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DECOLORIZATION OF VEGETABLE OILS: A STUDY OF THE MECHANISM OF ADSORPTION OF β -CAROTENE BY AN ACID-ACTIVATED BENTONITE FROM CYPRUS

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Abstract—The mechanism of decolorization of crude maize and sunflower oils was studied by means of adsorption of β -carotene by a low-grade bentonite, containing mixed-layered illite-smectite. Decolorization depends on temperature and the time required for equilibrium decreases with increasing temperature. The study of the kinetics of adsorption showed that decolorization of maize oil is a first-order process which occurs in two steps: a first fast step with higher activation energy (25.6 kJ mol⁻¹), indicating the influence of a chemical interaction between the pigment and the clay surface, followed by a second slow step with low activation energy (12.3 kJ mol⁻¹), characteristic of physical adsorption on the previously adsorbed molecules. Decolorization of sunflower oil is also a first-order process, described by a single mechanism with intermediate activation energy (19.0 kJ mol⁻¹). Adsorption isotherms of decolorization of maize oil follow the Freundlich equation, indicating the existence of heterogeneous adsorption sites on the solid's surface. Heterogeneity is attributed both to different active centers on the smectite surface (Brönsted and Lewis centers) and to the different phases present in bentonite, such as illitic layers and clinoptilolite, which also have active centers on their surfaces.

Key Words—Acid-activated Bentonite, Activation Energy, Active Centers, Adsorption Kinetics, β -carotene, Decolorization, Freundlich Isotherm, Reaction Order, Vegetable Oils.

INTRODUCTION

Bentonites are highly valued for their sorptive properties which stem from their high surface area and their tendency to adsorb molecules in their interlayer sites. These properties are enhanced with acid activation and treatment with organics (Odom, 1984; Rupert et al., 1987; Boyd and Jaynes, 1994). Acid-activated bentonites are mainly used for the purification, decolorization and stabilization of vegetable oils. They remove phospholipids, soaps, trace metals, organic compounds (carotenoids, such as β -carotene and their derivatives, xanthophylls, chlorophyll, pheophytin, tocopherols and gossypol) and their degradation products which impart undesirable colours to the edible oils (Siddiqui, 1968; Kheok and Lim, 1982; Zschau, 2001). Moreover, during bleaching they remove undesirable products such as hydroperoxides formed by oxidation, unsaturated fatty acids and glycerides. The coloring agents are not adsorbed in the interlayer space of smectites (Christidis et al., 2002).

Important physical changes in acid-activated smectites are the increase of specific surface area and average pore-volume, depending on acid strength, time and temperature of treatment (Kheok and Lim, 1982; Morgan *et al.*, 1985; Srasra *et al.*, 1989; Taylor *et al.*, 1989; Rhodes and Brown, 1992; Christidis *et al.*, 1997). The specific surface area and surface acidity of activated smectites control decolorization properties. With some

* E-mail address of corresponding author: christid@mred.tuc.gr DOI: 10.1346/CCMN.2003.0510309 exceptions (Christidis *et al.*, 2002) decolorization is usually not associated with maximum surface area (Morgan *et al.*, 1985; Christidis *et al.*, 1997).

Decolorization or the bleaching capacity of acidactivated bentonites for crude edible oils is usually expressed in terms of adsorption of β -carotene (e.g. Khoo et al., 1979; Sarier and Güler, 1988; Srasra et al., 1989; Boki et al., 1992a; Christidis et al., 1997, 2002) or less often chlorophyll (Brimberg, 1982). Adsorption of β -carotene has been found to follow a first-order rate law (Khoo et al. 1979; Brimberg, 1982). In the case of rapeseed oil, an apparent first-order rate constant of 7.0×10^{-5} s⁻¹ has been calculated (Khoo *et al.*, 1979) for low temperatures up to 35°C. Although a Langmuirtype isotherm has been postulated for adsorption of β-carotene from acid-activated montmorillonite (Khoo et al., 1979; Sarier and Güler, 1988), decolorization of mineral oils has been described satisfactorily by means of the Freundlich isotherm (Siddiqui, 1968; Boki et al., 1992b; Zschau, 2001).

