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ORIGINAL PAPER

Obtaining Butter Oil Triacylglycerols Free from β-Carotene and α-Tocopherol via Activated Carbon Adsorption and Alumina-Column Chromatography Treatments

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Abstract It is difficult to remove β-carotene from oils with alumina-column chromatography, because β-carotene is even less-polar than triacylglycerols (TAGs) are. The objective of this study was to obtain butter oil TAGs free from β-carotene and antioxidants via sequential treatments with activated carbon (AC) adsorption and alumina column chromatography. The AC used was prepared from waste apricots. The effects of AC dosages, temperatures and time courses on β-carotene adsorption were studied. The Langmuir and Freundlich isotherms were used to describe the adsorption of β-carotene onto AC, and it was found to be more consistent with the Freundlich isotherm with a higher R^2 value (0.9784). Adsorption kinetics of β-carotene was analyzed by pseudo-first order and pseudo-second order models. The pseudo-second order model was found to explain the kinetics of β-carotene adsorption more effectively ($R^2 = 0.9882$). The highest β-carotene reduction was achieved (from 31.9 to 1.84 mg/kg) at an AC dosage of 10 wt%, temperature of 50 °C, and adsorption time of 240 min. A considerable amount of α-tocopherol was also adsorbed during the AC treatment. Remaining portions of α-tocopherol were completely removed with alumina adsorption chromatography. The method described may be used for purification of vegetable oil TAGs, which will be used as model compounds in model oxidation studies.

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Introduction

β-Carotene is an oil soluble and natural pigment of many oils, such as palm, olive and butter oils. In addition to its use as a food coloring, β-carotene has a strong antioxidant activity. It has been shown to protect lipids from autooxidation by reacting with peroxyl radicals, thereby inhibiting propagation and promoting termination of the oxidation chain reaction [1]. β-Carotene is also an effective quencher of singlet oxygen and thus it inhibits photooxidation [2]. It was reported that the stability of oil could be improved by β-carotene addition [3–5]. It is well known that the antioxidants act not only individually but also cooperatively and in some cases even synergistically.

In order to determine the effects of antioxidants in oils, triacylglycerols (TAGs) free from antioxidants have been produced and used in some model system oxidation studies [6–11]. Alumina is one of the most commonly used adsorbents in glass chromatography columns. However, it is difficult to remove β-carotene from oils with alumina, because alumina adsorbs polar compounds and β-carotene is even less-polar than TAGs are. Although, strong cooperative actions of β-carotene with other antioxidants have been reported [12–14], it is worth noting that in many studies cooperative actions of β-carotene have been neglected. Residues of β-carotene and other antioxidants cause similar effects in oxidation experiments where oils without purification are used [15–18].

Apricot processing plants purchase apricots from farmers as sulphurated/dried forms and are pooled and stored until packaging. Apricots, which are injured, deformed or smaller than acceptable dimension, are discarded during processing. Based on the producers' information, approximately 0.5 kg waste is generated in the plants per 100 kg processed dried apricots. To promote an economic utilization of this cheap and abundant waste, it has been used for the preparation of activated carbon [19].

There are some studies on β-carotene adsorption from different oils, e.g. from soy oil using clay [20], rapeseed oil using sepiolite [21], palm oil using synthetic polymer [22], and kaolin-carbon adsorbents [23]. AC prepared from waste apricots has been successfully used for adsorption of dyes [19]. In this study we take a similar approach and apply AC to absorb β-carotene from butter oil (BO) and also discuss adsorption isotherms and kinetic parameters.

The objective of this study was to obtain BO TAGs free from β-carotene and antioxidants via sequential treatments of AC adsorption and alumina column chromatography. Purified BO TAGs would be used in oxidation studies.

