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ScienceDirect

Food Chemistry 110 (2008) 562–570

FOOD CHEMISTRY

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Regeneration of thermally polymerized frying oils with adsorbents

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Received 7 June 2007; received in revised form 1 February 2008; accepted 11 February 2008

Abstract

Two thermally polymerized palm oils used continuously for deep-fat frying of legume-based snacks for 30 and 36 h were treated with various adsorbents as such and in binary and quaternary blends, in an attempt to regenerate them. Activated charcoal powder (ACH), aluminum oxide (ALO), aluminum hydroxide (ALH), activated clay (ACL), celite (CE) and silica gel (SG), activated carbon (ACA), frypowder (FP), britesorb (BR) and magnesol (MA) were evaluated for their efficacy in regenerating the oils in terms of their effects on physicochemical parameters such as free fatty acids (FFA), total polar materials (TPM), *p*-anisidine value (*p*-AV), conjugated dienes, viscosity and colour. Binary and quaternary adsorbent treatments were better than single adsorbents in improving the overall quality of the oils studied. The efficacy of the best adsorbent blend was further evaluated in a highly polymerized cottonseed oil collected from a local eatery. Use of such adsorbents is recommended for small processing units in the unorganized sector, where such polymerized oil is generally discarded.

Keywords: Thermally polymerized oils; Adsorbents; Regeneration; Oil analysis

1. Introduction

Waste disposal problems, today, are in vogue, increasing the prospects of endangering the ecosystem. Disposal of oils is one such, with recycling of used frying oils being one of the viable ways to reducing the problem. The worldwide production of edible vegetable oil is about 60 million tonne a year (United States Department of Agriculture, 2000), the majority being used for frying foods and a significant quantity of the used frying oils being discarded. Once the oil is exposed to frying temperatures, a portion of the triacylglycerols is converted to a myriad of degradation products. Total polar materials (TPM) are considered to be one of the most important tests for assessing degrading oils. Colour, foaming and viscosity are generally the main criteria for discontinuing the use of frying oils (Ohta, 1985).

The degradation of oil during frying occurs due to factors such as heat, air and moisture resulting in polymerization, oxidation and hydrolysis (Gebhardt, 1996). Oxidation is greatly influenced by the presence of metal ions, especially copper and iron. Moisture is responsible for the hydrolysis of triacylglycerols resulting in the formation of free fatty acids, monoacylglycerols, diacylglycerols, and in some extreme cases, glycerol (Gebhardt, 1996). Extraneous matter also contributes to oil breakdown. The buildup of cracklings increases the rate of formation of free fatty acids (FFA), which when left in the fryer for extended periods of time at elevated temperatures, darken the oil, generate off-flavours, impede heat transfer, and ruin the appearance of fried foods. Besides, they continuously leach their components into the oil causing chemical degradation of the frying medium (Blumenthal, 1996).

Passive and active filtration systems are used to remove oil degradation products from oil. Active treatments remove surfactant materials carbonized on the surface as well as precursors of polymers formed from the frying oils, and reduces the frequency of cleanups and the amount of caustic cleaning compounds needed in this context. The active treatments are generally adsorbents powders such

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doi:10.1016/j.foodchem.2008.02.033

as diatomaceous earth, magnesium and calcium silicates, rhyolite and pumice materials, zeolites, and alumina. Passive treatments are filter aids as materials or systems, and perform a polishing function to remove solid particles, microemulsified water, and components such as free radical oxygen, copper or iron, that accelerate the oxidative reaction.

Regeneration of fried oil by selective removal of undesirable polar compounds has been sought by the industry for long. Commercially, the adsorbents are slurried with the oil in the fryer, circulated through the filter and back into fryer until a filter bed is established, and the fryer is free of fines and particles. Finally, the clean oil is pumped back into the fryer. These treatments maintain the frying life of fats and oils by controlling the buildup of free fatty acids without any adverse effect on flavour.

Addition of diatomaceous earth increases the efficiency of filtration due to the contaminants adhering to the powder (Cummings, 1984). In a study, filter pads with activated charcoal and activated silicates bonded by a system of resins and binders were found to be effective in removing prooxidation transition metals thus enhancing the stability of the frying oil; however, diatomaceous earth was inefficient in removing FFA (Zhang & Addis, 1992). 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, Kakuda, & Kamel, 1986).

Some synthetic adsorbents studied individually or combined with natural adsorbents for their ability to effectively reduce one or more components such as FFA, colour and TPM demonstrated magnesium oxide to decrease FFA, while all other treatments effectively reduced only the colour (Mancini-Filho, Smith, Creveling, & Al-Shaikh, 1986). Treatment with 10% of adsorbent combination (comprising of 4.5% clay, 0.5% charcoal, 2.5% magnesium oxide and 2.5% celite) demonstrated the highest effectiveness. Experiments were conducted with used frying oils in a flat membrane batch cell with polymeric membranes (Miyagi, Nakajima, Nabetani, & Subramanian, 2001). By using a combined approach of membrane and adsorption processes, the quality of the used frying oil could be improved to that of fresh frying oil. Silica gel with a small amount of magnesium oxide gave the best results in the adsorption process.

Information on thermally polymerized oils used previously for frying legume-based traditional Indian products such as *sev* and *chakli* are scant. The quality of such oils depends on the composition of the food fried in it. The present study compares ten adsorbents with respect to their ability to regenerate thermally polymerized frying palm oils that were used to fry legume-based fried snacks. The physicochemical characteristics of the processed oils, including TPM, oxidation products, FFA, colour and viscosity were studied in detail to enable the selection of the most effective adsorbent combination that could further improve the quality of the used palm oil.

