Adsorptive Bleaching of Soybean Oil with Non-Montmorillonite Zambian Clays

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As an alternative to montmorillonite clay, three local Zambian clays have been used to bleach soybean oil. The bleaching action of the natural clays was poor when compared with commercial acid-activated montmorillonite (M-C) and activated charcoal (A-C) adsorbents. However, acid-activation of the Zambian clays profoundly increased their adsorptive activity. Reduction of 88% in soybean oil color (Lovibond Red) by each of the three activated Zambian clay samples represented an efficiency close to that of montmorillonite (94%) and better than activated charcoal (63%). Peroxide value (PV) of the oil was reduced by 85% (M-C) and 78% (A-C) while 68% was the highest reduction for the activated Zambian clays. After 12 wk of storage at ambient temperature, the bleached soybean oil samples showed some oxidation. Consideration of the totox values indicated that the Zambian clay-bleached oil was more stable over this length of storage when compared with the M-C bleached oil. The bleaching action shown by aluminum-exchanged clays was closely related to their acid-activated counterparts. These results demonstrate a dependency of adsorptive bleaching with Zambian clays on proton availability. Comparative powder x-ray diffraction analysis of the clays showed that quartz was the major mineral present, followed by kaolinite. No montmorillonite was detected. It was concluded that by appropriate treatment to generate Brönsted acidity (protons), Zambian clays can be converted into potent adsorbents for soybean oil impurities.

KEY WORDS: **Adsorption, Brönsted acidity, kaolinite, montmorillonite, quartz, silica, soybean oil.**

When refining vegetable oils, the bleaching process is an important step, intended to remove from the oil unwanted constituents by adsorption. This enables the production of a stable product with the required characteristic bland taste and light color (1). Unwanted constituents of soybean oil include excessive amounts of pigments, such as the carotenoid lutein (2), and substances implicated in color reversion, such as chroman-5,6-quinone (3) and nonhydratable phosphatides (4).

In view of its relatively unsaturated nature, soybean oil is particularly prone to oxidative rancidity (5). This process is catalyzed by the presence of metals or other radical initiators (6). The resulting oxidation products, such as hydroperoxides and their breakdown compounds, *e.g.* ketones and aldehydes, along with the prooxidant metals, are undesirable in the oil.

Pigments and oxidation products are effectively removed or reduced from the oil by the process of adsorption onto clays (7,8). Removal of prooxidant transition metals, such as iron and copper, by adsorption onto clays is also suggested to take place (9).

Adsorbent materials used throughout the world by vegetable oil refiners are mainly acid-activated montmorillonite clays or activated carbon. However, in view of its relatively high cost, carbon is not as widely used as montmorillonite. Montmorillonite is a 3-layered sheet aluminosilicate mineral.

Non-montmorillonite minerals, such as kaolinites and micas (9), synthetic minerals, such as zirconium phosphate, and other types of 3-layered aluminosilicates (10) have been reported to be ineffective or inferior adsorbents. Although montmorillonite at present does seem to be the most effective adsorbent clay available to industry, evaluation of alternative cheaper sources has attracted great attention in recent years. Some workers (11) have shown that local Nigerian Okija clay can be modified into an effective adsorbent after acid-activation. Also, Proctor and Palaniappan (12) report that rice hull ash, following acid-activation, develops pronounced bleaching activity for lutein. The ash was shown to be composed of silica polymorphs, tridymite and cristobalite (13).

This present study of Zambian clays as possible alternative bleaching materials was undertaken mainly because of the nonavailability of a typical montmorillonite clay, which has to be imported into the country. Bleaching efficiency was estimated by assessment of oil color, PV, acid value, para-anisidine value and fatty acid composition before and after bleaching. Any possible effect on the storage life of the bleached oil samples was also investigated.

MATERIALS AND METHODS

Adsorbents. Natural clays N-S and N-Ls were supplied by ROP Limited (Ndola, Zambia), while N-Ch was supplied by the Geological Survey Department (Lusaka, Zambia). The three clay samples were obtained from three different parts of the country. Montmorillonite clay (ex ROP Limited) and activated charcoal (ex Fisons) are commercial adsorbents.