Materials and Methods

Materials

BO was produced by melting the butter produced from cow's milk (Karlidag Dairy Products, Malatya, Turkey) at 55 °C and filtering through a plain filter paper coated with anhydrous sodium sulfate at the same temperature. BO obtained was kept at −18 °C, and used in all experimental treatments. Waste apricot was supplied from different apricot plants and analyzed in duplicate according to AOAC methods [24] for dry matter content (920.151A), ash content at 550 °C (940.26A), protein content was calculated by multiplying the nitrogen content by a factor of 6.25 by the Kjeldahl method (978.04A), fat content by using petroleum ether with a Soxhlet apparatus. (920.39), total fibre (crude) content (962.09), and carbohydrate content was calculated by difference (i.e., carbohydrate content = dry matter − sum of other components). Chemical composition of waste apricot as weight percentage was 78.6 for dry matter which composed of ash, protein, fat, total fibre and carbohydrate at the percentage of 3.3, 3.7, 0.8, 2.8 and 68.0, respectively. Elemental analysis of the waste apricot was performed in a Leco CHNS 932 (Michigan, USA) analyzer. The weight percentages of carbon, hydrogen, nitrogen, sulphur and oxygen were 42.48, 6.04, 0.29, 0.39 and 50.80 (calculated by difference), respectively. HPLC grade organic solvents such as *n*-hexane and *iso*-propanol were obtained from Merck (Darmstadt, Germany).

Preparation of AC

AC was prepared from waste apricots according to the method of Akmil-Basar [19]. This method included several steps: drying of the waste apricots at 100 °C to a constant weight, mixing with $ZnCl_2$ at the weight ratio of 1:1 and kneading with distilled water, and then drying at 110 °C to prepare the impregnated product. Thermal activation of the product was achieved by keeping it in a quartz tube at 500 °C under N_2 flow (100 mL/min) for 60 min. After this treatment, it was cooled down under N_2 flow, treated with 0.5 N HCl, and washed sequentially several times with hot distilled water to remove residual chemicals until no reaction of chloride with $AgNO_3$ occurred. Finally, AC was dried at 110 °C and ground in a mortar to pass a 200-mesh screen. Detailed information regarding the AC have been given by Akmil-Basar [19].

Adsorption Experiments

Adsorption experiments were performed in a flask (100 mL) connected to a rotary evaporator with agitation (250 rpm) at different experiment temperatures under vacuum supplied by a water jet pump. After BO (25 g) was completely melted, the vacuum was broken with nitrogen gas and AC was added. In order to determine the effects of the amount of AC on adsorption of β-carotene, dosages of 1, 2, 3, 4, 5, 6, 8, and 10 wt% were used at a temperature of 50 °C for an adsorption period of 240 min. Similarly, adsorption times of 15, 30, 45, 60, 75, 90, 105, 120, 135, 150, 180, 210, 240, 300, and 360 min, at an AC dosage of 6 wt%, and a temperature of 50 °C were used to determine the effects of adsorption time. In addition, to determine the effects of temperature on adsorption, temperatures of 40, 50, and 60 °C were applied with an AC dosage of 6 wt% and an adsorption time of 240 min. The products were filtered with a 0.45 µm pore size syringe filter (Millipore, Bedford, MA, USA) and the filtrate was stored at −18 °C under nitrogen until further analysis.

The amount of β-carotene adsorbed onto AC, q_t (mg/g), was calculated by a mass- balance relationship Eq. 1

$$q_t = (C_0 - C_t)\frac{V}{W} \quad (1)$$

where C_0 and C_t are the liquid-phase concentration of the β-carotene (mg/L) at initial and any time t, respectively. V is the volume of the BO (L) and W is the weight of the dry AC (g). Mass of the BO used in adsorption experiments was converted to volume by using its density (0.887 kg/L).

Column Chromatography of BO

β-Carotene of BO (60 g) was removed using the same apparatus described in the previous section under the following conditions: a temperature of 60 °C, an adsorption time of 300 min, an AC dosage of 6 wt%. Thereafter, BO was stripped to remove pro- and antioxidants to yield purified BO TAGs, applying the method of Lampi et al. [25] with some minor modifications. Slurry of 150 g neutral aluminum oxide (Merck, Darmstadt, Germany) (activated at 100 °C for 16 h and 220 °C for 8 h) and 250 mL of *n*-hexane was applied to a double-jacketed glass chromatography column (300 × 28 mm i.d.) and *n*-hexane was allowed to flow through the column, until the solid phase was evenly packed. The mixture containing AC and BO obtained from adsorption experiment was suspended in an equal volume of *n*-hexane and loaded on the top of the chromatographic column. The column was washed with 150 mL of *n*-hexane. The column temperature was maintained at 37 °C by circulating water from a water bath. In order to prevent light-induced oxidation of the purified BO TAGs, the column and the collecting flask were wrapped in aluminum foil. The solvent was removed with a rotary evaporator at 37 °C under vacuum. The BO TAGs were then dried under nitrogen and stored at −18 °C until further analysis.