2. Materials and methods

2.1. Materials

Fresh refined palm oil and oils remaining after frying of legume-based snacks were obtained from a local processor in the small-scale unorganized sector. The used oils were labeled as P30 and P36 and were used for frying at 170–180 °C for 30 and 36 h, respectively, without any replenishment with fresh oil. Activated charcoal powder (ACH), aluminum oxide (ALO), aluminum hydroxide (ALH), activated clay (ACL), celite (CE) and silica gel (SG) (silica gel 60: particle size, 0.063–0.200 mm) were supplied by Merck Ltd. (Mumbai, India). Activated carbon (ACA) was supplied by ICI Americas Inc. (Marshall, TX, USA). Frypowder (FP) (composed of porous rhyolite and citric acid) was obtained from Mir Oil Company (Allentown, Pa., USA). Britesorb (BR) was procured from PQ Co. (Valley Forge, PA, USA) and magnesol (MA) (magnesium silicate) was obtained from Dallas group of America, Inc. (Whitehouse, NJ, USA).

2.2. Methods

2.2.1. Batch adsorbent treatment

This was carried out as reported by Lin, Akoh, and Reynolds (1998). Each adsorbent (10% based on the weight of the oil) was added to 150 g used frying oil after heating to 150 °C, stirred for 15 min, vacuum filtered through Whatman filter paper no. 41. The filtrate was stored in a sealed vessel at 4 °C after flushing with nitrogen.

2.3. Analytical methods

2.3.1. Percent free fatty acid (FFA)

FFA was determined using the AOCS (1989) method with few modifications. Thirty millilitres of ether/ethanol/water 3:3:2 (v/v/v) were used to dissolve 5 g of the sample and titrated against 0.1 N sodium hydroxide solution (Foglia, Petruso, & Feairheller, 1993). FFA was expressed as% oleic acid.

2.3.2. Total polar materials (TPM)

TPM was determined using the AOCS method (1998). A chromatographic column (21 mm i.d., 450 mm long with stopcock and ground glass joint) was filled with about 30 ml of a mixture of light petroleum and diethyl ether (87:13, v/v). A wad of glass wool was introduced at the lower end of the column with the aid of a glass rod. Silica gel (25 g) was slurried in about 80 ml of the solvent mixture and poured into the column. The elution solvent was drained through the column until its level was 10 cm above the silica gel level. About 4 g of sea sand were added and the supernatant was drained up to the sand layer.

For determination of TPM, 2.5 g of sample were dissolved in 20 ml of the solvent mixture containing light petroleum and diethyl ether (87:13, v/v) at room temperature

(30 ± 2 °C), with slight warming, if necessary. The volume was then made to 50 ml with the solvent mixture and 20 ml of resulting solution were introduced into the column, and drained off to the level of the sand layer. The non-polar compounds were eluted with 150 ml of the solvent mixture at a flow rate of 2.5 ml/min. TPM was calculated as

$$\%\ \text{TPM} = [(m - m_1)/m] \times 100$$

where m_1 is the mass (g) of the non-polar fraction and m is the mass (g) of the sample contained in 20 ml of the solution added to the column.

2.3.3. p-Anisidine value (p-AV)

The *p*-AV was determined as per AOCS (1998). The sample (0.5–4.0 g) was dissolved and diluted to volume with *iso*-octane in a 25 ml volumetric flask. The absorbance (A_b) of the solution was measured at 350 nm. Exactly 5 ml of the fat solution were transferred to a test tube and 5 ml of only the solvent were added to another test tube. One millilitre of *p*-anisidine reagent (2.5 g/l solution in glacial acetic acid) was added to each tube, and shaken. After exactly 10 min, the absorbance (A_s) of the solution in the first test tube was measured at 350 nm, using the solution in the second test tube as blank.

$$p\text{–AV} = [25 \times (1.2A_s – A_b)]/m$$

A_s is absorbance of the fat solution after reaction with the *p*-anisidine reagent, A_b is absorbance of the fat solution, m mass of the test portion in g.

2.3.4. Percent conjugated diene (CD)

CD was determined as per AOCS (1998). The sample (90–130 mg) was added to 75 ml of purified iso-octane in a 100 ml flask. The flask was warmed to completely dissolve the sample, cooled to room temperature, allowed to stand for 15 min, and then diluted to a final concentration of 0.01/l. The absorbance was then measured at 233 nm.

% CD was calculated as follows:

$$\%\ \text{CD} = 0.84[(A_s/bc) - K_o],$$

where K_o = absorptivity by acid or ester groups (0.07 for esters, 0.03 for acids), A_s = observed absorbance at 233 nm, b = cuvette length in cm, c = concentration of sample, g/l of the final dilution.

2.3.5. Viscosity

Viscosity was determined as per AOCS (1998) using Brookfield DV111 model digital rheometer at 30 °C using LV 2 spindle at 10, 20 and 50 rpm.

2.3.6. Colour

Colour was determined as per AOCS (1989), measured with a Lovibond Tintometer Model PFX990 (Wiltshire, UK), using an oil sample of 12 ml and an optical path length of 1". Results were expressed on *R* and *Y* scale. The oil samples to be analyzed were heated at 45 °C, and shaken well to bring each sample to a homogenous liquid state. To minimize any experimental errors from temperature variations, the sample holding cell along with the sample vial and the Lovibond Tintometer was maintained at 45 °C in a built-in temperature control system.

