Effect of Adsorption and Solvent Extraction Process on the Percentage of Carotene Extracted from Crude Palm Oil

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ABSTRACT: Palm carotene was successfully concentrated from crude palm oil (CPO) by a batch adsorption process using a synthetic (polymer) adsorbent followed by solvent extraction. Carotene was concentrated to about 20,000 ppm, or about 33.3 times the original concentration in CPO. Carotene recovery varied from 16 to 74% depending on the process conditions. Adsorption times, isopropanol (IPA) extraction times, temperatures of adsorption and solvent extraction process, effect of agitation during IPA extraction process, and adsorbent lifespan were evaluated to determine their effects on the percentage of carotene extracted and carotene concentration. The minimum adsorption time required was 0.5 h. However, an adsorption time of 1.5 h gave a significantly higher carotene concentration than adsorption times of 0.5, 1.0, and 0.2 h. The IPA extraction time was determined based on the final carotene concentration desired. The suitable temperature for adsorption and solvent extraction process was 40°C. There was no significant difference in the percentage of carotene extracted and carotene concentration between the IPA extraction process with and without agitation.

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KEY WORDS: Adsorption, palm carotene, palm oil, solvent extraction, 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 and green leafy vegetables, which are considered to have significant quantities of pro-vitamin A activities (2). Various methods of carotenoid recovery from palm oil have been reported. These include saponification (3,4), adsorption (5), selective solvent extraction (6), and transesterification followed by distillation (7–10). Only the transesterification followed by distillation process has been further developed into a commercial-scale process. However, the CPO has to be converted to methyl esters, which are not edible.

Our research group has successfully developed a process of separating carotene from CPO by adsorption chromatography with a synthetic polymer adsorbent (11). However, this chromatographic process is still not commercially proven and may slow the refining process if the process is to be introduced to existing palm oil refining systems. 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. These studies evaluated the adsorption times, isopropanol (IPA) extraction times, temperatures of the adsorption and solvent extraction processes, effect of agitation during IPA extraction, and adsorbent lifespan on the percentage of carotene extracted and carotene concentration.

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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 850), also a SDVB copolymer, was obtained from the same company.

Adsorption. The adsorption process was conducted in a 2,000-mL round-bottomed flask. The adsorbent was treated with IPA for about 15 min at a fast stirrer speed. The adsorbent was separated from IPA and dried at room temperature before using it for the adsorption process. CPO was diluted with three parts of IPA. The adsorption process was conducted at three temperatures (40, 55, and 80°C) and for four time periods (0.5, 1.0, 1.5, and 2.0 h) by adding diluted CPO to the dried adsorbent in the round-bottomed flask at 10 mL/min, while maintaining stirrer speed at 120 rpm.

Solvent extraction. After the adsorption process had been completed, the CPO and adsorbent were put in a 2,000-mL Soxhlet extractor or jacketed extraction flask to extract the CPO from the adsorbent using IPA at specified extraction times (0.5, 1.0, 2.0, and 2.5 h) and temperatures (40, 55, and 80°C). Hexane was then used to extract the carotene from the adsorbent. The carotene extraction was carried out as described in Reference 12.

Adsorption time. The resin HP 20 (300 g) and CPO (75 g) were used in these experiments. The adsorption process was conducted at 50–55°C for 0.5, 1.0, 1.5, and 2.0 h. The IPA extraction process was carried out in a 2,000-mL Soxhlet extractor at 80–85°C for about 2.5 h. The quantities of IPA and hexane used were about 2,500 mL.

IPA extraction time. The experiments on the effect of IPA extraction time were carried out to determine the suitable

TABLE 1
Effect of Adsorption Time on the Percentage of Carotene Extracted[a]