HPLC Analysis of β-Carotene and α-Tocopherol

Normal-phase HPLC was used to analyze β-carotene and α-tocopherol [26] using a ThermoFinnigan HPLC system. The chromatographic separation was achieved with a Phenomenex Luna Silica column (4.6 mm i.d. 6,250 mm, 5 mm). The column temperature was maintained at 30 °C. Separation of the components was based on isocratic elution with *n*-hexane (99%) and *iso*-propanol (1%) at 1 mL/min. β-Carotene and tocopherols were monitored at 453 and 292 nm, respectively. β-Carotene and α-tocopherol were identified by comparing the retention times with those of pure standards of β-carotene from Merck (Darmstadt, Germany) and α-tocopherol from Calbiochem (La Jolla, CA), respectively. They were quantified on the basis of peak areas of those of the pure standards.

Statistical Analysis

All adsorption treatments were performed in duplicate. HPLC analyses of β-carotene and α-tocopherol were carried out in duplicate. SPSS version 9.0 (SPSS Inc., Chicago, IL, USA) was used to perform statistical calculations. A factorial design was performed using generalized linear models. Significant differences among treatment means were separated by using a LSD test and a one-way analysis of variance (ANOVA) procedure at a level of $P < 0.05$.

Results and Discussion

Effect of Adsorption Parameters on Adsorption of β-Carotene

The adsorption of β-carotene onto AC as a function of its dosage (%) is presented in Fig. 1 in terms of percent adsorption versus per unit weight of AC. Increasing the AC dosage provides more surface area for adsorption. There was a clear reduction in β-carotene content when increasing the AC dosage from 1 to 10 wt%. It can be seen that the increase of β-carotene adsorption was drastic up to the 4 wt% dosage and slowed down above it. At the AC dosages of 6 and 8 wt%, adsorptions of β-carotene were 87 and 93%, respectively. The highest β-carotene adsorption on AC was achieved at the AC dosage of 10 wt%, when the initial β-carotene content of BO (31.9 mg/kg) decreased to 1.84 mg/kg (Table 1). β-Carotene content of BO before and after a few adsorption experiments are presented in Table 1. The AC dosages had an important effect on β-carotene contents of BO ($P < 0.05$).

Total surface area (S_{BET}) of the AC prepared from waste apricots was 1,060 m^2/g [19]. The required surface area

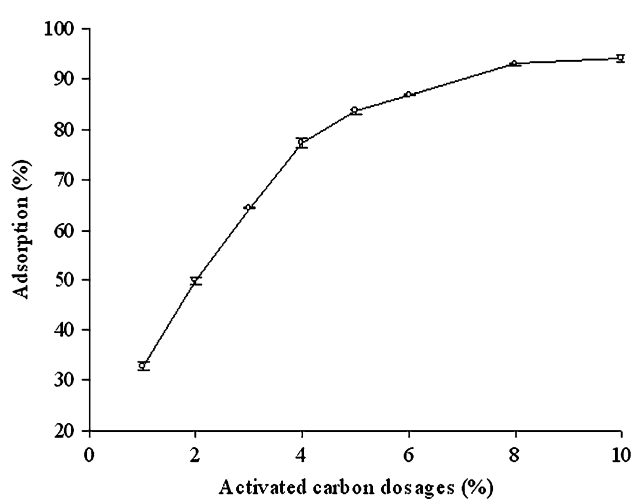

Fig. 1 Adsorption of β-carotene by AC both in terms of percent adsorption and per unit wt of AC (The amount of BO = 25 g, temperature = 50 °C and adsorption time = 240 min), two replicates from each of AC dosage treatments were analyzed individually in duplicate

