Application of coconut fiber and shell in the bleaching of soybean oil

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SUMMARY: The bleaching process is an important stage in the edible oil refining operation, and is carried out by using acid-activated bleaching earths. The aim of this study was to evaluate the efficiency of coconut fiber ash, shell ash, acid-activated fiber ash and acid-activated shell ash as compared to the commercial bleaching earth in the bleaching of neutralized soybean oil. Bleaching materials were added to neutralized oil at the concentration of 1% (w/v) with agitation under vacuum at 110 °C for 30 minutes. The values for red and yellow colors, carotenoids, chlorophylls, peroxide value, p-anisidine value, free fatty acid contents, copper and iron levels of the bleached samples were determined. The results indicated that all coconut-based adsorbents have been significantly more effective than commercial bleaching earth in reducing color and the greatest reductions in carotenoid (84.25%) and chlorophyll (82.30%) contents were obtained by using acid-activated fiber ash. The peroxide value for all treatments decreased. The amounts of iron and copper as peroxide compounds decreased considerably (44.59% and 23.53%) by using acid-activated fiber ash and acid-activated shell ash, respectively. Therefore, coconut fiber and shell as agricultural wastes which have been ignored in the past might be employed as effective agents to bleach crude oils, particularly soybean oil, in refining operations.

KEYWORDS: Adsorbents; Agricultural waste; Bleaching; Coconut; Soybean oil.

RESUMEN: Aplicación de fibra y cáscara de coco para decolorar aceite de soja. El proceso de decoloración es una etapa importante en la operación de refinación de aceites comestibles que se lleva a cabo utilizando tierras decolorantes activadas con ácido. El objetivo de este estudio fue evaluar la eficiencia de las cenizas de fibra de coco, cenizas de cáscara, cenizas de fibra activada por ácido y cenizas de cáscara activada con ácido, en comparación con la tierra decolorante comercial, en la decoloración de aceite de soja neutralizado. Los materiales de decoloración se añadieron al aceite neutralizado a una concentración del 1% (p/v) con agitación a vacío a 110 °C durante 30 minutos. Se determinaron los valores de colores rojo y amarillo, carotenoides, clorofilas, índice de peróxido, índice de p-anisidina, contenido de ácidos grados libres, niveles de cobre y hierro de las muestras decoloradas. Los resultados indicaron que todos los adsorbentes basados en coco han sido significativamente más efectivos que la tierra decolorante comercial para reducir el color y la mayor reducción en los contenidos de carotenóido (84,25%) y clorofila (82,30%) se obtuvo mediante el uso de ceniza de fibra activada con ácido. El índice de peróxido en todos los tratamientos disminuyó. Las cantidades de hierro y cobre como compuestos peroxidantes disminuyeron considerablemente (44,59% y 23,53%) al usar ceniza de fibra activada por ácido y ceniza de cáscara activada por ácido, respectivamente. Por lo tanto, la fibra y la cáscara de coco como desechos agrícolas que se han ignorado en el pasado podrían emplearse como agentes efectivos para decolar los aceites crudos, particularmente el aceite de soja en las operaciones de refinación.

PALABRAS CLAVE: Aceite de soja; Adsorbentes; Coco; Decoloración; Residuos agrícolas.


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1. INTRODUCTION

The coconut fruit contains three layers: the exocarp, mesocarp, and endocarp. Both the exocarp (the glossy outer skin, usually yellow-green to yellow-brown in color) and the mesocarp (middle fibrous coat, called coir) make up the “husk” of the coconut, while the endocarp makes up the hard coconut “shell” (Emojevwe, 2013). Therefore, the coconut plant has some useful waste materials such as fronds, husk and shell, which have many traditional and commercial uses.

Coir (the fiber from the husk of the coconut) is used in ropes, mats, doormats, brushes, and sacks, brooms, as caulking for boats, and as stuffing fiber for mattresses. It is also used in horticulture for potting compost (Pauline, 2000).

Different studies have been carried out for the application of these lignocellulosic agricultural wastes in polymeric composites (Ikumapayi et al., 2020), the textile industry (Martins and Sanches, 2019), and the oil and gas industry as adsorbents for industrial wastewater (Johari et al., 2014). Yuan et al. (2021) synthesized an efficient adsorbent by simple doping of Mg–Al composite oxide on coconut shell fiber to remove of phosphorus from domestic sewage. Taksitta et al. (2020) modified and used coconut husk as adsorbents for metal ion removal from wastewater.

