Evaluation of Different Types of Synthetic Adsorbents for Carotene Extraction from Crude Palm Oil

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ABSTRACT: Palm carotene was successfully concentrated from crude palm oil (CPO) by an adsorption process using synthetic adsorbents followed by solvent extraction. This process was a modified process for separation of palm carotene from CPO by adsorption chromatography with a synthetic polymer adsorbent. Carotene was concentrated to about 15,000 ppm, which is about 25 times the original concentration in CPO. Carotene recovery varied from 30 to 62% depending on the process conditions. Different types of adsorbents, combinations of adsorbents, and adsorbent/CPO ratios were evaluated to determine the effect on the percentage of carotene extracted. Commercial synthetic adsorbents HP 20 (styrene-divinyl copolymer); synthetic aromatic porous resin SP 850, SP 825; and synthetic adsorbents Relite Exa 32 and Relite Exa 50 were capable of adsorbing substantial amounts of carotene from CPO. Combinations of adsorbents types HP 20 and SP 850 slightly increased the percentage of carotene extracted. An adsorbent/CPO ratio of 4 was most suitable for this process for optimal recovery and concentration of carotene.

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KEY WORDS: Adsorption, crude palm oil, palm carotene, synthetic adsorbents.

Crude palm oil (CPO) is the world's richest source of natural plant carotenoids in terms of retinol (pro-vitamin A) equivalent (1). It contains about 15 to 300 times more retinol equivalent than carrots, green leafy vegetables, and tomatoes (2). Various methods of carotenoid recovery from palm oil have been reported. These include saponification (3,4), adsorption (5), selective solvent extraction (6,7), transesterification followed by distillation, and others (8–12). However, in all of these processes, CPO has to be converted to methyl esters, which are not edible.

A process of separating carotene from CPO by adsorption chromatography with a synthetic polymer adsorbent was successfully developed by our research group (13). However, this chromatographic process is still not commercially proven and may slow down the refining process if the process is to be introduced in the existing palm oil refining. Therefore, the objective of this study was to develop a modified process of carotene extraction from CPO by adsorption with synthetic adsorbent that could speed up the carotene extraction process and maintain the edible oil quality of CPO. In this study different types of synthetic adsorbents, combinations of adsorbents, and adsorbent/CPO ratios were evaluated.

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MATERIALS AND METHODS

Materials. CPO was obtained from Golden Jomalina Food Industries (Teluk Panglima Garang, Selangor, Malaysia). All solvents used were of industrial grade. Synthetic highly porous resin (HP 20), a styrene-divinyl benzene (SDVB) copolymer, was obtained from Mitsubishi Chemical Corporation (Tokyo, Japan). Synthetic porous resin (SP) series (SP 850, SP 825, and SP 207) were obtained from the same company. Synthetic adsorbents Relite Exa 31, Relite Exa 32, and Relite Exa 50 were obtained from Resindion (Milano, Italy). The physical properties of the synthetic adsorbents are shown in Table 1.

Adsorption. The adsorption was conducted in a 2000-mL round-bottomed flask. Adsorbents were washed with isopropanol (IPA) for about 15 min with virogous agitation. The adsorbents were separated from IPA and dried at room temperature before using them for the adsorption process. All of the feed CPO that was used in this study was diluted with three parts of IPA. The adsorption process was initiated by adding diluted CPO to the washed adsorbent in the round-bottomed flask at 10 mL/min, with mixing; over a period of 1 h about 600 mL of diluted CPO was added. The flask was maintained at 50–55°C by immersion in a controlled-temperature water bath.

TABLE 1
Physical Properties of the Synthetic Adsorbents

	Physical properties[c]		
Synthetic adsorbent	Pore volume (mL/g)	Pore radius (Å)	Surface area (m^2/g)
HP 20[a]	1.30	260	511
SP 850[a]	1.20	38	995
SP 825[a]	1.39	57	977
SP 207[a]	1.08	105	627
Relite Exa 31[b]	1.20	175	470
Relite Exa 32[b]	1.30	250	600
Relite Exa 50[b]	1.40	70	950

[a]Manufactured by Mitsubishi Chemical Corporation (Tokyo, Japan).
[b]Manufactured by Resindion (Milano, Italy).
[c]Data from Reference 15 and from P. Caimi (personal communication, Resindion, Mitsubishi Chemical Corporation, Italy, 1998).