Table 1 β-Carotene and α-tocopherol content (mg/kg) of BO before and after some adsorption conditions

	AC dosage (%)	Temperature (°C)	Adsorption time (min)	β-Carotene	α-Tocopherol
BO				31.39 ± 0.45	22.07 ± 0.74
After adsorption with AC (residual contents)[a]					
Condition 1	6	50	240	4.15 ± 0.16	5.95 ± 0.17
Condition 2	10	50	240	1.84 ± 0.10	5.46 ± 0.03
Condition 3	6	50	360	2.59 ± 0.08	5.56 ± 0.23
Condition 4	6	40	240	9.67 ± 0.15	6.38 ± 0.12
Condition 5	6	60	240	2.40 ± 0.01	6.04 ± 0.07
Stripped BO TAGs				3.85 ± 0.11	ND

Values are means ± SD for two replicates from each of the treatments, analyzed individually in duplicate

BO butter oil, *AC* activated carbon, *ND* not detected

[a] BO of 25 g was used in all conditions

for 1 mg/kg β-carotene adsorption using conditions 1 (Table 1) could be calculated as about 58 m^2/g by using the adsorbed amount of β-carotene (27.24 mg/kg) and the amount of AC (1.5 g) that provided a surface area of 1,590 m^2/g. So, β-carotene content of the oils can successfully be reduced with many of the ACs commercially available, which should have similar surface properties.

A plot of adsorption (%) versus adsorption time (min) is shown in Fig. 2. It was observed that the adsorption of β-carotene increased considerably up to 180 min (the level of adsorption was 86.6%), and thereafter the adsorption proceeded at a slower rate until an steady state was reached, i.e. when the rate of adsorption of β-carotene onto the surface of AC was the same as the rate of desorption. Adsorption times had an important effect on the β-carotene contents of BO ($P < 0.05$). Only results from adsorption time experiments of 240 and 300 min (conditions 1 and 3) are given in Table 1.

The adsorption of β-carotene was found to be endothermic indicating that the adsorption would be enhanced at higher temperatures. As can be seen from Fig. 3, the percent adsorption of β-carotene increased when the temperature increased from 40 to 60 °C. Higher temperatures than 60 °C were avoided, because higher temperatures may enhance oxidation of the oil. This is important because the main aim of the study was to produce TAGs for oxidation studies, and such a material should be non-oxidized. β-Carotene contents of BO were affected significantly by the adsorption temperatures ($P < 0.05$). Results from adsorption experiments conducted at temperatures of 40, 50 and 60 °C (conditions 1, 4 and 5) are given in Table 1.

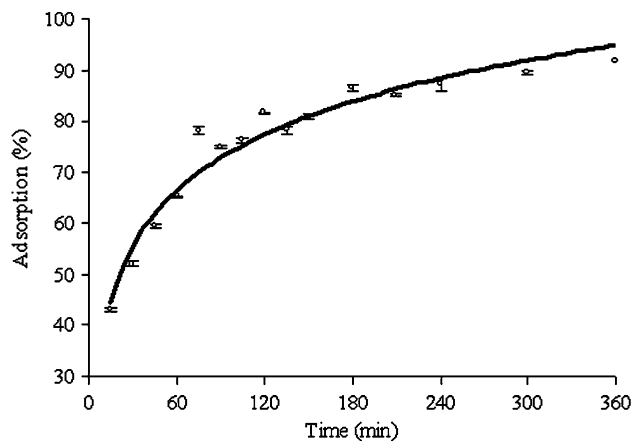

Fig. 2 Effect of adsorption time (min) on adsorption of β-carotene (The amount of BO = 25 g, AC dosage = 6 wt% and temperature = 50 °C), two replicates from each of time treatments were analyzed individually in duplicate