One of the applications of adsorbents in the food industry concerns the bleaching process in oil refineries. Bleaching is one of the refining stages of oil and fat industries which removes not only pigments but also other minor impurities such as residual soaps, metal, and oxidation products to provide an acceptable product to the consumer with the highest stability. Acid-activated bleaching earth containing silicates combined with metal oxides such as aluminum, magnesium, calcium, iron, sodium, and potassium activated by sulfuric or hydrochloric acids is employed in the conventional bleaching operation (Erten, 2004).

Some researchers have proposed the use of nut shells as adsorbents. Shruthi and Parithra (2018) studied the efficiency of groundnut shells for the removal of lead and copper from wastewater. The ability of groundnut shell to remove toxic metals from industrial wastewater was achieved by Aarti Sowmya et al., 2018. Almasi et al. (2016) stated that the walnut shell has suitable physical properties for the production of activated carbon. Forozan Sepehr et al. (2020) used walnut shell ash for the bleaching of soybean oil and reported a reduction in color, carotenoid and chlorophyll contents during this process. Coconut shell ash has been reported to produce the highest activated carbon among the agro-waste materials that can be used as adsorbents (Ikumapayi et al., 2020).

Usman et al. (2012) indicated that there is a poor correlation between the chemical composition of clays and their adsorptive power. This means that poor adsorbents may have identical composition to active types. Therefore, the scientific basis for evaluating the adsorbent’s functionality involves actual testing in the laboratory. According to the literature, the application of coconut fiber and shell is not receiving much application in the food industry. Therefore, the aim of this research is to study the application of these agro wastes as bio adsorbents in the bleaching of neutralized soybean oil.

2. MATERIALS AND METHODS

2.1. Materials

Coconut was supplied from a local market in Tehran, Iran. Neutralized soybean oil was obtained from the Behshahr Vegetable Oil Company (Tehran, Iran). Commercial activated bleaching earth, Bentonite Type KF, with pH of 3.3, moisture content of 11% and density of 0.88 g/cm³ was purchased from Kanysaz Jam Industries Ltd., (Tehran, Iran). All the chemicals used in the experiments were pure and of analytical grade, purchased from Merck Chemical Co. (Germany) and Sigma Aldrich Co. (USA).

2.2. Preparation of adsorbents

Coconut fibers and shell were separated from the fruits and dried at 103 ± 2 °C, then ground in a mill (Triplex, France), and passed through a 200-mesh sieve separately. The coconut fiber and coconut shell powders were carbonized in air atmosphere and then heated in a muffle furnace at 800 °C for 5h to prepare the ash. The ash samples were cooled in a desiccator at room temperature, passed through a 200-mesh sieve and stored in amber glass bottles (Forozan Sepehr et al., 2020).

In order to acid activate the ash samples, they were mixed with 12N HCl in the ratio of 1:3 (w/v) separately. The suspension was agitated at 750 rpm
Application of coconut fiber and shell in the bleaching of soybean oil • 3

at 80 ± 2 ºC for 2 h and then diluted with distilled water up to pH of 3.5. The slurry was filtered and dried at 103 ± 2 ºC. Activated ashes were ground and passed through a 200-mesh sieve (Forozan Sepehr et al., 2020).

The specific surface area of adsorbents was measured according to Kashani Motlagh et al. (2011) by the N₂-BET method with a Micromeritics Gemini 2360 instrument.

2.3. Soybean oil bleaching

100 ml of neutralized soybean oil and 1% (W/V) adsorbent (commercial acid-activated bleaching earth, coconut fiber ash, acid-activated coconut fiber ash, coconut shell ash, acid-activated coconut shell ash separately) were placed into a special three-neck flask equipped with a vacuum pump, thermometer and magnetic stirrer. Vacuum at 9 mmHg was applied and the temperature was increased to 110 ºC and stirring was continued at medium speed to mix the oil and adsorbent for 30 minutes. Heating was discontinued after this period but vacuum and agitation were continued for a further period of 15 min. The temperature of the bleached oil was reduced to 50 ºC. Bleached oils were filtered under vacuum by using Watman No. 41 filter paper to remove the adsorbent particles and obtain a clear oil. The treated oils were stored for further analysis in sealed vessels at 4 ºC after flushing with nitrogen (Abdi et al., 2021).