Absorbent time (h)	Fractions	Oil quantity (g)	Carotene Content (mg)	Carotene Recovery (%)	Carotene Concentration (ppm)
0.5	IPA	69.88 ± 1.81	18.88 ± 6.59	40.22 ± 14.02	270 ± 91
	Hexane	4.83 ± 1.87	21.09 ± 2.77	44.92 ± 5.90^{A}	4,739 ± 1,470^{C}
1.0	IPA	70.66 ± 1.98	22.27 ± 1.77	47.44 ± 3.77	315 ± 19
	Hexane	4.00 ± 1.92	19.82 ± 2.69	42.21 ± 5.72^{A}	5,458 ± 1,624^{C}
1.5	IPA	71.97 ± 0.69	26.60 ± 2.04	55.51 ± 4.34	363 ± 25
	Hexane	2.53 ± 0.61	21.32 ± 3.41	45.42 ± 7.27^{A}	8,633 ± 1,602^{B}
2.0	IPA	69.62 ± 2.10	22.38 ± 1.26	47.67 ± 2.69	321 ± 10
	Hexane	5.08 ± 2.05	20.86 ± 1.37	44.42 ± 2.92^{A}	4,449 ± 1,294^{C}

[a]Basis of calculation: crude palm oil (CPO) feed with original carotene concentration (about 600 ppm) determined by absorbance at 446 nm and calculated as β-carotene. Three hundred grams of a synthetic highly porous resin (HP 20; Mitsubishi, Tokyo, Japan) of adsorbent (HP 20) and 75 g of CPO were used in these experiments. The adsorption process was conducted at 50–55°C. The isopropanol (IPA) extraction process was carried out in a 2,000-mL Soxhlet extractor at 80–85°C for about 2.5 h. Carotene extraction was carried out at 60–65°C and was continued until the adsorbent became clear (about 4 h). The quantities of IPA and hexane used were 2,500 mL. Results have been expressed as mean ± standard deviation of three experiments. Means with different superscripts are significantly ($P < 0.05$) different.

amount of IPA to be used in the extraction of CPO from the adsorbent. In these experiments, 300 g of HP 20 and 75 g of CPO were used. The adsorption process was conducted at 50–55°C for about 1 h. The IPA extraction process was carried out in a 2,000-mL Soxhlet extractor at 80–85°C for 0.5, 1.0, 1.5, 2.0, and 2.5 h. The quantities of IPA and hexane used were about 800 mL.

Temperature of adsorption and solvent extraction process. Three hundred grams of two synthetic porous resins (70% of HP 20 and 30% of SP 850) and 75 g of CPO were used in these experiments. The adsorption and IPA extraction process was conducted at 40, 55, and 80°C. The adsorption time was 0.5 h. The IPA extraction was conducted in a 2,000-mL jacketed extraction flask. IPA (600 mL) at 60 mL/min was used to extract the CPO from the adsorbent. The carotene extraction was carried out in a 2,000-mL Soxhlet extractor at 60–65°C. Hexane (2,500 mL) was used to extract the carotene from the adsorbent.

Agitation during IPA extraction. The experiments on the effect of agitation during the IPA extraction process were carried out using 300 g of HP 20/SP 850 (70:30) and 30 g of CPO. The adsorption process was conducted at 50–55°C for 0.5 h. The IPA extraction was conducted in a 2,000-mL round-bottomed flask using 1,000 mL of IPA with agitation for about 10 min. This process allowed the CPO that was adsorbed on the surface of the adsorbent to transfer into the IPA. At the end of the process, the mixtures, the IPA and CPO, and adsorbent were kept for a while to allow the adsorbent to settle. The IPA and CPO were then decanted from the adsorbent. This IPA extraction process was repeated 10 times. Hexane (2,500 mL) was used for carotene extraction process. A similar method was applied for the experiments without agitation as a comparison, except that the IPA extraction process was conducted in a 2,000-mL jacketed extraction flask.

Adsorbent lifespan. In these experiments 300 g of HP 20 and 75 g of CPO were used. The adsorption process was carried out at 50–55°C for about 0.5 h in a 2,000-mL jacketed extraction flask. The temperature for IPA extraction was maintained at 50–55°C, and 6,000 mL of IPA, at 60 mL/min, was used to extract the CPO from the adsorbent. Hexane (2,500 mL) was used to extract the carotene from the adsorbent.

Analysis. The carotene content was determined as described in References 12 and 13.

Statistical analysis. Data were statistically analyzed as described in References 12 and 14.