Solvent extraction. After the adsorption process had been completed, the CPO/adsorbent slurry was put in a 2,000-mL Soxhlet extractor to extract the CPO from the adsorbent using IPA. The IPA extraction time was about 2.5 h at 80–85°C. Hexane was then used to extract the carotene from the adsorbent. The carotene extraction process was carried out at 60–65°C and was continued until the adsorbent became clear (about 4 h). Solvents were removed from the IPA fractions, which contained CPO, and hexane fractions, which contained carotene, in a vacuum evaporator.

Analysis. The carotene content was determined by diluting a 1-mL aliquot of each fraction with hexane to the appropriate dilution and measuring absorbance in a Shimadzu UV-1601 (Shimadzu Corporation, Kyoto, Japan) at 446 nm.

Statistical analysis. Data were statistically analyzed by a one-way analysis of variance procedure using an SAS (14) software package. Significant differences ($P < 0.05$) between means were further determined by Duncan's multiple-range test.

RESULTS AND DISCUSSION

Evaluation of different types of adsorbents. Synthetic highly porous resin (HP 20), synthetic porous resin (SP 850, SP 825, and SP 207), and synthetic adsorbents Relite Exa 31, Relite Exa 32, and Relite Exa 50 were used for the evaluation of carotene extraction from CPO. For evaluation of HP 20, SP 850, SP 825, and SP 207, 700 g of adsorbents and 175 g of CPO were used. For evaluation of Relite Exa 31, Relite Exa 32, and Relite Exa 50, the quantities of adsorbents and CPO were 120 and 30 g, respectively. Quantities of IPA and hexane for all these experiments were about 2,500 mL.

Table 2 shows the result of carotene extraction by different types of adsorbents. All of the synthetic adsorbents tested were capable of adsorbing substantial amounts of carotene from CPO except for SP 207 and Relite Exa 31. The percentage of carotene extracted in the hexane fraction ranged from 44 to 70%, with the concentration ranging from 1,200 to 3,700 ppm. The capability of the above-mentioned adsorbents to adsorb carotene from CPO is due to the similarity of the molecular structures of carotene and the adsorbents and also to hydrophobic interaction between the adsorbents and carotene (13).

The synthetic adsorbent HP series and SP series are three-dimensional cross-linked polymers with macropores. They do not possess ion exchange or other functional groups; however, they have a large surface area and are able to adsorb a variety of organic substances by means of van der Waals' forces (15). HP series resins were the first SDVB synthetic adsorbents developed by Mitsubishi Chemical Corporation, Japan. As they have fairly large pores (1.30 mL/g) and a specific surface area of 511 m^2/g, they are well suited to the adsorption of large molecules. Because adsorbed substances can be easily eluted from the HP series resins, the resins are used in many different industrial fields. HP 20 is the most widely used among the whole series, especially in pharmaceutical and food industries.

For the SP 800 series, an aromatic porous resin matrix has been specially treated to increase its specific surface and to introduce a uniform pore network. SP 850 has a large specific surface (995 m^2/g) and smaller pores (1.20 mL/g) than the HP series and a sharp pore distribution, so they can adsorb large quantities of small molecules. SP 850 gave the highest percentage of carotene extracted (69.47%) compared to other adsorbents; it has the largest specific surface area. SP 825 has a slightly smaller specific surface (977 m^2/g) and slightly larger pores

TABLE 2
Effect of Different Types of Adsorbent on the Percentage of Carotene Extracted[a]

			Carotene		
Type of adsorbent	Fractions[a]	Oil quantity (g)	Content (mg)	Recovery (%)	Concentration (ppm)
HP 20	IPA	112.53	31.56	33.6	281
	Hexane	35.57	57.65	61.4	1,621
SP 850	IPA	114.07	23.33	21.3	205
	Hexane	59.37	76.11	69.5	1,282
SP 825	IPA	124.41	24.14	24.5	194
	Hexane	48.88	63.25	64.2	1,294
SP 207	IPA	129.44	17.47	20.7	136
	Hexane	20.32	9.67	11.5	476
Relite Exa 31	IPA	29.59	15.42	90.0	521
	Hexane	0.08	0.14	0.8	1,743
Relite Exa 32	IPA	27.06	6.60	37.7	244
	Hexane	2.70	9.96	56.8	3,688
Relite Exa 50	IPA	27.35	4.84	27.6	177
	Hexane	2.42	7.71	44.0	3,185