Sample preparation and activation. Working clay fractions were prepared by screening through a 45-micron sieve after pulverizing in a pestle and mortar. Mineral acid (H_2SO_4) activation based on the method described by Nihal and Guler (14) was found to be satisfactory and adopted in this study. The filtered clay was dried overnight in an oven at 120°C and re-screened before use. Activated clays were designated A-S, A-Ls and A-Ch.

Cation exchange. The method described by Yariv, *et al.* (15) was employed to prepare aluminum-exchanged clays Al-S, Al-Ls and Al-Ch.

X-ray diffraction analysis of clay samples. The analysis was carried out with a Philips x-ray diffractometer comprised of the following units: PW 1130/00 generator set at a voltage of 40 kv and a current of 40 mA; PW 2233/20 copper target—source for Cu K alpha radiation; PW 1050/25 goniometer (with detection and counting facilities) set to scan 2θ range of Bragg angles between 3° and 65° at a speed of 1 degree per minute. Clay films suitable

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for analysis were prepared by using appropriate slides.

Bleaching. This was carried out under a vacuum of 90 mm Hg between 100 and 104°C with a contact time of 30 min. Stirring and heating was carried out by means of an electric hot plate and a magnetic stirrer. A clay dosage of 6% w/w of oil was used in all cases. A predegummed commercial soybean oil of U.S. origin and supplied by ROP Limited, designated as crude Sbo, was used for all the experiments.

Oil color. Assessment of color was carried out in the Lovibond Tintometer Model E. A one-inch cell instead of the recommended 5.25″ cell was used because of sample size limitations. Results obtained were converted to 5.25″ cell values by multiplying by 2.5 (Anglia Oils, Hull, UK, Dave Denman, personal communication).

Peroxide value (PV), para-anisidine value (p-AV) and acid value (AV). These determinations were performed by using the IUPAC standard method 2.504 for p-AV (16) and the methods described by Egan *et al.* (17) for PV and AV.

GLC analysis of fatty acids (FAMES). A rapid methyl ester preparation method in a heating block was used (18). The prepared fatty acid methyl esters in isooctane were injected directly onto a DB wax capillary column in a Perkin-Elmer chromatograph Model 8420 (Norwalk, CT). The chromatograph was programmed as follows:

$$40^\circ\mathrm{C} \xrightarrow{30^\circ/\mathrm{min}} 150^\circ\mathrm{C} \xrightarrow{30^\circ/\mathrm{min}} 230^\circ\mathrm{C}$$

(0 min)	(4 min)	(0 min)
Initial		Final

RESULTS AND DISCUSSION

Important x-ray diffraction peaks, characteristic of the acid-activated montmorillonite clay employed, are shown in Figure 1. These peaks appear between 24.5° and 27.5° 2θ Bragg angles. Two of these peaks at 25.15° and 26.32° are well defined and almost of equal intensity. In contrast, none of the natural or acid-activated Zambian clays gave similar 2θ patterns. In fact, all of them showed only one strong intense peak between 26° and 26.5°. Traces of the acid-activated clays are shown in Figures 2 to 4 to illustrate the difference. The weaker peak intensity of the A-Ch clay may be attributed to the mineral dilution effects, due to the possible presence of amorphous materials. Fahn (8) suggests that during the acid-activation process, amorphous silicic acid develops in the montmorillonite crystal, which in combination with the remaining intact crystalline portion is responsible for the high efficiency of the mineral. It is, therefore, not surprising that peaks of the montmorillonite clay are less intense than for the other clays. Slight variations in the position of the main peak of the test clays may be due to differences in the type of cations associated with the clays in their natural state. The d-spacings of 3.34Å–3.39Å derived for the peak were,

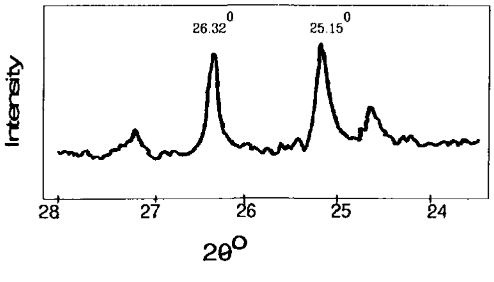

FIG. 1. Powder XRD pattern of montmorillonite clay.