2.4. Column adsorbent treatment

An adsorbent combination as determined from the previous study was packed in a column. A known quantity of used frying oil heated to 150 °C was poured into the column and allowed to pass through the adsorption layer by gravity. The filtrate was stored in a sealed vessel at 4 °C after flushing with nitrogen.

2.5. Evaluation of efficiency of adsorption process

All adsorbents were applied to the batch adsorption process at 150 °C for 15 min. The oil after filtration was analyzed for FFA, CDV, *p*-AV, TPM, viscosity and colour "*R* and *Y*" values. Based on the results obtained, two potential adsorbents were physically blended in the ratio of 1:1, 1:3, and 3:1 by weight. Finally, a combination of the best two sets of adsorbents (maximum 10% concentration), as determined from the adsorbent combination study was packed in a column. All adsorbents and their combinations were evaluated for their performance in improving oil quality. This was determined by calculating percentage improvement as

$$\text{Percentage Improvement } (\%\text{PI}) = \frac{(\text{Value of untreated oil} - \text{Value of treated oil})}{(\text{Value of untreated oil})} \times 100$$

The percentage improvement of adsorbents for both P30 and P36 was calculated and reported as average percentage improvement (API).

3. Results and discussion

3.1. Analysis of the fresh and polymerized oil

Table 1 shows the baseline values of fresh palm oil, and P30 and P36 prior to adsorbent treatment. P30 and P36 had higher values of FFA, CDV, viscosity, *p*-AV, TPM and colour (*R*, *Y*) values compared to the fresh oil, indicating oxidative deterioration in the sample. P30 and P36 were subjected to each of the ten adsorbents and the adsorbent efficiency in oil recovery was compared for fresh and adsorbent-treated P30 and P36 oils. Percentage improvement was calculated as detailed in Section 2.5.

3.2. Screening of individual adsorbents

The efficiency of adsorption depends on the polarity, surface active sites, surface area, porosity, particle size,

Table 1
Evaluation of the thermally degraded oils *vis-à-vis* fresh oil^{A,B}

Parameters	Fresh oil	Thermally polymerized palm oil	
		P30	P36
% FFA	0.05 ± 0.01^{a}	0.70 ± 0.03^{b}	0.92 ± 0.04^{c}
p-AV	2.33 ± 0.45^{d}	15.30 ± 0.45^{e}	22.71 ± 0.51^{f}
% CD	0.04 ± 0.03^{g}	0.19 ± 0.01^{h}	0.22 ± 0.01^{h}
Viscosity (cP, 30 °C)	78.13 ± 0.05^{i}	97.12 ± 0.45^{j}	98.60 ± 0.32^{k}
% TPM	5.41 ± 0.52^{l}	12.88 ± 0.50^{m}	18.62 ± 0.46^{n}
Colour "*R*" value	0.9 ± 0.61^{o}	1.9 ± 0.25^{p}	5.5 ± 0.2^{q}
Colour "*Y*" value	5.4 ± 0.01^{r}	26.0 ± 0.01^{s}	70.0 ± 0.35^{t}

[A] Results are mean ± SD of three individual determinations.
[B] Values in the same row with different superscripts are significantly different ($P = 0.05$) as measured by Duncan's multiple-comparison test.

pH and moisture content (Zhu, Yates, & Caldwell, 1994). Use of magnesol and filtrite as adsorbents at 1%, 2% and 3% levels and treatment time of up to 8 min showed a maximum improvement of 7.0-8.8, 15.2–18.0, 11.7–14.6 and 4.5–5.9% for capacitance, viscosity, photometric colour index and FFA, respectively (Phogat, Mittal, & Kakuda, 2006). Mancini-Filho et al. (1986) demonstrated a 10% total adsorbent concentration (4.5% clay, 0.5% charcoal, 2.5% magnesium oxide and 2.5% celite) to reduce dielectric constant, colour and FFA by 18%, 37% and 74%, respectively. Hence, the amount of the adsorbents in this study was fixed at 10% of the weight of oil. Researchers suggest different treatment times for different adsorbent products. Britesorb has been recommended to be circulated or stirred with oil for 2 min, while frypowder be allowed for 15–20 min before being filtered out of the oil (Lin, Akoh, & Reynolds, 1999). In the present study, total adsorbent exposure time for 15 min at initial oil temperature of 150 °C was adopted.

3.2.1. Percent FFA

FFA value is an indication of the degree of hydrolysis of oil. Controlling its level within a reasonable range of 0.4% (Berger, 1997) prevents acceleration of breakdown of fats, and also assists heat transfer. When the fatty acid content of the oil exceeds the objectionable amount, it must be discarded. The properties of P30 and P36 that were treated with individual adsorbents are shown in Tables 2 and 3, respectively. For both P30 and P36, ALH remarkably reduced FFA by an average 59.06%. The average percent improvement (API) for FFA by MA, ACH, SG, ALO and ACA were 55.49%, 40.07%, 44.76%, 37.37% and 29.55%, respectively. BR, FP, ACL and CE were not very effective in improving FFA. The citric acid component in FP could be responsible for poor removal of FFA (Lin

Table 2
Effect of single adsorbent treatment on quality of thermally polymerized palm oil, P30^{B,C,D}

