A Method for Bleaching Rice Bran Oil with Silica Gel

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The color of bleached rice bran oil can be improved by silica gel treatment of the oil miscella before or after dewaxing. A silica gel/oil/solvent ratio of 1:5:5 (wt/wt/vol) is suitable. Silica gel treatment can be carried out either by column percolation or by merely shaking the miscella with the gel followed by decantation. However, column percolation is more efficient, with 30–72% color reduction *vs.* 19–36% reduction for shaking and decanting.

KEY WORDS: Bleaching, miscella decolorization, oil color removal, oil-miscella bleaching, rice bran oil, silica gel bleaching, silica gel oil-miscella shaking, silica gel percolation, silica gel treatment.

Rice bran oil (RBO) obtained by solvent extraction of bran has been reported to be colored dark brown, dark greenish brown or greenish yellow, depending on the extent of bran deterioration during storage, method of extraction and processing conditions (1,2). Generally, the dark color of RBO is not totally eliminated during bleaching. The Indian standard specification for acceptable color of refined and bleached rice bran oil prescribes a value of not more than 20 Lovibond units (generally given as 5 × red color units + 1 × yellow color units, represented in short as 5R + Y Lovibond units) in a 2.5-cm cell (3). This is rather high in comparison with the color values prescribed for peanut oil, which are 3.0 and 0.0 Lovibond units for refined oil and bleached oil, respectively (4). Also, refining losses for RBO are rather high compared to other oils (1,5). These high losses have been attributed to the presence of wax and oryzanol (ferulic acid esters of triterpene alcohols) present in the oil (5). In the present study, attempts have been made to develop a laboratory method for producing a clear, bleached RBO of light color.

MATERIALS AND METHODS

Materials. RBO obtained by solvent extraction of rice bran, expeller-pressed peanut oil, and refined peanut oil were obtained from local factories around Mysore, India. RBO was degummed at 75°C with 1% aqueous phosphoric acid (3 mL/100 g oil) as outlined in an earlier communication (5). Dewaxing was accomplished by chilling the oil at 7–8°C for 48 h and then allowing the oil to equilibrate to ambient temperature. The supernatant dewaxed oil was decanted. For column percolation, 60–120-mesh silica gel (Glaxo Laboratories, Bombay, India) was used. Other solvents and chemicals were AR grade.

Methods. Free fatty acid (FFA) contents of the oils were determined by the AOCS method (6) with 5 ± 0.1 g oil. Color of the oil was measured with a Lovibond Tintometer in a 1-cm cell and expressed as 5 × red units + 1 × yellow units (5R + Y). Refining of oil was done by the AOCS cup method (7) with 100–200-g oil samples. Bleach testing of the refined oil was done on 100-g oil samples as per AOCS method (8). Whenever the sample size was a limiting factor, refining was done on 10-g samples in quadruplicates as described in an earlier communication (5). The refined oils so obtained from four experiments (respective fractions from individual experiments) were pooled to get two sets of samples in sufficient quantities for the bleaching test. For bleaching experiments, 6 g of the refined oil (in duplicate) was transferred to a 10-mL conical flask, 120 mg of bleaching earth (SVC-15, S.V. Earths and Chemicals Pvt. Ltd., Hyderabad, India) was added, and the mixture was heated for 5 min at 120 ± 1°C. The contents were filtered through Whatman No. 4 filter paper, and the filtered oil was taken for color measurement. Means of duplicate values of color were reported.

Silica gel column percolation for bleaching. RBO in hexane (1:1, wt/vol) was fed to a silica gel (moisture content 7.5%) column (30 × 1 cm). The flow rate ranged from 0.40 ± 0.02 mL/min, and 10-mL fractions were collected until the eluent was as colored as the initial oil, indicating exhaustion of the column. Approximately 10 × 10-mL fractions were collected. After collection of the fractions, the column was regenerated by successively eluting with hexane (40 mL), benzene (40 mL) and methanol (25 mL). Each of these fractions was collected separately for analysis. The column was finally eluted with more hexane (40 mL) and was ready for the next set of experiments. The oil in each fraction was freed from solvent and, after reading the color, was used for refining and bleaching experiments.

