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Research Article
Use of Carbonized Seed Hulls as Alternative to Bleaching Clay During Miscella Bleaching of Oils

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Abstract
Soybean oil (SBO) was miscella bleached in hexane using carbonized hulls of Jojoba (Jo), Jatrova (Ja), Peanuts (PN) and Pistachios (P) as alternatives to bleaching clays. Evaluation of bleached crude SBO with carbonized hulls was based on their delta-Free Fatty Acids (ΔFFA), reduction in Peroxide Value (PV), carotenoid content, color index and bleachability. Fuller's Earth (FE) and Tonsil N (TN) were used for comparison with the carbonized hulls. Three oil: hexane ratios, 1: 0.5, 1:1 and 1:1.5 by volume and at Room Temperature (RT) and 50°C were used. It was found that oil hydrolysis during miscella bleaching and using seed hulls was very little in all treatments resulted in ΔFFA% between 2.65-3.12 at RT and 2.69-3.09 at 50°C compared to 3.29 ΔFFA% of crude SBO. The results proved that highest reduction in PV was achieved at 50°C and an oil to hexane ratio1:1.5 reaching 73.89 reduction percentage when using PN hulls. Also, Jo hulls resulted in more reduction in PV than FE under all conditions. Whereas Ja, PN and P gave more reduction percentage than TN in all cases. Concerning the effect, of using seed hulls in bleaching SBO, on carotenoid content the results showed that Jo and Ja gave the highest reduction in carotenoid content at oil to hexane ratio of 1:1 and at RT in comparison to the other hulls, TN and FE. Regression analysis indicate a polynomial correlation between the oil characteristics (ΔFFA%, reduction percentage in PV, carotenoid content and bleachability with the three oil: hexane ratios at the two temperatures, RT and 50°C, with r = 1. This study proved that miscella bleaching with carbonized hulls resulted in oils with less FFA, less PV and less carotenoids than the crude SBO. It also proved that it cannot act as a single bleaching agent by itself but it can be bleached with other clays.

Key words: Miscella bleaching, carbonization jojoba, Jatrova, peanut and pistachio hulls, crude soybean oil

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Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Bleaching is an essential step in the process of the production of edible vegetable oils. Bleaching is the process of adsorption of mainly coloring matter (pigments) and other minor constituents of vegetable oils used. During the bleaching of vegetable oils peroxides are degraded and removed, traces of soap and a portion of Cu and Fe are removed and traces of phospholipids are adsorbed. The resistance of oil to rancidity is reduced because some of the natural antioxidants such as tocopherols are removed and partial hydrolysis of the oil takes place (Patterson, 1992; Hui, 1996; Omar *et al*., 2003).

Natural, neutral or non-activated bleaching clays are derived from clay mineral deposits "Bentonite". The clays used in the edible oil industry range from natural neutral clays to heavily acid activated clays. Carbonaceous adsorbents may be classified into two main classes, chars or activated carbons. Chars are the carbonization products from wood, fruit shells, seed hulls, brown coals, lignites, bone char and a range of other natural materials and highly volatile coals. Gnanasambandam *et al*. (1998) produced carbon adsorbents from soybean hulls by pyrolysis and used it to bleach crude soybean.

There is growing interest in using low cost materials for adsorption as an alternative to activated carbons. A suitable adsorbent has to meet the following criteria: it must have a high affinity and high adsorption capacity for the adsorbate; it must result from a safe and economically viable treatment, it must be renewable, if possible.

Seed hulls are attractive low cost materials. Peanut hulls proved to be good adsorbents in the industry. They are good adsorbents for the removal of metals from wastewater (Periasamy and Namasivayam, 1994; Brown *et al*., 2000), the removal of cationic dyes from aqueous solutions (Gong *et al*., 2005). Omar *et al*. (2003) reported cottonseed, peanut, sunflower, soybean, faba beans and lupines hulls, to be potential alternatives to bleaching clays, especially when acid activated. Other research studies reported the use of carbon in processing sesame oil miscella (Toro-Vazquez and Rocha-Uribe, 1993).

In the vegetable oil industry, carbonaceous materials are used either as a small part of readymade mixtures with bleaching clays, where the ratio of the carbon does not exceed 5-10% of the weight of the clay, or by bleaching with activated carbon prior to bleaching with the clay (Patterson, 1992). Carbon is used in addition to clay because they are highly selective to phospholipids, thus leaving the adsorption sites on the clay free for the pigment adsorption (Gnanasambandam *et al*., 1998). Active carbon also possess a high capacity to adsorb polycyclic aromatic hydrocarbons to which activated clays are not similarly effective (Patterson, 1992). All the bleaching clays used in the egyptian oil industry are imported thus posing a big load of hard currency for a developing country like Egypt. It would be very advantageous if part of the imported clays can be replaced by locally available carbonaceous materials.

