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Research article

Improving the quality of used frying niger seed oil with adsorbent treatment

Zehara Nuru, Paulos Getachew *

Addis Ababa University, College of Natural and Computational Sciences, Center for Food Science and Nutrition, P.O. Box: 1176, Addis Ababa, Ethiopia

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ABSTRACT

High temperature continuous deep fat frying of foods will result in the frying oil and food quality deterioration. Although the quality can be retained by using fresh oil, this approach will increase the production cost. In this study, quality improvement of used niger seed oil using adsorbent treatment was evaluated. Each adsorbent was mixed with 20 h used niger seed oil (15% w/v) at 150 °C and stirred for 30 min. The oil was recovered through centrifugation at 4200 rpm for 15 min. The tested chemical parameters of the oil increased after 20 h of frying (acid value (AV) (2.24–8.31) mg KOH/gm oil, free fatty acid (FFA) (1.13–4.17) %, and peroxide value (PV) (1.00–13.97 mEq oxygen/Kg of oil). The improvement in free fatty acid, peroxide value and oil recovery upon treatment of the fried oil with ash, bentonite, bleaching earth, silca gel and magnesium oxide (MgO) was (61, 57, 80), (66, 43, 88), (56, 21, 85), (61, 50, 70), and (73, 64, 40) % respectively. Ash and MgO effectively improved the physico-chemical characteristics of the used oil. Thus, the two were selected for further optimization of effective concentration and to evaluate their synergetic effect. Treatments with 2.5, 5.0, 7.5, 10.0, 12.5 and 15.0 % of ash reduced the AV of the fried oil by 26, 39, 46, 53, 53 and 60 % respectively ($p < 0.05$). Also the combination of ash and MgO (1:1) improved the physico-chemical properties of the frying oil to nearly fresh quality.

1. Introduction

Deep-fat fried (DFF) foods are popular among consumers due to its desirable flavor, color and crispy texture (Asokapandian et al., 2019; Nawaz et al., 2019; Segura et al., 2019; Boskou et al., 2006; Serjouie et al., 2010). However, DFF (150–190) ^{o}C in the presence of oxygen, moisture, trace elements and free radicals will result in physico-chemical reactions such as thermo-oxidation, hydrolysis, polymerization, and isomerization. This will lead to decomposition of the frying oil and formation of non-volatile monomeric/polymeric oxidative products (Manjunatha et al., 2019; Mondale and Dash, 2017; Sayyad 2017; Hidayatullah and Bangash, 2007; Andrikopoulos et al., 2002). As a result, DFF increases foaming, color, viscosity, density, and the free fatty acid content of frying oils. The oxidized products induce off-flavour to both the frying medium and fried foods as well (Sayyad 2017; Lin and Yoo, 2001). Beyond hampering the sensorial quality, ultimately the degradation of the frying oil can cause adverse health effects to the consumer (Que et al., 2019; Falade et al., 2017; Yilmaz and Bulut, 2012). Even disposing the used oil before catalytic conversion would lead to environmental pollution (Sani et al., 2017).

Replenishing with fresh oil, blending different oils to increase oxidative stability and treatment with adsorbents can improve the quality of used oil. Among which, treatment with adsorbents demonstrated being cost effective and easily applicable. With the same token Hidayatullah and Bangash (2007) reported quality improvement of *Silybum marianum* oil using activated charcoal and MgO treatments. Treatment of fried oil with combination of adsorbents like Hubersorb 600, Magnesol and Britesorb (Lin et al., 1999) and natural zeolite, lime and diatomaceous earth (Yilmaz and Bulut, 2012) reduced free fatty acids, total polar material, viscosity, turbidity, peroxide value, conjugated dienes, and improved the color.

In Ethiopia, the consumption of DFF foods is increasing and the oil is used over and over again on daily basis. Yet, the quality of the prolonged fried oil and treating the oil to improve the quality has not been investigated as to our knowledge. Therefore, this study aimed to evaluate the physico-chemical composition of commonly used-fried niger seed oil. The study also evaluated the effects of various adsorbents to improve the quality of the used fried oil.

