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THE QUALITY AND CHARACTERISTICS OF COTTON AND SUNFLOWER OIL BLEACHED USING CLAYS FROM ILIRI, IN NORTH EASTERN UGANDA

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ABSTRACT: *Bleaching is known to alter the composition of edible oils as it removes impurities and certain food nutrients. The characteristics of bleached oil are strongly related to type bleaching medium, temperature at which bleaching is done and other factors. In this study we compare peroxide, free fatty acid, acid and iodine values, copper and iron content of bleached and crude oils to establish the quality and characteristics of cotton and sunflower oils bleached using clays from Iliri. A known mass of bleached oil (0.2 g) digested in the perchloric-nitric-hydrofluoric acid mixture (3.0 mL) then with distilled water as aspirated to atomic absorption spectrophotometer Shimadzu-AA-6200 and absorbance of copper recorded at 324.8 nm. Similarly, another oil portion was treated, aspirated and absorbance of iron was determined at 478 nm when ammonium thiocyanate had been added. Oil dissolved in ethanoic acid-chloroform-water- potassium iodide-starch indicator was titrated with sodium thiosulphate to obtain peroxide value of oil. And oil dissolved in butan-1-ol was titrated with ethanolic potassium hydroxide solution to get acid and free fatty acid values. The percentage decrease in copper content was higher than for iron. The content of iron in cotton oil decreased by 66.4 % when bleached with iliri clay leached in 30% hydrochloric or sulfuric acids yet that in sunflower fell by 62.9 and 60.0% when respectively bleached in 30% hydrochloric and sulfuric acid. The content of copper in cotton oil decreased by 82.5 % when bleached with Iliri clay leached in 30% hydrochloric acid and 85.0% for 30% sulfuric acid leached clay. That in sunflower fell by 73.3% when bleached with clay leached 30% hydrochloric acid and 83.3% when bleached with 30% sulfuric acid. The acid values showed that the acidity in sunflower oils is largely due to oleic acid, cotton-seed oil corresponded to linoleic acid. The levels of free fatty acid were found to lie in range from 3.8-3.2 for all clays used showing no significant rise. The peroxide values of bleached oils lay between 1.2 and 0.8. The bleached oils were found to be fit for human use because the quality was high.*

KEYWORDS: Bleached Oil, Clays, Trace Metals, Acid, Peroxide, Iodine Values.

INTRODUCTION

Vegetable oils are bleached to remove coloring matter, traces of heavy elements, phospholipids, poly-aromatics and oxidation products (Mag 1990) so as to improve the quality and oxidation stability of oils (De Greyt and Kellen, 2000). It was reported that iron and copper present in the bleached oils affect quality of oil produced. The quantity of trace elements in oils was shown to progressively decrease as the concentration of acid used to leach the clays increased (Boyd, 1988; Mukasa-Tebandeke et al 2014, Ujeneza et al, 2014). Similarly, the decrease in copper content in vegetable oils was observed during bleaching (Leonardis et al, 2000).

The selected clays from Central and Eastern Uganda were reported to have reduced the content of copper in cotton and sunflower oils decreased from 0.5ppm to 0.1ppm; iron from 1.6 to 0.1ppm; free fatty acids to 3.2 ppm and peroxide value to 0.8ppm (Mukasa-Tebandeke et al, 2014). The iodine values of oils published by the Journal of American oil Chemists indicted which the iodine value for cotton-seed oils to lie in the range 108-110 and for sunflower oils it is in 109-135 range (Firestone, 1993; Firestone D, 1993). This showed that bleaching increases the level of conjugated trienes and reduces the content of conjugated dienes as these have molar masses lying in range between 232 and 270 (Girgis, 2005; Hoffmann, 1989; Morrison, 1975; Topallar, 1998).

Sunflower-seed, cotton-seed, Olive, corn, soybeans and all other seed oils fall into the general family of oils known as vegetable oils. Vegetable oil is one of the liquid substances extracted from the vegetables. Vegetable oil is almost entirely made up of the fat of the vegetable. It can be liquid at room temperature, as in the case of corn, cottonseed, soybean, or olive oil. In the case of cocoa butter, coconut, or palm oil, the oil is solid at room temperature. Some vegetable oils are extracted from the seed of the vegetable, as in corn, soybeans, peanuts, hazelnuts, and sunflowers. Some vegetable oils come from the “fruit of the vegetable,” as in Olives and palms.