Two unconventional oilseeds planted recently in Egypt are Jojoba and Jatrova. They are non-edible oils with a hard shell, which is discarded and pose a problem to get rid of them. Because of the low price of seed hulls and their availability it seemed worthwhile to investigate their power in the bleaching process. Hassanein *et al*. (2011) using carbonized peanut hulls during bleaching, they recommended miscella bleaching over the conventional. Thus it seemed worthwhile to investigate the ability of some seed hulls in miscella bleaching of soybean oil.

The aim of this study was to evaluate carbonized hulls of Jo, Ja, PN and P (as alternative to bleaching clays) in miscella bleaching of crude SBO. Miscella bleaching was carried out using three different oil: hexane ratios (1:0.5, 1:1 and 1:1.5, v/v) and at room temperature, about 25°C and 50°C. A comparison of the results of miscella bleaching with the four carbonized hulls and with two standard bleaching clays, Fullers earth and Tonsil N, was done. Evaluation of the bleached oils was done on the basis of their free fatty acid content, peroxide value, carotenoid content, color index and bleachability.

MATERIALS AND METHODS

Materials: Jojoba (Jo), Jatrova (Ja), Peanuts (PN) and Pistachios (P) were brought from the local market. All seeds were manually dehulled and the hulls were washed well with distilled water, dried in an oven at 100°C over night, ground in a ball mill and sieved to pass a mesh size screen of 100 µm. Freshly extracted soybean oil (SBO) was supplied in 2014 from Agricultural Research Centre, Cairo, Egypt (2014) and dried over anhydrous sodium sulphate. Fuller's Earth (FE) a product of BDH Chemicals Ltd. Liverpool, England; Tonsil N (TN) is a products of Süd Chemie, A.G., München Germany.

Methods

Carbonization of hulls: Dry ground hulls were placed in aluminium crucibles in a muffle furnace that was previously heated to the desired temperature, under a limited supply of air. The investigated temperature was 500°C and the time of carbonization was 30 min (the best conditions reported by

Hassanein *et al.* (2011). The carbonized hulls were cooled and kept in desiccator until use (Gnanasambandam and Proctor, 1997; Omar *et al.*, 2003).

Bleaching experiments: Basic experiments of bleaching comprises: a sample of soybean oil (SBO, 20 g of FFA 3.29%, PV 13.5 meq kg^{-1} and Carotenoids 84.48 ppm) was stirred together with 0.4 g of the carbonized seed hull samples or bleaching earth (2% wt. of oil) in a rotary evaporator (BUCHI Labortechnik AG) at Room Temperature (RT) and at 50°C in a hot water bath under reduced pressure for 20 min. The oil was then filtered through a Whatman No. 2 filter paper to remove carbonaceous adsorbent or bleaching earth (Gnanasambandam and Proctor, 1997; Omar *et al.*, 2003). Bleaching experiments were carried out using the following clays: (TN and FE) and the following samples of carbonized hulls of Jo, Ja, PN and P.

Miscella bleaching was carried out as in the above conventional bleaching method but at room temperature (RT, ca 25°C) and at 50°C, with an oil to hexane ratio 1:0.5, 1:1, 1:1.5 (v/v) according to Megahed (2002) and Hassanein *et al.* (2011).

Analysis

Acid value: The acid value is the number of milligrams of potassium hydroxide necessary to neutralize free acids in one gram of sample (AOCS., 1998).

Peroxide value: Peroxide value is milliequivalents of peroxide per 1000 g of sample, which oxidize potassium iodide under the conditions of the test. It is determined iodometrically according to standard methods for oils analysis and the results were expressed in meq kg^{-1} oil (AOCS., 1998).

Carotenoid contents: Carotenoid contents in the samples were analyzed by ultraviolet-visible spectrophotometer at 446 nm using MPOB test method (Dauqan *et al.*, 2011).

Color index and bleachability: Color index and bleachability were calculated according to Hassanein *et al.* (2011).

Calculations:

- The percentage of ΔFFA = [percentage of FFA in crude oil-percentage of FFA of bleached oil/ percentage of FFA in crude oil]×100
- Reduction percent in PV= [(PV of crude oil−PV of bleached oil)/PV of crude oil]×100
- CI = [the sum of 16 readings from 400-550 nm]×10
- Bleachability percent= [CI of crude oil−CI of bleached oil)/CI of crude oil]×100

Bleaching experiments were replicated twice and analysis of resulting oils were carried out in triplicates.

Statistical analysis: All determinations were carried out in triplicates and values were expressed as Means±Standard Deviation (SD). Significant statistical differences of investigated parameters were determined and analyzed using one way analysis of variance (ANOVA PC-STAT, 1985 Version IA copyright, University of Georgia). A confidence interval at the 95% level and a probability (p) value less than 0.05 were considered statistically significant at 5% significance level ($p<0.05$).

