Journal of Nuts

Journal homepage: ijnrs.damghaniau.ac.ir

Investigation of Soybean Oil Bleaching by Using Walnut Shell

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A R T I C L E I N F O

Keywords:

Adsorbent;
Bleaching;
Soybean Oil;
Walnut Shell

A B S T R A C T

In this research, the application of walnut shell ash, as an adsorbent for soybean oil bleaching, has been investigated. Therefore, neutralized soybean oil was bleached with 1 and 2% of walnut shell ash as well as commercial bleaching earth. Then, a series of chemical tests such as amounts of carotenoids, chlorophylls, peroxide value, and free fatty acid content of bleached oils and oil retention of adsorbents were determined. The results indicated that bleaching with 2% walnut shell ash reduced carotenoids and chlorophyll contents up to 37.46 and 33.4%, respectively. Moreover, the red and yellow colors reduced in the oil bleached with 2% walnut shell ash and reached to 1.23 and 50 Lovibond, respectively. The oil retention by walnut shell ash (36.99%) was significantly lower than commercial bleaching earth (45.33%). Therefore, as a food waste, walnut shell ash can be used alone or in combination with acid activated earths or activated carbons for oil bleaching as a low cost adsorbent.

Introduction

Crude vegetable oils contain some impurities such as free fatty acids, phospholipids, waxes, oxidation products and pigments including carotenoids and chlorophyll that decrease the oil nutritional or technological qualities (Akoh & Min, 2008). Therefore, the refining process consisted of degumming, neutralization, bleaching, and deodorization with the aim of removing these impurities and improving the oil quality is necessary (Naji *et al*., 2009).

The bleaching of oils and fats by the absorption process removes oil soluble pigments or colloidal particles spreadable in oils (Kaynak *et al*., 2004). The most commonly adsorbents used for bleaching edible fats and oils are acid activated earths containing silicates combined with metal oxides such as aluminum, magnesium, calcium, iron, sodium, and potassium activated by sulfuric or hydrochloric acids (Erten, 2004). According to Almeida *et al*. (2019) who compared the mechanisms of adsorption of carotenes from hybrid palm oil onto two kinds of bleaching earths widely used by industrial refiners (acid-activated and neutral), acid activated adsorbent showed micropore volumes twice larger than the neutral. In addition, FTIR analysis of adsorbent after adsorption demonstrated that active site was Si–O–Si for both adsorbents. Acidic activation causes some physical and chemical changes on the surface of adsorbents creating motive to increase the absorption power of the bleaching earths (Hussein *et al*., 2001). Activated carbon is another adsorbent used for oil bleaching but its application has been limited due to higher oil retention and difficulties in filtration that increases process cost.

According to FAO statistical reports, the world production of walnut with shell had been 3.8 million

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Received: 31 December 2019; Received in revised form: 3 March 2020; Accepted: 8 June 2020
DOI: 10.22034/jon.2020.1889666.1076

tonnes in 2017. It is estimated that shell contains about 45-60% of the total weight of walnut (Pragya *et al*., 2013; Hassankhah *et al*., 2017). Almasi *et al*. (2016) stated that walnut shell, as an agricultural waste with low cost, has suitable physical properties for the production of activated carbon. Qui and Yang (2010) proposed that high amounts of lignin in the wooden shell of walnut facilitate creation of activated carbon. Mirzabe *et al*. (2014) also measured physical properties of walnut.

Gao *et al*. (2017) produced activated carbons from walnut shell by fast activation with H_3PO_4 in a spouted bed. It was found that the activated carbons contained more carbonyl groups (C = O), carboxyl groups (COOH), and some P-containing functional group. According to Salehi *et al*. (2016) and Singh *et al*. (2017), the ash composition produced from walnut shell containing SiO_2 and combined with other metal oxides is very similar to bleaching earths.