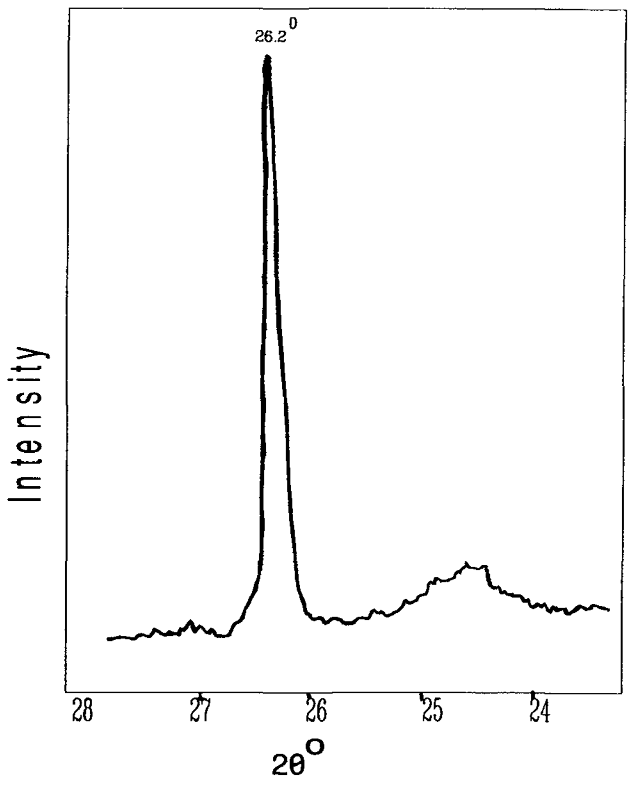

FIG. 2. Powder XRD pattern of activated Zambian clay (A-S).

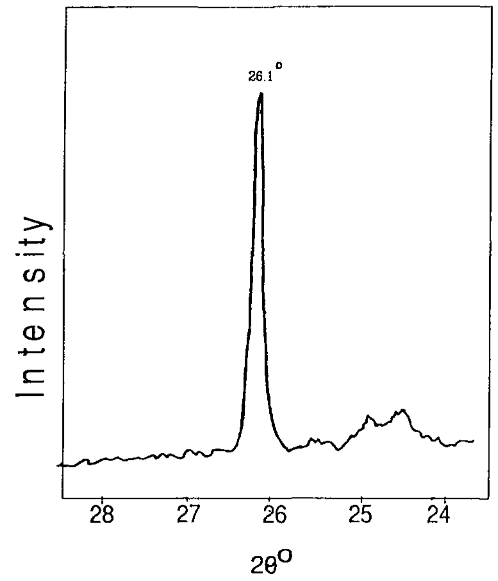

FIG. 3. Powder XRD pattern of activated Zambian clay (A-Ls).

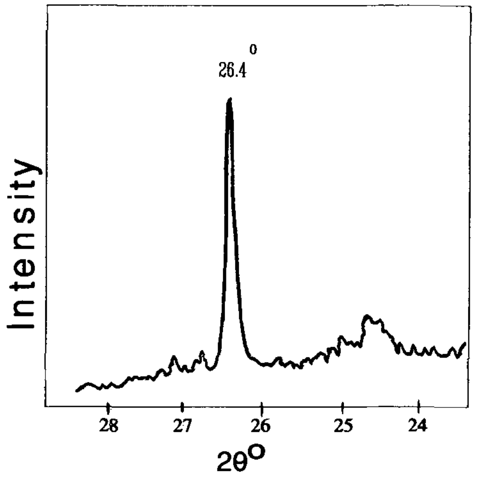

FIG. 4. Powder XRD pattern of activated Zambian clay (A-Ch).

therefore, taken to be typical of the mineral quartz. It was also deduced that kaolinite was the main mineral responsible for most of the remaining weaker peaks, which were not as well defined. Molak (19) reported higher levels of kaolinite mineral (82%) than quartz (8%) in a clay sample from one of the regions covered in the present study. The difference in the magnitude of the relative abundance of the minerals may be due to differences in the exact location and depth of the sampling point as well as to the particle size and purity of the fraction sampled. Table 1 summarizes adsorption capacities of the various adsorbents for the peroxide oxygen, free fatty acids, pigments and carbonyl compounds.