Regression analysis is concerned with describing and evaluating the relationship between a given variable (usually called the dependent variable) and one or more other variables (usually known as the independent variables). The independent variable is typically the variable being manipulated or changed and the dependent variable is the observed result of the independent variable being manipulated. Regression analysis models are used to predict the value of one variable from one or more other variables whose value can be determined. It is also used to predict which among the independent variables are related to the dependent variable and to explore the forms of these relationships. Linear regression is a statistical technique for fitting a straight line to a set of data points. The general form is:

$$Y= a+b.X+u$$

where, Y, is the value we are trying to predict, X, is the value we are using to predict, a is the intercept, b is the slope, u is the regression residual.

Polynomial regression fits data to this equation:

$$Y = A+B.X+ C.X^2+D.X^3$$

You can include any number of terms. If you stop at the second (B) term it is called a first order polynomial equation, which is identical for a straight line. Regression analyses were performed using SPSS Software version 13.0 for Windows; SPSS Inc., IL, USA, with $p<0.05$ regarded as statistically significant.

RESULTS AND DISCUSSION

Effect of miscella bleaching using carbonized hulls on the reduction of free fatty acid of bleached crude SBO: The seed hulls included in this study comprises: Jojoba (Jo), Jatrova (Ja), Peanuts (PN) and Pistachios (P) hulls together with Tonsil N clay (TN) and Fuller's Earth (FE) used as bleaching agents in the industry, for comparison. Miscella bleaching was carried out at two temperatures including, RT and 50°C and at three oil: hexane ratios 1:0.5, 1:1 and 1:1.5 (v/v).

It is well known that during bleaching partial hydrolysis of the oil takes place due to the acidic nature of the clays (Patterson, 1992; Hui, 1996; Omar *et al*., 2003). In contrary to this statement, it is clear from Table 1 that the oil hydrolysis during miscella bleaching was very little in all treatments resulted in ΔFFA% between 2.65-3.12 at room temperature and 2.69-3.09 at 50°C, compared to 3.29 ΔFFA% of the crude soybean oil. This result is probably due to the carbonized hull surface which is neutral, thus slight or no hydrolysis takes place. Omar *et al*. (2003) investigating seed hulls that were subjected to acid activation, steaming and carbonization, found that carbonized samples that possess neutral surfaces resulted in least hydrolysis of the oil. Hassanein *et al*. (2011) also reported least oil hydrolysis when bleaching cottonseed oil with peanut hulls. Proctor and Harris (1996) and Gnanasambandam and Proctor (1997), reported using carbonized soy hull to bleach soybean oil. Their results also show that free fatty acid content of the bleached oils decreased over those of crude oil. These results are in agreement with our results.

Effect of miscella bleaching using carbonized hulls on the reduction of PV of bleached crude SBO: A peroxide is a compound containing an oxygen-oxygen single bond or the peroxide anion, O_2. The O-O group is called the peroxide group or peroxo group. In contrast to oxide ions, the oxygen atoms in the peroxide ion have an oxidation state of −1 (https://en.wikipedia.org/wiki/Peroxide).

Detection of peroxide gives the initial evidence of rancidity in unsaturated fats and oils. Other methods are available but peroxide value is the most widely used. It gives a measure of the extent to which an oil sample has undergone primary oxidation. The peroxide value is the amount of peroxide oxygen per one kilogram of fat or oil and is a measure of the extent to which rancidity has reached (https://en.wikipedia.org/wiki/Peroxide_value).

Bleaching causes peroxides to decompose and one measure of the effectiveness of the bleaching process may be the peroxide value (Hui, 1996). Table 2 represents the reduction percentage in PV during bleaching of soybean oil with the four examined carbonized seed hull as well as FE and TN for comparison. The results in Table 2 reveal an appreciable reduction in the PV of all the oil samples resulting from miscella bleaching. There is a significant difference at ($p<0.05$) between almost all treatments, between different hulls at the

Table 1: Effect of miscella bleaching on the Δfree fatty acid percentage of crude soybean oil bleached with carbonized hulls at room temperature and 50°C and at three oil: Hexane ratios 1:0.5, 1:1 and 1:1.5 (v/v)

	RT			50°C		
Samples	1:0.5	1:1	1:1.5	1:0.5	1:1	1:1.5
FE	2.99±0.01[a]	3.05±0.01[b]	2.98±0.03	2.79±0.01[d]	2.74±0.003[d]	2.91±0.04[ab]
TN	2.77±0.01[b]	2.65±0.03[d]	2.86±0.11	2.88±0.02[c]	2.99±0.04[b]	2.89±0.07[bc]
Jo	2.77±0.02[b]	2.83±0.04[c]	2.82±0.02	3.02±0.03[b]	3.04±0.01[a]	2.79±0.02[de]
Ja	2.98±0.01[a]	3.12±0.01[a]	2.88±0.004	3.09±0.01[a]	3.04±0.02[a]	2.85±0.04[cd]
PN	2.75±0.03[b]	2.80±0.032[c]	2.80±0.01	2.82±0.03[d]	2.84±0.01[c]	2.83±0.00[de]
P	2.75±0.00[b]	2.68±0.06[d]	2.96±0.35	2.69±0.05[e]	3.03±0.00[a]	2.8±0.01[de]

