internal surface)
- Thermal stability
- Mechanical integrity during handling

- Low pressure drop over absorber bed
- Low cost for acquisition (also disposal)

Table 3 Main characteristics of technical adsorbents

Adsorbents	Nature	Average pore ,nm	Particle porosity %	Surface area m^2g^{-1}	Sorepative capacity Kg kg^{-1}
Activated alumina	Hydrophilic amorphous	4-14	50	320	0.1-0.33
Activated carbon	Hydrophobic amorphous	1-4	40-85	200-1200	0.3-0.7
Molecular sieve carbon	Hydrophobic structured	0.3-0.6	30-50	400	0.2-0.5
Molecular sieve zeolites	Hydrophilic crystalline	0.3-1	20-50	600-700	0.12-0.42
Polymeric adsorbents	Hydrophilic amorphous	4-25	40-60	80-700	0.45-0.55
Silica gel	Hydrophobic amorphous	2-5	47-71	300-850	0.35-0.5

Sources: (Seader et al., 1998) and (Perry et al., 1997)

B. Types of adsorbents

Absorbent materials for used oil can generally be deviced into three distinct categories, natural inorganic, natural organic and synthetic sorbents.

a) Natural inorganic sorbents – typically consists of mineral of mineraloid materials, such as clay granules, expanded glass, perlite, and vermiculite mica. They can absorb 1 to 20 times their weight in oil. Inorganic substances are inexpensive and readily available in large quantities.

b) Natural organic sorbents – typically consists of materials such as peat moss, straw, hay, sawdust, ground corncobs, wood pulp, cotton rags, and other readily available carbon-based products. Organic sorbents can soak up water as well as oil.

c) Synthetic sorbents – typically consists of polypropylene or polyethylene mats, pads, and socks that can be melt-blown, woven or non-woven. Most synthetic sorbents can absorb as much as 20 times their weight in oil, and some types can be cleaned and reused several times. Synthetic sorbents that cannot be cleaned after they are used can present difficulties because arrangements must be made for their temporary storage prior to disposal.

2.6.3.1. Properties of commercial adsorbents

a) Bentonite

Bentonite is the commercial designation of a natural clay mineral, the main component of which is montmorillonite. Bentonite is widely used as adsorbent due to its high specific surface area. Some studies showed that modified bentonite (i.e. inherent clay inorganic cations replaced with suitable quaternary amine cations) effectively removed organic contaminants from aqueous solution (Fuller et al., 2009, Li et al., 2007). In fact, there has been much interest in the use of organo-bentonites as adsorbent to prevent and remediate environmental contamination by dyes and other organic pollutants (Shen et al., 2002, Taylor, 1985).

In general, bentonite clay have a wide range of chemical and industrial uses. The structure and chemical composition, exchangeable ion type and small crystal size of smectite are responsible for its several properties (i.e. large chemically active surface area, a high cation exchange capacity and inter-lamellar surface having unusual hydration characteristics) (Ahmad et al., 2007). Bentonite consists predominantly of the mineral montmorillonite, and aluminium hydrosilicate structure applied as figure 7. Its crystal structure has distinct layers (i.e. a layer lattice). This type of compound is a lamella solid. Between the individual layers, exchangeable cations are inserted. Dependent on the condition under which a bentonite deposit had formed, these cations can be sodium, calcium or magnesium ions. The valency of the included ions is responsible for the swelling capacity, compared to lower bentonite swelling capacity when bivalent calcium or magnesium ions are present. The important properties of bentonite include its ability to exchange cations, its swelling and hydration capacity. Their sorption capabilities com from their high surface area and exchange capacities (Ahmad et al., 2005). Okiel et al. (2011) indicated that bentonite had the effect of adsorbing organic pollutants and Wonglamom and Rakariyatham (2014) has evaluated the effect of two-step adsorbent treatment in improving the quality of used vegetable oils by using the two adsorbents (bentonite and activated carbon). The other is as a partial fulfillment of Master's thesis, Siasakul (2005) has investigated improvement of used-frying oils by using three types of adsorbents (bentonite, activated carbon and celite).

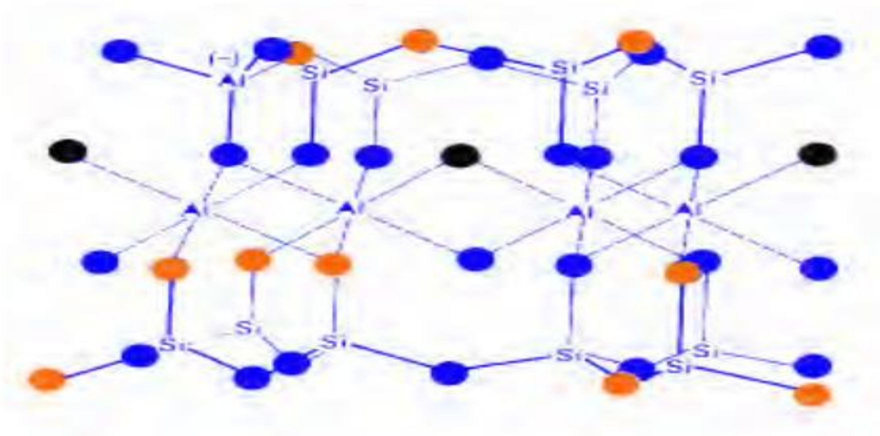


Figure 7 Chemical structure of bentonite clay

b) Silica gel

Silica gel's chemical surface characteristics made it as a starting material for the production of several different stationary phases in separation chemistry. Amorphous silica gel is produced by the condensation polymerisation of silicic acid. During the polymerisation, the SiO groups interlink and lead to the formation of colloidal particles and become gelatinous silica gel. The surface hydroxyl groups are polarised and some of them form hydrogen bonds (Hoffman and Knozinger, 1987 and Kondo et al., 1979). The gelatinous silica gel particles are covered by several successive layers of water molecules. The first layer is due to adsorption arising from the hydrogen bonding between silanol groups and water molecules. The other layers of water molecules build up on this first layer by intermolecular hydrogen bonding (Christy, 2012). Adsorption properties of silica gel have been attributed to the surface hydroxyl groups. Some hydroxyl groups are free standing and called free silanol groups. Some are hydroge bonded to neighboring silanol groups. Christy (2012) reported that high silanol number and balanced concentration proportionality between these two different types of hydroxyl groups is necessary for effective adsorption of water molecules.

Silicas are generally clear or faintly tinted, and transparent or translucent. Silica is used to separate hydrocarbons. Silica offers the greatest potential for the edible oil refining industry (Siasakul, 2005).

c) Bleaching earth

Bleaching earth is a clay .sometimes called diatoms earth. It improves quality of oil through reducing the tint of any colored oil to a lighter shade by changing the basic color units without altering the chemical properties of the oil (Okwara and Osoka, 2006). It is also responsible for the removal of pigments and other impurities, such as soap, trace metals, phospholipids, oxidation products and polyaromatics (Bayrak, 2003; Rossi et al., 2003). The two basic commercial bleaching earth types are natural and activated (Falaras et al.,1999). Activated bleaching earth is the most preferred due to a higher adsorption capacity (Falaras et al., 1999). In order to enhance the chemical and physical properties of bleaching earth, activation by acid and alkaline are the most commonly used techniques (Gunawan et al., 2010; Babaki et al., 2008). The increase in the specific surface area and pore volume upon these treatments will improve its adsorption capacity of metal impurities, phosphatides and coloring bodies.

d) Magnesium oxide (MgO)

Magnesium oxide takes the form of nano or micro sized powders. It is non-toxic, inflammable, with high electrical resistance, mechanical strength and antibacterial activity (Huang et al., 2005). These unique properties of MgO make it possible in a wide range of applications as a catalyst, adsorbents (Aramendía et al., 2003 and Malet et al., 1997). As adsorbent, it was reported that MgO improved used-fried *Silybum marianum* oil (Hidayatullah et al., 2007).

e) Wood Ash

Ash is a strongly alkaline material and its surface is negatively charged. Metal ions can be removed from aqueous solutions though precipitation, electrostatic adsorption (Cho et al., 2005) and ion exchange (Erol et al., 2005) mechanisms using ash. For the removal of toxic elements in different effluents, biosorption process can be applied. Hence, wood and bone ashes are proposed as adsorbent materials for removal of mainly Cr (III), Cd (II), Zn (II), Cu (II) and Ni (II) ions from aqueous solutions. It is a surface phenomenon and depends on the binding of metal ions to functional groups present on the sorbent (Jnacka and Michalak, 2009). The combustion of wood and agricultural residues generates large amounts of ashes (Reijnders, 2007). Previous studies indicated an increasing attention in the application of natural ashes as adsorbents (Das et al., 2007) due to its high adsorption capacity.

2.7. Quality parameters of edible oils

2.7.1. Physical parameters

a) Specific gravity

Specific gravity of oil depends on fatty acid composition and minor components as well as on the storing temperature. Hence, it is not the same for all oils. The standard specific gravity set by Ethiopian Standard Authority for palm and niger seed oil is reported in Table 1 and 2 respectively. Deep-fat frying increases foaming, color, viscosity, density, the amount of polymeric and polar compounds and the free fatty acid content of frying oils (Melton et al., 1994). Therefore, specific gravity was one of the physical parameters selected in this study to evaluate the impact of adsorbents in improving physico-chemical properties of used frying oils.

b) Viscosity

Viscosity controls the amount of oil that coats the fried product as it leaves the fryer. It has an important role in oil absorption and uptake of oxidized products by the fried food (Alim and Morton, 1974). As the oxidation accelerated by heat proceeds, the viscosity also progressively increases (Tyagi and Vasishtha, 1996) because of oxidation products including aldehydes, ketones, hydrocarbons and many polymeric compounds. Especially, polymeric compounds leads to changes in viscosity and heat-transfer efficiency of the oil. Formo (1979) and McGill (1980) reported that the rate of viscosity increase paralleled the rate of polymer formation. Hence, in this study viscosity was one of the physical parameters used to evaluate the quality of used and adsorbent treated vegetable oils.

c) Refractive index

The refractive index of oils can easily be measured using small amount of sample using refractometer. Refractive index varies with chain length, degree of saturation and to the ratio of cis/trans double bonds. Hence, specific refractive index of fat and oils can be used for identification (as shown in Table 1 and 2 for palm and niger seed oils respectively), checking purity and also provide hints on the oxidative damage (Hee, 2011). Triacylglycerols have higher values of refractive index than free fatty acids (Sheabar and Neeman, 1988). Together with viscosity, refractive index was used to evaluate the quality of used and adsorbent treated vegetable oils in this study.

2.7.2. Chemical parameters

a) Free fatty acid content

Free fatty acid (FFA) content is the most frequently used test to evaluate the quality of edible oils. The FFA content is given as percent FFA (% FFA), calculated in commonly in terms of oleic acid (Stauffer, 1996). Free fatty acid percentage reflects the amount of fatty acids hydrolyzed from triacylglycerols to form glycerol and free fatty acids (Fig 7) (Nielsen, 2010). The hydrolysis of ester bonds (lipolysis) may occur due to enzyme action, or by heating (frying), due to the presence of light and moisture, resulting in the liberation of free fatty acids (Nielsen, 2010). The maximum amount of free fatty acids allowed in refined palm and niger seed oils are 0.3% as shown in Table 1 and 2 respectively.

During frying, the steady rise in the formation of FFA (%) can be attributed partly to the hydrolysis and partly to the component carboxylic groups present in polymeric products of frying (Tyagi and Vasishtha, 1996). The acidity is mainly formed by hydrolysis of triglycerides, which is promoted by food moisture, oxidation, and reaction of oil with moisture formed during other deterioration reactions (Al-Harbi and Al-Kabtani, 1993). Hence, in this study FFA % was one of the chemical parameters used to evaluate the quality of used and adsorbent treated frying oils.