There are four basic steps are used to refine oil. These include; neutralization and separation, bleaching and deodorizing (Siddiqui, 1968). When oil is neutralized, sodium hydroxide, also known as caustic soda, is added to lower the acidity. This neutralizes the bitter taste of the crude oil by combining with the oil to create a sodium salt, which is then separated out from the oil and used for soap stock. The neutralized oil then is ready for bleaching.

Diatomaceous earth, clays, peroxides or carbon is added to bleach and adsorb the dark colored impurities in the oil in order to give it a clear color. Color impurities typically present in oils include, carotenoids, xanthophylls, xanthophyll esters, chlorophyll, tocopherols, as well as oxidized fatty acids and fatty acid polymers (Christidis, et al, 2003; Boki, et al, 1989). Some of oils may have a color that is objectionable to a consumer. The oils must be bleached to improve its color quality. Many oils are commonly treated with clays to reduce oil color values by adsorptive purification. Unpleasant smell that the oil may have is removed through deodorization, whereby oil is heated in vacuum to very high temperatures in a 12-metre tall deodorizer. Degumming removes carotenes, tocopherols, phytosterols and squalenes which have nutritional aspects (De Greyt, 1999; Goh, 1991). . Major phytosterols in palm oil include campesterol, stigmasterol and β-sitesterol, have pharmaceutical effects but are removed by bleaching (Chiew, 2007; Hedtmann, 1991; Khor, 1997; 1996). This makes bleached oils less nutritive but safe for human consumption.

Unbleached oils contain pesticide residues, oxidation products and heavy metals which can become harmful when consumed. So it is essential to bleach the oils (Pollard, 1993; Richardson, 1978). The bleaching of edible oils was accomplished using adsorptive bentonite clays (Richardson, 1978; Wiederman,1981). As early as 1933, the designing and testing procedures for bleaching clays had been published. The designed and tested procedures of bleaching and rating bleaching capacity of acid-leached clay samples were developed using petroleum (Nutting, 1933). Later, (Dandy, 1965; Richardson, 1978) decolorized cotton-seed oil by adsorption of color pigments on acid leached clays of Kajansi and Koki. Cotton-seed oil was bleached by selective adsorption of impurities on sulfuric acid-leached clays from Ghana. (Gadzekpo, and Mensah. 1991, Sabah and Sabri 2005). The adsorption of components of oils like carotenoids and peroxides during bleaching was reported (Toro-Vazquez., 1991).

It was reported further that degumming and bleaching removes gums, soaps, trace metals, vitamins, pigments and peroxides (Chiew, 2007; Mbah et al 2005; Ng, et al , 2004; Rossi, 2001). Oxidation products in the crude vegetable oils (Zchau, 1981) are removed by adsorption on the active surface of the bleaching earth to improve color and stability of the final oil. The effects of filtering through bleaching media on decrease of peroxide value of autoxidized soybean oil were investigated and shown to improve its quality (Bheemreddy, 2002; Shahidi, 1997; Zhang, 1992). Bleaching removes phospholipids, inorganic phosphates and gums from oils and the reduction in the total phosphorous present was proportional to the quantity of clay used (Kheok and Lim, 1982). Bleaching of vegetable oils is a very important component of oils production and sales (Proctor, 1978; Boukerroui, 2009). The bleaching of oils for human consumption is efficiently carried out using commercial bleaching earths.

This study has aimed at determining the effects of Iliri bleaching clays on trace elements, acid, iodine and peroxide values in cotton-seed and sunflower-seed oils to characterize the purity of the bleached oils.

MATERIALS AND METHODS

Location and geological settings of sampled clays

Iliri is located *in* Bokora Corridor Wildlife Reserve, which lies between Toror and Napak mountains in North Eastern Uganda's Karamoja region. The raw swelling clay from the deposit in Iliri was collected from the roadside from Katakwi to Moroto from a ditch 35 cm deep.

Preparation of clays

Raw samples of clays was soaked in distilled water, sieved to pass through a mesh 5.3 x 10^{-4} m diameter, dried at 105°C and ground to powder using porcelain mortar and pestle. The clay powders were stored for future use in desiccators.

Leaching of clays

Clay powder (100g, 0.25mol) was separately mixed with hydrochloric and sulfuric acid (500mL) at different concentrations (10, 20, 30% v/v) in a flask. The mixture was heated at 105°C for 4 hours; then cooled and filtered. The residue was washed to neutrality with distilled water; then dried at 105°C in the thermo-stated oven. The dried leached powders were labeled and stored for future use (Fahn 1976; Beneke and Lagaly, 2002; Didi et al, 2009).