2. Materials and methods

Sample collection

Potato and niger seed oil were purchased from open market in Addis Ababa, Ethiopia. Magnesium oxide, bentonite, silica gel, bleaching earth

* Corresponding author.
E-mail address: p_getachew@yahoo.com (P. Getachew).

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were purchased from local suppliers. Ash was prepared at home following the traditional method (i.e. white residue left after charcoal made from wood is combusted completely).

2.1. Sample preparation

Potato preparation

Potatoe samples washed and peeled under tap water. The washed potatoes were cut into slices of uniform size using a vegetable slicer for uniform heat transfer between the slices and the frying oil. The sliced potatoes were kept in water at room temperature. Then, blotted with tissue paper before weighing into 250 g batches for the frying process.

2.2. Frying experiment

The frying conditions were modified based on the information gathered from street food vendors in Addis Ababa and Serjouie et al. (2010). Briefly, 5.0 kg of frying oil poured into an electrical deep-fat fryer (Oppein, model-OP-81, China) with a frying basket. The temperature was raised to 200 °C, in which after 17 min frying started. A batch of 250 g raw sliced potatoes were fried for 3 min at 200 °C. Then, the fried slices were removed from the fryer and the frying operation was carried out for a new potato batch after 17 min. 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 h frying time. At the end of the 12^{th} frying in a day, the fryer was switched off, put on the lid and the oil was allowed to cool down overnight (Serjouie et al., 2010). Fried oil sample collected after 60^{th} frying cycle, cooled and kept in opaque bottle at room temperature. The volume of oil was never replenished to the original volume with fresh oil during frying.

2.3. Adsorbent treatment

Phase 1–30 g of the five adsorbents (bleaching earth, MgO, bentonite, ash, silica gel) (15 % w/v) were individually mixed with 200 mL of used frying niger seed oil at 150 °C and stirred for 30 min (Yilmaz and Bulut, 2012; Lin et al., 1999). Then, the whole content was centrifuged (Centrifuge CE, Model-800D, China) at 4200 rpm for 15 min.

Phase 2-among the adsorbents used the two with relative higher effects in improving the physico-chemical quality of the used-frying oil were selected. To determine the minimum concentration of the adsorbents improving the quality of the used oil, the selected adsorbents were mixed with the used oil in w/v ratios of (2.5, 5.0, 7.5, 10.0, 12.5) % at 150 °C, stirred for 30 min and separated through centrifugation at 4200 rpm for 15 min.

Phase 3-in order to evaluate their synergetic effect, the two selected adsorbents were blended together in 1:1 ratio, mixed with the used-frying oil, heated together at 150 °C, stirred for 30 min, separated by centrifugation at 4200 rpm for 15 min. In all the phases the treated oil samples were kept in brown glass bottles until analysis. Centrifugation was considered as a treatment to avoid its effect on the physico-chemical quality improvement of the oils. The study design and flow is summarized in Figure 1 below.

2.4. Analytical methods

2.4.1. Physical tests

Viscosity

Viscosity was determined by using BROOKFIELD DV-E viscometer (MA 023434666, 1031, USA) with spindle number 61 as per the specification of the instrument. 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.

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.

Specific gravity

Briefly, a clean 50 mL beaker was weighted (W_0). Then, the beaker was filled with distilled water, extra water was spilled out and reweighed (W_1). Same procedure was repeated, but using oil samples instead of water and weighted again (W_2) (AOAC, 2000). The specific gravity of the oil samples was calculated using the following formula (Eq. (1)):

$$\text{Specific Gravity} = \frac{W_2 - W_0}{W_1 - W_0} \quad (1)$$

where;

W_0 = Weight of empty beaker
W_1 = Weight of water + beaker
W_2 = Weight of oil sample + beaker

2.4.2. Chemical tests

Acid value (AV)

The acid value of the oil samples was determined using AOAC (2000) with slight modifications. Sufficient amount of oil sample weighed into erlenmeyer flask based on the expected acid value as shown in Table 1. Ethanol (97%) was heated at 70 °C until bubble formation 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 reached when the addition of a single drop of alkali produces a slight but definite pink color change persisting for at least 15 s. The AV was calculated following Eq. (2) below:

$$\text{Acid Value} = \frac{(56.1 * V * C)}{m} \quad (2)$$

where;