Decolorization is not considered merely a physical adsorption process since it also involves catalytic reactions, ion exchange and reactions due to surface acidity of the solid phase (Siddiqui, 1968; Khoo *et al.*, 1979; Morgan *et al.*, 1985; Sarier and Güler, 1988, 1989; Zschau, 2001). However, other studies have shown that β -carotene can be removed from synthetic systems and oils via physical adsorption by acid-activated clays (Boki *et al.*, 1992a) or by synthetic polymer adsorbents (Baharin *et al.*, 1998; Latip *et al.*, 2000).

With some exceptions (Brimberg, 1982) most previous attempts to describe the mechanism of adsorption of β -carotene from acid-activated montmorillonite have been carried out at low temperatures (1-40°C) using acetone or benzene solvents (e.g. Khoo et al., 1979; Sarier and Güler, 1988), possibly due to the high volatility of the solvents. Such temperatures are low compared with those employed during oil decolorization (Morgan et al., 1985; Srasra et al., 1989; Boki et al., 1992a, 1992b; Christidis, 1997, 2002). In a previous work, Christidis et al. (2002) activated a low-grade bentonite from Cyprus with HCl and evaluated its capacity to decolorize maize and sunflower oil by means of removal of β -carotene. It is the purpose of this contribution to study the mechanism of decolorization of vegetable oils by means of kinetics, with determination of the activation energy and construction of isotherms for the adsorption of β -carotene at temperatures used for decolorization.

MATERIALS AND METHODS

The samples were collected from bentonite beds in the Mitsero area in the northern part of the Troodos Ophiolite Complex, Cyprus. They contain 50-60% mixed-layered illite-smectite (I-S) with 80-85% expandable layers, minor clinoptilolite, quartz, opal-CT, carbonates (calcite and trace siderite) and trace amounts of illite, gypsum and kaolinite in places. The bentonite was described by Christidis et al. (2002). The materials were dried at 65°C overnight, ground in the ball mill and passed through a 125 µm sieve. Activation was carried out using HCl of analytical grade, with concentration 5 N for 6 h, at 70±2°C and a solid to liquid ratio of 1:10. These experimental conditions were found to yield material with optimum decolorization properties (Christidis et al., 2002). After treatment the clay was washed to pH 4, and the slurry was filtered under vacuum. The collected material was dried at 60°C and was ground using a pestle and mortar to pass through a 125 µm sieve.

The kinetics of adsorption of β -carotene were studied using crude maize and sunflower oil provided by ELAIS-UNILEVER S.A., at a solid:liquid ratio of 1:50 (0.5 g of clay in 25 mL of oil) under stirring. Adsorption was carried out at 45, 60, 75 and 85℃ for times ranging from 1 min to 9 h for the maize oil and from 1 min to 6 h for the sunflower oil. The temperature during adsorption was kept constant by means of a water bath. After completion of the reaction, the treated oils were filtered under vacuum and the concentration of β -carotene was determined spectrophotometrically at 430 nm (MILTON ROY SPECTRONIC 20D absorption spectrophotometer) by diluting 5 mL of bleached oil in 15 mL of chloroform. This is a well known procedure for determination of β -carotene in oils, since its spectrum shows three maxima at ~450, 430 and 480 nm (Khoo et al., 1979; Sarier and Gülar, 1988; Srasra et al., 1989; Boki et al., 1992b). By contrast, the spectrum of chlorophyll yields

maxima above 650 nm (Brimberg, 1982). The amount of β -carotene remaining in the oil was calculated by converting absorbance units to concentration of β -carotene using a calibration curve, which was constructed by dissolving β -carotene of analytical grade (Merck) in chloroform. The β -carotene adsorbed by the acidactivated bentonite was calculated by subtraction from that present in the crude oil. The steep part of the kinetic curves at each temperature was used to calculate the rate constant of the adsorption and the activation energy. The order of the reaction was determined using the method of integration (Laidler, 1987).