Degumming of vegetable oils

Crude oil (100g, 0.43mol) was placed in a flask, 85% phosphoric acid (1g,0.1mmol) was added, the mixture heated at 90°C while stirring at 900 revolutions per minute, for 10 minutes under nitrogen blanket. The oil was filtered under nitrogen (Saadia 1992).

Bleaching of vegetable oils

Degummed neutral oil (200g, 0.85mol) under nitrogen blanket was passed through columns containing appropriate neutral, acid-leached clay powders (5g, 1.24mmol) separately which had been heat-activated at various temperatures ranging from 40 to 130°C for two hours and left to elute bleached oils (Patterson, 1992).

Analysis of bleached oils

The bleached oils were analyzed for iron and copper content, peroxide value, free fatty acids value, iodine number, refractive index, transmittance and turbidity. The methods used are outlined below.

Determining content of iron and copper in bleached oils

The bleached oil (0.2g, 0.86mmol) was digested in the perchloric-nitric-hydrofluoric acid mixture (3.0mL, 0.13mol) then made up to 25.0mL with distilled water. The absorbance of copper was determined at 324.8 nm using the atomic absorption spectrophotometer Shimadzu-AA-6200. Similarly iron was determined at 478 nm when ammonium thiocyanate solution had been added to complex the ions (Allen et al, 1998; Leonardis et al, 2000).

Determining peroxide value of bleached oils

Bleached oil (2.0g, 8.6mmol) was placed in a 250mL flask. Ethanoic acid(30 mL, 0.43mol) added together with chloroform (15mL, 0.24mol) to give 9.1:5.0 ratio. The mixture was stirred, water (50mL, 2.7mol) added and standard potassium iodide (0.5mL, 0.001mmol), followed by starch indicator (2 drops) and water (100mL, 5.4mol). The mixture was titrated with 0.01M sodium thiosulphate to discharge the blue color (AOCS, 2001. The values of the peroxide values were computed using equation 1.

$$PV = \frac{1000M(A-B)}{W} \quad \text{.....................................} 1$$

Where A is titre obtained with sample of sodium thiosulphate/cm$^{3.}$

B is blank titre of sodium thiosulphate/cm$^{3.}$

M is molarity of sodium thiosulphate.

W is mass in g of test portion.

Determining free fatty acid value of bleached oils

Bleached oil (2g, 8.6mmol) was placed in flask; butan-1-ol (10mL, 0.12mol) added. The mixture was titrated with 0.5M ethanolic potassium hydroxide solution to the faint pink phenolphthalein end point (AOCA 94048). The experiment was repeated thrice.

Determining iodine value of bleached oils

Resublimed iodine (1.3g, 5.1mmol) was dissolved in ethanoic acid (100mL, 1.3mol) and slight excess chlorine bubbled through it. Oil (0.1g, 0.43mmol) was placed in the 250mL volumetric flask containing chloroform (10mL, 3.1mmol) excess 0.1M iodine (15mL, 1.5mmol) was added, stirred and mixture boiled, then cooled. The amount of unreacted iodine was determined by back titration with standard thiosulfate solution (Pockington, 1990). Using the average titres obtained from titration and applying equation 2, the iodine values (Iv) can be calculated.

Iodine value is given by:

$$Iv = \frac{12.69T(V3-V4)}{M} \quad \text{.....................................} 2.$$

T is exact molarity of sodium thiosulphate = 0.1M.

V3 is number of cm^3 of $Na_2S_2O_3$, used on blank test.

V4 is number of cm^3 of $Na_2S_2O_3$, used on test portion.

M is mass of test portion in grams.

Determining acid value of bleached oils

The test portion (0.1g, 0.43mmol) was placed in a reaction flask and dissolved in 1:1 (v/v) mixture of 95% ethanol (15ml, 0.26mmol) and ethoxyethane(15mL, 0.16mmol). The solution was titrated with standard 0.1M ethanolic potassium hydroxide solution, using phenolphthalein indicator. The determinations were duplicated for each batch of bleached and unbleached oils. The acid value, AV was calculated using equation 3;

$$AV = \{56.1 \times V \times T\}/ M \qquad 3$$

V is volume of standardized potassium hydroxide solution used/mL.

T is the molarity of the standardised potassium hydroxide solution used

M is mass in grams of the oil portion taken (AOAC 94048). The experiment was repeated to get comparing results used to calculate mean acid values.