Silica gel mixing with miscella. The oil (8% FFA) was heated to 80°C to dissolve wax, cooled to 50°C and mixed with hexane (1:1, wt/vol). Silica gel (20 g) and hexane (40 mL) were taken in a 250-mL Erlenmeyer flask. The miscella (40 mL) was poured into the flask and held at about 50°C on a waterbath while the contents were swirled frequently. After holding for 5 min, the contents were cooled under tap water and left at ambient temperature for settling. The supernatant was decanted. To the silica gel in the flask, 40 mL of additional miscella were added, and the process of heating, settling and decanting was repeated three more times. In total, 200 mL of miscella were treated with the same batch of 20 g silica gel. The silica gel was then regenerated by successively shaking and decanting with 40 mL of hexane, 40 mL of benzene, 40 mL of methanol, and, finally 3 × 20 mL of hexane, which was added to the methanol fraction. The eluted oil was desolventized, weighed and measured for color.

RESULTS AND DISCUSSION

Silica gel column percolation for bleaching. The effect of percolation of RBO miscella through the silica gel column on color of the bleached oils is given in Table 1. Conventionally bleached oil had a color of 7.0 Lovibond units, and about 70% color reduction could be achieved after silica gel treatment, up to a gel/oil/solvent ratio of 1:1:1. With a 10-g silica gel column and up to 10 × 10 mL fractions, the color value could be reduced by approximately 36% (from 7.0 to 4.5 Lovibond units). However, with larger columns and larger sample sizes, the color reduction was more effective, enabling use of a silica gel/oil ratio of 1:5

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TABLE 1

Efficacy of Silica-Gel Column Percolation for Bleaching Rice Bran Oil

Fraction from silica gel column[b]	Color of oil after processing[a]			
	Dewaxed oil		Refined oil	
	5R + Y units[c]	Color reduction (%)	5R + Y units[c]	Color reduction (%)
1 (1:0.5:0.5)	1.5	78.6	—	—
2 (1:1:1)	2.0	71.4	—	—
5 (1:2.5:2.5)	3.0	57.1	4.0	20.0
10 (1:5:5)	4.5	35.7	4.5	10.0
20 (1:10:10)	5.5	21.4	—	—
Starting oil	7.0	—	5.0	—

[a]Fraction of miscella obtained from the silica gel column was subjected to desolventization in both cases. The fraction of refined oil was only subjected to bleaching and the fraction of dewaxed oil was subjected to refining and bleaching.

[b]Values in brackets are approximate ratio of silica gel/oil/solvent predicted from volume and quantity of eluted miscella.

[c]Means of values obtained from four experiments.

(Table 2). With this procedure, both solvent-extracted RBO and dewaxed RBO could be bleached. But refined RBO of high color value could not be further bleached by the above procedure (Tables 1 and 2, 0–10% color reduction).

The elution pattern of the colored material from the oil (Table 3) indicates that the constituents are more polar than the neutral lipids of RBO. The methanol fraction contained 6.8% oryzanol and unidentified oxidation products of monoglycerides (Gopala Krishna, A.G., unpublished data).

The color adsorption capacity of the silica gel did not seem to be affected by the moisture content (0–15%) of gel, but the particle size and acidity of the gel had an effect. For example, particle sizes of silica gel used were 4–20, 60–120 and 100–200 mesh with pH values of 7.0, 6.3 and 6.3, respectively. Silica gel of 4–20 mesh was an

TABLE 2

Effect of Rice Bran Oil-Miscella Percolation Through Silica Gel Column on Color of Bleached Oil

Sample	Color[a] after bleaching	
	Centrifuge method	AOCS Cup method
1. Dewaxed oil (control)	5.5	9.0
2. Oil 1 after SGP[b]	2.0 [63.6%][c]	3.0 [66.7%][c]
3. Crude oil (control)	5.5	—
4. Oil 3 after SGP[b]	1.5 [72.7%][c]	—
5. Refined oil (control)	3.3	8.8
6. Oil 5 after SGP[b]	3.3 [0%][c]	—

[a]Color is expressed as 5R + Y Lovibond units in a 1-cm cell.