Adsorbent treatment^{A}	% FFA	% CD	Viscosity (cP) at 30 °C	*p*-AV	% TPM	Colour	
						R	*Y*
Control (P30)	0.70 ± 0.03^{a}	0.19 ± 0.01^{b}	97.12 ± 0.45^{a}	15.30 ± 0.45^{a}	12.88 ± 0.50^{a}	1.90 ± 0.25^{a}	26.0 ± 0.01^{a}
FP	0.68 ± 0.01^{a} (2.25)	0.10 ± 0.01^{a} (47.02)	95.27 ± 0.52^{b} (1.90)	11.68 ± 0.74^{b} (23.62)	8.84 ± 0.34^{b} (31.31)	1.50 ± 0.25^{a} (20.10)	17.5 ± 0.35^{b} (32.51)
BR	0.62 ± 0.01^{a} (10.74)	0.13 ± 0.02^{b} (30.57)	96.33 ± 0.76^{a} (0.81)	14.00 ± 0.22^{c} (8.51)	8.15 ± 0.46^{b} (36.66)	0.80 ± 0.78^{b} (57.30)	8.9 ± 0.21^{c} (65.50)
ALH	0.26 ± 0.1^{b} (62.17)	0.13 ± 0.02^{b} (28.77)	86.30 ± 0.64^{d} (11.14)	9.12 ± 0.14^{d} (40.40)	6.27 ± 0.5^{d} (51.29)	0.65 ± 0.08^{c} (65.40)	9.1 ± 0.03^{c} (65.10)
ACH	0.42 ± 0.01^{c} (39.97)	0.10 ± 0.15^{b} (43.52)	95.14 ± 1.11^{b} (2.11)	9.92 ± 0.18^{e} (35.13)	9.93 ± 0.27^{c} (22.84)	0.10 ± 0.01^{d} (94.73)	3.5 ± 0.24^{d} (86.53)
CE	0.67 ± 0.02^{a} (4.14)	0.18 ± 0.01^{b} (3.78)	95.23 ± 0.15^{b} (1.94)	14.78 ± 0.57^{a} (3.37)	11.53 ± 0.20^{e} (10.42)	0.60 ± 0.32^{e} (68.42)	8.4 ± 0.57^{c} (67.54)
SG	0.41 ± 0.01^{c} (40.83)	0.10 ± 0.01^{a} (47.12)	84.40 ± 0.36^{e} (13.09)	11.63 ± 0.1^{b} (23.95)	5.57 ± 0.11^{d} (56.73)	0.65 ± 0.04^{f} (65.57)	7.3 ± 0.04^{e} (71.69)
ACA	0.49 ± 0.05^{c} (30.28)	0.13 ± 0.01^{b} (32.01)	91.20 ± 0.60^{f} (6.09)	11.11 ± 0.16^{b} (27.35)	7.35 ± 0.65^{b} (42.93)	0.60 ± 0.23^{g} (68.25)	4.1 ± 0.47^{d} (84.2)
MA	0.29 ± 0.04^{b} (58.59)	0.08 ± 0.01^{a} (59.45)	89.50 ± 1.36^{c} (7.84)	6.73 ± 0.40^{f} (58.17)	9.92 ± 0.20^{c} (22.98)	0.62 ± 0.19^{h} (67.35)	6.0 ± 0.70^{f} (76.76)
ACL	0.69 ± 0.01^{a} (1.86)	0.14 ± 0.01^{b} (23.24)	88.40 ± 0.27^{c} (8.97)	10.41 ± 0.12^{e} (31.96)	9.60 ± 0.85^{c} (25.46)	0.51 ± 0.17^{j} (73.14)	6.8 ± 0.37^{f} (73.84)
ALO	0.44 ± 0.02^{c} (36.50)	0.06 ± 0.01^{a} (68.10)	93.77 ± 0.15^{g} (3.44)	12.57 ± 0.24^{g} (17.80)	9.23 ± 0.24^{c} (28.33)	1.40 ± 0.54^{a} (25.78)	24.8 ± 0.27^{g} (4.61)

[A] Adsorbents used at 10% (w/w) based on weight of the oil.
[B] Results are mean ± SD of three individual determinations.
[C] Values in parenthesis indicate the percent improvement with respect to control.
[D] Values in the same column with different superscripts are significantly different ($P = 0.05$) as measured by Duncan's multiple-comparison test.

et al., 1998). In the present study, the order of adsorbent ability to reduce free fatty acids was ALH > MA > SG > ACH > ALO > ACA > BR > CE > FP > ACL.

3.2.2. Percent conjugated diene (% CD)

When polyunsaturated fatty acids are oxidized, a shift in one of the double bonds occurs. This produces the diene conjugation of unsaturated linkages present. The % CD of the treated oil by the individual adsorbents is shown in Tables 2 and 3. ALO and MA reduced the CD of P30 and P36 by 67.97% and 63.87%, respectively. SG, FP and ACH were less effective and showed a reduction of 42.97%, 42.48% and 39.81%, respectively. In the present study, the order of adsorbent ability in reducing the % CD was ALO > MA > FP > SG > ACH > ACA > BR > ALH > ACL > CE.

3.2.3. Viscosity

The formation of polymers during frying is mainly responsible for the changes in the viscosity of the oil (Paul & 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 & Mittal, 1997). As can be seen from Tables 2 and 3, the adsorbents that satisfactorily reduced viscosity were SG (14.39%), ALH (9.8%), ACL (9.2%), MA (7.21%) and ACH (7.05%). FP, BR, CE, ACA and ALO were not very effective in reducing viscosity. In the present study, the order of adsorbent ability to reduce viscosity was SG > ALH > ACL > MA > ACA > ALO > CE > FP > ACH > BR.