RESULTS AND DISCUSSION

Acid activation

The concentration of hydrochloric and sulfuric acid varied from 10 to 30%, was used to attack the interlayer lamellar cations and replace them with hydrogen ions (Didi et al, 2009). The extent of removal of octahedral ions would influence the bleaching capacity of the product formed. Retention of acid in the clay matrix is known to reduce bleaching power (Beneke and Lagaly, 2002). Hence the bleaching efficiency of clays depends mainly on amount of hydrated silica in the bleaching clay. Bleaching efficiency was shown to increase with concentration of acid and temperature of activation by several authors (Motlagh et al., 2011; Mukasa-Tebandeke et al, 2015., Ujeneza et al, 2014). Reacting natural clays or silicates with sufficiently strong acids leads to formation of silica which strongly enhances the clarifying and bleaching effect. Silicates have to be reacted with acid until they are decomposed to silica to a large extent.

Bleaching

Mixture of the degummed, neutralized oil (200.0 g, 0.85 mol) and appropriate clay powder masses (2.0 g,) was placed in 250 cm^3 Pyrex glass flasks, fitted with a magnetic stirrer. The flask was immersed in a thermo-stated iso-electric mantle at 90 ^oC. The mixture was heated while stirring continuously for a further two hours at the set temperature under high vacuum (Patterson, 1992). The hot oil and clay mixture was filtered in nitrogen atmosphere using a vacuum suction pump. Acid activated Iliri clay decolorized cotton and sunflower-seed oils by removing color bodies by over 80% and met the requirements for application in oil decolorization (Rožic et al, 2010). The filtrate oil was tested by determining content of copper and iron; acid, iodine and peroxide values.

Effect of bleaching on content of metals in oils

Vegetable oils are bleached to remove coloring matter, traces of heavy elements, phospholipids, poly-aromatics and oxidation products (Mag 1990) so as to improve the quality and oxidation stability of oils (De Greyt and Kellen 2000) it was found necessary to determine the amount of iron and copper present in the bleached oils as test on quality of oil produced. The data in Table 1 was obtained. The data in Table 1 has been presented in Figure 1 as a bar chart.

The amount of copper (II) and iron(III) ions in oils progressively decreased as the concentration of acid used to leach the clay increased from 10 to 30%. As seen in Table 1, the content of copper and iron in the bleached oils decreased with increase in concentration of the acid used per fixed mass of clay (Boyd, 1988). The decrease in copper content of cotton oils has been observed to change from 0.4ppm to 0.07 ppm using clay leached in 30% sulfuric acid yet using clay leached in 30% hydrochloric acid it decreased to 0.06 ppm (Leonardis et al 2000). This showed that both leached clays were effective in removing copper. The content of copper in sunflower bleached using clay leached in 30% sulfuric acid decreased from 0.3 to 0.08 ppm yet that leached in 30% hydrochloric acid showed a decrease to 0.06 ppm; indicating that the hydrochloric acid leached clay worked better that the sulfuric acid leached clay.

Table 1: The content of iron and copper in bleached and unbleached oils

	Raw oil		A10		A20		A30		B10		B20		B30	
Metal ion/ ppm	Cu^{2+}	Fe^{3+}	Cu^{2+}	Fe^{3+}	Cu^{2+}	Fe^{3+}	Cu^{2+}	Fe^{3+}	Cu^{2+}	Fe^{3+}	Cu^{2+}	Fe^{3+}	Cu^{2+}	Fe^{3+}
Cotton oil	0.40	2.68	0.27	1.80	0.20	1.20	0.07	0.90	0.25	1.40	0.15	1.10	0.06	0.90
Change%			32.5	32.8	50.0	55.2	82.5	66.4	37.5	44.8	62.5	59.0	85.0	66.4
Sunflower oil	0.30	1.75	0.23	1.00	0.19	0.80	0.08	0.65	0.20	1.00	0.12	0.90	0.05	0.70
Change%			23.3	42.9	36.7	54.3	73.3	62.9	33.3	42.9	60.0	48.6	83.3	60.0

The decrease in content of iron in cotton oils has been observed to change from 2.68 ppm to 0.90 ppm using clay leached in 30% hydrochloric and sulfuric acid (Leonardis et al, 2000). This showed that both leached clays were equally effective in removing iron. The content of iron in sunflower bleached using clay leached in 30% sulfuric acid decreased from 1.75 to 0.65 ppm yet that leached in 30% hydrochloric acid showed a decrease to 0.70 ppm; indicating that the hydrochloric and sulfuric acid leached clays performed similarly. From Figure 1 it can be observed that bleaching cotton and sunflower oils using clay leached in 30% acid had the strongest reducing power on the content of copper and iron in oils. Figure 1