[b]SGP = silica gel percolation followed by refining and bleaching for samples 2 and 4; sample 6, after silica gel percolation, was subjected to bleaching only.

[c]Values in brackets are the color reduction after silica-gel column-percolation treatment followed by refining and bleaching.

TABLE 3

Elution Patterns of Color Constituents of Rice Bran Oil from Silica-Gel Column Percolation of Oil Miscella[a]

Fraction from silica gel column	Color of oil as 5R + Y Lovibond units		Weight of fraction (g)	
	a	b	a	b
I fraction (hexane)	19	19	23.8	21.0
II fraction (benzene)	40	40	8.0	9.6
III fraction (methanol)	(25)[b]	(25)[b]	2.0	1.9
Starting oil	40	40	34.0	33.0

[a]a and b are replicates.

[b]Dark material; color value is for 2.3% solution of the dark material fraction.

absorbent gel and others were adsorbent-type gels. Absorbent silica gel of 4–20 mesh was not effective even after activation at temperatures of 120 to 600°C for 8–24 h. Decreasing the particle size of this gel to 60–120 mesh by grinding, followed by activation (as given above for 4–20 mesh gel) also did not improve its color adsorption capacity, indicating that it is not the particle size that is important, but the pH (acidity) of the gel. In two other cases, decreasing the particle size of silica gel (of the same pH) from 60–120 mesh to 100–200 mesh improved the color adsorption capacity of the gel, but it reduced the flow rate of the column to <0.1 mL/min. Therefore, it may be argued that both particle size and acidity of the adsorbent silica gel had an effect on the color adsorption from oil-miscella.

Silica gel mixing with miscella. A ratio of gel/oil/solvent of 1:5:5 (wt/wt/vol) as determined by the column percolation procedure can be maintained by treatment of silica gel/oil/solvent in 1:1:1 (wt/wt/vol) ratio in five batches. This was done to avoid the problems of slow flow rate and plugging of the column, due to precipitation of wax when RBO was used for color removal by the column percolation procedure. The data on color removal with silica gel by mixing with miscella in five batches (on the same adsorbent) is presented in Table 4. Recovery of miscella after silica gel treatment of up to five batches, followed by washing the silica gel in the flask with hexane (sixth batch) and methanol (seventh batch), showed that in each batch 50–85% of oil of less color can be recovered successively, but the efficiency of the gel to remove color per gram came down to 19–36% (Table 4) compared with 30-72% (Tables 2 and 5) for the column percolation procedure.

The present method consists of passing the oil miscella through a silica gel (60-120 mesh size) column (gel/oil/solvent ratio of 1:5:5 wt/wt/vol), followed by collecting the eluent, which after solvent removal gives oil of less color. After further processing (as given in Table 6) it produces an oil similar in color to refined peanut oil. After completion of miscella percolation (*i.e.*, when no more eluent comes out of the column), the gel was regenerated by washing with 70% hexane-absolute ethanol mixture (gel/solvent ratio of 1:5 wt/vol), and the eluent was collected. Then the column, after one wash with fresh hexane, can be reused for color removal from a fresh batch

TABLE 4

Color and Recovery Values of Rice Bran Oil by Repetitive Shaking of Oil Miscella with Silica Gel[a]

Batch number	Recovered miscella				Color		
	Total volume (mL)		Oil weight (g)		Lovibond units		Mean reduction[b] (%)
	a	b	c	d	e	f	
1	32	27	16.0	12.8	24	24	22.6
2	34	31	16.9	17.6	24	24	22.6
3	37	41	19.6	22.3	25	24.5	19.4
4	38	38	20.4	17.8	25	25	19.4
5	40	38	10.8	11.0	25	21	25.8
6	42	41	6.5	6.7	20	20.5	35.5
7	82	84	8.5	8.8	59	69	—[c]
Total	305	300	98.7	96.9	—	—	—
Recovery (%)	—	—	98.7	96.9	—	—	—

[a]a and b, c and d, and e and f are replicates.