[a]Basis of calculation; crude palm oil (CPO) feed with original carotene concentration of about 600 ppm. For evaluation of HP 20, SP 850, SP 825, and SP 207, 700 g of adsorbents and 175 g of CPO were used. For evaluation of Relite Exa 31, Relite Exa 32, and Relite Exa 50, the quantity of adsorbents and CPO were 120 and 30 g, respectively. Quantities of isopropanol (IPA) and hexane used for all these experiments were 2500 mL. Results have been expressed as the arithmetic mean of three results. Total recoveries in the two extract fractions were not 100% because the adsorbents retained some of

compared to SP 850. As the chemical structure of the adsorbing matrix of both adsorbents is exactly the same as in the HP series, adsorbed substances can be eluted from the resin with the same ease.

SP 207 is a highly porous, styrene-based adsorption resin with bromine groups chemically bonded to the cross-linked polystyrene matrix to enhance hydrophobic adsorption properties. SP 207 has much better adsorption capacity than conventional HP series. But in some cases, elution of adsorbed material is more difficult due to the greater adsorption forces, and more eluant is required. Therefore, for these experiments, the quantity of IPA used may not have been enough to elute all the oil adsorbed onto the adsorbent. The total percentage of carotene extracted (IPA and hexane fractions) was only about 33% whereas for the other adsorbents, the total percentage of carotene extracted was 72–95% (from Table 2).

Relite Exa 31 is a new type of synthetic adsorbent with a methacrylic highly porous matrix, having a calibrated pore structure and a medium hydrophobicity value. The percentage of carotene extracted from CPO by using Relite Exa 31 was very low, only about 0.8% (hexane fraction), and most of the carotene was eluted together with the oil during the IPA extraction process (Table 2).

Relite Exa 32 and 50 are highly porous synthetic adsorbents based on a SDVB copolymer with a uniform pore structure and a high degree of hydrophobicity. The physical properties of Relite Exa 32 are very similar to those of HP 20, whereas those of Relite Exa 50 are very similar to those of SP 825 (Table 1).

Combination of adsorbents (HP 20 and SP 850). The evaluation of the combination of adsorbents (Table 3) and the effect on the percentage of carotene extracted from CPO were conducted.

The pore radii of the HP 20 and SP 850 are 260 and 38 Å, respectively (16). Therefore, the combination of adsorbents will increase the specific surface area of the adsorbents, which can provide more adsorbing capability. The combination of 80% HP 20/20% SP 850, 70% HP 20/30% SP 850, and 60% HP 20/40% SP 850 gave a significantly ($P < 0.05$) higher percentage of carotene extracted than the other combinations. In general, these results indicated that the combination of adsorbents increased the percentage of carotene extracted. Based on the highest mean, the combination of 70% HP 20 and 30% SP 850 gave the highest percentage of carotene extracted (54.55%).

Adsorbent/CPO ratio. Experiments were conducted to determine the optimal adsorbent/CPO ratio for the highest yield of carotene extraction from CPO. For those experiments 40, 50, 60, 75, 100, 150, and 200 g of CPO were used with 300 g HP 20. The quantities of IPA and hexane used were 800 mL for each. Table 4 shows the effect of adsorbent/CPO ratio on the percentage of carotene extracted. The percentage of carotene extracted increased with the increase of adsorbent/CPO ratio as more carotene was adsorbed on the surface of the adsorbent. This is due to increased binding site availability. The percentage of carotene extracted ranged from 30 to 62%, and the carotene concentration ranged from 6,513 to 14,280 ppm. However, for these experiments, the adsorbent/CPO ratio of 4 seemed to be the most suitable condition where the percentage of carotene extracted was 53.93% and the carotene concentration was 7,212 ppm. Further increase in the adsorbent/CPO ratio did not significantly affect the percentage of carotene extracted.

The selection of the adsorbent/CPO ratio of 4 was also based on the selection matrix as shown in Table 5 (17). Table 5 is based on the Juran's Breakthrough for Quality Improvement Process. There are six steps involved in this process: (i) identify a project; (ii) establish the project; (iii) diagnose the cause; (iv) remedy the cause; (v) hold the gains; and (vi) replicate results and nominate new projects. In the process of getting the most effective and appropriate remedy (step 4), a remedy selection matrix is used. The selection matrix normally contains identified remedies, the weight of each remedy, and the rating. Rating is based on the set criteria. The most effective and appropriate remedy is chosen based on the highest total rating. In this study, carotene recovery, adsorbent/CPO ratio and carotene concentration were chosen as the criteria for selection. The highest weight was given to carotene recovery because it was the main objective of this study. Second-highest was given to the adsorbent/CPO ratio because of its impact on the cost of the extraction process. The lowest weight was given to carotene concentration because the result obtained was only an indication and a further purification process should be developed to achieve higher carotene concentration. Therefore, based on the set criteria and the highest total rating (83.3%), an adsorbent/CPO ratio of 4 was the most suitable condition for this experiment.