Almasi *et al*. (2016) used walnut shell as a natural adsorbent for the removal of Reactive Red 2 form aqueous solution. Li *et al*. (2020) studied the adsorption mechanism of Congo red and Methylene blue dyes in aqueous solution through using walnut shell and showed that the adsorption occurred via physical interactions at different temperatures where the removal process was endothermic. Naghizadeh *et al*. (2015) removed NOMs from its aqueous solution using walnut shell modified with Zinc Oxide (ZnO) nano particle as an adsorbent. Jiang (2017) prepared activated carbon from walnut shell to remove it from industrial wastewater. Furtherore, the catalytic activity of the walnut shell ash was investigated in the biodiesel production by the sunflower oil methanolysis by Miladinović *et al*. (2020).

Therefore, the aim of this research is to investigate soybean oil bleaching using walnut shell.

Materials and Methods

Material

The degummed water and neutralized soybean oil and acid activated bleaching earth were obtained from Behshahr Vegetable Oil Co. (Tehran, Iran). Walnut shells were obtained from Pars Rafsanjan Factory (Kerman, Iran). All the chemicals used in this research were purchased from Merck Chemical Co. (Germany) or Sigma Aldrich Co. (USA).

Methods

Preparation of acid activated walnut shell ash

First, the walnut shells were washed with distilled water, dried at 103±2°C, crushed in the mill (Triplex, France), and passed through a 200-mesh sieve. The walnut shell powder was carbonized in air atmosphere and then heated in muffle furnace at 800 °C for 5h. The ash sample was cooled in a desiccator at ambient temperature, and stored in amber glass bottles (Dai *et al*., 2014).

For acid activation, walnut shell ash was mixed with 12 HCl at the ratio of 1:3 (w/v). Suspension was heated with stirring at 80 ± 2ºC for 2h and then diluted with distilled water up to pH reached to 3.5. The slurry was filtered and dried at 103°C. Activated ash was grounded and passed through a 200-mesh sieve (Ghasemi Afshar *et al*., 2014).

Bleaching process of soybean oil

A 1 liter round bottom three-neck quick fit glass equipped with means for agitation, temperature control, and creation of vacuum (9mmHg) was employed during the course of bleaching. One or two percent of acid activated walnut shell ash and commercial acid activated earth employed separately. The adsorbent was added to the oil before the top operating temperature and mixed with the oil at 110°C for thirty minutes. Heating was discontinued after this period; however, vacuum and agitation were continued for further period of fifteen minutes. Bleached oils were filtered under vacuum through a Whatman No. 41 filter paper to remove the adsorbent. Treated oils were stored for further analysis in sealed vessels at 4°C after flushing with nitrogen (Ghasemi Afshar *et al*., 2014).

Physical and chemical tests

A series of physical and chemical tests were carried out on the neutralized and bleached oils according to the British Standard and AOCS Official Methods.

For determining the amounts of carotenoids, the light absorption of oil solution was measured by a UV-visible spectrophotometer at 455 nm and total carotenoid contents based on β-carotene was calculated according to BS 684, UK.

The chlorophyll contents of neutralized and bleached oil samples were determined by the AOCS method (Cc 13d-55) using a UV-Visible spectrophotometer at 630, 670, and 710 nm.

Free fatty acid contents were determined by dissolving the oil in diethyl ether-ethanol (1:1) solution and titration with a standard solution of 0.01 N potassium hydroxide solution in the presence of phenolphthalein by the AOCS method, Cd 3d-63.

Peroxide value was determined immediately after oils bleaching according to AOCS method, Cd 8–53 by dissolving the oil in acetic acid-chloroform (3:2) solution, and titration with 0.01 N sodium thiosulfate solution in the presence of potassium iodide and starch indicator.

Color measurement was carried out by Lovibond Tintometer apparatus in 5.25-inch cell according to AOCS standard method, Cc13e-92.

Oil retention was calculated according to equation (1) (Usman *et al*., 2012).

$$Oil\ Retention\ (\%) = \frac{W1-(W2-W3)}{W1} \quad (1)$$

W1= Weight of filter cake (g)

W2= Weight of bleaching earth (g)

W3= Weight of H_2O (g)

Statistical analysis

All the experiments and/or measurements were carried out in triplicate order. The data were statistically analyzed using the Statistical Analysis System software package on replicated test data. Analyses of variance were performed by ANOVA. Significant differences between the means were determined using the Duncan multiple range test.