Acid value of crude soybean oil (SBO) = 6.58±1.09E-15, %FFA = 3.29, [a-e]Means with the same small letters superscripts within the same column are not significantly different, Significance level ($p<0.05$), RT: Room temperature, FE: Fuller's earth, TN: Tonsil N, Jo: Jojoba, Ja; Jatrova, PN: Peanuts. P: Pistachio

Table 2: Effect of miscella bleaching on the reduction percentage of peroxide value of crude soybean oil bleached with carbonized hulls at room temperature and 50°C and at three oil: Hexane ratios 1:0.5, 1:1 and 1:1.5 (v/v)

	RT			50°C		
Samples	1:0.5	1:1	1:1.5	1:0.5	1:1	1:1.5
FE	24.20±2.013[d]	18.74±0.65[cd]	54.80±1.19[c]	27.20±3.59[e]	48.82±1.00[bc]	63.17±1.93[c]
TN	36.86±0.44[a]	16.73±3.03[d]	47.89±1.04[d]	37.62±0.63[d]	33.99±2.03[e]	70.88±0.59[ab]
Jo	37.89±0.02[a]	55.83±2.36[a]	64.89±0.11[a]	55.69±0.104[a]	49.97±1.02[b]	69.38±0.34[b]
Ja	29.68±0.02[c]	52.29±0.89[b]	53.18±0.25[c]	44.97±4.15[c]	47.16±0.96[c]	63.78±2.04[c]
PN	34.22±0.98[b]	53.11±2.08[ab]	54.99±1.92[c]	50.89±1.83[b]	55.23±1.19[a]	73.89±0.07[a]
P	34.18±0.84[b]	20.59±1.14[c]	58.89±0.52[b]	53.71±1.25[ab]	42.74±0.53[d]	60.99±3.44[c]

Peroxide value of crude soybean oil (SBO) = 13.5±0.05, [a-e]Means with the same small letters superscripts within the same column are not significantly different, Significance level ($p<0.05$), RT: Room temperature, FE: Fuller's earth, TN: Tonsil N, Jo: Jojoba, Ja; Jatrova, PN: Peanuts. P: Pistachio same oil: Hexane ratio and between the three oil: hexane ratios for the same hull, bleached at room temperature and at 50°C. Highest reduction percentage in PV was achieved at 50°C and an oil to hexane ratio 1:1.5 reaching 73.89 reduction percentage in PV when using PN hulls. Results demonstrate that Jojoba hulls resulted in more reduction in PV than FE under all conditions. When comparing reduction percentage in PV for all samples bleached using Ja hulls with TN it can be said that most of the samples were better than the TN. The same can be said for PN and P hulls. Many authors reported that bleaching has a positive effect on PV of the bleached oil (Gnanasambandam and Proctor, 1997; Aly and Girgis, 2000; Hassanein *et al*., 2011). Boki *et al*. (1989) studying the effects of filtering through bleaching media on decrease of peroxide value of autoxidized soybean oil. Sixteen kinds of filtering and bleaching media were employed. The standard activated clay was the most effective in decreasing the peroxides in autoxidized soybean oil. The relations between the decrease of PV and the physical or the chemical properties of the media were examined. It was found that peroxides are reduced in proportion to the amount of acid at the highest acid strength range +1.5-5.6 rather than amount of acid at the lower acid strength range, total amount of acid or specific surface area.

The Brooks *et al*. (2013), described as a process of mixing oil and clay adsorbent to remove color, the bleaching operation effectively removes some of the color, reduces the contents of chlorophyll, residual soap and gums, trace metals, oxidation products and indirectly impacts on deodorized oil color. While, the bleaching process appears to be a simple mixing of adsorbent and oil followed by filtration, the chemical and physical reactions occurring are complex.

Effect of miscella bleaching using carbonized hulls on Carotenoid content of bleached crude SBO: Bleaching is a critical step in oil refining due to the reduction of impurities such as color and oxidation products namely hydroperoxides (Agatemor, 2008; Foletto *et al*., 2011). Removal of these substances is essential in the refining of oils as it improves the stability and the sensory quality of the oils (Agatemor, 2008). Improvement in color is due to the removal of organic compounds such as carotenoids, especially *beta*-carotene and their derivatives, xanthophylls, chlorophyll, pheophytin, gossypol and their degradation products, that impart undesirable color to the oils (Agatemor, 2008). This removal is usually achieved by adsorption of these color pigments on to an adsorbent such as activated bleaching earths, a clay that have been widely used in the oil industry.