RESULTS AND DISCUSSION

Adsorption time. Table 1 shows the results of carotene extraction at different adsorption times. The percentage of carotene extracted in the hexane fraction ranged from 42 to 45%, with the concentration ranging from 4,500 to 8,600 ppm. According to the supplier of this resin (15), more than 90% of cephalosporin was adsorbed in 1 h using this resin. However, based on our experiments, the minimum adsorption time required for carotene extraction from CPO was 0.5 h. Any further increase in the adsorption time did not have a significant ($P > 0.05$) impact on the percentage of carotene extracted. This is due to the adsorption capacity of the adsorbent having reached its maximum at even shorter adsorption times. In other words, the adsorbent and the surrounding fluid (diluted CPO) reached equilibrium (16). An adsorption time of 1.5 h gave a significantly ($P < 0.05$) higher carotene concentration in the hexane fraction than adsorption times of 0.5, 1.0, and 2.0 h. Extractions between adsorption times of 0.5, 1.0, and 2.0 h produced results that were not significantly ($P > 0.05$) different from each other.

TABLE 2
Effect of IPA Extraction Time on the Percentage of Carotene Extracted[a]

IPA extraction time (h)	Fractions	Oil quantity (g)	Carotene Content (mg)	Carotene Recovery (%)	Carotene Concentration (ppm)
0.5	IPA	51.03 ± 1.03	10.50 ± 0.86	23.93 ± 1.95	206 ± 21
	Hexane	23.05 ± 1.53	31.68 ± 0.11	72.19 ± 0.26^{A}	1,378 ± 86^{F}
1.0	IPA	51.03 ± 1.03	11.51 ± 2.33	26.22 ± 5.30	215 ± 38
	Hexane	23.05 ± 1.53	32.39 ± 0.05	73.81 ± 0.12^{A}	1,559 ± 74^{F}
1.5	IPA	63.70 ± 0.22	13.37 ± 2.73	30.47 ± 6.21	210 ± 44
	Hexane	10.37 ± 0.47	27.05 ± 0.02	61.65 ± 0.05^{B}	2,610 ± 97^{E,F}
2.0	IPA	65.28 ± 0.57	15.05 ± 1.86	34.30 ± 4.23	231 ± 30
	Hexane	8.69 ± 0.67	26.70 ± 0.18	60.84 ± 0.41^{B}	3,084 ± 217^{E}
2.5	IPA	71.21 ± 0.28	17.88 ± 3.30	40.75 ± 7.53	251 ± 46
	Hexane	3.26 ± 1.02	22.95 ± 3.09	51.16 ± 7.05^{C}	7,212 ± 1,563^{D}

[a]Basis of calculation: CPO feed with original carotene concentration (about 600 ppm) determined by absorbance at 446 nm and calculated as β-carotene. Three hundred grams of adsorbent (HP 20) and 75 g of CPO were used in these experiments. The adsorption process was conducted at 50–55°C. The IPA extraction process was carried out in a 2,000-mL Soxhlet extractor at 80–85°C. Carotene extraction was carried out at 60–65°C and was continued until the adsorbent became clear (about 4 h). The quantities of IPA and hexane used were 800 mL. Results have been expressed as mean ± standard deviation of three experiments. Means with different superscripts are significantly ($P < 0.05$) different. For abbreviations and manufacturer see Table 1.

IPA extraction time. Table 2 shows the result of carotene extraction at different IPA extraction times. The percentage of carotene extracted in the hexane fraction ranged from 51 to 74% with the carotene concentration ranging from 1,400 to 7,200 ppm. The IPA extraction times of 0.5 and 1.0 h gave significantly ($P < 0.05$) higher percentages of carotene extracted than the IPA extraction times of 1.5, 2.0, and 2.5 h. Between the times of 0.5 and 1.0 h, IPA extractions were not significantly ($P > 0.05$) different from each other; and IPA extractions between 1.5 and 2.0 h were also not significantly ($P > 0.05$) different from each other. The IPA extraction time of 2.5 h gave significantly ($P < 0.05$) higher carotene concentration than extraction times of 0.5, 1.0, 1.5, and 2.0 h. The results for IPA extraction times of 1.5 and 2.0 h were not significantly ($P > 0.05$) different from each other, and those for between 0.5, 1.0, and 1.5 h were also not significantly ($P > 0.05$) different from each other. Based on these results, the percentage of carotene extracted increased with shorter IPA extraction time. At a fixed solubility, use of a lower IPA volume would mean a lower quantity of carotene extracted together with CPO, leaving more carotene to be extracted later with hexane. However, the carotene concentration is lower at shorter IPA extraction times owing to incomplete CPO extraction by IPA. Therefore, the suitable IPA extraction time is based on the targeted final carotene concentration.

