Benefits and Limitations of a Novel Chlorophyll Adsorbent

D.M. Chapman*
W.R. Grace Co.-Conn., Washington Research Center, Columbia, Maryland 21044

Silica hydrogels acidified with strong mineral acids, such as sulfuric acid, are highly effective chlorophyll and phospholipid adsorbents relative to traditional acid-activated bleaching earth (ABE), but they are not effective β-carotene adsorbents. When an acidified silica is used as the only bleaching agent, sulfuric acid leaches into the oil, and after deodorization, Tintometer red and yellow (R/Y) numbers are higher than those for ABE-bleached and deodorized oils. The fixed R/Y colors do not arise solely from the decomposition of β-carotene during deodorization. Sequential treatments of canola oils with sulfuric acid/silica and ABE can be performed to overcome all of the drawbacks associated with sulfuric acid/silica treatment alone, such that finished oils can be produced by lower overall adsorbent dosages.

KEY WORDS: **Bleaching earth, canola oil, chlorophyll adsorption, silica.**

The removal of pigments and various other trace constituents from triglyceride oils by adsorption is one of the most important steps in the processing of edible oils. The removal of pigments, notably chlorophyll, is generally accomplished by bleaching-earth adsorbents, although activated carbon, metal oxide and metal phosphate adsorbents have been described (1,2). In addition, Pryor *et al.* (3,4) patented acidified silica hydrogels as chlorophyll and phospholipid adsorbents.

Generally, the chlorophyll saturation capacities of bleaching earth, activated carbon and metal oxide adsorbents are low, roughly 1–3 mg chlorophyll per gram of adsorbent (5). By comparison, saturation capacities of proteins onto silica are typically 100–200 mg/g (6). Recently, we concluded that competitive adsorption was the main factor that limited the uptake of chlorophyll from edible oils (7).

Silica hydrogel/mineral acid mixtures, however, demonstrated substantially improved chlorophyll capacities. Thus, we undertook a study to determine the benefits and limitations of such adsorbents in the purification of canola oil. The results showed that these adsorbents could be used to produce good-quality finished oils at lower overall adsorbent dosages, provided that ABE was used in conjunction with the acidified silicas.

EXPERIMENTAL PROCEDURES

The starting super-degummed canola oils were obtained from CSP Foods (now CanAmera Foods, Russell, Manitoba, Canada) and had the trace-element impurity levels shown in Table 1. The impurity levels were measured by inductively coupled plasma (ICP) spectrophotometry.

The acid-activated bleaching earth (ABE) was Filtrol F160 (Englehard Corp., Edison, NJ), which contained 18% volatile water (measured at 550°C). The acidified silicas (AS) were prepared simply by physically mixing concentrated sulfuric acid (96% reagent grade; J.T. Baker, Phillipsburg, NJ) with commercially available TriSyl® silica (W.R. Grace & Co.-Conn, Columbia, MD). The initial TriSyl® silica contained 65% volatile water and 35% silica. AS3 contained an additional 3 wt% sulfuric acid on a hydrous basis; AS6 contained 6 wt% sulfuric acid; and AS10 contained 10 wt% sulfuric acid.

TABLE 1

Starting Oil Characterization

Impurity	Oil A level (ppm)	Oil B level (ppm)
Phosphorus	28.4	27.4
Copper	0.0	0.0
Calcium	15.5	16.4
Magnesium	3.9	4.4
Iron	0.98	0.37
Sulfur	5.5	6.7
Chlorophyll	21.1	14.3
Free fatty acids (wt%)	0.35	0.41
Red (1-cm cell)	7.7	4.9
Yellow (1-cm cell)	>70	>70

Chlorophyll adsorption was carried out at 100°C for 30 min with vigorous stirring at 10–20 mbar pressure. Treatments for phospholipid adsorption were carried out at 70°C for 30 min with vigorous stirring at 1.01 bar pressure. The sequential adsorption treatments were performed by treating the oil with AS at 70°C for 20 min at 1.01 bar pressure with stirring, followed by ABE addition and further treatment at 100°C for 30 min with stirring at 10–20 mbar. In these experiments, the AS adsorbent was not filtered off prior to ABE addition. Deodorizations were carried out at 260 ± 3°C for 1 h at 1–2 mbar with injection of 2–3 wt% H_2O. Oils were stored in a refrigerator when not in use.