3.2.4. *p*-Anisidine value (*p*-AV)

This test primarily measures secondary oxidation products, namely α- and β-unsaturated aldehydes. Oxidation products, such as peroxides, aldehydes, ketones, hydroperoxides, polymers, and oxidized monomers, can cause clinically harmful effects (Paul & Mittal, 1997). The adsorbents that significantly reduced *p*-AV of P30 and P36 were MA (60.63%) and ALH (41.33%). The adsorbents effective to a lesser extent were ACH (34.53%), SG (28.02%), FP (25.69%) and ACL (26.9%) (Tables 2 and 3). BR, CE and ALO did not significantly reduce the *p*-AV. Generally, the *p*-AV values of good quality oil should be less than 2.0. However, even after adsorbent treatment, values were much higher than the specifications. This is due to the large amount of oxidation products present in the control samples. In the present study, the order of adsorbent ability

Table 3
Effect of single adsorbent treatment on quality of thermally polymerized palm oil, P36[B,C,D]

Adsorbent treatment[A]	% FFA	% CD	Viscosity (cP) at 30 °C	*p*-AV	% TPM	Colour	
						R	*Y*
Control (P36)	0.92 ± 0.04^{d}	0.22 ± 0.01^{c}	98.60 ± 0.32^{b}	22.71 ± 0.51^{b}	18.62 ± 0.46^{e}	5.5 ± 0.2^{e}	70.0 ± 0.35^{c}
FP	0.90 ± 0.02^{d} (1.99)	0.14 ± 0.01^{b} (37.94)	95.80 ± 0.1^{c} (2.83)	17.77 ± 1.16^{a} (21.76)	13.08 ± 0.19^{a} (29.75)	3.9 ± 0.35^{c} (29.09)	39.0 ± 0.25^{b} (44.28)
BR	0.84 ± 0.01^{c} (8.33)	0.16 ± 0.01^{b} (29.12)	96.80 ± 0.55^{c} (1.82)	21.06 ± 0.25^{e} (7.29)	13.28 ± 0.60^{a} (28.67)	3.0 ± 0.17^{d} (53.90)	48.6 ± 0.01^{e} (69.57)
ALH	0.41 ± 0.01^{a} (55.96)	0.17 ± 0.01^{b} (25.00)	90.25 ± 0.43^{a} (8.46)	13.11 ± 0.11^{f} (42.26)	9.72 ± 0.46^{c} (47.79)	2.2 ± 0.26^{a} (59.82)	39.3 ± 0.12^{b} (56.21)
ACH	0.56 ± 0.02^{b} (39.38)	0.14 ± 0.01^{b} (36.10)	95.80 ± 1.15^{c} (2.84)	15.00 ± 0.18^{c} (33.94)	14.65 ± 0.36^{b} (21.32)	0.9 ± 0.15^{b} (83.63)	5.9 ± 0.24^{f} (91.57)
CE	0.87 ± 0.04^{c} (5.79)	0.21 ± 0.01^{c} (6.53)	95.76 ± 0.20^{c} (2.88)	22.36 ± 0.45^{b} (1.52)	16.20 ± 0.71^{e} (12.97)	1.9 ± 0.24^{a} (65.28)	21.1 ± 0.34^{g} (69.85)
SG	0.47 ± 0.02^{a} (48.70)	0.14 ± 0.01^{b} (38.83)	83.11 ± 0.72^{e} (15.70)	15.37 ± 0.46^{c} (32.31)	8.81 ± 0.63^{d} (52.65)	2.1 ± 0.23^{a} (61.81)	18.0 ± 0.18^{a} (74.28)
ACA	0.65 ± 0.04^{e} (28.82)	0.15 ± 0.01^{b} (34.37)	90.70 ± 0.52^{a} (8.01)	15.19 ± 0.21^{c} (33.09)	9.62 ± 0.22^{c} (48.33)	1.4 ± 0.17^{b} (74.54)	8.8 ± 0.18^{i} (87.42)
MA	0.44 ± 0.01^{a} (52.39)	0.07 ± 0.01^{a} (68.30)	92.10 ± 1.35^{d} (6.59)	8.38 ± 0.12^{d} (63.09)	12.29 ± 0.59^{a} (33.99)	1.6 ± 0.04^{a} (70.90)	19.53 ± 0.41^{h} (72.10)
ACL	0.90 ± 0.01^{d} (1.78)	0.17 ± 0.05^{b} (2.32)	89.30 ± 0.65^{a} (9.43)	17.75 ± 0.46^{a} (21.84)	14.73 ± 0.26^{b} (20.89)	1.2 ± 0.16^{b} (78.18)	18.6 ± 0.08^{a} (73.42)
ALO	0.57 ± 0.01^{b} (38.24)	0.07 ± 0.01^{a} (67.85)	95.52 ± 0.69^{c} (3.12)	18.11 ± 0.18^{a} (20.23)	12.25 ± 0.28^{a} (34.20)	4.4 ± 0.50^{c} (20.00)	68.9 ± 0.42^{d} (1.47)

[A] Adsorbents used at 10% (w/w) based on weight of the oil.

[B] Results are mean ± SD of three individual determinations.

[C] Values in parenthesis indicate the percent improvement with respect to control.

to reduce *p*-AV was: MA > ALH > ACH > ACA > SG > ACL > FP > ALO > BR > CE.