Table 3 demonstrates the effect of miscella bleaching on carotenoid content of soybean oil bleached with four carbonized seed hulls and under different conditions. Miscella bleaching of soybean oil resulted in highest adsorption of carotenoids content from 31.42-37.86 ppm when TN was used, compared to 84.48 ppm in crude SBO. The PN and P hulls adsorbed least amount of carotenoids at 1:1 and 1:1.5 oil: hexane ratio and bleaching at room temperature. Adsorption of carotenoids on TN resulted generally in higher adsorption than the other seed hulls. Thus the studied seed hulls are not recommended as alternatives to bleaching clays. No literature was found on the adsorption of carotenoids by seed hulls.

Afshar *et al*. (2014) working on the bleaching of vegetable oils with press mud obtained from sugar industry. They examined the effect of bleaching with the press mud on soybean, canola and sunflower oils. They reported that in all oil samples *beta*-carotene contents significantly decreased after bleaching with 1 and 2% of adsorbents. Bleaching efficiency varied depending on the experimental parameters, namely adsorbents type, activation method and dosage. Egbuna and Omotioma (2013) activated the clay obtained from Inyi in Oji River Province of Enugu State using tetraoxosulphate (VI) acid. The results of the characterization of the clay showed it to be montmorillonite with more of metallic oxides than the standard activated Fulmont AA bleaching earth. The physical properties of Bulk density, moisture content, percent of non clay residue and ignition and

Table 3: Effect of miscella bleaching on the carotenoid content (ppm) of crude soybean oil bleached with carbonized hulls at room temperature and 50°C and at three oil: Hexane ratios 1:0.5, 1:1 and 1:1.5 (v/v)

	RT			50°C		
Samples	1:0.5	1:1	1:1.5	1:0.5	1:1	1:1.5
FE	66.02 ± 0.59^{e}	74.41 ± 0.91^{b}	71.54 ± 1.06^{c}	64.70 ± 0.72^{d}	69.85 ± 0.91^{a}	65.41 ± 0.89^{e}
TN	37.86 ± 1.05^{f}	34.84 ± 0.96^{e}	32.50 ± 1.02^{d}	34.45 ± 0.98^{e}	31.42 ± 0.90^{f}	33.63 ± 0.96^{f}
Jo	76.25 ± 0.92^{a}	29.54 ± 0.89^{f}	79.69 ± 1.02^{b}	75.26 ± 1.17^{a}	73.31 ± 0.86^{b}	80.70 ± 1.09^{a}
Ja	71.34 ± 1.23^{c}	37.44 ± 1.06^{d}	80.33 ± 0.85^{b}	73.36 ± 1.09^{b}	69.26 ± 0.99^{c}	74.45 ± 1.11^{b}
PN	74.27 ± 1.06^{b}	81.57 ± 1.04^{a}	81.43 ± 0.95^{ab}	76.55 ± 1.01^{a}	63.67 ± 1.07^{e}	72.61 ± 0.96^{c}
P	68.81 ± 1.15^{d}	72.55 ± 0.97^{c}	82.51 ± 1.06^{a}	70.50 ± 0.99^{c}	67.46 ± 0.95^{d}	67.39 ± 0.90^{d}

Carotenoids content in crude soybean oil (SBO) = 84.48±1.03 ppm, [a-f]Means with the same small letters superscripts within the same column are not significantly different, Significance level ($p<0.05$), RT: Room temperature, FE: Fuller's earth, TN: Tonsil N, Jo: Jojoba, Ja; Jatrova, PN: Peanuts. P: Pistachio the chemical properties like silica, alumina and ferric oxide were found to be in agreement with the standard values. However, the metal oxides were found to be somewhat higher than the standard values, although, with little or no contribution to the bleachability of the activated clay. The bleaching performance of the activated clay in terms of color reduction (carotenoids) showed that it is a veritable material in the bleaching of palm oil. It was observed that acid addition increases the bleaching efficiency of activated clay (Egbuna and Omotioma, 2013; Afshar *et al*., 2014).

Effect of miscella bleaching using carbonized hulls on the Color Index of bleached crude SBO: The color scale of edible oils may not seem like an important factor in the quality of oil products. In truth, consumers rarely notice the color of the edible oils they are using, until that color scale starts to show variations. Even slight changes in color indicate to consumers that something is not right with their product or that the quality has changed, even if the integrity of the oil remains the same. Color is a huge factor in consumer opinion and choice and maintaining an even color scale in the production of edible oils is an important step in process monitoring and quality control.

When measuring oil color, the chemical compounds that are present in the sample often exhibit specific color attributes. These differences can easily be detected with spectrophotometers using a color scale that bases its measurements on both visible and ultraviolet (UV) spectroscopy. A color scale for specific compounds such as chlorophyll will be in the green color range on the color scale and can be used to indicate final color outcome. Chlorophyll detection in oils through UV spectrophotometry has also been linked to measuring and quantifying this compound in relation to the antioxidant health benefits that it provides. This information is valuable for the proper labeling and promotion of these health claims and can increase the value of the product.