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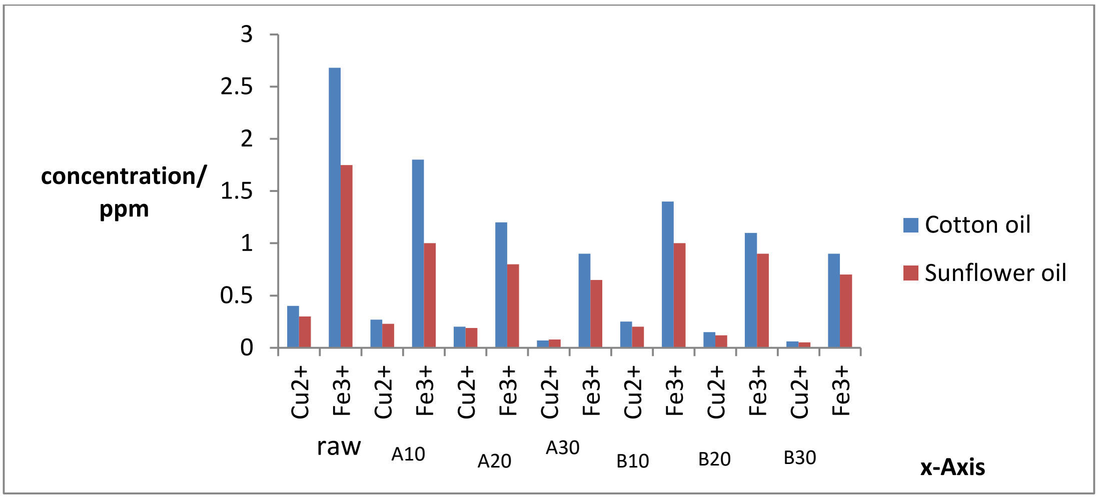

Figure 1: Content of trace metals in bleached oils using Iliri clay activated at 90ºC

Further shows that the quantity of copper and iron in oil decreased with increase in mass percent of the acid used to leach the clay. So to effectively remove trace elements from oils, one needs to bleach the oil with clay which nearly lost all interlayer lamellar ions through leaching (Balaras et al, 1999). The data in Table 1 was used to compute the percentage decrease in metal content of oils. A bar chart developed using the percentage decrease in metal content of oils is presented in Figure 2.

The percentage decrease in content of iron was highest for cotton and sunflower oils bleached using clay leached in 30% sulfuric acid. The highest percentage decrease in content of copper was observed when cotton and sunflower oils were bleached using clay leached in 30% hydrochloric acid. Basing on the percentage change, hydrochloric and sulfuric acids were effective in producing the needed bleaching earth from the Iliri clay.

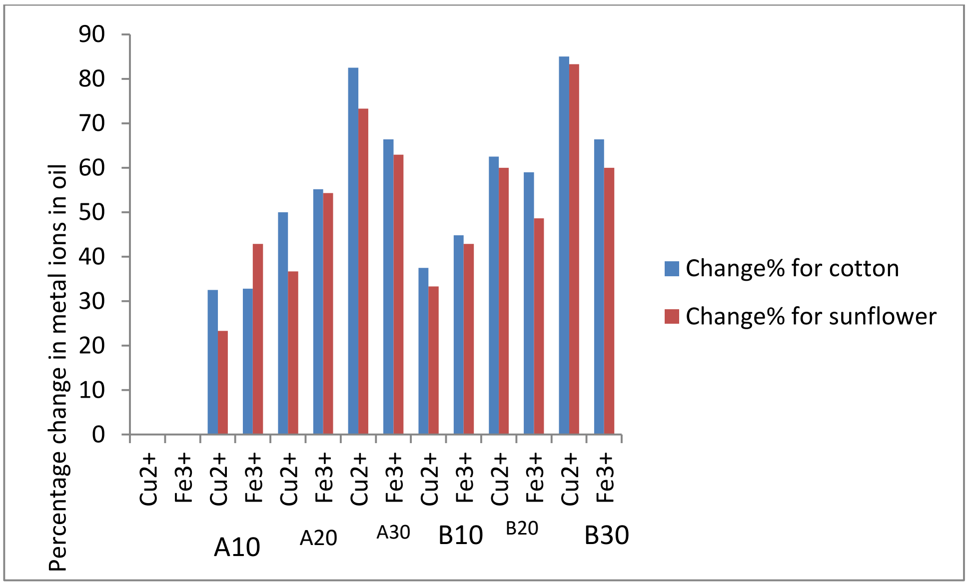

Figure 2: Percentage change in content of metals in bleached oils using Iliri clay

Generally, the percentage decrease in iron content was less than for copper showing that hydrochloric and sulfuric acid leached were more effective at binding coloring materials containing copper than iron.