V = Volume (mL) of potassium hydroxide
C = Concentration of potassium hydroxide (0.5M)
56.1 = Molar mass (g/mole) of potassium hydroxide
m = Mass (g) of the test portion

Percentage of free fatty acids (% FFA)

The free fatty acids (%) was determined using AOAC (2000) method and calculated using Eq. (3) below:

$$\text{Free Fatty Acid } (\%) = \frac{\text{Acid value}}{1.99} \quad (3)$$

Peroxide value (PV)

Peroxide value was measured following the method by AOAC (2000). On 5 g of oil sample in 250 mL erlenmeyer flask, 30 mL of glacial acetic acid-chloroform (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 0.01M sodium thiosulfate solution 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 following Eq. (4) below.

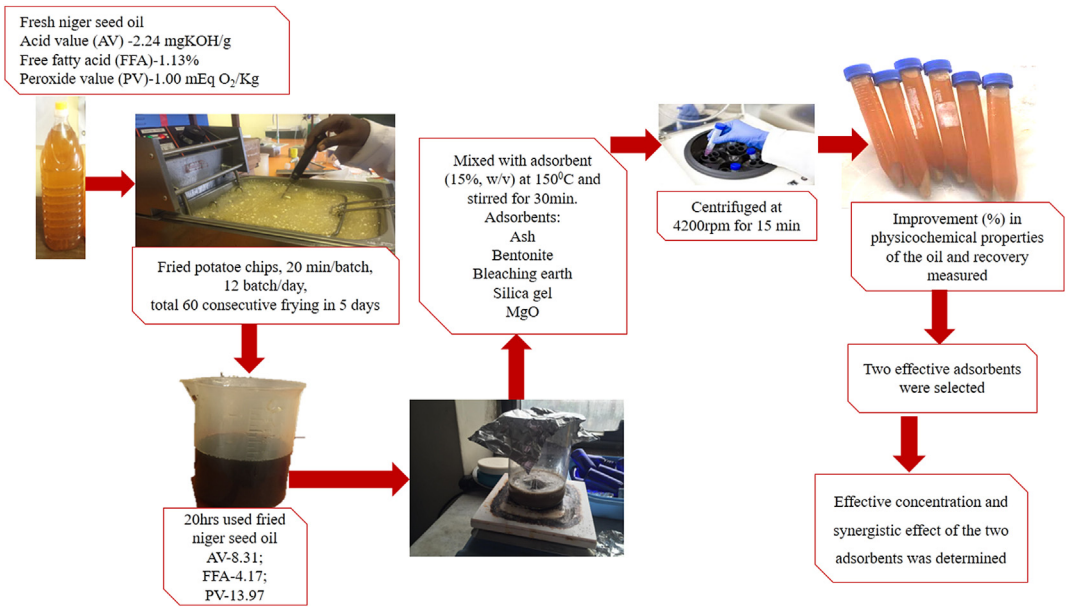

Figure 1. Pictorial representation of the study design and flow.

Table 1. Mass of test portion of oil based on the expected acid value.

Expected acid value (mg KOH/g oil)	Mass of test portion (g)
<1	20
1 to 4	10
4 to 15	2.5
15 to 75	0.5
>75	0.1

Source: Ethiopian Standard (ES ISO 660: 2009).

$$\text{Peroxide value (milli equivalent of oxygen / Kg oil)} = \frac{V*M*1000}{m} \quad (4)$$

where;

V = Volume of $Na_2S_2O_3$ (blank corrected) and
M = Molarity of $Na_2S_2O_3$
m = Mass (g) of the test portion

Iodine value

Iodine value was conducted according to AOAC (2000). About 0.25 g of oil sample 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) and then the solution was left to stand in the dark for 30 min with occasional shaking. Potassium iodide (10 mL) (15%, w/v) added, shaken thoroughly followed by addition of 100 mL distilled water to rinse down any iodine on the stopper. The solution then titrated with 0.01N thiosulfate solution using starch as indicator (1 mL) till yellow color formation. Then, 2–3 drops of starch solution added resulting in blue color. The titration continued until the blue color disappeared and the volume (mL) of $Na_2S_2O_3$ recorded (S). The same 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 Eq. (5) below:

$$\text{Iodine Value} = \frac{(B-S)*0.127*N\ Na_2S_2O_3*100}{W} \quad (5)$$

where;

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

For both chemical and physical tests percentage of improvement upon adsorbent treatment of the used-frying oil was calculated using Eq. (6) below:

$$\text{Improvement (\%)} = \frac{(A-B)*100}{A} \quad (6)$$

where;

A = Value in untreated oil
B = Value in treated oil.