The concentration of β -carotene at the plateaux of the kinetic curves (remaining β -carotene in the oil at equilibrium) vs. the concentration adsorbed per unit mass of bentonite was used to construct the adsorption isotherms. Due to the low concentration of β -carotene in the sunflower oil, adsorption isotherms were constructed only for the maize oil. Since crude maize oil has a fixed concentration of β -carotene, isotherms were constructed using different adsorbent-to-oil ratios (1:10 to 1:1000). With this experimental approach, the amount of β-carotene adsorbed per unit mass of bentonite at each temperature changed, and the influence of the amount of clay on adsorption of β -carotene was estimated. The time allowed for acquisition of equilibrium during adsorption varied with temperature of the reaction and was determined from the kinetic curves (see below).

RESULTS

The kinetic curves results for adsorption of β -carotene from maize and sunflower oil are shown in Figure 1. The curves are clearly separated in the case of maize oil, but not in the case of sunflower oil at high temperatures. Temperature affects both the time of approaching equilibrium and the equilibrium concentration of β -carotene after each experiment. Temperature dependence is better expressed in maize oil, for which equilibrium is attained after 2 h at 45°C and after 30 min at 85°C. By contrast, for sunflower oil, adsorption is considerably faster; at 45°C equilibrium is observed after 40 min, while at 85°C, after 15 min. The observed difference is attributed to the smaller concentration of β -carotene in the sunflower oil.

Application of the method of integration yielded rate constants for adsorption of β -carotene at various temperatures for both oils. According to this method, an assumption of the order of the reaction is made and the experimental results are modeled using equations which describe the reaction order each time. The order that better describes the experimental results is regarded as order of the reaction. In first-order reactions, the experimental points plot on a straight line in the semilogarithmic plot ln C/C_o vs. time, where C is the concentration of β -carotene at each time and C_o the original concentration in the oil. The semi-logarithmic plots of $\ln C/C_o vs.$ time for maize oil yielded two straight lines (Figure 2), which correspond to a two-stage reaction, namely an initial period of rapid adsorption, followed by a period of slow adsorption. Although, according to Brimberg (1982), this type of reaction is frequently observed in vegetable oils, Khoo *et al.* (1979) observed a single adsorption stage of β -carotene from palm oil. The reaction rates for the two stages (k1 and k2) obtained from the slopes of the straight lines in Figure 2 are listed in Table 1. At each temperature, both k1 and k2 are larger than the value calculated by Khoo *et al.* (1979) (7 × 10⁻⁵ s⁻¹) probably due to the higher temperature of the reaction (45–85°C vs. 27°C). Moreover, both k1 and k2 increase with increasing temperature confirming that temperature



Figure 1. Kinetic curves of adsorption of β -carotene by acidactivated Cyprus bentonite: (a) maize oil; (b) sunflower oil.

Table 1. Reaction rate (k) (s⁻¹) and activation energy (E_a) obtained for maize oil and sunflower oil. In the case of maize oil, k1 is the reaction rate for the first fast adsorption step and k2 the rate for the second slow step.