The percentage decrease in copper and iron content of cotton oil bleached using clay leached in 10% and 20% sulfuric acid were 32.5, 32.8, 50.0 and 55.2% respectively showing that clay showed nearly equal adsorptive tendencies for the pigments containing these ions. However, this similarity is not reflected for adsorption of pigments in sunflower oils. Degumming and bleaching removed trace metals like copper and iron. Presence of these elements is known to increase ease of oxidation of oils, so their removal must increase the shelf life of the bleached oils (Wei et al, 2004). Clays are known to adsorb metal ions like Cd^{2+}, Pb^{2+}, Ni^{2+}, PO_4^{3-} (Bhattacharyya, 2006; Sen Gupta and Bhattacharyya, 2006). Similarly, acid-activated sepiolite adsorbed phosphorus from rapeseed oil (Sabah and Mehmet Sabri 2005; Sabah, 2009). But free metal ions do not exist in vegetable oils. The decrease in content of iron and copper in the bleached oils was greatest for clay leached in 30% acid because it acquired the highest bleaching capacity to adsorb metal ions from oils during the bleaching process. This probably indicates that maximally efficient bleaching earth was produced by leaching the clay in 30% hydrochloric or sulfuric acid (Berbesi, 2006; Ujeneza et al, 2014).

Effect of bleaching on acid value and free fatty acids content

Vegetable oils bleached using acid leached clays may acquire increased acidity because the bleaching solid acids may catalyze hydrolysis of fats by water present in oils or clays (Mag1990). Similarly, solid acids may suppress ionization of glycerrides thereby limiting acidity of bleached oils (Mukasa-Tebandeke et al, 2014). So it was necessary to determine the amount acid present in the bleached oils by titrating portions of oil with 0.1M ethanolic potassium hydroxide solution using phenolphthalein indicator. The titres obtained were used to calculate the acid values presented in Table 2 for the clays used.

Table 2: The average acid values

	Unbleached oil	A10	A20	A30	B10	B20	B30
Acid value							
Cotton oil	271-279	270- 279	272-277	275-282	272-278	275-278	276-290
Sunflower oil	281-283	280-283	282-287	281-289	281-284	283-287	283-288

The calculated acid values showed that the acidity in sunflower oils is largely due to oleic acid as the average value for acids is in the range close to the molar mass of 282 for oleic acid. The calculated acid values for cotton-seed oil correspond to average value for linoleic acid, molar mass 279. The acid values for the unbleached and bleached oils are almost constant showing that bleaching did not cause the triglycerides to hydrolyze (Girrgis, 2005). Similarly, it was reported that acid values for vegetable oils were not affected by the bleaching procedure, but a slight shift in the absorption maximum of the bleached cottonseed oil was observed (Falaras, et al 1999; Girgis; 2005).

It was also reported that if vegetable oils are bleached at elevated temperatures and in presence of water, there occurs significant rise in levels of free fatty acids because the triglycerides are hydrolyzed by the water present in clays or oils or significantly dissociate when heated at temperatures as high as 200°C (Mag, 1990). Basing on this, it often necessary to determine the free fatty acid content of vegetable oils bleached with acid-leached clays. Free fatty acids give a bitter taste to the oil, which is undesirable. The data obtained in experiments to deduce the level of acidity of bleached clays has been presented in tabular form in Table 3.

The bleached oils were subjected to determination of free fatty acids (FFAs) content of oils to investigate the effect of bleaching on fatty acid levels in oils. The data tabulated in Table 3; showed that bleaching cotton and sunflower oils had no significant changes on the free fatty acid content of bleached oils as compared to unbleached oils.