Color. Soybean oil color is mainly due to the presence of carotenoids, such as lutein (2). Reduction in the color of the oil from a Lovibond Red of 8.75 to 0.5 by montmorillonite represents an adsorptive capacity of 94%, while the reduction to 3.25 Red by carbon showed a capacity of only 63%. All activated clays reduced the color of the oil to 1 Red, representing an adsorptive capacity of 88%. This reduction is significant considering that most high-quality refined cooking oils in Zambia have a color of about 2 Red. The adsorptive activity of the activated clays for lutein is thus comparable to montmorillonite and superior to activated charcoal used under the conditions of the test.

Whereas the preliminary tests showed that natural clays were poor adsorbents, the increase in pigment removal by acid-activated clays implies that the bleaching efficiency is influenced by H^+ ions on the surface of the clay. The performance of aluminum-exchanged clays was in the range of acid-activated clays. According to Jones *et al.* (20), small, highly charged cations cause pronounced polarization of the water molecules in the interlayer space of sheet silicates, such as montmorillonite (Fig. 5). This process is accompanied by the generation of protons. In aluminum-exchanged clays, therefore, the activity observed may be related to the protons (H^+) generated from water polarization effects of Al^{3+}. Proton release from water associated with Al^{3+} can be represented as follows:

$$[Al\,(H_2O)_6]^{3+} \rightleftharpoons [Al\,(H_2O)_5(OH)]^{2+} + H^+$$

$$[Al\,(H_2O)_5(OH)]^{2+} \rightleftharpoons [Al(H_2O)_4(OH)_2]^{+} + H^+$$

Having established that quartz is the main mineral in the Zambian clays, followed by kaolinite, it is not certain whether the adsorption behavior of the clays is due to quartz alone, kaolinite alone, or both, or whether the action of one depends on the other. Also, the effect of any amorphous material, if present, is not known.

If quartz were responsible for the decolorizing action, it would be expected that the characteristic visible spectrum of lutein in the bleached oil would appear similar to that observed with tridymite and cristobalite (13),

TABLE 1

Effect on the Quality of Soybean Oil Treated with Different Adsorbents[a]

	Soybean oil quality changes[b]				
Soybean oil treatment	Color (Lovibond Red units[c])	PV (meq/kg)	p-AV	TotoxV (2PV + p-AV)	AV (mg KOH/g)
Crude Sbo	8.75	7.3	1.97	16.57	2.26
M-C[d]	0.50	1.1	3.53	5.73	2.32
A-C[e]	3.25	1.6	3.64	6.84	2.06
A-S	1.00	3.4	11.43	18.23	2.54
A-Ls	1.00	2.3	7.75	12.35	2.09
A-Ch	1.00	2.7	9.43	14.83	2.48
Al-S	1.25	3.2	7.64	14.04	2.17
Al-Ls	1.00	3.5	10.03	17.03	2.38
Al-Ch	1.00	3.1	6.05	12.25	2.28

[a] Results for natural clays have been omitted because preliminary tests showed them to be poor adsorbents.

[b] All the results shown are means of duplicate determinations.

[c] Lovibond—5.25″ cell.

[d] Montmorillonite clay.

[e] Activated charcoal (carbon).

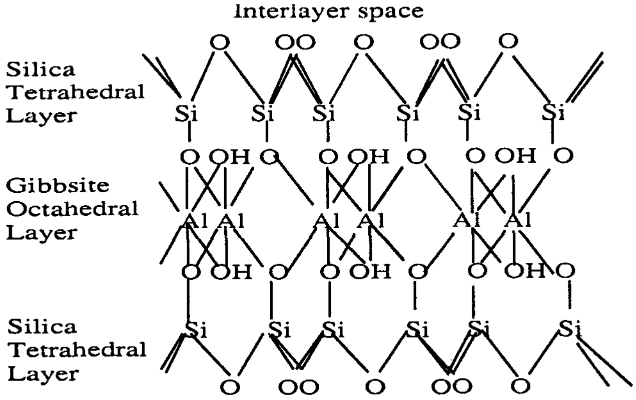

FIG. 5. Montmorillonite—part of the crystal structure showing the arrangement of the three layers making up the mineral (not drawn to scale). Some of the Al atoms in the octahedral layer are substituted by Mg atoms. (This is the principal isomorphous substitution in montmorillonite.)

because all these minerals are polymorphs of silica, which is a three-dimensional framework silicate of formula SiO_2. In fact, the spectrum characteristic of lutein in soybean oil was completely removed (results not shown), implying that quartz may not be the mineral responsible. The observed effectiveness of the aluminum-exchanged clays would seem to favor involvement of a sheet crystal structure. It would, therefore, appear reasonable to assume that kaolinite, which is a two-layered sheet aluminosilicate (Fig. 6), could be the mineral actively involved in adsorption. Quartz is formed of (SiO_4) tetrahedra arranged in helical chains (21).