2.4. Physical and chemical analyses

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.

The carotenoid contents of the neutralized and bleached oil samples were determined by a UV-VIS spectrophotometer at 450 nm (PG Instruments T60U UV/VIS Spectrophotometer) according to BS 684, UK (BS, 1993).

The chlorophyll contents of the neutralized and bleached oil samples were determined according to the AOCS method (Cc 13d-55) by a UV-VIS spectrophotometer at 630, 670 and 710 nm (AOCS, 2017a).

A color measurement was carried out according to the AOCS standard method, Cc13e-92, by Lovibond Tintometer apparatus in 5.25-inch cell (AOCS, 2009).

The free fatty acid contents of the neutralized and bleached oil samples were determined by dissolving the oil in a diethyl ether-ethanol (1:1) solution followed by titration with a standard solution of 0.01 N potassium hydroxide in the presence of phenolphthalein according to the AOCS method, Cd 3d-63 (AOCS, 2017b).

The peroxide value determination of the neutralized and bleached oil samples was carried out according to the AOCS method, Cd 8–53 by dissolving the oil in an acetic acid-chloroform (3:2) solution, followed by titration with a 0.01 N sodium thiosulfate solution in the presence of potassium iodide and starch indicator (AOCS, 2003).

The determination of the p-anisidine value (pAV) of the neutralized and bleached oil samples was carried out following the ISO 6885:2006 method (ISO, 2006). A solution of the oil in iso-octane was reacted with p-anisidine in glacial acetic acid to form yellowish reaction products. Then absorbance was measured by a UV-VIS spectrophotometer at 350 nm (PG Instruments T60U UV/VIS Spectrophotometer).

The amounts of copper and iron in the neutralized and bleached oil samples were determined by Atomic Absorption Spectrometer according to the AOCS standard method, Ca 15–75. Oils dissolved in methyl isobutyl ketone were analyzed for metals by direct aspiration (AOCS, 2017c).

2.5. Statistical analysis

All the experiments and/or measurements were carried out in triplicate. 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 among the means were determined using the Duncan multiple range test.

3. RESULTS AND DISCUSSION

Although carotenoids as the main pigments in most vegetable oils have antioxidant properties, they might act as pro-oxidant under elevated temperatures during oil processing (Zeb and Murkovic, 2011; Zeb and Murkovic, 2013). Therefore, the removal of these compounds from the oil might be desirable for their subsequent applications.
Table 1 indicates the amounts of carotenoids in soybean oils bleached with different adsorbents. Although the amounts of carotenoids were significantly decreased in all bleached treatments, the highest reduction was obtained by using acid-activated treatments. The percentages of carotenoid reduction in treatments obtained from acid-activated fiber ash and acid-activated shell ash were 84.25 and 71.63%, respectively. Therefore, fiber ash had a better efficiency in reducing carotenoid pigments compared to shell ash. The removal of carotenoids is due to the reaction between these pigments and the active sites of the adsorbents (Jummao et al., 2008). The textural characteristics and surface chemistry of adsorbents which can be modified by acid activation play important roles in their functionality (Hussin et al., 2011). Hambley et al. (2021) stated that acid activation attacks and partly dissolves the layered mineral structure, leaving a partially amorphous material with a higher surface area and porosity. The specific surface area of coconut fiber and shell ashes were obtained at 78 and 92 m²/g, respectively, which were increased by acid activation and reached up to 156 and 143 m²/g for acid-activated fiber and shell ashes, respectively. Therefore, structural modification of adsorbents is an effective factor in their better efficiency.