3.2.5. Total polar material (TPM)

TPM is a chemical index used to determine the degree of cumulative degradation of oil, and is an excellent predictor of frying oil quality (Blumenthal, 1996). TPM includes polar substances, such as monoacylglycerols, diacylglycerols, and FFA, which occur in unused oils, as well as polar compounds, that are formed during the heating of foodstuffs. Non-polar materials are mostly unaltered triacylglycerols (AOCS, 1998). TPM is essentially the non-triacylglycerol fraction of the oil, which is broadly grouped into polymerized and decomposed products based on molecular weight and polarity. The maximum permissible limit for TPM allowed in frying oils is less than or equal to 25%. As can be seen from Tables 2 and 3, SG showed maximum removal of TPM (54.69%) followed by ALH (49.54%) and ACA (45.63%). Adsorbents like BR (32.66%), ALO (31.26%), FP (30.53%), MA (28.48%), ACH (22.08%) and ACL (14.17%) were reasonably effective in reducing TPM. The ability of SG to reduce TPM can be attributed to its polar nature, which selectively separates particles on the basis of its molecular weight and surface area (430 m^2/g), thus entrapping higher molecular weight decomposition products. The effectiveness of SG in overall improvement in TPM is in agreement with the results obtained by Miyagi, Subramanian, and Nakajima (2003). van der Waals forces dominate adsorption on a non-polar surface like ACA with a surface area of 824 m^2/g. Polarizability is the main factor governing the magnitude of the van der Waals energy, and is roughly proportional to the molecular weight. The effectiveness of ACA to reduce TPM had been previously reported by McNeill et al. (1986). CE showed the lowest reduction in TPM owing to its very low surface area (<10 m^2/g). Its ineffectiveness to reduce TPM has been previously reported by Yates and Caldwell (1992). Fritsch (1981) reported determination of TPM in frying fat as the most reliable measure of the extent of deterioration. In this context, a higher reduction of TPM indicates the feasibility of recycling used frying oil and retaining the fried food quality over a longer duration of fryer operation. In the present study, the order of adsorbent ability to reduce TPM was SG > ALH > ACA > BR > ALO > FP > MA > ACL > ACH > CE.

3.2.6. Colour

Surveys have indicated that colour to be the main criterion for discontinuing usage of frying oil (Kajimoto, 1994). Regulations in several countries stipulate colour as a criterion for discarding frying oils (Firestone, Stier, & Blumenthal, 1991). Colour development is an indication of oxidation, polymerization, and formation of carbonyl compounds. It increases dramatically during frying and is influenced by frying temperature, although the quantitative amount of chemicals causing the increase in colour is small (Paul & Mittal, 1997). One of the benefits of active treatments is improvement in color. As can be seen from Tables 2 and 3, ACH improved the colour of both P30 and P36 frying oils significantly. Other adsorbents like SG, CE, ACA, ALH, ACL, MA and BR were also effective in decolorizing the used oils. MA containing magnesium silicate is believed to have the ability to remove coloured bodies as it has a high concentration of both acidic and basic sites (Lin et al., 1998; Zhu et al., 1994). ALO showed the least improvement in the oil colour. In the present study, the order of adsorbent ability to reduce "*R*" and "*Y*" values was ACH > ACL > ACA > MA > CE > SG > ALH > BR > FP > ALO and ACH > ACA > SG > ACL > MA > CE > ALH > FP > BR > ALO.

4. .Selection and use of binary adsorbent combination

Adsorbent combination was selected on screening of each adsorbent, ranked on the basis of their overall percentage improvement (API) values across all the analysis parameters. ALO and MA showed significant reduction in FFA, CD, colour and *p*-AV. ALH also reduced TPM considerably, while ACA demonstrated excellent colour bleaching characteristics, and TPM reduction. SG reduced the TPM and all other values satisfactorily. Although BR reduced TPM marginally better than MA, it was not effective in removing other decomposition products present in the oil. MA performed well in this study on all tests, especially on FFA and colour. Hence, MA, ALH, SG and ACA were selected for preparing blends to check the efficiency of removal of all parameters monitored. Two adsorbent sets, one comprising of ALH and ACA [A – ALH:ACA (1:3), B – ALH:ACA (1:1) and C – ALH:ACA (3:1)], and the other comprising of MA and SG [D – MA:SG (1:3), E – MA:SG (1:1) and F – MA:SG (3:1)] were formulated and evaluated at a total adsorbent concentration of 10%.

4.1. Evaluation of the adsorbent blends

The efficacy of six combinations of four adsorbents that were evaluated are shown in Tables 4 and 5. Among these, formulation F gave the best improvement of 55.71%, again confirming the effectiveness of MA and SG in reducing FFA (Tables 4 and 5). This was followed by formulation C (43.98%), A (39.4%), B (30.95%), E (27.95%) and D (18.05%). Single adsorbent treatment with ALH and MA were more efficient in reduction of FFA than all the blends chosen in the study.

The best reduction of 83.65% in CD was achieved by formulation F. This was followed by A (76.1%), E (59.94%), C (48.72%), B (48.86%), and D (28.11%). Single treatment with MA reduced CD by 63.87%. The highest reduction in viscosity of 8.83% was achieved by formulation A, followed by F (7.99%), C (7.09%), E (5.89%), D (5.18%) and B (2.71%). SG alone at 10% reduced viscosity by 14.39%.