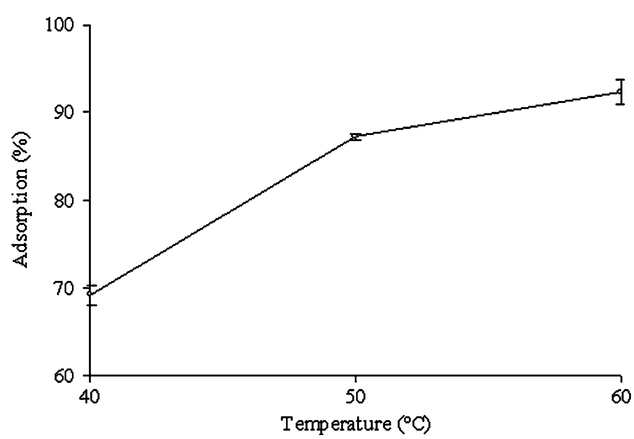

Fig. 3 Effect of temperature (°C) on adsorption of β-carotene (The amount of BO = 25 g, AC dosage = 6 wt% and adsorption time = 240 min), two replicates from each of temperature treatments were analyzed individually in duplicate

Adsorption Isotherms

Adsorption of β-carotene was analyzed using widely applied models, named Langmuir and Freundlich isotherms. Because the coefficient of determination value of the Freundlich model ($R^2 = 0.9784$) was greater than that of the Langmuir model ($R^2 = 0.9382$), assessments for the Langmuir model were not given here. Adsorption of β-carotene onto AC prepared from waste apricots was consistent with the Freundlich isotherm. The Freundlich equation is an empirical model; it is widely used to describe vegetable oil adsorption bleaching [27]. It can be expressed as follows [28]:

$$\log q_e = \log k_f + \frac{1}{n}\log C_e \tag{2}$$

where q_e is the amount of β-carotene adsorbed at equilibrium time (mg/g), C_e is the equilibrium concentration of β-carotene (mg/L), k_f (L/g) and n are isotherm constants which indicate the capacity and intensity of the adsorption, respectively.

The plot of log q_e versus log C_e is given in Fig. 4 which is in harmony with Freundlich isotherm ($R^2 = 0.9784$). The values of k_f and n were calculated from the slope and intercept of the plot of log q_e versus log C_e as 3.9777 L/g and 2.188, respectively. The calculated Freundlich constant ($n = 2.188$) was in the range of 1–10 [29] indicating that the β-carotene adsorption by AC was the most favorable at a temperature of 50 °C.

Adsorption Kinetics

The increase in adsorption of β-carotene onto AC from BO with time was applied to the first and the second order models. The coefficient of determination values was significantly greater in second order ($R^2 = 0.9882$) model compared to that of first order ($R^2 = 0.9393$). Therefore, the present study suggests a pseudo-second order model [30], and the measured data fitted to the model proposed in Eq. 3.

$$\frac{dq_e}{dt} = k(q_e - q_t)^2 \tag{3}$$

The integrated form of Eq. 3 becomes:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \tag{4}$$

where and q_e and q_t are the amounts of β-carotene adsorbed (mg/g) at equilibrium and time t (min), respectively, and k is the rate constant of pseudo-second order adsorption (g/mg min).

The plot of (t/q_t) versus t for the pseudo-second order model given in Eq. 4 is shown in Fig. 5. The q_e and k values were calculated from the slope and the intercept of this as 0.0508 mg/g and 0.760 g/mg min, respectively. The calculated (0.0508) and experimental q_e (0.0480 mg/g) values were found to be close to each other, and therefore, we can accept that the pseudo-second order model is suitable for the adsorption of the β-carotene with AC.

Column Chromatography of BO

Preliminary studies using alumina chromatography with nonpolar solvent (hexane) showed that it did not remove β-carotene fully from BO while α-tocopherol was completely separated (data not shown). In order to purify BO TAGs from β-carotene and α-tocopherol, some sequential steps were studied. Firstly, β-carotene was removed via AC treatment. AC has broad nonpolar surface cavities that provide specific adsorption towards β-carotene. However, α-tocopherol could not been completely adsorbed on AC although a considerable reduction was achieved as shown in