Temperature (°C)	Maize oil		Sunflower oil	
I	k1 (s ⁻¹)	k2 (s ⁻¹)	k (s ⁻¹)	
45	2.8×10^{-4}	8.6×10^{-5}	1.6×10^{-4}	
60	3.9×10^{-4}	1×10^{-4}	2.5×10^{-4}	
75	5.6×10^{-4}	1.3×10^{-4}	3.3×10^{-4}	
85	8.2×10^{-4}	1.4×10^{-4}	3.6×10^{-4}	
$(E_{\rm a})$ (kJ mol ⁻¹)	25.6	12.3	19.0	



Figure 2. In (C/C_o) vs. time (s) curves for adsorption of β -carotene: (a) maize oil, (b) sunflower oil. C_o = initial concentration of β -carotene at t = 0, C = concentration of β -carotene at time t.

affects decolorization of vegetable oils. In the case of sunflower oil, a single straight line is obtained at each temperature (Figure 2), while the corresponding reaction rates are intermediate between the k1 and k2 obtained for the maize oil (Table 1). The existence of a single adsorption stage is attributed to faster reaction due to a significantly lower concentration of β -carotene in crude sunflower oil. It was not possible, therefore, to distinguish different adsorption stages. It has been shown recently (Christidis *et al.*, 2002) that activated Cyprus bentonite adsorbs greater amounts of β -carotene from maize oil than from sunflower oil.

The rate constants obtained for both oils were used to determine the activation energy (E_a) of adsorption according to the Arrhenius equation:

$$\mathbf{k} = A_{\mathrm{e}}^{-E_{\mathrm{a/RT}}} \tag{1}$$

where k is the rate constant and A is the pre-exponential (frequency) factor. The Arrhenius plots obtained for the two oils are shown in Figure 3. For maize oil, two plots were constructed, for k1 and k2, respectively. Activation energy was calculated from the slopes of the plots (Table 1). For the maize oil, E_a for the initial rapid step was 25.6 kJ mol⁻¹ whereas for the slow step it was 12.3 kJ mol⁻¹. For the sunflower oil an intermediate value of E_a (19.0 kJ mol⁻¹) was obtained.

The role of the amount of clay used expressed as solid:liquid ratio is important for the decolorization process (Table 2). At low clay:oil ratios the removal of β -carotene is more efficient, since most active centers are occupied by β -carotene molecules. With gradual increase of clay content, more β -carotene is adsorbed but an increasing number of active sites is not occupied. Increase of temperature enhances adsorption.

The β -carotene adsorption isotherms determined for maize oil at various temperatures are shown in Figure 4a. They are typical Freundlich isotherms (*x/m* = K_fC^{1/n}), as can be seen in Figure 4b where analytical data are projected in a logarithmic plot (Laidler, 1987). The slope of straight lines in Figure 4b gives n. K_f and n are empirical constants and are listed in Table 3. Although n does not change with temperature, K_f increases with temperature, and its increase is more gradual at lower temperatures (Table 3). A Freundlich



Figure 3. Arrhenius plots for maize and sunflower oil. k1 and k2 correspond to the fast and slow adsorption stages, respectively, of β -carotene from maize oil. Activation energy is calculated from the slopes of the straight lines.

isotherm may suggest heterogeneity of adsorption sites on the solid's surface (Laidler, 1987; Drever, 1997). Adsorption would take place initially at the sites with the strongest binding energy, which correspond to the steep part of the isotherm. As the sites are filled, adsorption occurs at low-energy sites, decreasing the slope of the isotherm (Drever, 1997). The results obtained are considerably different from those of Sarier and Güler (1988), who observed a multi-step isotherm or from those of Khoo *et al.* (1979) who observed a Langmuirtype isotherm during adsorption of β -carotene by acidactivated montmorillonite.

INTERPRETATION AND DISCUSSION

Decolorization of maize and sunflower oil depends on temperature, in agreement with previous studies. Both systems reach equilibrium after some time depending on the temperature of reaction (Figure 1). The activation energies obtained are smaller than those calculated by Khoo *et al.* (1979) (41.8 kJ mol⁻¹) for

Table 2. Concentration of β -carotene adsorbed by maize oil (moles $g^{-1} \times 10^{-6}$) during decolorization by acid-activated Cyprus bentonite as a function of the clay:oil ratio.