Results

Fig. 1 presents the amounts of carotenoids in the neutralized and bleached oil samples. Neutralized soybean oil contains 28.64ppm carotenoids. In all bleached treatments, the amount of these pigments reduced significantly ($p<0.05$) so that the reduction percentage in carotenoids after bleaching with 1 and 2% of commercial acid activated earth reached 48.39 and 60.50%, respectively. Although the commercial bleaching earth efficiency was more than walnut shell ash, the carotenoids reduction percentage by oil bleaching with 1 and 2 % of walnut shell ash were obtained 31.05 and 37.46%, respectively. Moreover, it is observed that in both adsorbents the proportion of 2% of adsorbents resulted in more reduction in carotenoids.

According to Fig. 2, the chlorophyll content decreased in all treatments so that there are significant differences ($p<0.01$) between all samples except oils bleached with 1 % commercial bleaching earth and 2% walnut shell ash.

The reduction percentage in chlorophyll content of oils bleached with 1 and 2% of commercial bleaching earth were obtained 33.63 and 49.98%, respectively. Furthermore, the amount of this pigment reduced up to

27.44 and 33.4% in oils bleached with 1 and 2 % of walnut shell ash, respectively.

Figs. 3 and 4 indicate yellow and red colors of neutralized and bleached oil samples, respectively. Both red and yellow colors reduced by bleaching process and using 2% adsorbent provided more reduction in oil color than using 1 %.

Thus, reduction percentage in yellow color of oils bleached with 2 % of commercial bleaching earth and walnut shell ash were obtained 72.85% and 28.57%, respectively, as compared to 45.71 % and 22.38 % reduction by using 1% of these adsorbents. In addition, the results of the red color of oils were similar to the yellow color, with the most reduction (79.84 %) in oil sample bleached with 2% of commercial bleaching earth. The results show no statistically significant difference between the red color of oil bleached with 1% commercial bleaching earth and oil bleached with 2% walnut shell ash ($p<0.01$).

Figs. 5 and 6 indicate peroxide value and acid value of neutralized and bleached oil samples, respectively.

According to the results, the walnut shell ash adsorbed lower amounts of oil (36.99 %), consequently, less oil waste as compared to commercial bleaching earth (45.10%) (Fig. 7).

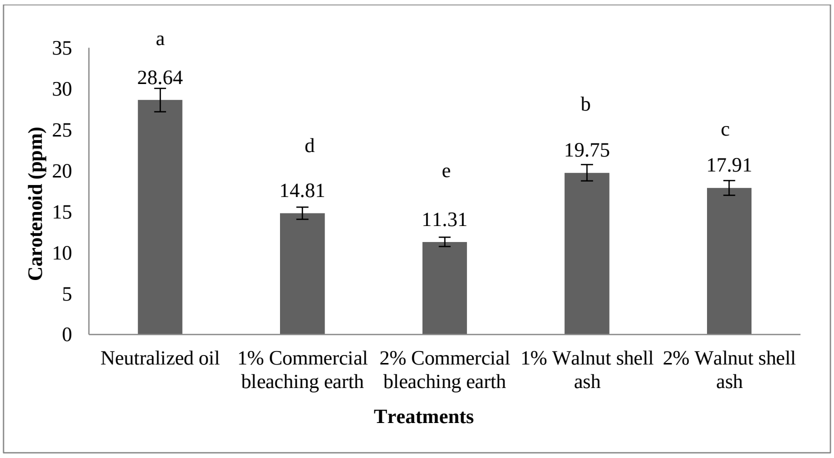

Fig. 1. Carotenoid contents in neutralized and bleached oil samples
Different letters indicate significant differences (P< 0.05).