Peroxide value. Table 1 shows that reduction of PV was highest with the commercial adsorbents montmorillonite (85%) and activated charcoal (78%). Test clays eliminated between 60% and 70% of the peroxides originally present in the oil. Although these reductions are not as significant, all the Zambian clay-bleached oil samples were more resistant to further oxidation (totox values) than montmorillonite-bleached oil on prolonged storage (see Table 2). The fact that oil bleached with carbon produced the lowest totox value on storage could indicate that these changes are also related to Brönsted acidity.

Antioxidant effects of any residual tocopherol and phosphatides (22) may also play a part. The extent of their removal by each of the adsorbents would thus determine the degree of any antioxidant activity left in the oil.

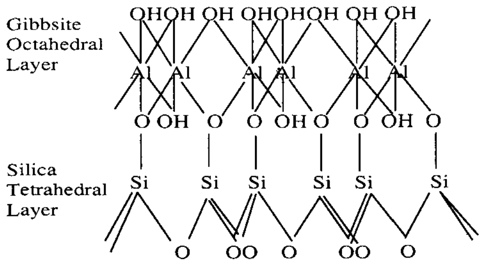

FIG. 6. Part of the crystal structure of kaolinite showing interleaving of Gibbsite layer with silicate network (not drawn to scale).

TABLE 2

Quality Changes After 12 Wk of Storage at Ambient Temperatures (16°C–25°C) of Soybean Oil Treated with Various Adsorbents

Soybean oil treatment	Soybean oil quality changes[a]		
	PV (meq/kg)	p-AV	Totox value (2PV + p-AV)
Crude Sbo	44.20	2.11	91.11
M-C	59.80	5.00	124.60
A-C	26.50	4.22	57.22
A-S	39.00	10.95	88.95
A-Ls	29.70	7.05	66.45
A-Ch	32.80	7.47	73.07
Al-S	36.40	9.51	82.31
Al-Ls	35.00	10.04	80.04
Al-Ch	33.60	6.81	74.04

[a] All the results shown are means of duplicate determinations.

TABLE 3

Effect on the Major Fatty Acid Distribution of Soybean Oil Treated with Various Adsorbents

Soybean oil treatment	%Fatty Acids[a]				
	C16:0	C18:0	C18:1	C18:2	C18:3
Crude Sbo	10.41	3.14	21.83	54.48	7.90
M-C	10.55	2.90	22.44	55.09	8.61
A-C	10.51	3.42	22.11	54.63	8.36
A-S	10.48	2.92	22.42	55.19	8.19
A-Ls	10.14	3.41	21.56	53.85	7.94
A-Ch	10.49	2.75	22.49	54.73	7.75
Al-S	10.60	3.03	22.43	55.75	7.86
Al-Ls	10.25	2.95	21.85	53.97	9.26
Al-Ch	11.01	3.22	21.68	53.64	7.98

[a] All the results shown are means of duplicate determinations.

Para-anisidine value. All the adsorbents caused an increase in the p-AV which suggests the possibility of a surface-chemical reaction involving the breakdown of hydroperoxides (12,8). The fact that higher p-AVs were obtained for the test clays implies that stronger Brönsted sites may be present in these clays.

Acid value. Changes in the AV were relatively small. Slight variations observed may be due to small differences in the amount of free or bound acidity on the clays.

Fatty acid profile. Table 3 summarizes the effect of the clays on the major triglyceride fatty acid content. None of the adsorbents employed resulted in any significant changes of these acids, including the unsaturates C18:2 and C18:3. This is a desirable feature considering their nutritional significance.

Further studies of the bleaching behavior of the Zambian clays are in progress.

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