Table 2. Lovibond color in soybean oils bleached with 1% of different adsorbents*

<table>
<thead>
<tr>
<th>Treatments with</th>
<th>Red units</th>
<th>Yellow units</th>
</tr>
</thead>
<tbody>
<tr>
<td>No treatment (Neutralized oil)</td>
<td>3.2 ± 0.20 a</td>
<td>60.0 ± 0.12 a</td>
</tr>
<tr>
<td>Commercial Bleaching Earth</td>
<td>2.4 ± 0.10 a</td>
<td>10.0 ± 0.20 b</td>
</tr>
<tr>
<td>Fiber Ash</td>
<td>2.5 ± 0.07 ab</td>
<td>8.0 ± 0.12 ac</td>
</tr>
<tr>
<td>Acid Activated Fiber Ash</td>
<td>2.9 ± 0.12 abc</td>
<td>8.5 ± 0.07 c</td>
</tr>
<tr>
<td>Shell Ash</td>
<td>3.0 ± 0.07 ab</td>
<td>7.0 ± 0.05 d</td>
</tr>
<tr>
<td>Acid Activated Shell Ash</td>
<td>2.7 ± 0.05 ab</td>
<td>5.0 ± 0.05 e</td>
</tr>
</tbody>
</table>

*The values are expressed as means ± standard deviation, n=3. Different letters in each column indicate significant differences (P < 0.05) using Duncan’s multiple range test.

One objective of oil bleaching is to remove the green pigments, chlorophylls, due to their decomposition into phaeophytins by heat treatment (Zheng et al., 2017) and acting as photooxidation sensitizers which enhance the oxidation reaction (Diosady, 2005), which results an opaque and dark oil with undesirable flavors.

The Removal of chlorophyll as green pigments present in crude soybean oil is considered more difficult than carotenoid pigments (Subramanian, 2001; El-Hamidi and Zaher, 2016) and according to the results shown in Table 1, the amount of chlorophyll in all the bleached oil samples was decreased significantly (p < 0.05). Most of the chlorophyll reduction (82.31 %) was obtained by using acid-activated fiber ash and there were no significant differences with commercial bleaching earth. Breaking the tetrapyrrrole ring in the chlorophyll structure might be one of the reasons for decreasing chlorophyll content during oil bleaching (Jung et al. 1989). Due to the application of acid-activated bleaching agents and materials, the Mg in the center of chlorophyll might be removed and might affect the color intensity.

Bleaching efficiency might be monitored by measuring the reduction in color bodies according to the Lovibond method. The greatest reductions in red
presence of hydrogen ions (Mustapha et al., 1992; Usman et al., 2012). Considering the effective role of the acidic adsorbents in providing the main purposes of bleaching, slight increases in free fatty acid contents during oil bleaching is not noticeable because these components could be removed simply from the oil during the deodorization stage.

Furthermore, the free fatty acid content in neutralized oil which was originally 0.44 g/100g was considerably reduced (50% and 25%) during bleaching with fiber ash and shell ash, and reached 0.22 and 0.33 g/100g, respectively. Bleaching with acid-activated adsorbents increased the acid value so that the free fatty acid content of oils bleached with acid-activated fiber ash and acid-activated shell ash reached 0.67 and 0.78 g/100g, respectively. The application of commercial acid-activated earths produced similar results. Different studies have indicated that oil bleaching with acidic adsorbents slightly increases the acid value of oils, which is due to triglyceride hydrolysis and subsequent production of free fatty acids (Boki et al., 1992; Usman et al., 2012). Considering the effective role of the acidic adsorbents in providing the main purposes of bleaching, slight increases in free fatty acid contents during oil bleaching is not noticeable because these components could be removed simply from the oil during the deodorization stage.

Silva et al. (2014) indicated that acid-activated bleaching earths might act as an oxidizer. Therefore, peroxide and p-anisidine values were determined as primary and secondary oxidation products, respectively. Table 3 presents the peroxide and p-anisidine values for neutralized and bleached oils after treatment by different adsorbents. The peroxide value of neutralized soybean oil was determined as 4.55 meq O₂/kg oil. Bleaching by different adsorbents decreased the peroxide value by 25.27 – 72.31%. The lowest peroxide value (1.26 meq O₂/kg oil) was obtained for oil bleached with shell ash, which indicates better function compared to commercial bleaching earth. According to the peroxide value results, a slight increase in secondary oxidation products occurred due to decomposition of primary oxidation products. There are significant differences between the p-anisidine value of the neutralized and bleached oils with different adsorbents (p < 0.05).

Usman et al. (2012) indicated that peroxides are decomposed into aldehydes and ketones due to further oxidation which might be catalyzed by the acidic nature of adsorbents. These decomposition products are also adsorbed to the bleaching agent (Subramanian et al., 2001; Mirrezaie Roodaki et al., 2016).