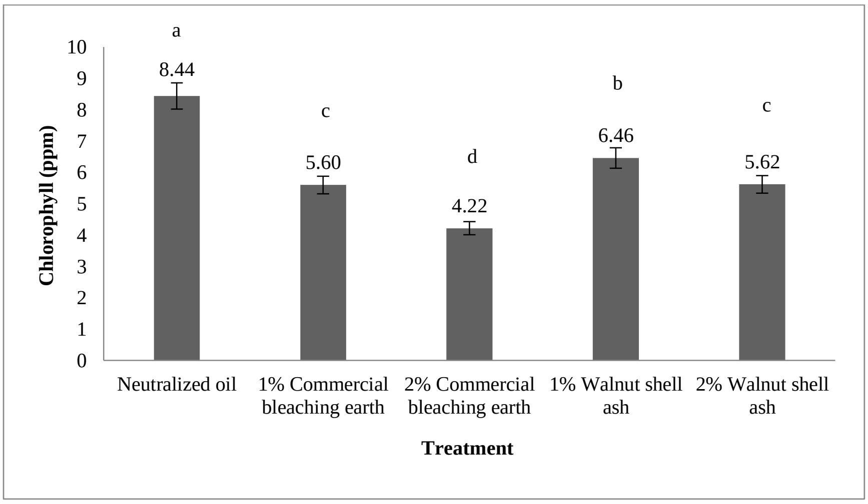

Fig. 2. Chlorophyll contents in neutralized and bleached oil samples
Different letters indicate significant differences (P< 0.05).

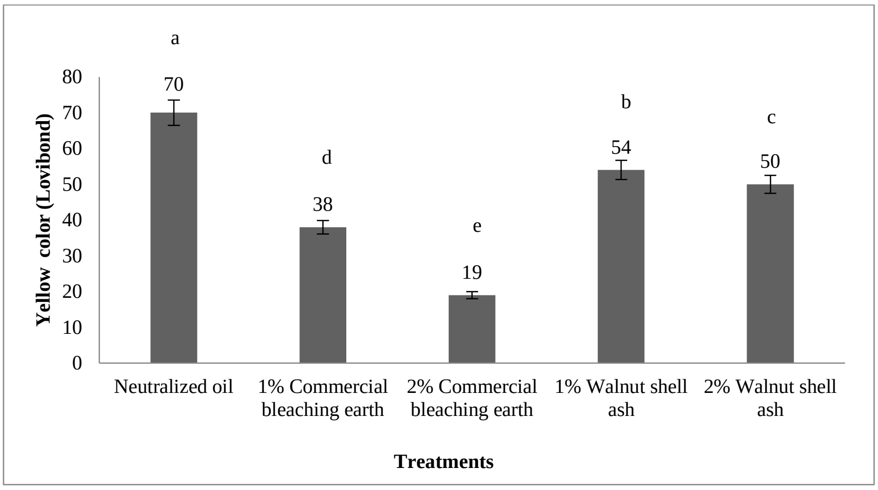

Fig. 3. Yellow color of neutralized and bleached oil samples
Different letters indicate significant differences (P< 0.05).

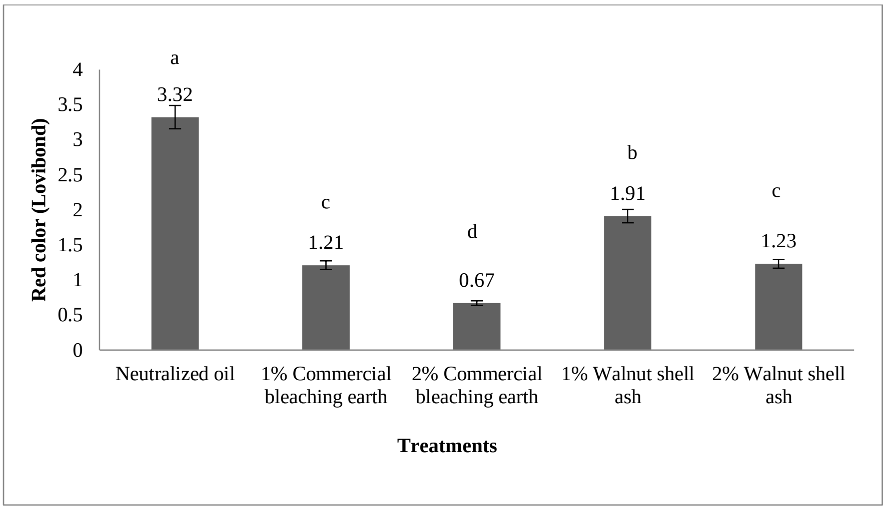

Fig. 4. Red color of neutralized and bleached oil samples
Different letters indicate significant differences (P< 0.05).