The β-carotene (Sigma Type III, from carrots, 80–90% β-isomer; Sigma Chemical Co., St. Louis, MO) was used without further purification. To spike a bleached oil with carotene, 142 mg of the pigment was added to 285 g oil that was bleached with 3.0 wt% F160 (anhydrous basis) to give 0.03 ppm chlorophyll The oil/carotene mixture was then heated to 50°C, to dissolve the carotene, and cooled to 25°C. The β-carotene that did not dissolve was then removed by filtration.

Ultraviolet and visible (UV/VIS) spectroscopic data were obtained in a Perkin-Elmer Lambda 3A spectrophotometer with 3600 Data Station (Palo Alto, CA). Chlorophyll a levels and Lovibond red and yellow (R/Y) values were obtained with a Lovibond AF950 Tintometer (HF Scientific, Ft. Myers, FL). Oxidative stability was measured in a Rancimat (Metrohm Model 617; Metrohm Herisau, Switzerland) at 100°C. Free fatty acids titrations were performed according to AOCS Method Ca 5a-40 (8).

RESULTS AND DISCUSSION

Chlorophyll adsorption data for experimental adsorbents and ABE are shown in Table 2. The data show that the chlorophyll capacities for the AS adsorbents increase with increasing sulfuric acid content. For AS10, only 0.75 wt% adsorbent is necessary to reduce chlorophyll to <0.05 ppm, and by comparison, 3.05 wt% ABE is necessary to

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*Address correspondence at W.R. Grace, Washington Research Center, 7379 Rt. 32, Columbia, MD 21044.

TABLE 2

Tintometer Red/Yellow Numbers After Chlorophyll Adsorption from Oil A

		Tintometer number[b]	
Adsorbent (wt%)[a]	Chlorophyll A (ppm)	Red	Yellow
1.83 ABE	0.21	6.9	>70
2.44 ABE	0.11	4.3	>70
3.05 ABE	0.04	3.1	52
3.66 ABE	0.04	2.7	50
0.25 AS10	3.13	10.0	>70
0.50 AS10	0.21	7.6	>70
0.75 AS10	0.03	6.5	>70
0.25 AS6	13.30	10.0	>70
0.50 AS6	0.29	7.6	>70
0.75 AS6	0.14	7.1	>70
0.25 AS3	18.90	9.9	>70
0.50 AS3	0.94	9.0	>70
0.75 AS3	0.38	7.9	>70

[a] Adsorbent dosages reported on a hydrous basis.

[b] For acid-activated bleaching earth (ABE), R/Y numbers measured in a 5.25″ cell; for acidified silicas (AS), R/Y numbers measured in a 1.0-cm cell.

TABLE 3

Phospholipid and Sulfur (S) Adsorption from Oil A[a]

Adsorbent (wt%)[b]	Elemental P (ppm)	S (ppm)
0.25 TriSyl®	22.2	3.1
0.50 TriSyl	16.1	4.2
0.75 TriSyl	8.5	4.3
1.00 TriSyl	3.2	3.3
0.25 AS3	19.9	20.4
0.50 AS3	7.1	20.1
0.75 AS3	3.6	16.3
1.00 AS3	3.0	18.3
0.25 AS6	13.8	32.2
0.50 AS6	6.6	31.7
0.75 AS6	3.5	22.7
1.00 AS6	2.2	17.3
0.25 AS10	16.4	31.1
0.50 AS10	8.4	43.8
0.75 AS10	4.0	27.5
1.00 AS10	2.6	20.1
0.25 ABE[c]	9.3	5.6
0.50 ABE	3.2	5.1
0.75 ABE	2.6	4.2
1.00 ABE	0.5	6.0

[a] Treatments at 70°C, 30 min, 1.01 bar. TriSyl from W.R. Grace & Co.-Conn., Columbia, MD. See Table 2 for abbreviations.

[b] Adsorbent dosages reported on a hydrous basis.