According to the results, the amount of iron was increased in bleached oils treated with fiber ash and shell ash, which might be due to the nature of the adsorbents used which contain different metals. Although iron content was significantly decreased in all samples treated with acidic adsorbents, the greatest reduction (44.59 %) was obtained in the oil bleached with acid-activated fiber ash, which might be due to the dealumination of the structure, resulting in organic acid activation.

### Table 3. Amounts of peroxide value, p-anisidine value, free fatty acids, iron and copper in soybean oils bleached with 1% of different adsorbents

<table>
<thead>
<tr>
<th>Treatments with</th>
<th>Peroxide Value (meq/kg oil)</th>
<th>p-Anisidine Value</th>
<th>Free Fatty Acids (g/100g)</th>
<th>Iron (mg/kg)</th>
<th>Copper (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No treatment (Neutralized oil)</td>
<td>4.55 ± 0.25 ‡</td>
<td>2.79 ± 0.13 ‡</td>
<td>0.44 ± 0.04 †</td>
<td>0.74 ± 0.12 ‡</td>
<td>0.17 ± 0.01 ab</td>
</tr>
<tr>
<td>Commercial Bleaching Earth</td>
<td>2.74 ± 0.35 †</td>
<td>2.92 ± 0.04 ab</td>
<td>0.56 ± 0.12 f</td>
<td>0.63 ± 0.05 d</td>
<td>0.15 ± 0.00 c</td>
</tr>
<tr>
<td>Fiber Ash</td>
<td>1.40 ± 0.05 d</td>
<td>3.04 ± 0.02 s</td>
<td>0.22 ± 0.01 f</td>
<td>0.92 ± 0.11 b</td>
<td>0.18 ± 0.05 s</td>
</tr>
<tr>
<td>Acid-Activated Fiber Ash</td>
<td>2.60 ± 0.12 †</td>
<td>2.98 ± 0.21 ab</td>
<td>0.67 ± 0.00 b</td>
<td>0.41 ± 0.07 f</td>
<td>0.16 ± 0.05 bc</td>
</tr>
<tr>
<td>Shell Ash</td>
<td>1.26 ± 0.09 ‡</td>
<td>2.90 ± 0.03 ab</td>
<td>0.33 ± 0.11 e</td>
<td>0.86 ± 0.05 b</td>
<td>0.18 ± 0.01 s</td>
</tr>
<tr>
<td>Acid-Activated Shell Ash</td>
<td>3.40 ± 0.07 b</td>
<td>2.97 ± 0.17 ab</td>
<td>0.78 ± 0.00 e</td>
<td>0.48 ± 0.00 e</td>
<td>0.13 ± 0.00 a</td>
</tr>
</tbody>
</table>

* The values are expressed as means ± standard deviation, n=3. Different letters in each column indicate significant differences (P < 0.05) using Duncan’s multiple range test.
Usman et al. (2012) stated that a number of metal ions in the octahedral layer, such as aluminum, magnesium, and iron cations and impurities such as calcite are also removed by leaching with a mineral acid at elevated temperatures.

The results for changes in the amount of copper in the treated samples are similar to the results obtained for the iron content so that copper content was decreased in the oil treated with acidic adsorbents. However, these changes are not statistically significant.

According to the results, these adsorbents might be recommended for post-bleaching processes carried out after oil hydrogenation with the aim of removing nickel from hydrogenated oil.

4. CONCLUSIONS

Coconut fiber and shell are agricultural wastes and their application in the food industry has received limited attention. Therefore, the efficiency of these compounds for the bleaching of edible oil has been investigated in this research. The results showed that these adsorbents were quite effective in achieving the main goals of the oil bleaching process, reducing oil color and carotenoid and chlorophyll contents. In this respect, acidic treatments with fiber and shell have shown to be more effective, which might be due to the structural modification of adsorbents by acid activation.

Regarding the effect of these compounds on the oil quality factors, the peroxide value and the amounts of iron and copper as prooxidant compounds decreased in all treatments. Although the content in free fatty acids increased in adsorbents with acidic nature, they could be removed from the oil during the deodorization process. Due to the competitiveness of acid-activated coconut fiber and shell with commercial bleaching earth, the use of these low-cost biosorbents can be considered for oil bleaching. Also, based on the effectiveness of the acid-activated fibers compared to acid-activated shells, acid-activated coconut fibers are recommended as adsorbent in the oil industry.

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