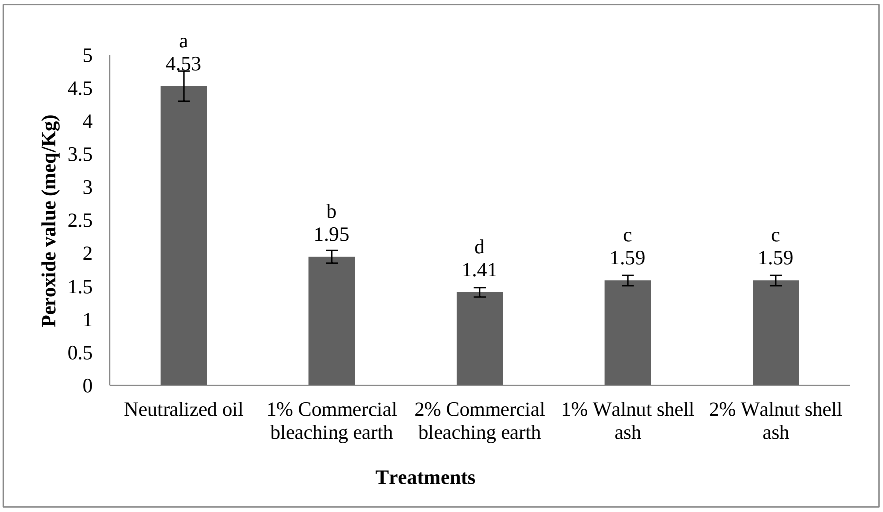

Fig. 5. Peroxide value in neutralized and bleached oil samples
Different letters indicate significant differences (P< 0.05).

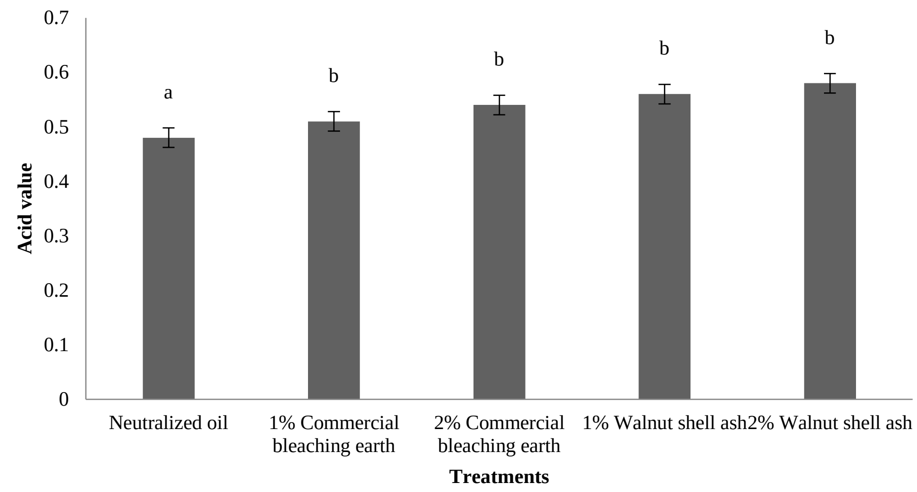

Fig. 6. Acid value in neutralized and bleached oil samples
Different letters indicate significant differences (P< 0.05).

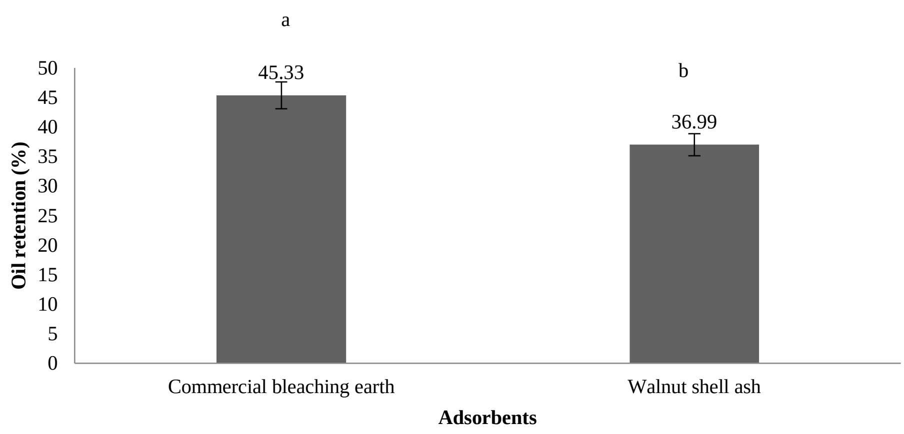

Fig. 7. Oil retention in different adsorbents (%).