TABLE 3
Effect of Combination of Adsorbents on the Percentage of Carotene Extracted[a]

Combination of adsorbents	Carotene recovery (%)
100% HP 20	$44.92 \pm 4.19^{c,d}$
90% HP 20/10% SP 850	$47.56 \pm 5.39^{a,b,c,d}$
80% HP 20/20% SP 850	53.95 ± 3.59^{a}
70% HP 20/30% SP 850	54.55 ± 5.09^{a}
60% HP 20/40% SP 850	54.28 ± 3.37^{a}
50% HP 20/50% SP 850	$49.04 \pm 4.71^{a,b,c}$
40% HP 20/60% SP 850	$52.14 \pm 0.16^{a,b}$
30% HP 20/70% SP 850	$48.72 \pm 3.36^{a,b,c}$
20% HP 20/80% SP 850	$46.71 \pm 2.34^{b,c,d}$
10% HP 20/90% SP 850	$48.79 \pm 3.10^{a,b,c}$
100% SP 850	41.39 ± 1.49^{d}

[a]Basis of calculation; CPO feed with original carotene concentration of 600 ppm. Three hundred grams of adsorbents (HP 20 and SP 850) and 75 g of CPO were used in these experiments. The quantities of IPA and hexane used were 800 mL. Results have been expressed as mean ± standard deviation of three experiments. Means with different roman superscripts are significantly ($P < 0.05$) different. For abbreviations and adsorbent properties see Tables 1 and 2.

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TABLE 4
Effect of Adsorbent/CPO Ratio on the Percentage of Carotene Extracted[a]

Adsorbent CPO ratio	Fractions[a]	Oil quantity (g)	Carotene Content (mg)	Carotene Recovery (%)	Carotene Concentration (ppm)
1.5	IPA	192.28	65.93	59.8	342
	Hexane	6.79	33.10	30.3	6914
2.0	IPA	141.57	45.70	53.6	321
	Hexane	7.33	32.36	38.3	10,588
3.0	IPA	95.62	28.77	50.5	299
	Hexane	3.51	27.14	48.1	14280
4.0	IPA	71.21	17.91	42.0	251
	Hexane	3.26	22.91	53.9	7,212
5.0	IPA	56.90	13.99	41.0	245
	Hexane	2.65	18.07	53.2	7,665
6.0	IPA	46.86	10.40	36.8	222
	Hexane	2.70	17.80	62.5	6,513
7.5	IPA	38.06	8.17	36.0	214
	Hexane	2.21	13.28	58.6	6,626

[a]Basis of calculation; crude palm oil (CPO) feed with original carotene concentration of about 600 ppm. Synthetic adsorbent HP 20 (300 g) and 40, 50, 75, 100, 150, and 200 g of CPO were used in these experiments. The quantities of IPA and hexane used were 800 mL. Results have been expressed as the arithmetic means of three results. For abbreviations see Table 2.

TABLE 5
Selection Matrix for Adsorbent/CPO Ratio[a]

Criteria	Weight	Adsorbent/CPO ratio 1.5	2.0	3.0	4.0	5.0	6.0	7.5
1. Carotene recovery	50%	1	1	2	3	3	3	3
2. Adsorbent/CPO ratio	30%	3	3	2	2	1	1	1
3. Carotene concentration	20%	1	3	3	2	2	1	1
Total rating (%)	100%	53.3	66.7	73.3	83.3	73.3	66.7	66.7

[a]Rating:

Carotene recovery		Adsorbent/CPO ratio		Carotene concentration	
Less than 40%	1	Equal to or more than 5	1	Less than 7000 ppm	1
40 to 50%	2	More than 2 but less than 5	2	7000 to 10,000 ppm	2
More than 50%	3	Equal or less than 2	3	More than 10,000 ppm	3

Total rating (%) = {[(rating for criterion no. 1 × weight)/total rating] + [(rating for criterion no. 2. × weight)/total rating] + [(rating for criterion no. 3 × weight)/total rating]} × 100%

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