Changes in Color Index (CI) and bleachability percentage of miscella bleached crude SBO samples is demonstrated in Table 4 and 5. Definitely all the oils bleached with the seed hulls examined resulted in decrease of the color index of the oils. The TN and FE had a better absorption capacity than the seed hulls examined.

Table 4 showed a significant differences in Color Index (CI) of the oil when treated at RT and at the three oil: hexane ratios for the four seed hulls of: Jo, Ja, PN, P and to the FE and TN used at the same conditions. Another statistical significant differences were noticed in CI at 50°C when FE and TN were used with the three oil: hexane ratios and also for the four seed hulls samples. It can be conclude that with all the three oil: hexane ratios and at RT and 50°C for FE and TN, the CI is

Table 4: Effect of miscella bleaching on the color index of crude soybean oil bleached with carbonized hulls at room temperature and 50°C and at three oil: Hexane ratios 1:0.5, 1:1 and 1:1.5 (v/v)

	RT			50°C		
Samples	1:0.5	1:1	1:1.5	1:05	1:1	1:1.5
FE	386.60±0.52^{e}	396.58±0.57^{c}	376.14±0.63^{e}	396.38±0.56^{c}	388.13±0.57^{bc}	195.92±0.57^{f}
TN	389.24±0.59^{d}	365.03±0.56e	394.13±0.59^{d}	377.03±0.58^{e}	398.41±0.59^{ab}	368.32±0.57^{e}
Jo	428.003±0.59^{a}	398.88±0.56^{b}	396.49±0.58^{c}	405.62±0.58^{a}	395.84±0.58^{c}	399.12±0.57^{b}
Ja	402.96±0.56^{b}	400.84±0.54^{a}	437.43±0.53^{a}	392.84±0.54^{d}	396.54±0.59^{abc}	395.12±0.54^{d}
PN	403.17±0.57^{b}	394.62±0.56^{d}	402.32±0.54^{b}	396.93±0.56^{c}	402.01±0.54^{a}	458.93±0.58^{a}
P	397.74±0.59^{c}	395.83±0.57^{c}	396.91±0.59^{c}	402.89±0.59^{b}	404.40±0.58a	396.94±0.54^{c}

CI of crude SBO= 486.84±0.25, $^{a-f}$Means with the same small letters superscripts within the same column are not significantly different. Significance level (p<0.05), RT: Room temperature, FE: Fuller's earth, TN: Tonsil N, Jo: Jojoba, Ja; Jatrova, PN: Peanuts. P: Pistachio

Table 5: Effect of miscella bleaching on the Bleachability percentage of crude soybean oil bleached with carbonized hulls at room temperature and 50°C and at three oil: Hexane ratios 1:0.5, 1:1 and 1:1.5 (v/v)

	RT			50°C		
Samples	1:0.5	1:1	1:1.5	1:05	1:1	1:1.5
FE	20.86±0.37^{a}	18.84±0.61^{bc}	23.03±0.55^{a}	18.88±0.63^{bc}	20.79±0.54^{a}	19.04±0.83^{b}
TN	19.97±0.64^{ab}	23.66±0.78^{a}	19.12±0.68^{b}	22.99±0.77^{a}	18.76±0.75^{bc}	23.09±0.78^{a}
Jo	17.69±0.75^{c}	18.66±0.79^{bc}	19.02±0.81^{b}	17.04±0.75^{d}	19.05±0.53^{b}	18.02±0.46^{b}
Ja	17.72±0.73^{c}	17.93±0.63^{c}	14.65±0.51^{c}	19.67±0.55^{b}	18.99±0.86^{bc}	19.10±0.52^{b}
PN	17.82±0.67^{c}	19.64±0.84^{b}	18.72±0.57^{b}	19.46±1.00^{b}	17.85±0.63^{cd}	18.93±0.64^{b}
P	18.82±0.73^{bc}	18.86±0.68^{bc}	18.81±0.64^{b}	17.78±0.71^{cd}	17.01±0.47^{d}	18.85±0.62^{b}

$^{a-d}$Means with the same small letters superscripts within the same column are not significantly different, Significance level (p<0.05), RT: Room temperature, FE: Fuller's earth, TN: Tonsil N, Jo: Jojoba, Ja; Jatrova, PN: Peanuts. P: Pistachio almost lower in comparison with that of the four seed hulls used at the same conditions of FE and TN and the all samples were significantly differences.