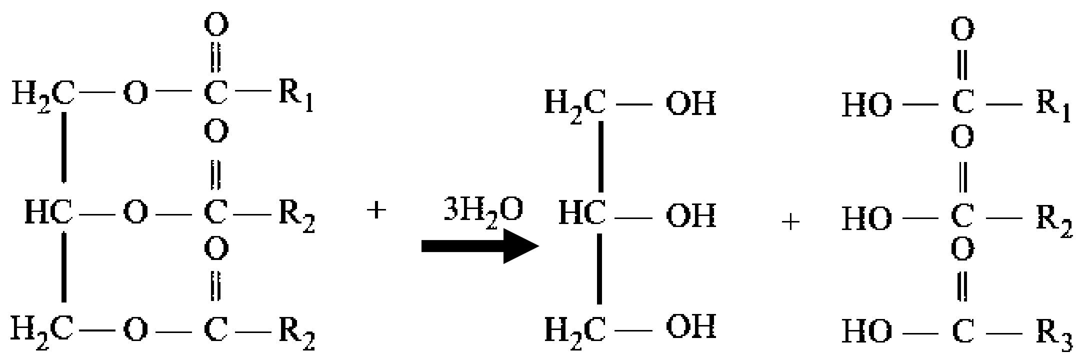


Figure 8 Hydrolysis of neutral fat/oil into glycerol and fatty acids

b) Acid value

Acid value is the amount of potassium hydroxide required to neutralize the free fatty acids present in one gram fat. The value is expressed as percent of free fatty acid as oleic acid (Sheabar and Neeman, 1988). The expected acid value for refined edible palm and niger seed oil is 0.6 as shown in Table 1 and 2.

c) Peroxide value

The primary products of lipid oxidation are hydroperoxides, which are generally referred to as peroxides. Peroxides are unstable organic compounds formed from triglycerides. The peroxide value is the classical method for determining the extent of oil oxidation (Rossell, 1983) and measures the formation of intermediate hydroperoxides in milli equivalents of active oxygen per Kilogram of oil. Hydroperoxides formed by oil oxidation react with iodide ions to form iodine, which in turn is measured by titration with thiosulphate. The change in peroxide values versus time exhibits an induction stage, where a steep increase in peroxide value occurs, and a decrease as lipid oxidation proceeds. Hydroperoxides break down at a faster rate than their formation. Low-quality oil will have shorter induction periods (Sheabar and Neeman, 1988).

Peroxides are unstable under frying conditions. An increase in the peroxide value during the initial stage of frying would be expected to be followed by a decrease with further frying because the hydroperoxides tend to decompose at 180°C to form secondary oxidation products (Chatzilazarou et al., 2006; Perkins, 1967). Further frying results in another increase in peroxide value. The overall increase in peroxide value occurs particularly during the cooling period, where the frying oil is exposed to air at high temperature (Augustin and Berry, 1983). Peroxide and hydroperoxides, although flavorless, provide an indication of impending flavor deterioration (Gray, 1978). Therefore, in this study peroxide value was one of the chemical parameters used to evaluate the quality of used and adsorbent treated frying oils. The peroxide value requirement in refined palm and niger seed oils is 10 milliequivalent of oxygen per Kg of oil as indicated in Table 1 and 2.

d) Iodine value

The iodine value of oil is a measure of average level of unsaturation, and an index of the number of double bonds (capable of reaction with halogen). Therefore, it is a very useful quality parameter during frying (Rossell, 1983; Roth and Rock, 1972). Iodine value is reported in terms of the grams of iodine that will react with 100 g of fat or oil under specified conditions. Iodine value tends to decrease with frying time due to increased rate of oxidation (i.e. consumption of double bonds by oxidation and polymerization) (Abdel-Aal and Karara, 1986; Alexander, 1978; Chang et al., 1978). Alim and Morton (1974) reported that the decrease in iodine value is a result of complex physicochemical changes during frying. Oxidation reactions involve the double bond through chain reactions to form VDPs (Gray, 1978). The required iodine value in refined edible palm and niger seed oils are (45-56) and (128-134) g/100g respectively (Table 1 and 2).

3. MATERIALS AND METHODS

3.1. Sample collection

Palm oil and potatoes were purchased from open market in Addis Ababa, Ethiopia; while niger seed oil was obtained from local processer named Kibe Lemine Oil Company located in Addis Ababa, Ethiopia free of charge. Among the adsorbents, magnesium oxide, bentonite, silica gel were purchased from chemical suppliers' Wise plc in Addis Ababa, Ethiopia; while bleaching was donated by Addis Modjo Edible Oil Processing Company. Ash was prepared at home following the traditional method (i.e. white residue left after charcoal made from wood is combusted completely). The deep-fat frying experiment and most of the quality parameter tests were conducted at Center for Food Science and Nutrition laboratory of Addis Ababa University. Refractive index was measured at Institute of Technology, School of Chemical and Food Engineering laboratory of Bahir Dar University, Bahir Dar, Ethiopia.

3.2. Potato Preparation

The potatoes were peeled and washed under tap water. The washed potatoes were cut into slices of uniform size using a vegetable slicer. The uniform size was essential for uniform heat transfer between the potato slices and the frying oil. The sliced potatoes were kept in water at room temperature (25 ^{0}C). Then, blotted with tissue paper before weighing into 250 g batches for the frying process.

3.3. Frying experiment

The frying conditions were modified based on the information gathered from street food vendors in Addis Ababa and Serjouie et al. (2010). Approximately, 5.0 Kg of frying oil was put into an electrical deep-fat fryer with a frying basket (Oppein, model-OP-81, China) (Fig 8). The temperature was raised to 200 ^{0}C. Frying was started 17 min after the temperature reached 200 ^{0}C. A batch of 250 g raw sliced potatoes were fried for 3 min at 200 ^{0}C at 17 min intervals between each batch of frying. After 3 min, the fried slices were removed from the fryer. Then, the frying operation was carried out for a new potato sample. Total frying period per day was 4 h. With this rate, the frying was conducted for five consecutive days, which is equivalent to 12 times per day and therefore the oil was subjected to 60 consecutive fryings for five days. The fryer was left uncovered throughout the 4.0 h frying time. At the end of the 12th frying the fryer was switched off, put on the lid and the oil was allowed to cool down overnight (Serjouie et al., 2010). In order to determine the effect of frying on the oil properties, frying oil was withdrawn after 60th frying cycle, cooled and kept in opaque bottles at room temperature. The volume of oil was never replenished to the original volume with fresh oil after any of the fryings.

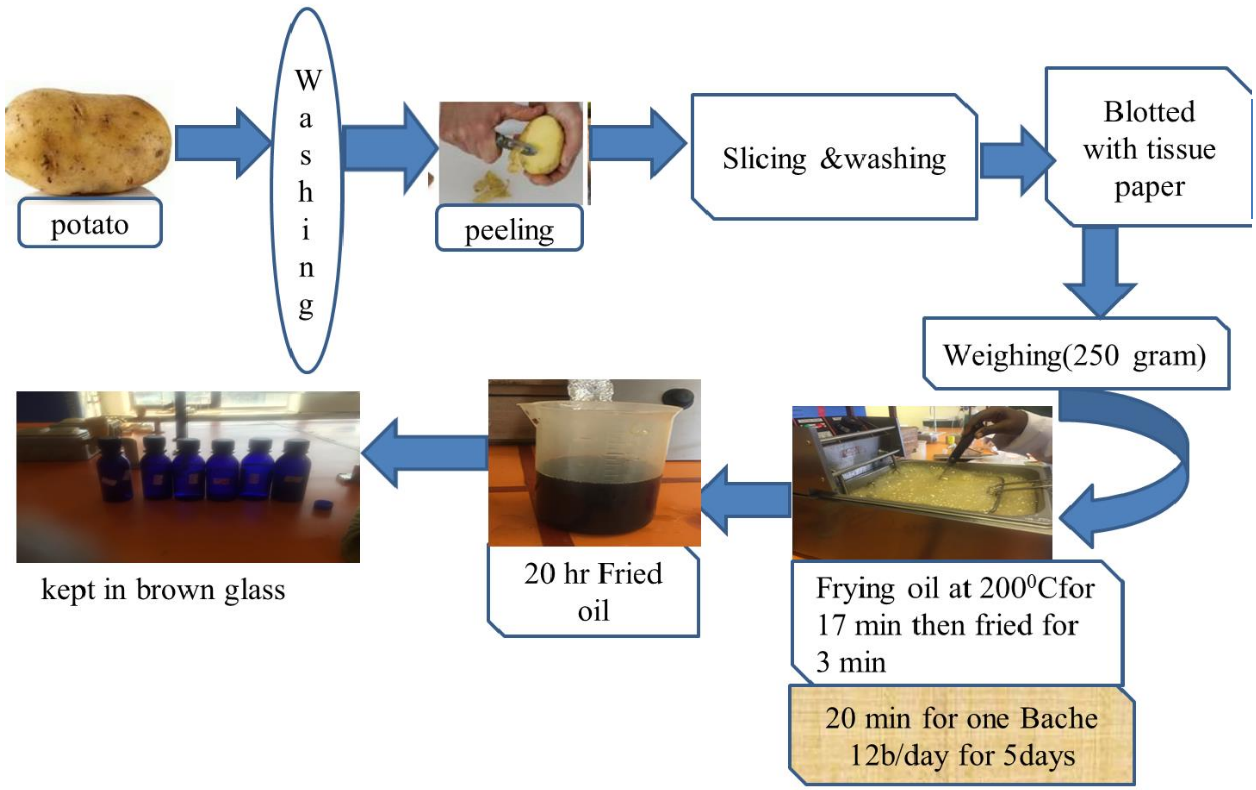


Figure 9 Frying experiment flow chart

Figure 10 Commercial fryer used to make potato chips (Oppein, model-OP-81, China)

3.3. Adsorbent treatment

Thirty gram of five adsorbents (bleaching earth, magnesium oxide, bentonite, ash, silica gel) (15 % w/v) were individually mixed with 200 mL of used vegetable frying oils (palm and niger seed) at 150°C and stirred for 30 min (Yilmaz and Bulu, 2012; Lin et al., 1999). The mixture of the adsorbent and the used frying oils were separated through centrifugation (Centrifuge CE, Model-800D, China) at 4200 rpm for 15 min. The treated oil samples were kept in brown glass bottles until analyzed.

Then, among the adsorbents used the two with relative higher effects in improving the physic-chemical quality of the used-frying oils were selected. To determine the minimum amount of the adsorbents that can improve the quality of the used oils, the selected adsorbents were mixed with the used oils in percentages of (2.5, 5.0, 7.5, 10.0, 12.5 %) (w/v) at 150°C, stirred for 30 min and separated through centrifugation (Centrifuge CE, Model-800D, China) at 4200 rpm for 15 min. Treated oil samples were kept in brown glass bottles until being analyzed.

Finally, the synergetic effect of the two selected adsorbents in improving the quality of used vegetable oils were evaluated. With this regard, the two selected adsorbents were mixed together in 1:1 ratio. Then it was mixed with the used-frying oils (at 150°C), heated together at 150°C, stirring for 30 min, separated by centrifugation (Centrifuge CE, Model-800D, China) at 4200 rpm for 15 min. Treated oil samples were kept in brown glass bottles until being analyzed. In all the three phases of this study, centrifugation was considered as a treatment to avoid its effect on the physico-chemical quality improvement of the oils.