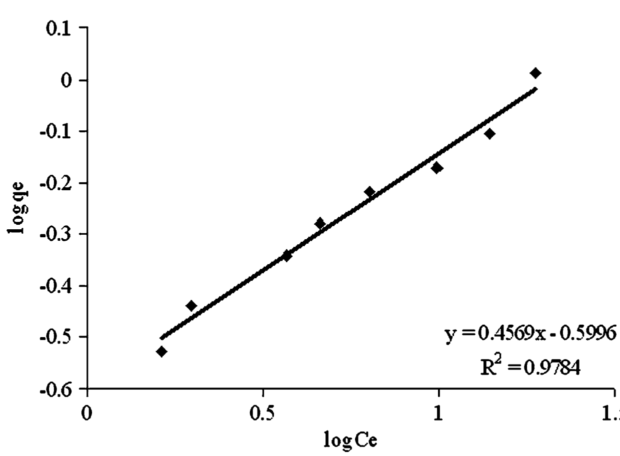

Fig. 4 Freundlich isotherm plots corresponding to the adsorption of β-carotene. q_e is the amount of β-carotene adsorbed at equilibrium time (mg/g), C_e is the equilibrium concentration of β-carotene (mg/L)

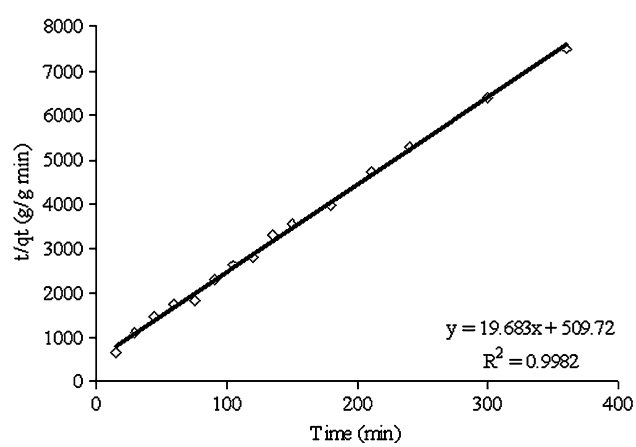

Fig. 5 The plot of the pseudo-second order model for β-carotene adsorption

Table 1 (conditions from 1 to 5), and that adsorption conditions had an important effect on the BO products α-tocopherol contents after AC treatment ($P < 0.05$). Secondly, the remaining portion of α-tocopherol was completely removed via alumina adsorption chromatography.

After AC and alumina chromatography treatments β-carotene content of BO reduced from 31.39 to 3.85 mg/kg (Table 1). It may possible to reduce it even more by extending the AC adsorption time, increasing the AC dosage and the adsorption temperature as shown in Table 1 (conditions1–3, conditions 1–2 and conditions 4–1–5, respectively).

During the evaluation of the HPLC chromatograms of BO, two unidentified small peaks were detected in addition to those of β-carotene and α-tocopherol. Based on our experiences, it was predicted that they might belong to tocopherol isomers and they were not found in the chromatograms of the samples, which were treated with AC and alumina chromatography. α-Tocopherol contents of BO TAGs, which were obtained from different adsorption treatments, fluctuated and it may be explained by changes in adsorption/desorption rate, which effected by adsorption conditions. There are some literature data regarding to β-carotene adsorption using column chromatography packed with activated alumina, silica, and HP 20 [22, 31]. Though, there is no information on the α-tocopherol adsorption capabilities of these adsorbents, it was shown in our study that a considerable amount of α-tocopherol reduction is possible with AC treatments, even without alumina chromatography treatments (Table 1).

In conclusion, adsorption of β-carotene onto AC prepared from waste apricots is consistent with the Freundlich isotherm. It was also indicated that the pseudo-second order expressions may represent the removal kinetics of β-carotene. It may be possible to use of AC for adsorption of β-carotene from different oil sources, such as palm oil. β-Carotene and α-tocopherol were successfully removed from BO with high percent adsorption values. It appears that the BO TAGs obtained via AC adsorption and alumina-column chromatography treatments are suitable to be used as model compounds in oxidation studies to determine individual or synergistic benefits of antioxidants, which will be added.

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