Discussion

According to the results, it seems that the removal of carotenoid pigments is due to the reaction between the pigments and the active sites of the adsorbents, where particle size of the adsorbents plays an important role in this reaction (Jummao *et al*., 2008).

Carotenoids are the main responsible factor for the yellow color of oils and fats; therefore, it is expected that the yellow color of the oils will be reduced by removing these pigments during the bleaching process. In addition, it should be noted that the possibility of structural changes of pigments or breaking their molecular bonds due to the presence of hydrogen ions in acid activated adsorbents is affected by color reduction (Mustapha *et al*., 2013).

The presence of chlorophylls is usually undesirable in the oils; since they might be decomposed into pheophytins by heat treatments that consequently the oil becomes opaque and dark (Zheng *et al*., 2017). Moreover, chlorophylls may act as photooxidation sensitizer enhancing the oxidation reaction and production of undesirable flavors. Therefore, one of the aims of oils bleaching is removing these green pigments (Diosady, 2005).

Jung *et al*. (1998) stated that tetrapyrrole ring of chlorophyll structure might be broken by the effect of acidic adsorbents making the oil pale.

Due to the significant reduction in the amounts of chlorophyll and carotenoids by bleaching with the used adsorbents, a decrease in the intensity of yellow and red colors of the oil samples is expected.

Although the main purpose of oil bleaching is to reduce the amount of pigments and the intensity of the oil color, other impurities, particularly oxidation products, decrease during this process. Acceptable limit of peroxide value, primary oxidation product, in soybean oil is 5 meq/Kg. According to Fig. 5, the peroxide value significantly reduced by application of both adsorbents. Based on the results, application of 1% of walnut shell ash had more effective role in reducing of peroxide value than commercial bleaching earth that might be due to selective absorption manner of adsorbent. Besides, it should be noted that peroxide might be decomposed in bleaching process due to high temperature (Tai & Lin, 2007).

As shown in Fig. 6, the acid value of bleached oils increased slightly that might be due to the acidic nature of the used absorbents and their inconsiderable moisture content (Erten, 2004). Although the acceptable limit of acid value in soybean oil is 0.1, minor increasing in free fatty acid contents during oil bleaching does not matter; since these compounds are volatile and removed simply in the next step of refining called deodorization.

Baranowsky *et al*. (2001) estimated 25–45% of oil losses as the result of bleaching with acid activated bleaching earths (Usman *et al*., 2012). Some researchers reported 30-70% oil retention in bleaching earths (Subermanian *et al*., 2001, Erten 2004). It Should be noted that total oil retention depends on a number of variables including adsorbent characteristics (e.g. particle size distribution and mineral type) and its dosage, permeability of the filter bed, incoming feedstock quality, cleanliness of the filter screen and the conditions used to purge the filter before disposal of the “spent” filter cake (Brooks *et al*., 2014).

Conclusions

The results indicated that bleaching with walnut shell ash reduced carotenoid, chlorophyll, red and yellow colors, and peroxide value of soybean oil. Although the results showed the higher efficiency of commercial acid activated bleaching earth than walnut shell ash in bleaching process, oil retention by walnut shell ash was significantly lower than commercial bleaching earth. Therefore, as a food waste, walnut shell ash might be used with alone or in combination with acid activated earths or activated carbons for oil bleaching as a low cost adsorbent.

Acknowledgements

Authors gratefully express their sincere thanks to Razi Research Complex Laboratories, Science and Research Branch, Islamic Azad University (Tehran, Iran), as well as Behshahr Vegetable Oil Co. (Tehran, Iran) and Pars Rafsanjan Factory (Kerman, Iran) for supporting this research.

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