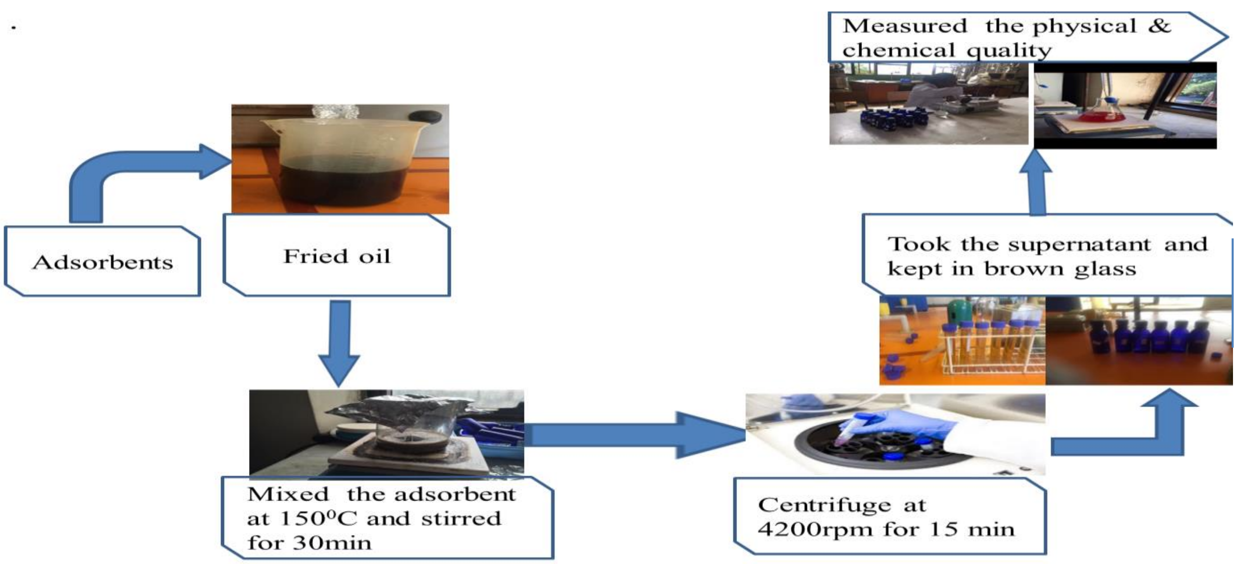


Figure 11 Adsorbent treatments flow chart

3.4. Analytical Methods

I. Physical tests

a) Viscosity

Viscosity was determined by using BROOKFILED DV-E viscometer (MA 023434666, 1031, USA) with a selection of spindle number 61 which was properly fixed to the holder. The container having the oil was carefully placed below the rotor holding the spindle. The spindle was immersed deep into the oil. The meter was turned on and adjusted to a speed of 100 rpm. Then, it was allowed to rotate in the oil for a period of 2-3 min until stable reading displayed and viscosity was recorded in centipoises.

b) Refractive index

According to the AOAC (2000) refractive index was measured using automatic digital refractometer (ATAGO RX-5000 I plus, Japan). Before reading the refractive index, the prisms were cleaned and calibrated using distilled water. A few drops of oil sample was put on the prism and values were recorded.

c) Specific gravity

According to AOAC (2000) for the determination of specific gravity of oils, a clean 50 mL beaker was weighted (W_0). Then, the bottle was filled with distilled water, extra water was spilled out and reweighed (W_1). Same process was repeated, but using oil samples instead of water and weighted again (W_2). The specific gravity of the all oil samples were calculated using the following formula:

$$\textbf{Sepecific Gravity} = \frac{W2-W0}{W1-W0} \qquad \text{Eq. [1]}$$

Where;

W_0 = Weight of empty beaker

W_1 = Weight of water + beaker

W_2 = Weight of oil sample + beaker

II. Chemical tests

a) Acid value (AV)

The acid value in the oil samples was determined using AOCS (2000) with slight modifications. Sufficient amount of oil sample was weighed into Erlenmeyer flask based on the expected acid value as shown in Table 4. Ethanol (97%) was heated at 70 ^{o}C until bubble formation was observed. Then, 50 mL of the heated ethanol was mixed with the weighed oil sample together with 0.5 mL phenolphthalein indicator. Then, the whole content was neutralized with a solution of 0.5 M potassium hydroxide. The end point of the titration was reached when the addition of a single drop of alkali produces a slight but definite pink color change persisting for at least 15 seconds. The AV was calculated as follows in equation 2:

$$\textbf{Acid Value} = \frac{(\mathbf{56.1*V*C})}{\mathbf{m}} \qquad \text{Eq. [2]}$$

Where;

V = Volume (mL) of potassium hydroxide

C = Concentration (moles per liter) of potassium hydroxide (0.5N)

M = Molar mass (gm/mole) of the acid used to express the acid value as per Table 5

m = Mass (g) of the test portion

Table 4 Mass of test portion of oil based on the expected acid value

Expected acid value (mg KOH/g oil)	Mass of test portion (g)	Accuracy of weighing of the test portion
<1	20	0.05
1 to 4	10	0.02
4 to 15	2.5	0.01
15 to 75	0.5	0.001
>75	0.1	0.0002

Source: Ethiopian Standard (ESISO 660: 2009)

Table 5 Type of fatty acids to determine acid value of oil samples

Type of fat	Expressed as	Molar mass (g/mol)
Coconut oil and plam oil	Lauric acid	200
Palm oil	Palmitic acid	256
Oils from certain cruciferae	Erucic acid	338
All other fats and rapeseed oil having a maximum erucic acid content of 5% (m/m)	Oleic acid	282

Source: Ethiopian Standard (ES ISO 660:2009)

b) Percentage of free fatty acids (% FFA)

The percentage of free fatty acids was determined using AOCS (2000) method with slight modifications. Sufficient amount of oil sample was weighed into Erlenmeyer flask in accordance with the values given in Table 4 (based on the expected acid value). Ethanol (97%) was heated at 70^{o}C until bubble formation was observed. Then, 50 mL of the heated ethanol was mixed with the weighed oil sample together with 0.5 mL phenolphthalein indicator. The whole content was neutralized with a solution of 0.5 M potassium hydroxide. The end point of the titration was reached when the addition of a single drop of alkali produces a slight but definite pink color change persisting for at least 15 seconds. The FFA (%) was calculated as follows in equation 3:

$$\textbf{Free Fatty Acid}\ (\%) = \frac{\textbf{Acid value}}{\textbf{1.99}} \qquad \text{Eq. [3]}$$

c) Peroxide value (PV)

Peroxide value was measured following methods of AOAC (2000). About 5 g of oil sample was placed in 250 mL Erlenmeyer flask. Then, 30 mL of glacial acetic acid-chloroform solution (3:2) and 0.5 mL of saturated potassium iodide (KI) solution were added, and kept for a minute in a dark at ambient temperature. Then, 30 mL of distilled water was used to stop the reaction followed by addition of 2 mL of saturated starch solution as indicator. The resultant mixture showing dark purple to dark brown color was titrated with standardized 0.01 N sodium thiosulfate solutions until the color of the mixture turned from ivory to white color. The peroxide value was expressed as mill equivalent of oxygen/Kilogram of oil as shown in equation 4.

$$\textbf{Peroxide value}\ (\textbf{milli equivalent of oxygen/Kg oil}) = \frac{\mathbf{V*M*1000}}{\mathbf{m}} \qquad \text{Eq. [4]}$$

Where;

V = Volume of $Na_2S_2O_3$ (blank corrected) and

M = Molarity of $Na_2S_2O_3$

d) Iodine value

Iodine value was conducted according to AOAC (2000). About 0.25 g of oil sample was weighed into 250 mL conical flask. Then, 10 mL of chloroform and 30 mL of hanus iodine solution (i.e. prepared by dissolving 18.2 g of iodine in 1L of glacial acetic acid followed by adding 3 mL of bromine water to increase the halogen content) and then the solution was left to stand in the dark for 30 min with occasional shaking. Potassium iodide (10 mL) (15%) was added, shaken thoroughly followed by addition of 100 mL distilled water to rinse down any iodine on the stopper. The solution was then titrated with 0.01N thiosulfate solution using starch as indicator (1 mL) till yellow color was formed. Then, 2-3 drops of starch solution was added resulting in blue color. The titration was continued until the blue color disappeared. Volume (mL) of $Na_2S_2O_3$ was recorded and represented as (S). The same above procedure was repeated without oil sample, and the volume (mL) of $Na_2S_2O_3$ at end point was represented as B). Then, the iodine value was calculated following equation 5 as shown below:

$$\textbf{Iodine Value} = \frac{(B-S)*0.127*N\ Na2S2O3*100}{W} \qquad \text{Eq. [5]}$$

Where;

B=Volume of standard $Na_2S_2O_3$ solution (mL) used to titrate the the blank sample

S=Volume of standard $Na_2S_2O_3$ solution (mL) used to titrate the sample

N=Normality of the standard $Na_2S_2O_3$ solution

W=Weight of the oil sample (g)

In both chemical and physical tests percentage of improvement upon adsorbent treatment of the used-frying oil was calculated as shown below in equation 6:

$$\textbf{Improvement}\ (\%) = \frac{(\mathbf{A-B})*\mathbf{100}}{\boldsymbol{A}} \qquad \text{Eq. [6]}$$

Where;

A- Value of untreated oil

B- Value of treated oil

3.5. Statistical analysis

Each analysis was done in triplicate and the readings were reported in terms of mean ± SE. The data was interpreted using SPSS statistics 17.0 using one way ANOVA software and mean values are considered significantly different at $p < 0.05$.

4. RESULTS and DISCUSSION

4.1. Effect of adsorbents on physical quality improvement of fried palm oil

a) Specific Gravity (S.G)

As reported in Table 6, frying potato chips in palm oil at 200 ^{o}C for a total of 20 hrs increased the specific gravity of the oil significantly ($p< 0.05$). The formation and accumulation of non-volatile decomposition products are responsible for physical changes in the frying oil such as increase in viscosity and foaming (Maskan and Bagcl, 2003). Melton et al. (1994) reported that upon deep-fat frying the amount of polymeric compounds in the frying medium increased. As a result, foaming, color, viscosity and relative density of the oil also increased. Similarly, in the present study the increased value of the specific gravity from 0.8989 to 0.9993 upon prolonged frying might be related with the formation of polymeric compounds. Specific gravity is one of the important edible oil physical quality parameters, in which the maximum value according to compulsory standard set by Ethiopian Standard Authority for refined palm oil is 0.899 (CSE 301: 2015). Thus, the S.G value reported for palm oil upon frying in this study is beyond the limit indicating the importance of improving this quality parameter. Accordingly, when the fried palm oil was treated with 15% (ash, MgO, bleaching earth) (150^{o}C, 30 minute then centrifuged at 4200 rpm), the S.G value in the fried oil improved significantly by 9%, 8% and 7% respectively. This might be due to the adsorbents' capability in removing the polymeric substances formed upon prolonged frying. In contrast, the least improvement was found upon bentonite and silica gel treatments (Table 6). But none of the adsorbents decrease the specific gravity to the recommended level.

b) Viscosity (VISCO)

The formation of polymers during frying is mainly responsible for the changes in the viscosity of oil (Paul and Mittal, 1997). The viscosity of the frying oil is an indicator of oil sticking in large cavities of the crust of the food product. Higher viscosity results in larger volume of the oil in the food product (Paul and Mittal, 1997). Similar with S.G, the viscosity of the fried palm oil in the present study increased significantly than the value in the fresh palm oil ($p < 0.05$) (Table 6). As the oxidation of oil accelerated by heat proceeds, the viscosity also progressively increases (Tyagi and Vasishtha, 1996) due to the formation of oxidation products (i.e. aldehydes, ketones, hydrocarbons and polymeric compounds). Specifically, the formation of polymeric compounds was reported to lead to changes in viscosity and heat-transfer efficiency of the oil. In fact, deterioration in colour, foaming and viscosity are the main criteria for discontinuing the utilization of used frying oils.

In the present study, treatment of the fried palm oil using different adsorbents improved the viscosity by (2-4) % as compared from the value in the fried oil (Table 6). The highest improvement was upon MgO treatment. This might be due to its powerful adsorption capability in removing the polymeric substances formed upon prolonged frying. Similarly, Bhattacharya et al. (2008) reported that magnesol ($MgO_2.6SiO_2.H_2O$), silcagel and activated charcoal powder improved the viscosity of fried oil by 14%, 7% and 7% respectively. In another study by Maskan and Bagcl (2003), beleching earth and activated charcoal reduced the viscosity of the fried oil more than the other adsorbents.

c) Refractive Index

Refractive index of oil varies with chain length, degree of saturation and to the ratio of cis/trans double bonds. Hence, specific refractive index of fat and oils can be used for identification, checking purity and indicator of oxidative damage of oils (Hee, 2011). In this study, RI value increased in the fried palm oil, which might be due to the increase in foaming, color, viscosity, density, etc during deep-fat frying (Melton et al, 1994). Similarly, Farag and El-Anany (2006) reported that frying soybean, sunflower, palm and cottonseed oils at 180°C for 12hrs led to gradual and significant increases in the values for refractive index. All adsorbent treated fried palm oil showed a decreased RI value compared with the fried one (Table 6).