2.5. Statistical analysis

Each analysis was done in triplicate and results were expressed as mean ± SE. Comparisons between the adsorbent treatments was conducted using One-Way-Analysis of Variance (ANOVA) using SPSS software version 22.0 (SPSS Inc. Illinois, USA). P-values < 0.05 were considered statistically significant.

3. Results and discussion

3.1. Effect of adsorbent treatment in improving physical quality of used frying niger seed oil

As presented in Table 2, after 60 consecutive fryings, the specific gravity, viscosity and refractive index of the fried niger seed oil increased significantly from the value in the fresh oil ($p < 0.05$). According to the compulsory standard set by Ethiopian Standard Authority (CES 20:2013) the S.G for crude niger seed oil is 0.927, which was 1.0016 in the used fried oil. This might be due to the formation of polymeric compounds upon prolonged frying (Melton et al., 1994). Treatment of the fried oil with ash, silca gel and MgO improved the S.G by 5%, 6% and 6% respectively, while the least improvement was upon bentonite and

Table 2. 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	$0.9502 \pm 0.00^{b,c}$	5	57.13 ± 0.17^{b}	3	1.47704 ± 0.00^{d}	NI
Bentonite	$0.9820 \pm 0.00^{a,b}$	2	$56.32 \pm 0.02^{b,c}$	4.	1.47702 ± 0.00^{c}	NI
Bleaching earth	$0.9728 \pm 0.01^{a,b}$	3	$56.46 \pm 0.07^{b,c}$	4	1.47711 ± 0.00^{b}	NI
Silica gel	$0.9445 \pm 0.02^{b,c}$	6	56.08 ± 0.03^{c}	5	1.47692 ± 0.00^{c}	NI
MgO	$0.9427 \pm 0.00^{b,c}$	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 at ($p < 0.05$). S.G (Specific Gravity), VISCO (Viscosity), RI (Refractive Index), "NI"-No Improvement; "ND"-Not Determined.

bleaching earth treatments (Table 2). In contrast, Phogat et al. (2006) reported no significant improvement in S.G of fried oil treated with Magnasol and Filtrite. In fact, the adsorbent concentration used was lower than in the present study.

Viscosity of edible oil will increase as oxidation is accelerated by heat (Jurid et al., 2020; Sahasrabudhe et al., 2017; Tyagi and Vasishtha, 1996). This is due to the simultaneous formation of oxidation products including aldehydes, ketones, hydrocarbons, and polymeric compounds. In this study, all adsorbent treatments improved the viscosity of the used oil, the highest being silca gel (5%) and MgO (6%) (Table 2). 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. Phogat et al. (2006) attained a maximum improvement of viscosity of fried oil in a range of (15.2–18.0)% using different adsorbent treatments.

3.2. Effect of adsorbent treatment in improving chemical quality of used frying niger seed oil

Acid value and free fatty acid

Upon frying for 20 h, the AV and FFA% of niger seed oil increased to 8.31 mg KOH/g oil and to 4.17%, respectively (Table 3), which is beyond the permissible limit for edible oil as per compulsory standard set by Ethiopian Standard Authority (CES 20:2013). Moisture from the fried product accelerates the hydrolysis of oil. Also the prolonged frying accelerates formation of secondary oxidation products, thus increased AV and FFA (Liu et al., 2019; Debnath et al., 2012). As reported in Table 3, all adsorbents reduced the increased AV and FFA significantly ($p < 0.05$). The highest reduction of both was found in the MgO treated oil (73%). Ash, bentonite, bleaching earth and silca gel also reduced the AV and FFA % significantly by (40, 61)%, (66, 66)%, (56, 56)% and (40, 61)% respectively from the value in the fried niger seed oil ($p < 0.05$). This improvement might be due to the specific adsorption affinity of each adsorbent for small molecular substances (Baptiste et al., 2020; Soprano et al., 2019; Christy 2012; Okiel et al., 2011; Hidayatullah and Bangash, 2007). Phogat et al. (2006) reported a maximum improvement of FFA% (4.5–5.9) % upon Magnasol and Filtrite treatment of degraded oil, which is a lower improvement from the present study.