Temperature of adsorption and solvent extraction process. Table 3 shows the results of carotene extraction at different adsorption and IPA extraction temperatures. A temperature of 40°C for adsorption and solvent extraction gave a significantly ($P < 0.05$) higher percentage of carotene extracted in hexane fraction than temperatures 55 and 80°C. An 80°C temperature of adsorption and solvent extraction gave significantly ($P < 0.05$) higher carotene concentrations than temperatures of 40 and 55°C. Results when the temperatures of adsorption and solvent extraction were 40 and 55°C were not significantly ($P > 0.05$) different from each other. Based on these results, the percentage of carotene extracted in hexane fraction reached 43% at 40°C; at higher temperatures, the percentage of carotene extracted became lower. The carotene concentration was 6,400 ppm at 40°C and increased with increasing temperature because the degradation of carotene and the solubility of oil in IPA were increased. As the solubility of oil in IPA increased, more carotene is extracted together with the oil during IPA extraction, resulting in a lower percentage of carotene extracted and higher carotene concentration in hexane fraction. Therefore, the optimal temperature for adsorption and IPA extraction process was at 40°C.

Agitation during IPA extraction. Table 4 shows the result of carotene extraction with agitation and without agitation during IPA extraction. The percentage of carotene extracted in the hexane fraction ranged from 34 to 38% with the carotene concentration ranging from 8,000 to 9,600 ppm. There was no significant ($P > 0.05$) difference in the percentage of carotene extracted and carotene concentration between the IPA extraction process with and without agitation.

Adsorbent lifespan. The experiments on the carotene extraction from CPO by adsorption with the same adsorbent were conducted at least 10 times in order to determine the lifespan of the adsorbent used. Table 5 shows the results of carotene extraction in experiments which were conducted using the same adsorbent. The percentage of carotene extracted in hexane fraction ranged from 35 to 43% with the carotene concentration ranging from 5,400 to 14,000 ppm. According to the supplier of this adsorbent, the adsorbent can

TABLE 3
Effect of Temperature of Adsorption and IPA Extraction Process on Percentage of Carotene Extracted[a]

Adsorption and IPA extraction temperature (°C)	Fractions	Oil quantity (g)	Carotene Content (mg)	Carotene Recovery (%)	Carotene Concentration (ppm)
40	IPA	71.66 ± 0.54	23.13 ± 1.29	52.80 ± 2.93	323 ± 16
	Hexane	2.96 ± 0.53	18.61 ± 1.87	42.49 ± 4.28^{A}	6,353 ± 569^{E}
55	IPA	73.04 ± 0.34	28.39 ± 1.12	64.82 ± 2.56	389 ± 14
	Hexane	1.57 ± 0.34	14.67 ± 0.40	33.51 ± 0.92^{B}	9,619 ± 2,006^{E}
80	IPA	74.25 ± 0.07	28.88 ± 5.55	65.94 ± 12.68	389 ± 75
	Hexane	0.37 ± 0.05	6.82 ± 1.71	15.56 ± 3.90^{C}	18,571 ± 3,673^{D}

[a]Basis of calculation: CPO feed with original carotene concentration (about 600 ppm) determined by absorbance at 446 nm and calculated as β-carotene. Three hundred grams of combined adsorbents (70% of HP 20 and 30% SP 850, a synthetic styrene-divinyl benzene copolymer manufactured by Mitsubishi) and 75 g of CPO were used in these experiments. The adsorption was carried out for 0.5 h. The IPA extraction process was carried out in a 2,000-mL jacketed extraction flask. IPA (6,000 mL) at 60 mL/min was used to extract CPO from the adsorbent. Carotene extraction was carried out in a 2,000-mL Soxhlet extractor at 60–65°C and was continued until the adsorbent became clear (about 4 h). Hexane (2,500 mL) was used to extract the carotene from the adsorbent. Results have been expressed as mean ± standard deviation of three experiments. Means with different superscripts are significantly ($P < 0.05$) different. For abbreviations see Table 1.

be regenerated using an acid solution, an alkali solution, or various polar solvents (15). In these experiments, hexane was used to regenerate the resin. Based on these results, the adsorbent can be reused several times.