Table 6 Effect of different adsorbents on physical quality improvement of fried palm oil

Adsorbent treatment	S.G	S.G Improvement (%)	VISCO	VISCO Improvement (%)	RI	RI Improvement (%)
Fresh palm oil	0.8989 ± 0.00[e]	ND	57.08 ± 0.39[c]	ND	1.46574 ± 0.00[f]	ND
Fried palm oil	0.9993 ± 0.00[a]	ND	60.80 ± 0.30[a]	ND	1.46806 ± 0.00[a]	ND
Ash	0.9083 ± 0.02[d]	9	59.29 ± 0.07[b]	2	1.46663 ± 0.00[e]	NI
Bentonite	0.9559 ± 0.00[b,c]	4	58.87 ± 0.07[b]	3	1.46735 ± 0.00[c]	NI
Bleaching earth	0.9260 ± 0.00[c, d]	7	59.29 ± 0.04[b]	2	1.46662 ± 0.00[e]	NI
Silica gel	0.9905 ± 0.00[a,b]	1	58.75 ± 0.09[b]	3	1.46707 ± 0.00[d]	NI
MgO	0.9178 ± 0.03[c, d]	8	58.62 ± 0.40[b]	4	1.46672 ± 0.00[e]	NI
Centrifugation	0.9991 ± 0.02[a]	NI	59.36 ± 0.05[b]	2	1.46772 ± 0.00[b]	NI

Values are expressed as mean ± SE (n = 3). Means in the same column not sharing the same superscripts are significantly different based on Duncan's multiple range tests ($p < 0.05$). S.G (Specific gravity), VISCO (Viscosity), RI (Refractive Index). "NI"- No Improvement, "ND"- Not Determined

4.2. Effect of adsorbents on chemical quality improvement of fried palm oil and recovery of fried palm oil

a) Acid value and Free Fatty Acid (%)

The acid value in the fresh palm oil used in this study was 0.42 mg KOH/gm oil, which is within the set limit for edible palm oil according to compulsory standard set by Ethiopian Standard Authority (CES 301:2015). Upon frying for 20 hrs, the AV was increased to 1.4 mg KOH/gm oil (Table 7), which is beyond the permissible limit. Udomkun et al. (2018) also reported increased values of FFA% of soybean oil (0.3 to 0.6)% after 18 hrs of continuous frying, which also reached 1.0% after 36 hrs.This can be explained by the increase in the rate of hydrolysis when water from potatoe is introduced into the frying system. Besides, the formation and accumulation of non-volatile decomposition products are responsible for chemical changes such as increase in FFAs, carbonyl value, hydroxyl content and saponification value and decreases in unsaturation, with resulting increases in the formation of high molecular weight products (Hidayatullah et al., 2007; Cho et al., 2005; Maskan and Bagcl, 2003).

All adsorbent treatments reduced the increased AV significantly at $p < 0.05$. The highest reductions were found in the MgO and silca gel treated fried oil (65% upon both treatments). Similarly Hidayatullah et al. (2007) reported the effectiveness of MgO in improving the overall quality of used fried *Silybum marianum* oil. Ash, bentonite and bleaching earth also reduced the AV by 60% from the value in the fried palm oil. In fact, the AV in all the adsorbent treated oils was within the permissible limit set for palm oil by Ethiopian Standard Authority. This improvement might be due to the specific adsorption affinity of the treatments to small molecular substances such as free fatty acids and mono-glycerols (Wonglamom and Rakariyatham, 2014).

Moreover, MgO is a basic compound which might enabled it to attract acids and polar compounds (Li et al., 1998).

Similarly, the FFA% in the fresh palm oil was within the requirement according compulsory standard set by Ethiopian Standard Authority (CES 301 : 2015). Upon prolonged frying, the FFA % increased to 0.64% (i.e. beyond the acceptable limit for human consumption). Percentage FFA is an indication of the degree of hydrolysis of oil. When the fatty acid content of the oil exceeds the objectionable amount, it must be discarded (Bhattacharya et al., 2008). Yet, discarding to the environment will endanger the ecosystem (USAID, 2000). In this study, treatment of the fried palm oil with ash, bentonite, bleaching earth, silca gel and MgO reduced the FFA% by 55%, 45%, 35%, 65% and 61% (silca gel > MgO > ash > bentonite > bleaching earth) respectively. Bhattacharya et al. (2008) also reported the maximum reduction of Total Polar Material (TPM) (i.e. monoacylglycerols, diacylglycerols, and FFA) upon treating the fried oil using silca gel. Adsorption properties of silica gel have been attributed to the surface hydroxyl groups. Some hydroxyl groups are free standing and called free silanol groups. Some are hydrogen bonded to neighboring silanol groups. High silanol number and balanced concentration proportionality between these two different types of hydroxyl groups is necessary for effective adsorption of polar molecules (Christy, 2012). Similarly, Lin et al. (1999) reported that magnesium silicate, to have the largest surface area and the most active sites, which were responsible for the adsorption of degradation materials like FFA.

Similarly, activated charcoal was found effective to restore the amount of fatty acids in fried *Silybum marianum* oil (Hidayatullah et al., 2007). Also Mancini-Filho et al. (1986) demonstrated decreased FFA % upon treating used frying oil by MgO. Similar with the least reduction (35%)

of FFA % by bleaching earth in this study, Zhang and Addis (1992) also reported its inefficiency in removing the FFA% in fried oil. Lin et al. (1998) also found that diatomaceous earth was not effective on free fatty acids removal from prolonged hours fried oil. This might be due to the very low surface area in diatomaceous earth (<$10m^2/g$), whereas activated carbon, magnesium silicate, and Britesorb have very high surface area per gram (> $600m^2/g$). In fact, bleaching earth was observed not to adsorb any polar materials in the study by Lin et al. (1998). Moreover, bleaching earth showed very high acidic site concentration but almost zero basic site concentration (Lin et al., 1998). This might entail less adsorption capacity of free fatty acids.

This difference in regenerating the used fried oils depends on the polarity, surface active sites, surface area, porosity, particle size, pH and moisture content of the adsorbents (Zhu et al., 1994). Bhattacharya et al. (2008) reported a maximum reduction of FFA % (59.06%) (i.e. lower reduction as compared with the present study) upon treating the thermally polymerized frying oils using aluminum hydroxide. In their study, activated charcoal powder, silca gel and magnesol reduced the FFA % in the fried oil by 40.07%, 44.76% and 55.49% respectively. In the present study, higher improvement of FFA% was reported upon the same treatments.

b) Peroxide value

In this study, after 20 hrs of frying, the PV of the palm oil increased from 1.99 to 11.00 mEq oxygen/gm of oil. As expected, the frying time intensively affected the accumulation of PV that gradually increased along 20 hrs of frying (Table 7). Similarly, Udomkun et al. (2018) reported that after 36 hrs of frying the peroxide value of the frying oil increased to 12.70 from 3.20 meq peroxide/kg initial value.

Hence, the prolonged frying deteriorated the oil's PV to unacceptable level for human consumption according to compulsory standard set by Ethiopian Standard Authority (CSE 301:2015). Mainly, the thermoxdiation reaction between atmospheric oxygen and the frying oil is responsible for the increment (Houhoula et al, 2003; Cuesta et al., 1993; Peers and Swoboda 1982; Sanchez-Muniz et al., 1993). Oxidation products, such as peroxides, aldehydes, ketones, hydroperoxides, polymers, and oxidized monomers, can cause clinically harmful effects such as atherosclerosis and coronary heart disease (Subramanian et al., 2000; Paul and Mittal, 1997). Thus, improving the quality of the used fried oil is crucial.

The fried palm oil treated with 15% (W/V) of ash, bentonite, bleaching earth, silca gel and MgO improved the quality of the oil by reducing the PV by 55%, 37%, 9%, 28% and 64% respectively (Table 7) (MgO > ash > bentonite > silca gel > bleaching earth). The highest reductions were obtained upon ash and MgO treatments respectively. Upon all the treatments the PV was within the acceptable level for palm oil. Similarly Hidayatullah et al. (2007) reported the effectiveness of MgO and activated charcoal in improving the overall quality of used fried *Silybum marianum* oil. The effectiveness of magnesol ($MgO_2.6SiO_2.H_2O$) in removing secondary oxidation products was reported by Bhattacharya et al. (2008). In the same study activated charcoal powder reduced production of secondary oxidation products by 35%.

(Alinnor, 2007 and Erol et al 2005) reported that burning of coal produced small molecular substances with useful adsorption capacity. The ash used in the present study is produced at household level after completely burning wood made charcoal. This might led to the formation of molecules with specific adsorption capacity. Hence, ash treated fried palm oil showed the highest reduction of the PV next to MgO treatment. This result corresponded with the reports by, Bhattacharya et al. (2008) and Lin et al. (1999).

c) Iodine value

Iodine value expresses the concentrations of the unsaturated fatty acids, together with the extent to which they are unsaturated. Therefore, it is a simple and very useful quality parameter during frying (Rossell, 1983; Roth and Rock, 1972). The IV of the fresh palm oil used in this study was 49.35 mg I_2/g oil, which is within the compulsory standard set by Ethiopian Standard Authority (CSE 301:2015). However, there was no significant difference ($p<0.05$) in IV between the fresh, fried and adsorbent treated palm oil (Table 7). In contrast, studies like by Buczek (2012) reported the reduction of unsaturated substances expressed as the iodine value by almost 22% as a result of heat treatment of frying oil.

d) Oil recovery (%)

Bentonite treated fried palm oil showed the highest recovery of oil (88%). Meanwhile, the recovery for ash, bleaching earth, silca gel and MgO treated used oils was 75%, 85%, 70% and 40% respectively (Table 7).

Table 7 Effect of different adsorbents on chemical quality improvement and recovery of fried palm oil

Adsorbent treatment	AV (mgKOH/gm)	AV Improvement (%)	FFA (%)	FFA Improvement (%)	PV (mEq O_2/g)	PV Improvement (%)	IV (mg I_2/g)	IV Improvement (%)	Oil recovery (%)
Fresh palm oil	0.42 ± 0.00^{d}	ND	0.20 ± 0.00^{e}	ND	1.99 ± 0.00^{d}	ND	49.25 ± 2.97^{a}	ND	ND
Fried palm oil	1.40 ± 0.00^{a}	ND	0.64 ± 0.00^{a}	ND	11.00 ± 0.57^{a}	ND	48.43 ± 0.80^{a}	ND	ND
Ash	0.56 ± 0.00^{b}	60	0.29 ± 0.00^{d}	55	4.99 ± 0.00^{c}	55	47.00 ± 1.62^{a}	3	75
Bentonite	0.56 ± 0.00^{b}	60	0.35 ± 0.00^{c}	45	6.98 ± 0.57^{b}	37	45.23 ± 1.65^{a}	7	88
Bleaching earth	0.56 ± 0.00^{b}	60	0.42 ± 0.00^{b}	35	9.98 ± 0.00^{a}	9	48.10 ± 1.26^{a}	1	85
Silca gel	0.49 ± 0.07^{c}	65	0.22 ± 0.00^{e}	65	7.98 ± 0.00^{b}	28	46.80 ± 0.33^{a}	3	70
MgO	0.49 ± 0.07^{c}	65	0.24 ± 0.00^{e}	61	4.00 ± 0.00^{c}	64	47.58 ± 0.40^{a}	2	40
Centrifugation	1.40 ± 0.00^{a}	NI	0.64 ± 0.00^{a}	NI	10.99 ± 0.58^{a}	NI	48.51 ± 1.02^{a}	NI	ND

Values are expressed as mean ± SE (*n* = 3). Means in the same column not sharing the same superscripts are significantly different based on Duncan's multiple range test ($p < 0.05$).