Peroxide value

After 20 h of frying, the PV of the fresh niger seed oil increased from 1.00 to 13.97 mEq oxygen/Kg of oil (Table 3). The prolonged frying deteriorated the PV to unacceptable level for human consumption (i.e. >10 mEq oxygen/Kg) (Ethiopian Standard Authority (CES 20:2013)). Mainly this is associated with the thermo-oxidation reaction between atmospheric oxygen and the oil (Gao et al., 2020; Jiang et al., 2020; Houhoula et al., 2003; Cuesta et al., 1993; Sanchez-Muniz et al., 1993; Peers and Swoboda, 1982). Moreover, the high unsaturated fatty acid composition of niger seed oil accelerates the thermo-oxidation. 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 PV by (57, 43, 21, 50 and 64) % respectively (Table 3). The highest reductions were obtained upon MgO and ash treatments respectively. Similarly, Hidayatullah and Bangash (2007) reported the effectiveness of MgO and activated charcoal in improving the overall quality of used fried *S. marianum* oil. Also the effectiveness of magnesol ($MgO_2.6SiO_2.H_2O$) in removing secondary oxidation products was reported by Bhattacharya et al. (2008). The ash used in the present study was made at household level after completely burning wood made charcoal. This might lead to formation molecules of specific adsorption capacity towards oxidation products (peroxides) (Nadia et al., 2020; Lam et al., 2018; Alinnor, 2007; Erol et al., 2005).

Oil recovery (%)

Bentonite treated fried niger seed oil showed the highest oil recovery (88%). Meanwhile, the recovery for ash, bleaching earth, silca gel and MgO treated oil was (80, 85, 70 and 40) % respectively (Table 3). Based

Table 3. Effect of different adsorbents on chemical quality improvement and recovery of fried niger seed oil.

Adsorbent treatment	AV (mgKOH/g)	AV Improvement (%)	FFA (%)	FFA Improvement (%)	PV (mEq O_2/Kg)	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	$129.93 \pm 0.56^{a,b}$	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
Ash	3.36 ± 0.00^{b}	40	1.62 ± 0.00^{b}	61	$5.99 \pm 0.66^{d,e}$	57	$129.22 \pm 0.40^{a,b}$	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	$129.20 \pm 0.70^{a,b}$	NI	85
Silica gel	3.36 ± 0.00^{b}	40	1.62 ± 0.00^{b}	61	$6.99 \pm 0.57^{c,d}$	50	$128.50 \pm 0.30^{a,b}$	NI	70
MgO	2.24 ± 0.00^{b}	73	1.13 ± 0.00^{b}	73	5.00 ± 0.57^{e}	64	$128.95 \pm 0.00^{a,b}$	NI	40
Centrifugation	8.31 ± 1.55^{a}	NI	4.17 ± 0.78^{a}	NI	13.96 ± 1.15^{a}	NI	$127.98 \pm 2.82^{a,b}$	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 at ($p < 0.05$). FFA (Free Fatty Acid), AV (Acid Value), PV (Peroxide Value), IV (Iodine Value), "NI"-No Improvement, "ND"-Not Determined.