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TABLE 4
Effect of Agitation During IPA Extraction on Percentage of Carotene Extracted[a]

Experiments	Fractions	Oil quantity (g)	Carotene Content (mg)	Carotene Recovery (%)	Carotene Concentration (ppm)
With agitation	IPA	28.89 ± 1.01	10.26 ± 1.05	58.49 ± 5.96	355 ± 28
	Hexane	0.82 ± 0.10	6.59 ± 1.48	37.56 ± 8.45^{A}	8,035 ± 1,380^{B}
Without agitation	IPA	29.70 ± 0.50	11.57 ± 1.04	65.93 ± 5.91	389 ± 29
	Hexane	0.61 ± 0.08	5.89 ± 0.82	33.57 ± 4.67^{A}	9,619 ± 692^{B}

[a]Basis of calculation: CPO feed with original carotene concentration (about 600 ppm) determined by absorbance at 446 nm and calculated as β-carotene. Three hundred grams of combined adsorbent (70% of HP 20 and 30% of SP 850) and 30 g of CPO were used in these experiments. The adsorption process was conducted at 50–55°C. The IPA extraction process was conducted in a 2,000-mL rounded flask using 1,000 mL of IPA with agitation for about 10 min. This IPA extraction process was repeated 10 times. Hexane (2,500 mL) was used for carotene extraction process. A similar method was applied for the experiments without agitation, as a comparison; except that the IPA extraction process was conducted in a 2,000-mL jacketed extraction flask. Results have been expressed as mean ± standard deviation of three experiments. Means with different superscripts are significantly ($P < 0.05$) different. For abbreviations see Table 1.

TABLE 5
Adsorption Lifespan and the Effect on the Percentage of Carotene Extracted[a]

Trial[b] no.	Fractions	Oil quantity (g)	Carotene Content (mg)	Carotene Recovery (%)	Carotene Concentration (ppm)
1	IPA	72.01	23.04	52.61	320
	Hexane	2.62	18.90	43.14	7,212
2	IPA	71.64	22.78	52.01	318
	Hexane	3.02	18.49	42.40	6,121
3	IPA	71.14	22.05	50.35	310
	Hexane	3.03	16.47	37.61	5,437
4	IPA	72.21	24.55	56.05	340
	Hexane	2.6	18.20	41.56	7,001
5	IPA	73.21	23.13	52.82	316
	Hexane	1.70	17.89	40.84	10,522
6	IPA	72.01	19.54	49.43	271
	Hexane	2.20	16.31	41.33	7,412
7	IPA	71.05	27.64	63.10	389
	Hexane	1.10	15.41	35.19	14,013
8	IPA	71.01	27.84	63.55	392
	Hexane	1.99	15.87	36.23	7,974
9	IPA	71.01	28.48	65.01	401
	Hexane	1.29	15.29	34.91	11,852
10	IPA	72.96	27.21	62.13	373
	Hexane	1.79	15.35	35.06	9,032
Mean ± SD	IPA	71.83 ± 0.81	24.63 ± 3.01	56.7 ± 6.09	343 ± 43
	Hexane	3.13 ± 0.69	16.82 ± 1.41	38.81 ± 3.31	8,658 ± 2,711

[a]Basis of calculation: CPO feed with original carotene concentration (about 600 ppm) determined by absorbents at 446 nm and calculated as β-carotene. Three hundred grams of adsorbent (HP 20) and 75 g of CPO were used in these experiments. The adsorption process was conducted at 50–55°C for 0.5 h. The IPA extraction was conducted in a 2,000-mL jacketed extraction flask at 50–50°C. IPA (6,000 mL) at 60 mL/min was used. Carotene extraction was carried out in a 2,000-mL Soxhlet extractor at 60–65°C and was continued tunil the adsorbent became clear (about 4 h). Hexane (2,500 mL) was used to extract the carotene from the adsorbent.
[b]Reusing the same adsorbent. For abbreviations see Table 1.

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