FFA (Free Fatty Acid), AV (Acid Value), PV (Peroxide Value), IV (Iodine Value),"NI"-No Improvement; "ND"-Not Determined

4.3. Effect of adsorbents on physical quality improvement fried niger seed oil

As a major medium of reaction quality of frying oils is detrimental for the quality of fried foods. Oil stability is primarily determined by its fatty acid composition. The higher the concentration of unsaturated fatty acids, especially polyunsaturated fatty acids (i.e. linoleic, linolenic, eicospentanoic, docosahexanoic acids, etc) the more unstable the oil will become upon frying (Fatemi and Hammond, 1980). Hence, in this study to evaluate, the effectiveness of the adsorbents in improving the physico-chemical properties of the frying oils vegetable oils with high composition of saturated (palm oil) and unsaturated (niger seed oil) fatty acids were used. The effects of adsorbents in improving the physico-chemical properties of used frying niger seed oil is discussed below.

a) Specific Gravity (S.G)

The specific gravity of the fried niger seed oil has increased significantly from the value in the fresh oil ($p< 0.05$) (Table 8). Similar trend was observed in the fried palm oil also, which might be related with the formation of polymeric compounds upon prolonged frying (Melton et al., 1994). Treatment of the fried niger seed oil using ash, silca gel and MgO improved the S.G by 5%, 6% and 6% respectively, while the least improvement was found upon bentonite and bleaching earth treatments (Table 8). The improvement might be related with the removal of polymeric substances as mentioned in section 4.1 (a). Specific gravity is one of the important edible oil physical quality parameters, According to the compulsory standard set by Ethiopian Standard Authority (CES 20:2013) the S. G for crude niger oil is 0.927.

b) Viscosity (VISCO)

As reported in Table 8, the viscosity of the fried niger seed oil increased significantly than the value in the fresh oil ($p < 0.05$). As the oxidation accelerated by heat proceeds, the viscosity also progressively increases (Tyagi and Vasishtha, 1996). As a result, oxidation products including aldehydes, ketones, hydrocarbons and many polymeric compounds will be formed. The latter leads to changes in viscosity and heat-transfer efficiency of the oil. In this study, all adsorbent treatments improved the frying oil's viscosity, the highest being silca gel (5%) and MgO (6%). Similarly, Bhattacharya et al. (2008) reported that magnesol ($MgO_2.6SiO_2.H_2O$), silcagel and activated charcoal powder improved the viscosity of fried oil by 14%, 7% and 7% respectively.

c) Refractive Index (RI)

In this study, RI value increased in the fried niger seed oil, which might be due to the increase in foaming, color, viscosity, density, etc during deep-fat frying (Melton et al., 1994). All adsorbent treated fried niger seed oil showed a decreased RI value compared with the fried one (Table 8).

Table 8 Effect of different adsorbents on physical quality improvement of fried niger seed oil

Absorbent treatment	S.G	S. G Improvement (%)	VISCO	VISCO Improvement (%)	RI	RI Improvement (%)
Fresh niger seed oil	0.9229 ± 0.00[c]	ND	54.50 ± 0.64[d]	ND	1.47518 ± 0.00[f]	ND
Fried niger seed oil	1.0016 ± 0.01[a]	ND	58.97 ± 0.20[a]	ND	1.47716 ± 0.00[a]	ND
Ash	0.9502 ± 0.00[b, c]	5	57.13 ± 0.17[b]	3	1.47704 ± 0.00[d]	NI
Bentonite	0.982 ± 0.00[a, b]	2	56.32 ± 0.02[b, c]	4.	1.47702 ± 0.00[c]	NI
Bleaching earth	0.9728 ± 0.01[a, b]	3	56.46 ± 0.07[b, c]	4	1.47711 ± 0.00[b]	NI
Silica gel	0.9445 ± 0.02[b, c]	6	56.08 ± 0.03[c]	5	1.47692 ± 0.00[c]	NI
MgO	0.9427 ± 0.00[b, c]	6	55.65 ± 0.08[c]	6	1.47638 ± 0.00[e]	NI
Centrifugation	1.0016 ± 0.01[a]	NI	58.71 ± 0.43[a]	NI	1.47715 ± 0.00[a]	NI

Values are expressed as mean ± SE (n = 3) -. Means in the same column not sharing the same superscripts are significantly different based on Duncan's multiple range test ($p < 0.05$). S.G (Specific gravity), VISCO (Viscosity), RI (Refractive Index). "NI"-No Improvement; "ND" -Not Determined

4.4. Effect of different adsorbents on chemical quality improvement and recovery of fried niger seed oil

a) Acid value and free fatty acid (%)

The acid value in the fresh niger seed oil used in this study was 2.24 mg KOH/gm oil, which is not within the set limit for edible refined niger seed oil according to the compulsory standard set by Ethiopian Standard Authority (CES 20:2013). Upon frying for 20 hrs, the AV increased to 8.31 mg KOH/gm oil (Table 9), which is beyond the permissible limit for edible oil. Generally, there are two sources of free fatty acids during frying: from (1) the reaction of oil with water in the foods and (2) the secondary oxidation substances Farag and El-Anany (2006). In the 20 hrs fried palm oil the AV has increased by 3.3%, while in the same time fried niger seed oil the increament was 3.7%. This might be as a result of more unsaturation in niger seed oil; as fatty acids with double bonds are liable for oxidation during heating, owing to presence of pi (π) bonds, which consequently produces degradable products (Debnath et al., 2012). As reported in Table 9, all adsorbents reduced the increased AV significantly at $p < 0.05$. The highest reduction was found in the MgO treated oil (73%). Ash, bentonite, bleaching earth and silca gel also reduced the AV significantly by (40, 66, 56, and 40) % respectively from the value in the fried niger seed oil.

The FFA% in the fresh niger seed oil was higher than the requirement according to Ethiopian Standard (CES 20:2013). After frying potato chips for 20 hrs, the FFA % increased to 4.17 %, yet this value is beyond the acceptable limit for human consumption. The AV increased in the fried palm oil and niger seed oil by 3.2% and 3.7% respectively. The moisture coming from the fried product accelerates the hydrolysis of oil, as water can promote the hydrolysis of triacylglycerols to form combination of mono/di-acylglycerol and FFAs. Also, the increase in

FFA (%) is due to cleavage and oxidation of double bonds to form carbonyl compounds, which oxidized to lower molecular weight fatty acid during frying (Debnath et al., 2012).

Treatment of the fried niger seed oil by ash, bentonite, bleaching earth, silca gel and MgO reduced the FFA% by (61, 66, 56, 61 and 73) respectively. The improvement of both AV and FFA% upon adsorbent treatments might be due to the specific adsorption affinity for small molecular substances of each treatment (Christy 2012; Hidayatullah et al. 2007; Okiel et al., 2011).

b) Peroxide value

After 20 hrs of frying, the PV of the fresh niger seed oil increased from 1.00 to 13.97 mEq oxygen/gm of oil. Mainly, the thermoxdiation reaction between atmospheric oxygen and the frying oil is responsible for the increment (Houhoula et al., 2003; Cuesta et al., 1993; Peers and Swoboda 1982; Sanchez-Muniz et al., 1993). According to the compulsory standard set by Ethiopian Standard Authority (CES 20:2013) the maximum peroxide limit for crude niger seed oil is 10 mEq oxygen/gm. The prolonged frying deteriorated the oil's PV value to unacceptable level for human consumption (CES 20:2013). Due to the high unsaturated fatty acid composition of niger seed oil, the increment of PV value (13.97%) was higher than same hour fried palm oil (5.52%). These findings are in line with the degree of oil unsaturation. Fatemai (1980) mentioned that the higher the concentration of unsaturated fatty acids (linoleic and linoleic acid) the oil will be more unstable.

The fried niger seed oil treated with 15% (W/V) of ash, bentonite, bleaching earth, silca gel and MgO (150°C, 30 min) improved the quality of the oil by reducing the PV by (57, 43, 21, 50 and 64) respectively (Table 9). The highest reductions were obtained upon MgO and ash treatments respectively. Similarly, Hidayatullah et al. (2007) reported the effectiveness of MgO and activated charcoal in improving the overall quality of used fried *Silybum marianum* oil. The effectiveness of magnesol ($MgO_2.6SiO_2.H_2O$) in removing secondary oxidation products was reported by Bhattacharya et al. (2008). (Alinnor, 2007 and Erol et al 2005) reported that burning of coal produced small molecular substances with useful adsorption capacity. The ash used in the present study is produced at household level after completely burning wood made charcoal. This might led to the formation of molecules with specific adsorption capacity. Hence, ash treated fried niger seed oil showed the highest reduction of the PV next to MgO treatment.

c) Iodine value

The IV of the fresh niger seed oil used in this study was 129.93 mg I_2/g oil, which is within the compulsory standard set by Ethiopian Standard Authority (CES 20:2013). However, there was no significant difference ($p<0.05$) in IV between the fresh, fried and adsorbent treated oil (Table 9).

d) Oil recovery (%)

Bentonite treated fried niger seed oil showed the highest recovery of oil (88%). Meanwhile, the recovery for ash, bleaching earth, silca gel and MgO treated oils was (80, 85, 70 and 40) % respectively (Table 9). As it was reported in Tables 6, 7, 8 and 9, based on both physical and chemical quality improvement effectiveness ash and MgO were selected for further objectives of this study (i.e. effect of concentration and synergism by the two adsorbents). Since peroxide value is a good indicator of oxidative deterioration of used frying oils, these adsorbents were selected based on their effectiveness in improving the PV values of both 20 hrs fried palm and niger seed oils.

Table 9 Effect of different adsorbents on chemical quality improvement and recovery of fried niger seed oil

Adsorbent treatment	AV (mgKOH/gm)	AV Improvement (%)	FFA (%)	FFA Improvement (%)	PV (mEq O_2/g)	PV Improvement (%)	IV (mg I_2/g)	IV Improvement (%)	Oil recovery (%)
Fresh niger seed oil	2.24 ± 0.00^{b}	ND	1.13 ± 0.00^{b}	ND	1.00 ± 0.57^{f}	ND	129.93 ± 0.56$^{a, b}$	ND	ND
Fried niger seed oil	8.31 ± 1.55^{a}	ND	4.17 ± 0.78^{a}	ND	13.97 ± 0.00^{a}	ND	126.76 ± 0.70^{b}	ND	ND
Ash	3.36 ± 0.00^{b}	40	1.62 ± 0.00^{b}	61	5.99 ± 0.66$^{d, e}$	57	129.22 ± 0.40$^{a, b}$	NI	80
Bentonite	2.80 ± 0.32^{b}	66	1.40 ± 0.16^{b}	66	7.98 ± 0.00^{c}	43	130.49 ± 0.03^{a}	NI	88
Bleaching earth	3.68 ± 0.18^{b}	56	1.85 ± 0.09^{b}	56	10.99 ± 0.66^{b}	21	129.20 ± 0.70$^{a, b}$	NI	85
Silica gel	3.36 ± 0.00^{b}	40	1.62 ± 0.00^{b}	61	6.99 ± 0.57$^{c, d}$	50	128.50 ± 0.30$^{a, b}$	NI	70
MgO	2.24 ± 0.00^{b}	73	1.13 ± 0.00^{b}	73	5.00 ± 0.57^{e}	64	128.95 ± 0.00$^{a, b}$	NI	40
Centrifugation	8.31 ± 1.55^{a}	NI	4.17 ± 0.78^{a}	NI	13.96 ±1.15^{a}	NI	127.98 ± 2.82$^{a, b}$	NI	ND

Values are expressed as mean ± SE (*n* = 3). Means in the same column not sharing the same superscripts are significantly different based on Duncan's multiple range test ($p<0.05$). FFA (Free Fatty Acid), AV (Acid Value), PV (Peroxide Value), IV (Iodine Value). "ND"-Not Determined, "NI"-No Improvement

4.5. Concentration effect of ash and magnesium oxide in quality improvement of fried palm oil

After selection of the effective adsorbents in improving the quality of the used fried oils (ash and MgO), it was necessary to determine the minimum concentration of each in the oil-adsorbent mixture that can improve physico-chemical qualities of the oil. Therefore, six levels of the adsorbents (2.5–15.0 %, w/v) were used in the frying oil to select the minimum concentration.

4.5.1. Ash

i) Physical quality improvement of used palm oil with different concentrations of ash

As concentration of the ash increased (2.5-15) % in the treatment, the S.G improved from the value in the fried palm oil (Table 10). The highest improvement was upon 15% ash treatment (9%). Also, the viscosity of the fried palm oil improved by 2% only at higher concentrations of (12.5 and 15.0) % ($p < 0.05$), while with lower concentrations significant difference was not observed (Table 10). Similarly, with (10.0, 12.5 and 15.0) % ash treatments a significant reduction of the RI value compared with the fried palm oil was observed (Table 10). All concentrations except (2.5 and 5.0) % treatments, significantly reduced RI value from the fried palm oil with percent of improvement less than 1 %. Thus, 12.5% ash was the minimum concentration improving the physical qualities of fried palm oil (S. G (5%), VISCO (2%)) with same level as 15% concentration.