[c] ABE bleaches at 100°C, 30 min, 10–20 mbar.

achieve this same level. Thus, the chlorophyll capacity of AS10 is several times greater on a hydrous basis than that of ABE. Because the AS adsorbents contain roughly 60% volatile water, while the ABE adsorbent contains only 18% volatile water, the AS adsorbents are up to seven times more effective than ABE for chlorophyll removal on a solids basis. The levels of free fatty acids, measured for the AS-bleached oils, were not substantially greater than those measured for ABE-bleached oils (data not shown), provided that the bleachings were done under conditions (e.g., reduced pressure at 100°C) that favored the removal of water from the oil. These conditions minimized the amount of triglyceride hydrolysis.

Phospholipid adsorption data and residual sulfur data are shown in Table 3. These data reveal that all of the silica hydrogels are more effective than ABE for phospholipid removal, and that the AS adsorbents are slightly more efficient than TriSyl® silica. However, treatment of the oil with the AS materials causes an increase in oil sulfur levels. The residual sulfur levels are greatest for AS10, which contributes nearly 50 ppm sulfur to the oil at the lowest adsorbent dosage. This residual sulfur arises from the low but measurable oil solubility of H_2SO_4 under the treatment conditions. At the 1.00 wt% dosage for the AS10 adsorbent, a total of 1000 ppm sulfur could potentially dissolve in the oil. However, only about 1.5% of the initial sulfur is measured in the oil after treatment. Thus, the partition coefficient under these conditions strongly favors adsorption of the acid onto the silica.

The sulfur level in the oil generally increased as the level of sulfuric acid on the silica increased (Table 3). However, for a given level of sulfuric acid on silica, the amount of sulfur in the oil decreased with increasing dosage of sulfuric acid/silica. We believe that this latter trend is from the variation in solubility of sulfuric acid at the different equilibrium phospholipid levels (phospholipids can function as surfactants for the sulfuric acid).

Treatment of canola oil with the AS adsorbents resulted in unusual color changes. While the starting oil was brownish yellow, the bleached oils were red from appreciable levels of β-carotene, as shown in Figure 1. Thus, the AS materials do not adsorb or decompose β-carotene (and probably related carotenoids) as effectively as ABE because no β-carotene was observed after treatment with the latter at appropriate dosages. Interestingly, R/Y numbers were observed to increase after AS bleach treatments. However, electronic spectroscopy over the wavelength ranges from 550 to 350 nm for the starting oil, and an AS10-treated oil revealed that the optical density over this range was actually lower for the AS10 oil than for the starting oil. To investigate the nature of these color

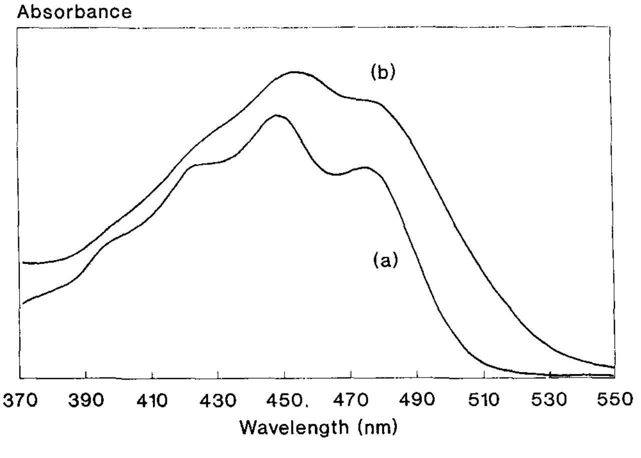

FIG. 1. Absorbance spectra for authentic β-carotene (a) and an AS10 bleached oil (b).

TABLE 4

The Effect of Deodorization on Bleached Oils

Oil description (wt% hydrous)	Chlorophyll A (ppm)	Tintometer number	
		Red	Yellow
2.13 ABE Bleached oil B	0.08	6.0	>70
Deodorized oil	0.05	0.7	3.8
0.80 AS10 Bleached oil B	0.05	7.9[a]	>70[a]
Deodorized oil	0.01	1.1	9.6

[a]Tintometer numbers measured in a 1.0-cm cell. See Table 2 for abbreviations.

phenomena, a green color filter (Tintometer R number = 0.0) and a red color filter (Tintometer R number = 11) were combined to produce a brownish-yellow composite color that had a Tintometer R number of 4.8. Thus, when an oil containing both green (chlorophyll) and red (β-carotene) pigments initially is treated so that the green pigments are preferentially removed, the oil becomes more red, both to the eye and as measured by the Tintometer. However, this does not necessarily mean that the optical density in the red region has increased; rather, the red color present initially is masked by the presence of the green color.