Table 3: Percentages of FFA in bleached vegetable oils

	Unbleached oil	A10	A20	A30	B10	B20	B30
FFA%							
Cotton oil	3.5	3.3-3.6	3.4-3.7	3.5-3.8	3.4-3.6	3.6-3.8	3.5-3.9
Sunflower oil	3.7	3.6-3.8	3.7-4.0	3.8-4.1	3.7-3.9	3.6-3.9	3.7-4.0

Because acid leached clay is acidic, the levels of free fatty acid did not rise significantly because this was not favored by the acidity of clay used. It is likely that the surface acidity of the clay matrices greatly retarded dissociation of the triglycerides. The slight increase in level of free fatty acids has been attributed acid activated low degree of hydrolysis of the triglycerides. As the oils feebly ionized in the acidic clay matrices, free fatty acid levels increased insignificantly in the bleached oils because there was little or no water to cause the triglycerides in vegetable oils to hydrolyze and the temperature at which bleaching was performed was low so the triglycerides could not dissociate to give free carboxylic acids (Mag1990). The rise in acidity was automatically checked by the exchange capacity of the clays so it was not significant. The slight rise in free fatty acids with increase in mass percent of acid used to leach the clay is in agreement with the results reported by Girgis (2005); Morgan et al. (1985) and Hoffmann (1989) who reported that free fatty acids increase in the bleached vegetable oils with acid leached earths.

Effect of bleaching of oils on peroxide value

Presence of peroxides and other oxidation products in vegetable oils imparts unpleasant odors and shorten the shelf life of the oil. The bleaching process combines catalytic action such as peroxide decomposition and equilibrium adsorption of pigments from oil (Reddy et al, 2001). The peroxides decompose to volatile aldehydes and ketones due to further oxidation, then they get adsorbed onto clay (Subramanian et al, 1993). Bleaching earths eliminate oxidation products and other impurities from oils (Mag1990; Topallar 1998) and in this way improve the quality shelf life of the oils (De Greyt and Kellen, 2000; Srasra and Trabelshi-Ayedi, 2000). It is therefore necessary to determine the quantities of peroxides that may be still present to find out if bleaching effectively eliminated oxidation products. The data obtained on these experiments has been summarized in Table 4.

The titres obtained during the titration of the iodine liberated when the peroxides in the bleached oil (0.1gm) reacted with potassium iodide in presence of acid were summarily used to calculate peroxide values given in Table 4 for cotton and sunflower oils. The values of the peroxide values were computed using the formula:

$$PV = \frac{1000M(A-B)}{W} \qquad \ldots 1$$

Where A is titre obtained with sample of sodium thiosulphate/$cm^{3.}$

B is blank titre of sodium thiosulphate/$cm^{3.}$

M is molarity of sodium thiosulphate.

W is mass in g of test portion.

The resulting ranges of peroxide values have been summarized in Table 4 below.

Table 4: Peroxide values for oils bleached at 90 °C

	A10	A20	A30	B10	B20	B30
Peroxide value						
Cotton oil	1.0-2.0	0.9-1.7	0.6-1.7	1.1-2.1	0.8-1.7	0.5-1.5
Sunflower oil	1.1-2.1	1.0-2.2	0.8-1.9	1.0-2.2	0.9-1.8	0.4-1.6

As shown in Tables 4 above, the values are negligibly small showing that freshly bleached sunflower and cottonseed oils are fit for human consumption. The reductions found in peroxide values of the cotton and sunflower seed oils after their bleaching with the different kinds of bleaching earths developed in this study agree with those presented by Girgis (2005), Young (1987), Boki et al. (1989) and Mag (1990) who showed that oxidation levels are reduced by the breakdown of hydroperoxide primary oxidation product on the adsorbent surfaces such as bleaching earth (Subramanian et al, 1993). It has been shown that decrease in peroxide value is due to the decomposition of peroxides by the strongest acid sites on the surface of bleaching clay (Boki et al 1989; Garido et al, 1994; Reddy et al, 2001). It is expected that peroxide values rise when the oils are stored for long to due to oxidation by air and this encourages rancidity. The primary oxidation products got removed significantly to lower levels as the concentration of the leaching medium increased. The peroxide values in Table 4 above decrease as the mass percent of acid used to leach the clay increases because the efficiency of adsorption of oxidation products is increased by increase in mass percent of the acid used to leach the clay (Boyd, 1988; Khor, 1997; Mukasa-Tebandeke, 2014; Wei , 2004). When the concentration of acid used to leach the clays is low, satisfactory removal of vegetable oil oxidation products is achieved. But when the concentration is increased, the peroxide values tend to zero. It was reported that when medium activation of the clay like treatment of Ca-montmorillonite with 4 N H_2SO_4, was found most effective in bleaching the cottonseed oil, resulting in the best color index and the lowest peroxide value (Falaras, et al 1999). To evaluate efficiency of bleaching required measurements peroxide value, free fatty acid content, iron concentration, and conjugation values (Mag, 1990).