Table 10 Concentration effect of ash in improving physical quality of fried palm oil

Adsorbent treatment	S.G	S. G Improvement (%)	VISCO	VISCO Improvement (%)	RI	RI Improvement (%)
Fresh palm oil	0.8989 ± 0.00^{d}	ND	57.08 ± 0.39^{g}	ND	1.46574 ± 0.00^{f}	ND
Fried palm oil	0.9993 ± 0.00^{a}	ND	60.80 ± 0.30^{a}	ND	1.46806 ± 0.00^{a}	ND
2.5%	0.9973 ± 0.04^{a}	NI	60.72 ± 0.09^{a}	NI	1.46806 ± 0.00^{a}	NI
5.0%	$0.9883 \pm 0.05^{a, b}$	1	60.96 ± 0.04^{a}	NI	1.46789 ± 0.00^{b}	NI
7.5%	$0.9862 \pm 0.00^{a, b}$	1	60.17 ± 0.03^{b}	1	$1.46793 \pm 0.00^{a,b}$	NI
10.0%	$0.9595 \pm 0.42^{a, b, c, d}$	4	$59.81 \pm 0.02^{b, c}$	2	1.46786 ± 0.00^{b}	NI
12.5%	$0.9425 \pm 0.00^{a, b, c, d}$	6	$59.37 \pm 0.00^{c, d, e}$	2	1.46766 ± 0.00^{c}	NI
15.0%	0.9083 ± 0.02^{d}	9	$59.29 \pm 0.07^{d, e}$	3	1.46663 ± 0.00^{e}	NI

Values are expressed as mean ± SE (n = 3). Means in the same column not sharing the same superscripts are significantly different based on Duncan's multiple range test ($p < 0.05$). S.G (Specific gravity), VISCO (Viscosity), RI (Refractive Index), "NI" No Improvement; "ND" Not Determined

ii) Chemical quality improvement of used palm oil with different concentrations of ash

As reported in Table 11, (2.5, 5.0, 7.5, 10.0, 12.5 and 15.0) % concentration of ash reduced the increased AV of fried palm oil gradient-wise by (30, 35, 40, 45, 50 and 60) % respectively ($p < 0.05$). With the same concentration gradient the FFA % also reduced from the value in the fried palm oil by (30, 35, 40, 45, 50 and 55) % respectively (Table 11). Treatments with 12.5% and 15.0% of ash improved the AV and FFA% to the recommended acceptable range for human consumption. Upon 2.5 and 5.0% of ash treatments of the fried palm oil, there was no significant difference from the value in the fried oil. However, with 7.5, 10.0, 12.5 and 15.0% treatments, the PV reduced by (13, 29, 38 and 55) % respectively ($p<0.05$) (Table 11). All the concentrations between (7.5-15.0) % improved the PV to the permissible level. In contrast, as shown in Table 11, there was no significant difference in IV between fresh, fried and adsorbent treated palm oil. The recovered fried palm oil percentage upon (2.5, 5.0, 7.5, 10.0, 12.5 and 15) % ash treatment was (90, 85, 83, 80, 78 and 75) % respectively (Table 11). Based on these, thus 12.5% of ash treatment of the fried palm oil was found to be the minimum concentration improving both acid value and free fatty acid % by 50% and the peroxide value by 38% (i.e. which is within the acceptable limit set by Ethiopian Standard Authority).

Table 11 Concentration effect of ash in improving chemical quality of fried palm oil

Adsorbent treatment	AV (mgKOH/gm)	AV Improvement (%)	FFA (%)	FFA Improvement (%)	PV (mEq O_2/g)	PV Improvement (%)	IV (mg I_2/g)	IV Improvement (%)	Oil recovery (%)
Fresh palm oil	0.42 ± 0.00^{f}	ND	0.20 ± 0.00^{i}	ND	1.99 ± 0.00^{h}	ND	49.25 ± 2.97^{a}	ND	ND
Fried palm oil	1.40 ± 0.00^{a}	ND	0.64 ± 0.00^{a}	ND	11.00 ± 0.57^{a}	ND	48.43 ± 0.80^{a}	ND	ND
2.5%	0.98 ± 0.00^{b}	30	0.45 ± 0.00^{b}	30	11.39 ± 0.12^{a}	NI	48.37 ± 1.69^{a}	NI	90
5.0%	$0.91 \pm 0.04^{b, c}$	35	$0.41 \pm 0.01^{b, c}$	35	11.19 ± 0.00^{a}	NI	50.95 ± 3.01^{a}	NI	85
7.5%	$0.84 \pm 0.00^{c, d}$	40	$0.38 \pm 0.00^{c, d}$	40	9.57 ± 0.22^{b}	13	50.42 ± 3.88^{a}	NI	83
10.0%	0.77 ± 0.04^{d}	45	$0.35 \pm 0.01^{d, e}$	45	7.80 ± 0.11^{c}	29	51.17 ± 3.31^{a}	NI	80
12.5%	0.70 ± 0.00^{d}	50	$0.32 \pm 0.00^{e, f}$	50	$6.80 \pm 0.23^{d, e}$	38	52.38 ± 2.60^{a}	NI	78
15.0 %	0.56 ± 0.00^{e}	60	$0.29 \pm 0.00^{f, g}$	55	4.99 ± 0.00^{f}	55	47.00 ± 1.62^{a}	3	75

Values are expressed as mean ± SE (n = 3). Means in the same column not sharing the same superscripts are significantly different based on Duncan's multiple range test ($p < 0.05$).

FFA (Free Fatty Acid), AV (Acid Value), PV (Peroxide Value), IV (Iodine Value). "NI"-No Improvement, "ND"- Not Determined

4.5.2. Magnesium oxide

i) Physical quality improvement of fried palm oil with different concentrations of MgO

As reported in Table 12, 12.5% and 15.0% MgO treatment of fried palm oil improved S.G value ($p < 0.05$) significantly by 7% and 8% respectively from the value in the fried oil. There is no significant difference in S.G value between the fresh and 12.5% and 15.0% MgO treated palm oil. Similar trend was observed in different concentrations of ash treated fried palm oil (Table 10). At higher concentrations of (10.0, 12.5 and 15.0) % MgO treatment, the viscosity of the fried palm oil was reduced by (3, 3 and 7) % ($p < 0.05$) respectively (Table 12). Similar trend was observed in different concentrations of ash treated fried palm oil (Table 10). Similarly, with (10.0, 12.5 and 15.0) % ash treatments, a significant reduction of the RI compared with the value in fried PO was observed (Table 10). Therefore, 10.0 % MgO treatment of fried palm oil was the recommendable minimum effective concentration to improve the S. G and VISCO by 3 %.

Table 12 Concentration effect of magnesium oxide in improving physical quality of fried palm oil

Adsorbent treatment	S.G	S.G Improvement (%)	VISCO	VISCO Improvement (%)	RI	RI Improvement (%)
Fresh palm oil	0.8989 ± 0.00^{d}	ND	57.08 ± 0.39^{g}	ND	1.46574 ± 0.00^{f}	ND
Fried palm oil	0.9993 ± 0.00^{a}	ND	60.80 ± 0.30^{a}	ND	1.46806 ± 0.00^{a}	ND
2.5 %	$0.9867 \pm 0.00^{a,b}$	1	60.77 ± 0.12^{a}	NI	1.46805 ± 0.00^{a}	NI
5.0 %	$0.9865 \pm 0.02^{a,b}$	1	60.00 ± 0.00^{b}	1	$1.46797 \pm 0.00^{a,b}$	NI
7.5 %	$0.9862 \pm 0.00^{a,b}$	1	$59.74 \pm 0.03^{b,c,d}$	2	1.46789 ± 0.00^{b}	NI
10.0 %	$0.9696 \pm 0.03^{a,b,c}$	3	$59.21 \pm 0.03^{e,f}$	3	1.46747 ± 0.00^{d}	NI
12.5 %	$0.9311 \pm 0.06^{b,c,d}$	7	$58.96 \pm 0.00^{e,f}$	3	1.46747 ± 0.00^{d}	NI
15.0 %	$0.9178 \pm 0.03^{c,d}$	8	58.62 ± 0.40^{f}	7	1.46672 ± 0.00^{e}	NI

Values are expressed as mean ± SE ($n = 3$). Means in the same column with different superscripts are significantly different based on Duncan's multiple range test ($p < 0.05$). S.G (Specific gravity), VISCO (Viscosity), RI (Refractive Index),"NI" No Improvement, "ND" Not Determined

ii) Chemical quality improvement of fried palm oil with different concentrations of MgO

As reported in Table 13, (2.5, 5.0, 7.5, 10.0, 12.5 and 15.0) % of MgO reduced the AV of fried palm oil gradient-wise by (30, 40, 45, 50, 60 and 60) % respectively ($p < 0.05$). According to CSE 301 (2015) the maximum limit of acid value for refined palm oil is 0.6. Based on this (10.0, 12.5, 15.0) % MgO and 15.0 % ash treated used fried palm oil were fit with the standard. With lower concentrations (2.5, 5.0) % of MgO, the PV was not reduced significantly as compared to the value in the fried palm oil. However, with (7.5, 10.0, 12.5 and 15.0) % of MgO, the PV was reduced by (24, 31, 41, 64) % respectively ($p < 0.05$) (Table 13) to acceptable level (CSE 301, 2015). Similar trend was found in the fried palm oil treated with the same concentrations of ash (Table 11). As shown in Table 13, there was no significant difference in IV between fresh, fried and adsorbent treated palm oil. This similar trend was observed in ash treated palm oil also. Hence, in this study iodine value was not a good indicator for quality deterioration and for improvement of used frying oils' quality as well. With (2.5, 5.0, 7.5, 10.0, 12.5 and 15.0) % MgO treated fried palm oil, the recovery was (73, 68, 63, 55, 45 and 40) % respectively (Table 13). Similar trend was found in the ash treated fried palm oil. However, for the same concentration treatment with ash yielded higher oil recovery. Thus, 10.0 % MgO treatment of fried palm oil was found to be the recommendable minimum concentration improving both AV and free fatty acid % by 50% and the PV by 31% .

Table 13 Concentration effect of magnesium oxide in improving chemical quality of fried palm oil

Adsorbent treatment	AV (mgKOH/gm)	AV Improvement (%)	FFA (%)	FFA Improvement (%)	PV (mEq O_2/gm)	PV Improvement (%)	IV (mg I_2/g)	IV Improvement (%)	Oil Recovery (%)
Fresh palm oil	0.42 ± 0.00^{f}	ND	0.20 ± 0.00^{i}	ND	1.99 ± 0.00^{h}	ND	49.25 ± 2.97^{a}	ND	ND
Fried palm oil	1.40 ± 0.00^{a}	ND	0.64 ± 0.00^{a}	ND	11.00 ± 0.57^{a}	ND	48.43 ± 0.80^{a}	ND	ND
2.5 %	0.98 ± 0.00^{b}	30	0.45 ± 0.00^{b}	30	10.79 ± 0.23^{a}	2	50.68 ± 3.88^{a}	NI	73
5.0 %	$0.84 \pm 0.00^{c,d}$	40	$0.38 \pm 0.00^{b,c,d}$	40	10.58 ± 0.34^{a}	4	47.11 ± 1.73^{a}	3	68
7.5 %	0.77 ± 0.04^{d}	45	$0.35 \pm 0.01^{d,e}$	45	8.38 ± 0.23^{c}	24	50.42 ± 3.88^{a}	NI	63
10.0 %	0.70 ± 0.00^{d}	50	$0.32 \pm 0.00^{e,f}$	50	$7.59 \pm 0.22^{c,d}$	31	50.15 ± 2.72^{a}	NI	55
12.5 %	0.56 ± 0.00^{e}	60	$0.26 \pm 0.00^{g,h}$	60	6.39 ± 0.22^{e}	42	49.65 ± 4.61^{a}	NI	45
15.0 %	0.49 ± 0.07^{e}	65	0.22 ± 0.01^{h}	62	4.00 ± 0.00^{g}	64	47.58 ± 0.40^{a}	1	40

Values are expressed as mean ± SE (n = 3). Means in the same column not sharing the same superscripts are significantly different based on Duncan's multiple range test ($p < 0.05$). FFA (Free Fatty Acid), AV (Acid Value), PV (Peroxide Value), IV (Iodine Value). "NI"-No Improvement; "ND"-Not Determined

4.6. Concentration effect of ash and magnesium oxide in quality improvement of fried niger seed oil

4.6.1. Ash

i) Physical quality improvement of fried niger seed oil with different concentrations of ash

As reported in Table 14, treating the fried niger seed oil by (10.0, 12.5 and 15.0) % of ash reduced the S.G value ($p < 0.05$) by (3, 4 and 5) % respectively. At higher concentrations of (10.0, 12.5 and 15.0) % ash treatment, the viscosity of the fried niger seed oil was reduced by (1, 2 and 3) % ($p < 0.05$), while with lower concentrations significant difference was not observed (Table 14). With (7.5, 10, 12.5 and 15.0) % ash treatments a significant reduction of the RI value compared with the fried niger seed oil was observed (Table 14). Thus, 12.5% ash was the minimum effective concentration to treat the fried niger seed oil improving its physical qualities to the same level as 15% treatment.