FE and TN in Table 5 exhibited, in general, higher bleachability than Jo, Ja, PN and P hulls in all conditions. Bleaching crude soybean oil with FE resulted in an oil which was statistically different from the oils resulting from oils bleached with Jo, Ja, PN and P, at RT and 1:0.5, oil: hexane ratio. Miscella bleaching of soybean oil at RT and 1:1 oil: hexane ratio using FE showed no significant difference with oils bleached with the four seed hulls. At RT and 1:1.5 oil: hexane ratio FE treated oil show a significant difference with the four examined seed hulls. Bleachability of oils treated at 50°C and at 1:0.5, 1:1.5 oil: hexane ratio reveal that Jo, Ja, PN, P treated hulls indicated no significant difference with FE while at 1:1 ratio there was a significant difference between FE and the four examined hulls. Comparing bleachability of the oils treated with TN and those treated with the other four seed hulls there was, generally, a significant difference between TN at RT and 50°C and at the three examined oil: hexane ratio. It can be concluded that bleachability percentage (which is the reduction percentage in color of oils) ranged between 17-23.6%. Omar *et al*. (2003) reported higher bleachability reaching 51% for carbonized PN hulls, bleached conventionally. Hassanein *et al*. (2011) reported 38 bleachability percentage for PN hulls carbonized at 500°C for 30 min.

Regression analysis: Results of the correlation coefficient study in Fig. 1-4 where Y represents the oil characteristic examined and X is the oil to hexane ratio. Results in figures (Fig. 1-4) indicate a polynomial correlation between all the oil characteristics (ΔFFA%, reduction percentage in PV, bleachability percentage and carotenoids content) with the three oil: hexane ratios (1: 0.5; 1:1; 1:1.5) at the two temperatures RT and 50°C, with (r = 1).

Figure 1a and 1b, show that there is an effect of temperature on the FFA. Oils bleached with Ja hulls at RT is the only oil that shows increase then decrease with oil: hexane ratio. As for oils bleached at RT with FE, PN and Jo pointed out that the effect of oil: hexane ratio was negligible (Fig. 1a). The P and TN hulls at RT showed a decrease in FFA then a slight increase with the increase in oil: hexane ratio. Oils bleached at 50°C with Jo, Ja and TN indicates an increase in FFA, then a decrease with the increase in oil to hexane ratio. Oils bleached with PN show a straight line relation of FFA of the oils with the oil: hexane ratio (Fig. 1b). Oils bleached with FE revealed

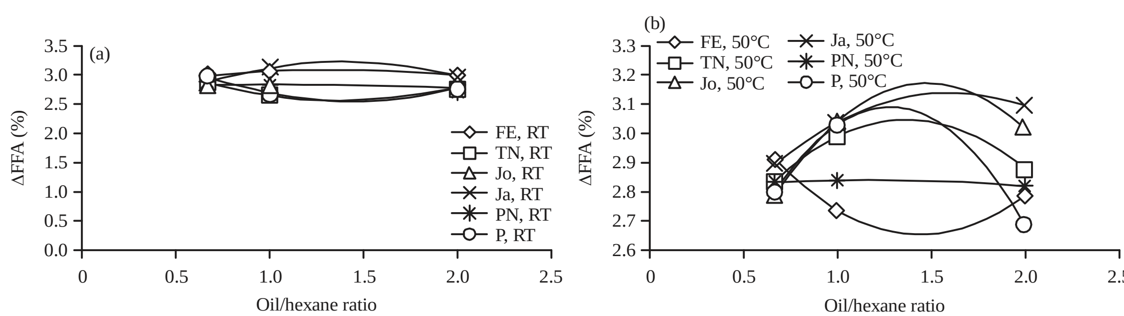

Fig. 1(a-b): Correlation between ΔFFA of crude SBO bleached with four seed hulls at (a) RT and (b) 50°C and at different oil to hexane ratio: 1:0.5, 1:1, 1:1.5 (v/v)

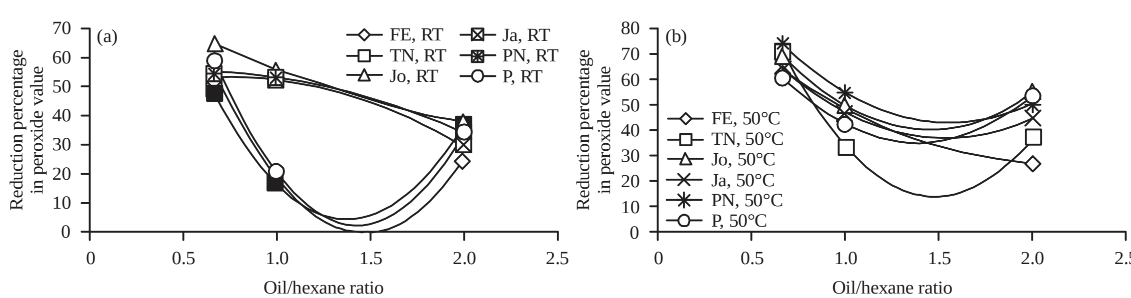

Fig. 2(a-b): Correlation between reduction percentage in PV of crude SBO bleached with four seed hulls at (a) RT and (b) 50°C and at different oil to hexane ratio: 1:0.5, 1:1, 1:1.5 (v/v)