Table 4. Effective concentration 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	1.475180 ± 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 %	0.9997 ± 0.00^{a}	NI	$58.86 \pm 0.07^{a,b}$	NI	1.477170 ± 0.00^{a}	NI
5.0 %	0.9997 ± 0.00^{a}	NI	$58.63 \pm 0.03^{a,b}$	NI	$1.477140 \pm 0.00^{a,b}$	NI
7.5 %	$0.9837 \pm 0.00^{a,b,c}$	2	$58.50 \pm 0.08^{a,b}$	NI	$1.477101 \pm 0.00^{b,c}$	NI
10.0 %	$0.9740 \pm 0.11^{c,d,e}$	3	$58.30 \pm 0.28^{b,c}$	1	$1.477120 \pm 0.00^{b,c}$	NI
12.5 %	$0.9605 \pm 0.00^{d,e,f}$	4	$57.76 \pm 0.11^{c,d}$	2.	1.477090 ± 0.00^{c}	NI
15.0 %	$0.9502 \pm 0.00^{e,f}$	5	$57.13 \pm 0.17^{e,f}$	3	1.477040 ± 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.

on effectiveness in improving both physical and chemical quality of the used oil ash and MgO were selected for further objectives of the study (i.e. obtaining minimum effective concentration and synergistic effect of the two adsorbents).

3.3. Effective concentration of ash and MgO in quality improvement of fried niger seed oil

3.3.1. Physical quality improvement of fried niger seed oil with different concentrations of ash

As reported in Table 4, treatment of the fried niger seed oil with (10.0, 12.5 and 15.0) % of ash improved the S.G and viscosity significantly ($p < 0.05$) by (3, 1) %, (4, 2) %, and (5, 3) % respectively. Meanwhile, with lower concentrations significant difference was not observed. Similarly, with (7.5, 10.0, 12.5 and 15.0) % ash treatments a significant reduction ($p < 0.05$) of the RI compared with the fried niger seed oil was observed (Table 3). Overall, 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. According to (Turan and Yalcuk, 2013), used frying oils were purified in a packed column using different amounts of silica gel, aluminum oxide, activated charcoal, bentonite, magnesol XL, calcium carbonate, zeolite, and bleaching earth. Similar with the present study, as the amount of adsorbent in the column increased, the physico-chemical properties of the oil improved.

3.3.2. Chemical quality improvement of fried niger seed oil with different concentrations of ash

With (2.5, 5.0, 7.5, 10.0, 12.5 and 15.0) % ash treatment the increased AV and PV of the fried niger seed oil reduced gradient-wise by (26, 14) %, (39, 27) %, (46, 30) %, (53, 40) %, (53, 46) %, (60, 57) % respectively ($p < 0.05$). With these concentrations the oil recovery was (90, 85, 85, 83, 81 and 80) % respectively (Table 5). Thus, considering the improvement of (AV and FFA) and PV by 50 % and 40 % to acceptable permissible level, 10.0 % ash treatment of the fried niger seed oil was recommended as effective concentration. Similarly, McNeill et al. (1986) reported that three levels of activated carbon or silica adsorbents blended found to reduce FFA%, PV, photometric color, polar compounds, and carbonyls by (28–59) %.

3.3.3. Physical quality improvement of fried niger seed oil with different concentrations of MgO

As reported in Table 6, (10.0, 12.5 and 15.0) % MgO treated fried niger seed oil improved S.G and viscosity significantly ($p < 0.05$) by (3, 2) %, (5, 3) %, (6, 4) % respectively from the value in the fried oil. Also with all MgO concentrations, a significant reduction of the RI compared with the fried niger seed oil was obtained (Table 6). MgO treatment (10.0 %) of fried niger seed oil was effective in improving the physical quality parameters to the same level with the 15 % treatment.

3.3.4. Chemical quality improvement of fried niger seed oil with different concentrations of MgO

As reported in Table 7, (2.5, 5.0, 7.5, 10.0, 12.5 and 15.0) % of MgO treatment reduced the AV and PV of the fried niger seed oil gradient-wise by (39, 17) %, (46, 24) %, (59, 28) %, (60, 40) %, (60, 47) %, (73, 64) % respectively ($p < 0.05$). The oil recovery was (73, 68, 64, 58, 48 and 40) % respectively (Table 7). Overall, 10.0 % MgO treatment of fried niger seed oil found to be the minimum effective concentration improving AV, FFA and PV within the acceptable range. Similarly, treatment with 10% of adsorbent combination (4.5% clay, 0.5% charcoal, 2.5% MgO, and 2.5% Celite) demonstrated the highest effectiveness, which reduced the FFA of used oil by 74% by Mancini-Filho et al. (1986).