Table 14 Concentration effect of ash in improving physical quality of fried niger seed oil

Adsorbent treatment	S.G	S.G Improvement (%)	VISCO	VISCO Improvement (%)	RI	RI Improvement (%)
Fresh niger seed oil	0.9229 ± 0.02[g]	ND	54.50 ± 0.64[i]	ND	1.47518 ± 0.00[j]	ND
Fried niger seed oil	1.0016 ± 0.01[a]	ND	58.97 ± 0.20[a]	ND	1.47716 ± 0.00[a]	ND
2.5 %	0.9997 ± 0.00[a]	NI	58.86 ± 0.07[a, b]	NI	1.47717 ± 0.00[a]	NI
5.0 %	0.9997 ± 0.00[a]	NI	58.63 ± 0.03[a, b]	NI	1.47714 ± 0.00[a, b]	NI
7.5 %	0.9837 ± 0.00[a, b, c]	2	58.50 ± 0.08[a, b]	NI	1.477101 ± 0.00[b, c]	NI
10.0 %	0.9740 ± 0.11[c, d, e]	3	58.30 ± 0.28[b, c]	1	1.47712 ± 0.00[b, c]	NI
12.5 %	0.9605 ± 0.00[d, e, f]	4	57.76 ± 0.11[c, d]	2.	1.47709 ± 0.00[c]	NI
15.0 %	0.9502 ± 0.00[e, f]	5	57.13 ± 0.17[e, f]	3	1.47704 ±0.00[e]	NI

Values are expressed as mean ± SE (n = 3). Means in the same column not sharing the same superscripts are significantly different based on Duncan's multiple range test ($p < 0.05$). S.G (Specific gravity), VISCO (Viscosity), RI (Refractive Index)."NI"- No Improvement, "ND"- Not Determined

ii) Chemical quality improvement of fried niger seed oil with different concentrations of ash

As reported in Table 15 (2.5, 5.0, 7.5, 10.0, 12.5 and 15.0) % concentration of ash reduced the increased AV of fried niger seed oil gradient-wise by (26, 39, 46, 53, 53 and 60) % respectively ($p < 0.05$). Similar trend was observed in ash treated fried palm oil. With ash concenterations of (2.5 to 15.0) %, the FFA% also reduced from the value in the fried niger seed oil gradient-wise (Table 15). The PV in the fried niger seed oil reduced concentration-wise (2.5, 5.0, 7.5, 10.0, 12.5 and 15.0) % ash treatment by (14, 27, 30, 40, 46 and 57) % respectively ($p < 0.05$) (Table 15). All concentrations between (7.5-15.0) % improved the PV to permissible level. As shown in Table 15, there was no significant difference in IV between fresh, fried and adsorbent treated niger seed oil. With (2.5, 5.0, 7.5, 10.0, 12.5 and 15.0) % ash treated fried niger seed oil, the recovery was (90, 85, 85, 83, 81 and 80) % respectively (Table 15). Considering the effect in improving both AV and FFA% by 50% and PV by 40% to acceptable level, 10.0% ash treatment of fried niger seed oil was recommended as effective concentration.

Table 15 Concentration effect of ash in improving chemical quality of fried niger seed oil

Adsorbent treatment	AV (mgKOH/gm)	AV Improvement (%)	FFA (%)	FFA Improvement (%)	PV ($mEqO_2/g$)	PV Improvement (%)	IV (mg I_2/g)	IV Improvement (%)	Oil recovery (%)
Fresh niger seed oil	2.24 ±0.00^{e}	ND	1.16 ± 0.00^{e}	ND	1.00 ± 0.57^{i}	ND	129.93 ± 0.56$^{a, b}$	ND	ND
Fried niger seed oil	8.31 ±1.55^{a}	ND	4.17 ± 0.78^{a}	ND	13.97 ± 0.00^{a}	ND	126.76 ± 0.70^{b}	ND	ND
2.5 %	6.17 ± 0.32^{b}	26	3.10 ± 0.33^{b}	26	12.00 ± 0.23^{b}	14	133.62 ± 4.38$^{a, b}$	NI	90
5.0 %	5.04 ± 0.31$^{b, c}$	39	2.53 ± 0.15$^{b, c}$	39	10.19 ± 0.35^{c,d}	27	132.13 ± 4.93$^{a, b}$	NI	85
7.5 %	4.49 ± 0.00$^{c, d}$	46	2.26 ± 0.00$^{b, c, d}$	46	9.79 ± 0.10^{c,d}	30	133.48 ± 0.07$^{a, b}$	NI	85
10.0 %	3.92 ± 0.32$^{c, d}$	53	1.97 ± 0.30$^{c, d, e}$	53	8.39 ± 0.23^{e}	40	132.16 ± 2.09$^{a, b}$	NI	83
12.5 %	3.92 ± 0.31$^{c, d}$	53	1.97 ± 0.16$^{c, d, e}$	53	7.58 ± 0.23$^{e ,f}$	46	135.40 ± 2.20$^{a, b}$	NI	81
15.0 %	3.36 ± 0.00$^{d, e}$	59	1.62 ± 0.00$^{d, e}$	61	5.99 ± 0.66^{g}	57	129.22 ± 0.40$^{a, b}$	NI	80

Values are expressed as mean ± SE (n = 3). Means in the same column not sharing the same superscripts are significantly different based on Duncan's multiple range test (p < 0.05).

FFA (Free Fatty Acid), AV (Acid Value), PV (Peroxide Value), IV (Iodine Value). "NI"-No Improvement; "ND"- Not Determined

4.6.2. Magnesium oxide

i) Physical quality improvement of fried niger seed oil with different concentrations of MgO

As reported in Table 16, (10.0, 12.5 and 15.0) % ash treated fried niger seed oil improved S.G value ($p < 0.05$) by (3, 5 and 6) % respectively from the value in the fried oil. At higher concentrations of (7.5, 10.0, 12.5 and 15.0) % ash treatment, the viscosity of the fried niger seed oil was reduced by 2, 3, 4 and 6% ($p < 0.05$) respectively (Table 16). With all the concentrations of MgO, a significant reduction of the RI value compared with the fried niger seed oil was observed (Table 16). Based on these results, 10.0 % MgO treatment of fried niger seed oil was found to be effective in improving the physical quality parameters to the same level with the 15% treatment.

Table 16 Concentration effect of magnesium oxide in improving physical quality of fried niger seed oil

Adsorbent treatment	S.G	S.G Improvement (%)	VISCO	VISCO Improvement (%)	RI	RI Improvement (%)
Fresh niger seed oil	0.9229 ± 0.02^{g}	ND	54.50 ± 0.64^{i}	ND	1.47518 ± 0.00^{j}	ND
Fried niger seed oil	1.0016 ± 0.01^{a}	ND	58.97 ± 0.20^{a}	ND	1.477160 ± 0.00^{a}	ND
2.5 %	$0.9977 \pm 0.00^{a, b}$	NI	$58.73 \pm 0.10^{a, b}$	NI	$1.477115 \pm 0.00^{b, c}$	NI
5.0 %	$0.9964 \pm 0.00^{a, b, c}$	NI	$58.62 \pm 0.05^{a, b}$	NI	1.476945 ± 0.00^{d}	NI
7.5 %	$0.9853 \pm 0.00^{a, b, c}$	1	$57.59 \pm 0.14^{d, e}$	2	1.476860 ± 0.00^{f}	NI
10.0 %	$0.9756 \pm 0.00^{b, c, d}$	3	$56.89 \pm 0.03^{f, g}$	3	1.476750 ± 0.00^{g}	NI
12.5 %	$0.95302 \pm 0.01^{e, f}$	5	$56.37 \pm 0.08^{f, g}$	4	1.476525 ± 0.00^{h}	NI
15.0 %	$0.9427 \pm 0.00^{f, g}$	6	55.65 ± 0.08^{h}	6	1.47638 ± 0.00^{i}	NI

Values are expressed as mean ± SE (n = 3). Means in the same column not sharing the same superscripts are significantly different based on Duncan's multiple range test ($p < 0.05$). S.G (Specific gravity), VISCO (Viscosity), RI (Refractive Index). "NI"-No Improvement, "ND"-Not Determined

ii) Chemical quality improvement of fried niger seed oil with different concentrations of MgO

As reported in Table 17, (2.5, 5.0, 7.5, 10.0, 12.5 and 15.0)% of MgO treatment reduced the AV of the fried niger seed oil gradient-wise by (39, 46, 59, 60, 60 and 73) % respectively ($p < 0.05$). Similar trend was observed in FFA% reduction also. For same concentration, MgO showed higher percentage improvement than ash in the fried niger seed oil. Fried niger seed oil treated by (2.5, 5.0, 7.5, 10.0, 12.5 and 15.0) % MgO reduced the PV by (17, 24, 28, 40, 47 and 64) % respectively ($p < 0.05$) from the value in the fried oil (Table 17). Treatments increasing from 7.5% reduced the PV to the allowed limit of niger seed oil. For (10.0, 12.5, 15.0)% MgO treatments higher improvement in PV was observed than same concentration ash treated niger seed oil. As shown in Table 17, there was no significant difference in IV between fresh, fried and adsorbent treated palm oil. With (2.5, 5.0, 7.5, 10.0, 12.5 and 15.0) % MgO treated fried niger seed oil, the recovery was (73, 68, 64, 58, 48 and 40) % respectively (Table 17). With same concentration ash treatment yielded higher recovery than MgO. Hence, 10.0% MgO treatments of fried niger seed oil was found to be the minimum effective concentration improving AV and FFA % by 60 % and the PV by 40 % (i.e. within the acceptable range set by Ethiopian Standard Authority).

Based on the above results, 12.5 % ash and 10.0 % MgO treatment of 20hrs fried palm oil improved the tested physical and chemical qualities. For 20hrs fried niger seed oil, the tested physical and chemical parameters were improved upon 12.5% a and 10.0% ash treatments respectively. Meanwhile, 10.0 % MgO treatment of the fried niger seed oil improved both the physical and chemical parameters within the acceptable range.

Table 17 Concentration effect of magnesium oxide in improving chemical quality of fried niger seed oil

Adsorbent treatment	AV (mgKOH/gm)	AV Improvement (%)	FFA (%)	FFA Improvement (%)	PV ($mEqO_2/g$)	PV Improvement (%)	IV (mg I_2/g)	IV Improvement (%)	Recovery (%)
Fresh niger seed oil	2.24 ± 0.00^{e}	ND	1.16 ± 0.00^{e}	ND	$1.00 \pm 0\text{-}.57^{i}$	ND	$129.93 \pm 0.56^{a, b}$	ND	ND
Fried niger seed oil	8.31 ± 1.55^{a}	ND	4.17 ± 0.78^{a}	ND	13.97 ± 0.00^{a}	ND	126.76 ± 0.70^{b}	ND	ND
2.5%	$5.05 \pm 0.32^{b, c}$	39	$2.54 \pm 0.09^{b, c, d}$	39	11.56 ± 0.22^{b}	17	127.18 ± 2.15^{b}	NI	73
5.0 %	$4.48 \pm 0.00^{c, d}$	46	$2.25 \pm 0.21^{c, d}$	46	10.6 ± 0.11^{c}	24	137.01 ± 2.11^{a}	NI	68
7.5 %	$3.37 \pm 0.00^{d, e}$	59	$1.69 \pm 0.00^{c, d, e}$	59	10.00 ± 0.11^{d}	28	137.16 ± 4.39^{a}	NI	64
10.0 %	$3.36 \pm 0.00^{d, e}$	60	$1.69 \pm 0.00^{c, d, e}$	60	8.38 ± 0.23^{e}	40	$129.67 \pm 2.39^{a, b}$	NI	58
12.5 %	$3.36 \pm 0.00^{d, e}$	60	$1.69 \pm 0.00^{c, d, e}$	60	7.39 ± 0.11^{f}	47	$134.11 \pm 3.22^{a, b}$	NI	48
15.0 %	2.24 ± 0.00^{e}	73	$1.13 \pm 0.00^{d, e}$	61	5.00 ± 0.57^{h}	64	$128.95 \pm 0.00^{a, b}$	NI	40

Values are expressed as mean ± SE ($n = 3$). Means in the same column with different superscripts are significantly different based on Duncan's multiple range test ($p < 0.05$).