Effect of bleaching of oils on iodine value

Vegetable oils are unsaturated containing double C=C bonds. The level of unsaturation of the oils may be expressed by the iodine values or numbers. Iodine numbers of bleached oils have been presented in Table 5 and used to identify the dominant acid in the oils. To test the efficiency of bleaching, determination of iodine value or number for conjugation values of the bleached oils was essential (Mag, 1990). Iodine value is proportional to molar mass of the fatty acid present in oils. The titre values for the blank and iodine solutions generated when iodine solution ($25cm^3$) was added to bleached oil sample (1g) which had been dissolved in trichloromethane ($15cm^3$) and the resulting mixtures separately titrated with 0.1M sodium thiosulphate solution after adding water and potassium iodide solution and labeled basing on oil bleached. Using the average titres obtained from titration and applying the formula below, the iodine values (Iv) were calculated and summarily presented in Table 5 as shown below.

Iodine value is given by:

$$Iv = \frac{12.69T(V3-V4)}{M}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..2$$

T is exact molarity of sodium thiosulphate = 0.1M.

V3 is number of cm^3 of $Na_2S_2O_3$, used on blank test.

V4 is number of cm^3 of $Na_2S_2O_3$, used on test portion.

M is mass of test portion in grams.

Table 5: Iodine values for oils bleached at 90 ^oC

	A10	A20	A30	B10	B20	B30
Iodine value						
Cotton oil	107-110	108-111	107-115	108-112	108-110	107-114
Sunflower oil	110-128	109-133	112-130	109-135	109-133	109-135

The iodine values for the vegetable oils bleached with raw and acid leached clays are low and are in same range showing that the structures of oils change negligibly as a result of bleaching.

The data adduced in this study compares very well with the internationally published data on iodine values of oils by journal of American oil Chemists in which the iodine value for cotton-seed oils lies in the range 108-110 and for sunflower oils it is in 109-135 range. This data has been deduced to indicate that the acid of formula $CH_3(CH_2)_7CH=CH(CH_2)_7COOH$, oleic acid is dominant in cotton oils yet the acid of formula $CH_3CH_2(CH=CHCH_2)_3(CH_2)_6COOH$, linolenic acid is dominant in sunflower oil (Firestone, 1993; Firestone D, 1993). The data in Table 6 lacks molecular masses 232 and 270 and so it gives similar inferences those reported by Girgis (2005), Morrison (1975), Hoffmann (1989) and Topallar (1998) who cited that bleaching increases the level of conjugated trienes and reduces the content of conjugated dienes as these have molar masses lying in range of 232 and 270.

CONCLUSION

The content of iron in cotton oil decreased by 66.4 % when bleached with iliri clay leached in 30% hydrochloric or sulfuric acids yet that in sunflower fell by 62.9 and 60.0% when respectively bleached in 30% hydrochloric and sulfuric acid. The content of copper in cotton oil decreased by 82.5 % when bleached with Iliri clay leached in 30% hydrochloric acid and

85.0% for 30% sulfuric acid leached clay. That in sunflower fell by 73.3% when bleached with clay leached 30% hydrochloric acid and 83.3% when bleached with 30% sulfuric acid. So the percentage decrease in copper content was higher than for iron. The percentage decrease in content of iron was highest for cotton and sunflower oils bleached using clay leached in 30% sulfuric acid (Mbah et al 2005).

The acid values showed that the acidity in sunflower oils is largely due to oleic acid; yet cotton-seed oil corresponded to linoleic acid. So the bleached oils contain different free fatty acids. The levels of free fatty acid were found to lie in range from 3.8-32 for all clays used showing no significant rise in acidity resulted from bleaching. The peroxide values of bleached oils lay between 1.2 and 0.8 showing that freshly bleached oils are fit for human consumption.

RECOMMENDATIONS

Iliri clay being a na-bentonite (montmorillonite) should be tested for surface properties to establish if acid leaching alters the clay structure. Isolation and purification of the clay should be carried out to confirm the components present in clays at Iliri. Survey must be carried out to establish quantity of this clay. The clay needs to be tested in industrial settings to pave way for Uganda’s bentonite industry.

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