[b]Color reduction (%) = (31 − (e + f) /2) × 100/31. Initial value was 31.

[c]Value not calculated, fraction 7 has all coloring constituents adsorbed by silica gel from fractions 1 to 6.

TABLE 5

Color and Recovery Values of Rice Bran Oil by Repetitive Silica-Gel Column-Percolation of Oil Miscella (present method)

Sample	RBO[a] subjected to present method					
	Color			Oil recovery (%)		
	a	b	c	a	b	c
1. Initial oil	40	40	11.5	—	—	—
2. After silica-gel column-percolation treatment	20 (50%)[b]	11 (72.5%)[b]	8.0 (30.4%)[b]	90.0	95.6	94.0
3. Adsorbed oil eluted with 70% hexane-ethanol mixture	—	—	—	10.0	4.4	6.0

[a]Rice bran oil (RBO) a and b were crude oil of 6.8 and 9.5% free fatty acid (FFA), and RBO c was a dewaxed oil of 10.1% FFA.

[b]Values in brackets represent the color reduction of RBO on duplicate samples.

TABLE 6

Modification of Processing Steps Suggested, Based on This Study

Normal practice in the industry	Suggested practice
1. Degumming	1. Silica-gel column-percolation
2. Dewaxing (1st time)	2. Degumming
3. Refining	3. Dewaxing
4. Bleaching	4. Refining
5. Dewaxing (2nd time) and deodorization	5. Bleaching and deodorization

of RBO. The eluent after solvent removal gives a dark-colored oil rich in oryzanol as a by-product (benzene and methanol were used earlier for regenerating the silica gel only for experimental purposes). The data in Table 5 show that color reduction of RBO of varied FFA content is possible to the extent of 30–72% by this method.

Commercially refined RBO's have intense brownish yellow color (16–20 Lovibond units), but the oil obtained by silica-gel column-percolation treatment of the dewaxed oil, followed by refining and bleaching, gave light-colored oil compared with commercially produced RBO (Table 2). However, color values could not be further reduced to a noticeable degree for RBO refined in the laboratory [by the AOCS cup method (7)], implying that commercially refined RBO of high color cannot be further improved by the present procedure. The method may be included for improving the color of RBO before or after dewaxing as indicated in Table 6.

Silica-gel treatment of miscella through column percolation was more efficient (30–72% reduction of color units) than batch treatment (19–36% reduction of color units, Tables 4 and 5). The silica-gel column-percolation technique has recovery values of 100.0, 100.8 and 99.0% for oils with 6.8, 9.5 and 10.1% FFA, respectively, and will be useful for making light-colored oil from solvent-extracted and dewaxed RBO. The color for silica gel-percolated oil was much lower than that for control oil (Table 2). The only disadvantage of the method was the slow flow rates of the oil miscella (especially for solvent-extracted crude RBO) through the silica gel column.

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REFERENCES

1. Cornelius, J.A., *Trop. Sci. 22*:1 (1980).
2. *Rice Chemistry and Technology,* edited by B.O. Juliano, The American Association of Cereal Chemists, Inc., St. Paul, 1985, p. 666.
3. Indian Standard Specification for Rice Bran Oil, IS:3448-1984, Indian Standards Institution, New Delhi, India, 1985.
4. Indian Standard Specification for Groundnut Oil, IS:544-1968, Indian Standards Institution, New Delhi, India, 1968.
5. Mishra, A., A.G. Gopala Krishna and J.V. Prabhakar, *J. Am. Oil Chem. Soc. 65*:1605 (1988).
6. *Official and Tentative Methods of the American Oil Chemists' Society,* Vol. I, 3rd edn., edited by W.E. Link, American Oil Chemists' Society, Champaign, 1973, Method Ca 5a-40.
7. *Ibid.,* Method Ca 9a-52.
8. *Ibid.,* Method Cc 8b-52.

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