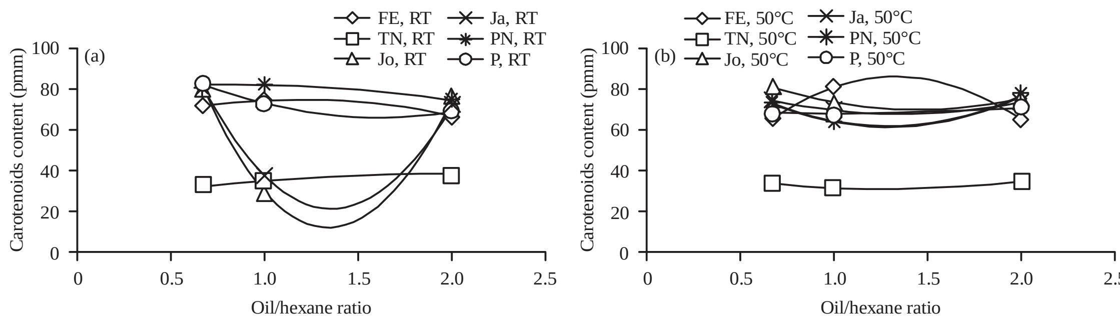

Fig. 3(a-b): Correlation between carotenoid content of crude SBO bleached with four seed hulls at (a) RT and (b) 50°C and at different oil to hexane ratio: 1:0.5, 1:1, 1:1.5 (v/v)

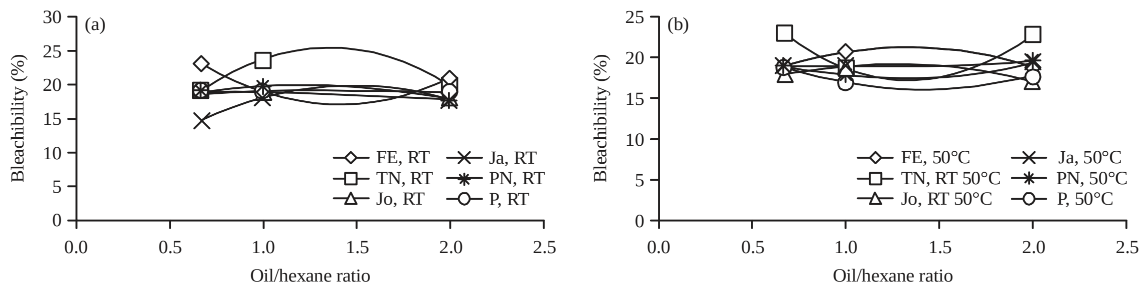

Fig. 4(a-b): Correlation between bleachability percentage of crude SBO bleached with four seed hulls at (a) RT and (b) 50°C and at different oil to hexane ratio: 1:0.5, 1:1, 1:1.5 (v/v)

a decrease then an increase in FFA content with the increase in oil: hexane ratio. As for reduction percentage in PV of oil, FE, TN and P hulls, bleached at RT (Fig. 2a), the oils revealed a decrease, followed by an increase in the reduction percentage of PV of the oils with the increase in oil: hexane ratio. The Ja, Jo and PN hulls caused a constant decrease in PV of bleached oils. Bleaching oils at 50°C (Fig. 2b) indicated that oils bleached with the hulls namely Jo, Ja, PN and P, FE and TN, all caused a decrease in the percentage PV reduction. Highest carotenoids content of oils bleached with hulls at RT (Fig. 3a) were in the following order: Ja>PN>FE>Jo>P>TN. Bleaching at 50°C (Fig. 3b) caused changes in sequence of carotenoid content , where highest content was in oil bleached with PN hulls followed by: Jo>Ja>P>FE>TN. As for bleachability percentage which is a very important criteria for bleached oils results also indicated a difference between bleachability at RT and at 50°C. Best bleached oil at RT (Fig. 4a) were in the following order: FE>TN>P>PN>Jo>Ja. When the bleaching was carried out at 50°C (Fig. 4b) the order of bleachability was changed to: TN>PN>Ja>FE>P>Jo.

CONCLUSION

Oil hydrolysis during miscella bleaching and using carbonized hulls was very little in all treatments. The use of carbonized seed hulls (Jo, Ja, PN and P) could be used in miscella bleaching of vegetable oil when blended with other clays. Highest reduction in PV was achieved at 50°C and an oil to hexane ratio 1:1.5 when using PN hulls. The Jo hulls resulted in more reduction in PV than FE under all conditions, whereas, Ja, PN and P gave more reduction than TN in all cases. Jo and Ja hulls gave the highest reduction in carotenoids at oil to hexane ratio of 1:1 and at RT in comparison with the other hulls, TN and FE. Since carbonization is a simple treatment, it is recommended over other methods of activation, this work proved that the carbonized hulls resulted in oils with less FFA, less PV and less carotenoids than the crude soybean oil. It cannot act as a single bleaching agent by itself but it can be blended with other clays.

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