FFA (Free Fatty Acid), AV (Acid Value), PV (Peroxide Value), IV (Iodine Value)."NI"- No Improvement; " ND"-Not Determined

4.7. Synergetic effect of ash and magnesium oxide in quality improvement of fried palm oil

4.7.1. Physical quality improvement

As reported in Table 18, (ash, MgO and (Ash + MgO) (1:1) significantly reduced the S.G of fried palm oil by (9, 8 and 4) % respectively ($p < 0.05$) from the value in the used fried palm oil. However, compared with the individual treatment the combination of the two adsorbents showed a less percentage improvement. As reported in Table 18 (ash, MgO and (Ash + MgO) (1:1) significantly reduced the viscosity of the fried palm oil by (2, 4 and 2) % respectively ($p < 0.05$).Yet, there is no significant difference between the individual and adsorbent combination treatments. Ash, MgO and (Ash + MgO) (1:1) significantly reduced the RI of fried palm oil ($p < 0.05$) (Table 18). In contrast, Mancini-Filho et al. (1986) reported that an adsorbent mixture of 4.5% clay, 0.5% charcoal, 2.5% MgO and 2.5% celite had a significant improvement in dielectric constant, FFAs and colour.

Table 18 Synergetic effect of ash and magnesium oxide in improving the physical quality of fried palm oil

Adsorbent treatment	S.G	S. G. Improvement (%)	VISCO	VISCO Improvement (%)	RI	RI Improvement (%)
Fresh palm oil	0.8989 ± 0.00^{c}	ND	57.08 ± 0.39^{c}	ND	1.46574 ± 0.00^{d}	ND
Fried palm oil	0.9993 ± 0.00^{a}	ND	60.80 ± 0.30^{a}	ND	1.46806 ± 0.00^{a}	ND
Ash	0.9083 ± 0.02^{c}	9	59.29 ± 0.07^{b}	2	1.46663 ± 0.00^{c}	NI
MgO	$0.9178 \pm 0.03^{b, c}$	8	58.62 ± 0.40^{b}	4	1.46672 ± 0.00^{c}	NI
Blend (ash + MgO) (1:1)	0.9604 ± 0.01^{b}	4	59.40 ± 0.09^{b}	2	1.46774 ± 0.00^{b}	NI

Values are expressed as mean ± SE ($n = 3$). Means in the same column not sharing the same superscripts are significantly different based on Duncan's multiple range test ($p < 0.05$). S.G (Specific gravity), VISCO (Viscosity), RI (Refractive Index).“NI”-No Improvement; “ND“-Not Determined

4.7.2. Chemical quality improvement

As reported in Table 19, (ash, MgO and (Ash + MgO) (1:1)) significantly reduced the AV of fried palm oil by (60, 65 and 60) % respectively ($p < 0.05$). Similar trend was observed in FFA% reduction also. Yet, the combination treatment couldn't show higher improvement rate than the individual treatments. As reported in Table 19, (ash, MgO and (Ash + MgO) (1:1) significantly reduced the PV of fried palm oil by (55, 64 and 46) % respectively ($p < 0.05$). Similarly, Udomkun et al. (2018) reported that combinations of (bentonite: activated carbon: celite = 3:4:1) and (bentonite: activated clay: celite =3:4:1 + 1% citric acid) significantly reduced PV of 36 hrs fried oil by 50.2 and 44.9% respectively. In the present study, the combination treatment couldn't show higher improvement rate than the individual treatments. This result may be due to the limited amount of adsorbent (i.e. active adsorbing site) that was present (Wonglamom and Rakariyatham, 2014). With (ash, MgO and (Ash + MgO) (1:1) the recovery was (75, 40 and 73) % respectively (Table 19).

Table 19 Synergetic effect of ash and magnesium oxide in improving the chemical quality of fried palm oil

Adsorbent treatment	AV (mgKOH/gm)	AV Improvement (%)	FFA (%)	FFA Improvement (%)	PV ($mEqO_2/g$)	PV Improvement (%)	IV (mg I_2/g)	IV Improvement (%)	Oil recovery (%)
Fresh palm oil	0.42 ± 0.00^{d}	ND	0.20 ± 0.00^{d}	ND	1.99 ± 0.00^{d}	ND	49.25 ± 2.97^{b}	ND	ND
Fried palm oil	1.40 ± 0.00^{a}	ND	0.64 ± 0.00^{a}	ND	11.00 ± 0.57^{a}	ND	48.43 ± 0.80^{b}	ND	ND
Ash	0.56 ± 0.00^{b}	60	0.29 ± 0.00^{b}	55	4.99 ± 0.00^{c}	55	47.00 ± 1.62^{b}	3	75
MgO	0.49 ± 0.07^{c}	65	0.22 ± 0.00^{c}	65	4.00 ± 0.00^{c}	64	47.58 ± 0.40^{a}	2	40
Blend (Ash + MgO) (1:1)	0.56 ± 0.00^{b}	60	0.29 ± 0.00^{b}	60	6.39 ± 0.23^{b}	46	50.95 ± 3.01^{b}	NI	73.5

Values are expressed as mean ± SE (n = 3). Means in the same column not sharing the same superscripts are significantly different based on Duncan's multiple range test ($p < 0.05$). FFA (Free Fatty Acid), AV (Acid Value), PV (Peroxide Value), IV (Iodine Value)."NI"-No Improvement; "ND"-Not Determined

4.8. Synergetic effect of ash and magnesium oxide in quality improvement of fried niger seed oil

4.8.1. Physical quality improvement

As reported in Table 20, ash, MgO and (Ash + MgO) (1:1)) significantly reduced the S.G of fried niger seed oil by (5, 6 and 4) % respectively ($p < 0.05$). The same treatments significantly reduced the viscosity of fried niger seed oil by (3, 6 and 1) % respectively ($p < 0.05$). As reported in Table 20 (ash, MgO and (Ash + MgO) (1:1) significantly reduced the RI of fried niger seed oil ($p < 0.05$).

4.8.2. Chemical quality improvement

As reported in Table 21, ash, MgO and (Ash + MgO) (1:1)) significantly reduced the AV of fried niger seed oil by (40, 73 and 60) % respectively ($p < 0.05$). There is no significant difference between each adsorbent. Similar trend was observed in FFA% reduction also, in which ash, MgO and (Ash + MgO) (1:1)) significantly reduced the FFA of fried niger seed oil by (61, 73 and 60) % respectively ($p < 0.05$). As reported in Table 21, ash, MgO and (Ash + MgO) (1:1)) significantly reduced the PV of fried niger seed oil by (57, 64 and 49) % respectively ($p < 0.05$). With (ash, MgO and (Ash + MgO) (1:1) the recovery was (80, 40 and 75) % respectively. Synergetic effect of the adsorbent combinations was not observed, though the combination treatment was effective enough in improving the physico-chemical properties of both fried oils. Studies involving treatment of frying oils with combinations of activated silica and carbon were found to reduce acid value, peroxide value, photometric colour, polar compounds, and carbonyls by 28–59% (McNeill et al., 1986).

Table 20 Synergetic effect of ash and magnesium oxide in improving physical quality of fried niger seed oil

Adsorbent treatment	S.G	S. G. Improvement (%)	VISCO	VISCO Improvement (%)	RI	RI Improvement (%)
Fresh niger seed oil	0.9229 ± 0.02^{c}	ND	54.50 ± 0.64^{c}	ND	1.47518 ± 0.00^{e}	ND
Fried niger seed oil	1.0016 ± 0.01^{a}	ND	58.97 ± 0.20^{a}	ND	1.47716 ± 0.00^{a}	ND
Ash	0.9502 ± 0.00^{b}	5	57.13 ± 0.17^{b}	3	1.47704 ± 0.00^{b}	NI
MgO	$0.9427 \pm 0.00^{b, c}$	6	$55.65 \pm 0.08^{b, c}$	6	1.47638 ± 0.00^{d}	NI
Blend (Ash : MgO) (1:1)	0.9619 ± 0.01^{b}	4	58.28 ± 0.15^{b}	1	1.47669 ± 0.00^{c}	NI

Values are expressed as mean ± SE ($n = 3$). Means in the same column with different superscripts are significantly different based on Duncan's multiple range test ($p < 0.05$). S.G (Specific gravity), VISCO (Viscosity), RI (Refractive Index). "NI" No Improvement; "ND" Not Determined

Table 21 Synergetic effect of ash and magnesium oxide in improving chemical quality of fried niger seed oil

Adsorbent treatment	AV (mgKOH/gm)	AV Improvement (%)	FFA (%)	FFA Improvement (%)	PV (mEq O_2/g)	PV Improvement (%)	IV (mg I_2/g)	IV Improvement (%)	Oil recovery (%)
Fresh niger seed oil	2.24 ± 0.00^b	ND	1.13 ± 0.00^b	ND	1.00 ± 0.57^d	ND	129.93 ± 0.56^a	ND	ND
Fried niger seed oil	8.31 ± 1.55^a	ND	4.17 ± 0.78^a	ND	13.97 ± 0.00^a	ND	126.76 ± 0.70^a	ND	ND
Ash	3.36 ± 0.00^b	40	1.62 ± 0.00^b	61	5.99 ± 0.66^c	57	129.22 ± 0.40^a	NI	80
MgO	2.24 ± 0.00^b	73	1.13 ± 0.00^b	73	5.00 ± 0.57^c	64	128.95 ± 0.00^a	NI	40
Blend (Ash : MgO) (1:1)	3.35 ± 0.00^b	60	1.68 ± 0.00^b	60	7.19 ± 0.22^b	49	130.13 ± 4.06^a	NI	75

Values are expressed as mean ± SE ($n = 3$). Means in the same column with different superscripts are significantly different based on Duncan's multiple range test ($p < 0.05$). FFA (Free Fatty Acid), AV (Acid Value), PV (Peroxide Value), IV (Iodine Value). "NI" No Improvement; "ND"Not Determined

5. CONCLUSION

In this study the effectiveness of different adsorbents was evaluated in improving the physico-chemical qualities of 20 hrs fried palm and niger seed oils. In conclusion, many of the oil quality parameters were significantly improved with the use of the different adsorbents. Among which, locally at house-hold level prepared ash and MgO were found to be effective in improving the qualities of prolonged fried PO and NO. With further investigation of the selected adsorbents concentration, 12.5 % ash and 10.0 % MgO treatments of the fried palm oil improved the tested physical and chemical quality parameters. For 20hrs fried niger seed oil, the tested physical and chemical parameters were improved upon 12.5% a and 10.0% ash treatments respectively. Meanwhile, 10% MgO treatment of the fried niger seed oil improved both the physical and chemical parameters within the acceptable range. The combination treatment of ash and MgO improved the chemical properties of both fried PO and NO to the acceptable level. Therefore, after further investigations, these adsorbents can be applied in improving the quality of edible oils used for prolonged time at high temperature frying process.

6. RECOMMENDATIONS

- Scale-up approach of the adsorbent treatments to the food industries and also for the street vendors.
- The ratio of the two selected adsorbents should be optimized to induce synergetic effect.
- Effect of sequential (two-step treatment) addition of the adsorbents should be studied.
- The frying quality of the adsorbent treated oils should be studied.
- Any possible particulate matter reminant in the treated oils need to be checked further.
- Cost-benefit analysis of the treatments should be done

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