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

Table 5. Effective concentration of ash in improving chemical quality of fried niger seed oil.

Adsorbent treatment	AV (mgKOH/g)	AV Improvement (%)	FFA (%)	FFA Improvement (%)	PV ($mEqO_2/Kg$)	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	$129.93 \pm 0.56^{a,b}$	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 %	6.17 ± 0.32^{b}	26	3.10 ± 0.33^{b}	26	12.00 ± 0.23^{b}	14	$133.62 \pm 4.38^{a,b}$	NI	90
5.0 %	$5.04 \pm 0.31^{b,c}$	39	$2.53 \pm 0.15^{b,c}$	39	$10.19 \pm 0.35^{c,d}$	27	$132.13 \pm 4.93^{a,b}$	NI	85
7.5 %	$4.49 \pm 0.00^{c,d}$	46	$2.26 \pm 0.00^{b,c,d}$	46	$9.79 \pm 0.10^{c,d}$	30	$133.48 \pm 0.07^{a,b}$	NI	85
10.0 %	$3.92 \pm 0.32^{c,d}$	53	$1.97 \pm 0.30^{c,d,e}$	53	8.39 ± 0.23^{e}	40	$132.16 \pm 2.09^{a,b}$	NI	83
12.5 %	$3.92 \pm 0.31^{c,d}$	53	$1.97 \pm 0.16^{c,d,e}$	53	$7.58 \pm 0.23^{e,f}$	46	$135.40 \pm 2.20^{a,b}$	NI	81
15.0 %	$3.36 \pm 0.00^{d,e}$	59	$1.62 \pm 0.00^{d,e}$	61	5.99 ± 0.66^{g}	57	$129.22 \pm 0.40^{a,b}$	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.

Table 6. Effective concentration 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.

Table 7. Effective concentration of magnesium oxide in improving chemical quality of fried niger seed oil.

Adsorbent treatment	AV (mgKOH/g)	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.

Table 8. 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 9. Synergetic effect of ash and magnesium oxide in improving chemical quality of fried niger seed oil.

Adsorbent treatment	AV (mgKOH/g)	AV Improvement (%)	FFA (%)	FFA Improvement (%)	PV (mEq O_2/Kg)	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.

As presented in Table 8, ash, MgO and (Ash + MgO) (1:1) (15 %, w/v) significantly reduced the S.G and viscosity of fried niger seed oil by (5, 3) %, (6, 6) %, (4, 1) % respectively ($p < 0.05$). These same treatments also significantly reduced the AV, FFA and PV by (40, 61, 57) %, (73, 73, 64) %, and (60, 60, 49) % respectively ($p < 0.05$). The respective oil recovery upon the treatments was (80, 40 and 75) % (Table 9). In this study, except ash all adsorbents were procured from commercial suppliers. Evaluating the synergetic effect of the two adsorbents, thus was to address economic feasibility of the treatments by using local available adsorbent (ash). Though synergetic effect of the adsorbent combinations was not observed, the combination treatment was effective enough in improving the physico-chemical properties of the fried oil. Studies involving treatment of frying oils with combinations of activated silica and carbon were found to reduce AV, PV, photometric colour, polar compounds, and carbonyls by (28–59) % (McNeill et al., 1986). 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).

4. Conclusion

This study evaluated the effectiveness of adsorbents in improving the physico-chemical quality of continuously fried niger seed oil. Accordingly, the specific gravity and viscosity of the used oil improved significantly upon treatments with ash, silca gel and MgO. Also MgO, ash, bentonite, bleaching earth and silca gel treatments reduced the AV, FFA, and PV of the used oil to permissible limits. Among all the adsorbents ash and MgO showed highest percentage improvement in the quality of the fried oil. Overall, 10 % ash and MgO was the minimum effective concentration improving the physico-chemical qualities of the used oil the same level as 15% treatment. Further studies on the effect of the adsorbents in retaining additional important quality parameters like total polar artefacts is highly recommended. Also the frying quality of the adsorbent treated oils should be studied.

Declarations

Author contribution statement

Zehara Nuru: Performed the experiments; Wrote the paper.

Paulos Getachew: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

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Data will be made available on request.

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The authors declare no conflict of interest.

Additional information

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