Formulation F gave maximum reduction of 63.57% in *p*-AV followed by E (58.58%), B (56.72%), D (53.23%),

Table 4
Regeneration of P30 with binary adsorbents[A,B,C,D]

Binary combination[E]	% FFA	% CD	Viscosity (Cp) at 30 °C	*p*-AV	% TPM	Colour	
						R	*Y*
Control (P30)	0.70 ± 0.03^{a}	0.19 ± 0.01^{a}	97.12 ± 0.45^{a}	$15.30 \pm \pm 0.45^{d}$	12.88 ± 0.5^{c}	1.90 ± 0.25^{a}	26.00 ± 0.01^{b}
A	0.43 ± 0.05^{a} (38.75)	0.30 ± 0.2^{a} (77.20)	90.9 ± 0.04^{b} (9.36)	8.31 ± 0.33^{b} (45.67)	6.60 ± 0.58^{d} (48.77)	0.59 ± 0.17^{b} (68.76)	6.16 ± 0.01^{a} (76.27)
B	0.48 ± 0.14^{a} (31.54)	0.23 ± 0.12^{a} (45.80)	96.8 ± 0.59^{a} (3.31)	6.21 ± 0.30^{a} (59.40)	7.83 ± 0.30^{a} (39.15)	1.00 ± 0.07^{c} (46.87)	11.23 ± 0.01^{c} (56.77)
C	0.39 ± 0.01^{b} (44.11)	0.36 ± 0.1^{a} (42.70)	93.62 ± 0.56^{c} (6.56)	8.99 ± 0.18^{b} (41.20)	8.46 ± 0.24^{b} (34.27)	0.98 ± 0.08^{c} (48.11)	11.67 ± 0.05^{d} (55.11)
D	0.55 ± 0.18^{a} (20.80)	0.14 ± 0.07^{a} (24.57)	95.74 ± 0.25^{d} (4.38)	6.99 ± 0.26^{c} (54.28)	7.72 ± 0.15^{a} (40.03)	0.78 ± 0.02^{b} (58.74)	9.48 ± 0.34^{e} (63.52)
E	0.50 ± 0.02^{a} (28.74)	0.58 ± 0.02^{a} (57.85)	94.49 ± 0.74^{e} (5.67)	5.69 ± 0.72^{a} (62.78)	8.27 ± 0.48^{b} (35.78)	0.91 ± 0.04^{c} (52.25)	7.61 ± 0.01^{f} (70.71)
F	0.30 ± 0.18^{b} (57.11)	0.27 ± 0.10^{a} (80.70)	92.09 ± 0.12^{f} (8.14)	5.03 ± 0.22^{a} (67.12)	7.52 ± 0.11^{a} (41.57)	0.65 ± 0.24^{b} (65.47)	6.62 ± 0.5^{a} (74.53)

[A] Adsorbents used at 10% (w/w) based on weight of the oil.
[B] Results are mean ± SD of three individual determinations.
[C] Values in parenthesis indicate the percent improvement with respect to control.
[D] Values in the same column with different superscripts are significantly different ($P = 0.05$) as measured by Duncan's multiple-comparison test.
[E] A – ALH: ACA (1:3), B – ALH: ACA (1:1), C – ALH: ACA (3:1), D – MA: SG (1:3), E – MA: SG (1:1), F – MA: SG (3:1).

Table 5
Regeneration of P36 with binary adsorbents[A,B,C,D]

Binary combination[E]	% FFA	% CD	Viscosity (Cp) at 30 °C	*p*-Av	% TPM	Colour	
						R	*Y*
Control (P36)	0.92 ± 0.04^{a}	0.22 ± 0.01^{a}	98.60 ± 0.32^{c}	22.71 ± 0.51^{d}	18.62 ± 0.46^{d}	5.50 ± 0.20^{a}	70.00 ± 0.35^{a}
A	0.55 ± 0.16^{b} (40.05)	0.06 ± 0.01^{b} (75.00)	90.40 ± 0.17^{a} (8.31)	13.01 ± 0.60^{b} (42.67)	10.04 ± 0.80^{c} (46.07)	2.06 ± 0.25^{c} (62.54)	14.20 ± 0.12^{b} (79.72)
B	0.49 ± 0.18^{b} (30.36)	0.11 ± 0.07^{a} (51.92)	96.50 ± 0.10^{d} (2.12)	10.43 ± 0.13^{a} (54.05)	10.77 ± 0.35^{b} (42.15)	3.03 ± 0.08^{b} (44.75)	34.12 ± 0.19^{c} (51.25)
C	0.52 ± 0.17^{b} (43.86)	0.10 ± 0.07^{a} (54.70)	92.59 ± 0.28^{b} (7.62)	14.26 ± 0.54^{c} (37.20)	11.91 ± 0.13^{a} (36.01)	2.63 ± 0.24^{b} (52.02)	28.09 ± 0.18^{d} (59.86)
D	0.78 ± 0.05^{a} (15.21)	0.15 ± 0.08^{a} (31.66)	92.70 ± 0.45^{b} (5.98)	10.85 ± 0.12^{a} (52.18)	11.64 ± 0.12^{a} (37.48)	2.16 ± 0.16^{c} (60.70)	23.00 ± 0.33^{e} (67.14)
E	0.67 ± 0.01^{b} (27.17)	0.08 ± 0.05^{a} (62.05)	91.17 ± 0.02^{e} (6.12)	10.36 ± 0.29^{a} (54.38)	12.38 ± 0.11^{a} (33.51)	2.50 ± 0.22^{b} (54.54)	20.00 ± 0.5^{f} (71.42)
F	0.42 ± 0.09^{b} (54.32)	0.03 ± 0.01^{b} (86.60)	90.20 ± 0.26^{a} (7.84)	9.08 ± 0.03^{e} (60.03)	11.01 ± 0.02^{b} (40.84)	2.00 ± 0.60^{c} (63.63)	19.04 ± 0.16^{g} (72.80)

[A] Adsorbents used at 10% (w/w) based on weight of the oil.
[B] Results are mean ± SD of three individual determinations.
[C] Values in parenthesis indicate the percent improvement with respect to control.
[D] Values in the same column with different superscripts are significantly different ($P = 0.05$) as measured by Duncan's multiple-comparison test.
[E] A – ALH: ACA (1:3), B – ALH: ACA (1:1), C – ALH: ACA (3:1), D – MA: SG (1:3), E – MA: SG (1:1), F – MA: SG (3:1).