Bleached oils produced with the AS10 material alone were deodorized and compared to ABE-bleached and deodorized oils as shown in Table 4. The results show that the AS10-deodorized oil had higher Tintometer R/Y numbers than the ABE-deodorized oil. Because the AS-treated oils had higher levels of β-carotene after the bleaching step than the ABE oils, as shown above, the effect of a high level of β-carotene in deodorization was examined. Thus, an ABE-bleached oil with 0.05 ppm chlorophyll and with Tintometer R/Y numbers of 0.3/6.4 (1.0-cm cell) was spiked with β-carotene so that the resultant Tintometer R/Y numbers were 17/>70 (1-cm cell). This red number is much higher than that (7.9) for the AS10-bleached oil. The spiked oil was then deodorized to give a finished oil with Tintometer R/Y numbers of 0.8/6.8 (1.0 cm cell). Because the β-carotene level in the spiked oil was initially higher than that present in the AS10 oil, and because the Tintometer numbers of the deodorized oil were lower for the spiked oil than for the AS10 oil, decomposition products of β-carotene do not account for the increased R/Y numbers for the AS-treated oils. The nature of the fixed R/Y pigments in AS-treated oils will be described in a subsequent paper (9).

Sequential adsorptive treatment of oils with silica and then ABE is an effective method of lowering overall adsorbent dosages necessary to produce high quality finished oils (10). Thus, the effect of sequential adsorption treatments on a super-degummed canola oil with AS10 and ABE was evaluated. It was anticipated that the AS10 would effectively remove phospholipids and chlorophyll and that subsequent treatment with ABE would remove R/Y pigments and residual sulfur.

In Table 5 are shown data for bleached and deodorized base-case and sequentially treated oils. These data show that 3.05 wt% ABE (hydrous basis) was necessary to produce a finished oil that contained <0.05 ppm chlorophyll, R/Y <1.0/7 (5.25″ cell) and which contained 2.5 ppm phosphorus and 2.6 ppm sulfur. Linear extrapolation of the R/Y data vs. ABE content for the sequential treatments demonstrates that finished oils with comparable or lower specifications can be obtained with 0.4 wt% AS10 (hydrous basis) and 1.95 wt% ABE (hydrous basis). Furthermore, the Rancimat stabilities of the oils treated with the sulfuric acid/silica adsorbent were improved compared to the base-case oils. Because AS10 contains only 31% silica, the overall adsorbent dosage level for sequential treatment is 1.91 wt% (anhydrous basis) vs. 2.50 wt% ABE (anhydrous basis) for the base-case. Thus, the overall adsorbent dosage can be lowered by 25% by sequential treatment with AS10 and ABE, compared to ABE treatment alone for this canola oil. While the sequential treatment does offer this overall benefit, a more desirable adsorbent system would be a material that offers the benefits of the AS materials, does not leach into the oil and adsorbs R/Y pigments.

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TABLE 5

Results for Sequential Treatments on Oil A[a]

Treatment description (wt% hydrous)	Chlorophyll A (ppm)	Tintometer numbers (5.25″)				
		Red	Yellow	P (ppm)	S (ppm)	Rancimat (h)
2.74 ABE bleached oil	0.08	3.5	69	3.8	4.9	—
Deodorized oil	0.02	1.3	8.8	3.8	3.1	17.5
3.05 ABE bleached oil	0.08	3.0	60	2.5	5.0	—
Deodorized oil	0.00	0.7	6.6	2.5	2.6	17.8
0.40 AS10; 1.58 ABE bleached oil	0.05	5.5	>70	>1	4.8	—
Deodorized oil	0.00	2.0	14	>1	2.9	18.2
0.40 AS10; 1.83 ABE bleached oil	0.03	4.4	>70	>1	4.5	—
Deodorized oil	0.00	1.3	10	>1	2.7	18.8

[a]See Tables 2 and 3 for abbreviations. Tintometer from HF Scientific, Ft. Myers, FL.

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