A (44.17%) and C (39.2%). Similarly, formulation A was most effective in reducing TPM (47.42%), followed by F (41.20%), B (40.65%), D (38.75%), C (35.14%), and E (34.64%). Treatment with only ALH or SG was relatively better than all the binary combinations used in the study.

The best adsorbent combination that reduced colour in terms of "*R*" value was formulation A (65.65%), followed by F (64.55%), D (59.72%), E (53.39%), C (50.06%) and B (45.81%). Formulation A showed best reduction of 77.99% for "*Y*" value, followed by F (73.66%), E (71.06%), D (65.33%), C (57.48%) and B (54.01%). ACA

Table 6
Effect of quaternary adsorbent combination treatment on quality of used palm frying oils and a heat-abused cottonseed oil^{A,B,C,D,E}

Parameters	Thermally polymerized				Heat-abused cottonseed oil	
	P30	P30, after treatment	P36	P36, after treatment	Control	Treated
% FFA	0.70 ± 0.03^{a}	0.39 ± 0.25^{a} (44.26)	0.92 ± 0.04^{a}	0.48 ± 0.12^{b} (48.04)	0.31 ± 0.11^{a}	0.19 ± 0.02^{a} (40.06)
p-AV	15.30 ± 0.45^{a}	6.98 ± 0.48^{b} (54.32)	22.71 ± 0.51^{a}	9.33 ± 0.18^{b} (58.91)	36.94 ± 0.06^{a}	17.28 ± 0.02^{b} (53.22)
CD	0.19 ± 0.01^{a}	0.05 ± 0.02^{b} (74.05)	0.22 ± 0.01^{a}	0.07 ± 0.05^{b} (70.08)	0.28 ± 0.09^{a}	0.07 ± 0.01^{a} (75.89)
Viscosity (cP at 30° C)	97.12 ± 0.45^{a}	82.50 ± 0.14^{b} (15.05)	98.60 ± 0.32^{a}	80.46 ± 0.23^{b} (18.39)	99.10 ± 0.31^{a}	82.50 ± 0.24^{b} (16.78)
% TPM	12.88 ± 0.50^{a}	7.50 ± 0.66^{b} (41.71)	18.62 ± 0.46^{a}	10.46 ± 0.85^{b} (43.82)	31.96 ± 0.75^{a}	14.12 ± 0.55^{b} (55.81)
Colour "*R*" value	1.9 ± 0.25^{a}	0.5 ± 0.06^{b} (73.68)	5.5 ± 0.2^{a}	1.30 ± 0.03^{b} (76.36)	9.70 ± 0.10^{a}	3.10 ± 0.08^{b} (68.04)
Colour "*Y*" value	26.0 ± 0.01^{a}	4.7 ± 0.11^{b} (81.91)	70.0 ± 0.35^{a}	18.3 ± 0.22^{b} (73.85)	85.00 ± 0.15^{a}	31.20 ± 0.23^{b} (63.24)

[A] Adsorbents used at 10% (w/w) based on weight of the oil.

[B] Results are mean ± SD of three individual determinations.

[C] Values in parenthesis indicate the percent improvement with respect to control.

[D] In each row, the two values, one before treatment and the other after treatment were considered separately for each parameter. Of the two values for each parameter, the ones with different superscripts are significantly different ($P = 0.05$) as measured by Duncan's multiple-comparison test.

[E] The quaternary adsorbent combination was a 1:1 blend of formulations A and F as indicated in Tables 4 and 5.

and MA could reduce "*R*" and "*Y*" value more than the adsorbent blends.

In conclusion, binary combination of adsorbents that performed best for most of the parameters evaluated were formulations F and A.

5. Selection of quaternary combinations and column treatment

A quaternary combination consisting of 1:1 ratio of binary adsorbent blends denoted by A and F (3.75% MA + 1.25% SG + 3.75% ACA + 1.25% ALH) in Section 4 was used. This was packed in a column and the thermally polymerized frying oils, heated to 150° C, were passed through the column. The results are shown in Table 6. This combination could reduce FFA by 46.15%, *p*-AV by 56.61%, CD by 72.06%, viscosity by 16.71%, TPM by.76%, "*R*" value by 75.02% and "*Y*" value by 77.87%. Similarly, a thermally polymerized cottonseed oil sample collected from a local eatery was subjected to the same treatment. The unknown sample had a high *p*-AV, CD, TPM and colour values, indicating severe polymerization of the same. The % FFA was low, possibly due to formation of other decomposition products. The percentage improvement for the unknown oil was 40.06% for FFA, 53.22% for *p*-AV, 75.89% for CD, 16.78% for viscosity, 55.81% for TPM, 68.04% for "*R*" value and 63.24% for "*Y*" value, respectively. The quaternary adsorbent combination recorded highest improvement for most parameters, and thus was effective in the overall regeneration of the fried oils.

6. Conclusions

Treatment of thermally polymerized palm oils with various adsorbents and adsorbent combinations could significantly improve its quality. MA, ACA, SG and ALH reduced FFA, CD, oxidation products and TPM, and also improved viscosity and colour, thus regenerating the heat-abused oils. Binary combination comprising of 7.5% MA and 2.5% SG consistently reduced all the parameters and was comparatively better than the single adsorbent treatments. Treatment with the quaternary combination comprising of 3.75% MA, 1.25% SG, 3.75% ACA and 1.25% ALH proved to be the best in reducing the oil decomposition products of the heat-abused palm and cottonseed oil.

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