Clay:oil	Concentr	Concentration of β -carotene adsorbed (moles $g^{-1} \times 10^{-6}$)		
ratio	45°C	60°C	75°C	80°C
1:25	0.907	0.929	0.948	0.977
1:50	1.610	1.681	1.763	1.956
1:100	2.144	2.343	2.437	3.013
1:250	3.748	4.002	4.506	5.227
1:500	5.514	6.080	6.562	7.455
1:1000	8.140	8.706	9.374	10.932



Figure 4. Freundlich isotherms (a) and logarithmic plots of the isotherms (b) of the adsorption of β -carotene from maize oil.

 β -carotene in the temperature range 1–30°C. Although the observed difference can be explained by the different experimental conditions used, there are other interrelated factors which contribute as well, which include (1) the nature and the rate of the reaction (physical adsorption or chemical reaction), (2) the influence of mass transfer from bulk oil to the oil-adsorbent interface, (3) the

Table 3. Values of log K_f and n (empirical constants in the Freundlich equation) obtained for the maize oil at various temperatures of decolorization.

Temperature (°C)	$\log K_{\rm f}$	n
45	-3.177	0.442
60	-3.152	0.440
75	-3.038	0.454
85	-2.954	0.453

existence of heterogeneous adsorption sites which need to be activated, and (4) the nature of the sorbent.

The rate of adsorption is controlled by mass transfer, because the adsorption rate of β -carotene is very fast compared to its transfer from the bulk oil to the clay surface. This is because during decolorization the activated bentonite breaks the stability of the pigments which form stable colloid systems in the oil (Brimberg, 1982; Taylor et al., 1989). The acetone-β-carotene system may be more stable than the oil-B-carotene colloid suspension due to electrophoretic phenomena caused by the Brönsted and/or Lewis acid centers on clay surfaces. Moreover, colloid stability may be adversely affected by interactions between different types of colloids present in the oil. These events are expected to facilitate pigment transfer from the oil to the adsorbent surface. Thus the E_a determined by Khoo *et al.* (1979) may not represent decolorization of real oils, which are complex systems. This is further supported by the fact that decolorization experiments yielded a twostep adsorption mechanism, while experiments with pure β -carotene yielded a single mechanism (Khoo *et al.*, 1979; Sarier and Güler, 1988). Therefore the E_a determined for maize oil is considered representative for decolorization of oils. Also, the $E_{\rm a}$ for sunflower oil may indicate an average value reflecting a two-step adsorption mechanism.

The exact mechanism of the reaction is not fully understood. Physical adsorption, known as van der Waals adsorption, which has been invoked for adsorption of β -carotene by synthetic polymer adsorbents (Baharin et al., 1998; Latip et al., 2000), does not require activation energy and the heat evolved is <20 kJ mol⁻¹ (Laidler, 1987). The activation energy calculated for the second slow step of decolorization of maize oil indicates mainly a physical adsorption mechanism. In contrast, the first fast step of decolorization of maize oil indicates, at least to some extent, the influence of chemical interaction on decolorization. Similarly, the activation energy calculated for sunflower oil is indicative of some type of chemical interaction. These interactions are related to hydrogen bonding with Brönsted sites and/or to direct binding at Lewis sites on clay surfaces (Sarier and Güler, 1989). The latter are broken bonds in the dissolved octahedral and tetrahedral sheets (Adams, 1987). The first fast step of adsorption represents the chemical interaction between the acid centers at smectite surface and β -carotene, while the second slow step may indicate physical adsorption of β-carotene on those molecules adsorbed during the first step.

Previous FTIR work has shown that β -carotene is the most important compound adsorbed during decolorization of maize oil (Christidis *et al.*, 2002). The absorption bands of pure β -carotene and smectite after decolorization are listed in Table 4. The spectrum of β -carotene contains C=O bonds at 1720 cm⁻¹ formed from oxidaTable 4. Characteristic FTIR adsorption bands (cm⁻¹) of pure β -carotene and β -carotene adsorbed on Cyprus bentonite during decolorization of maize oil.

β-carotene	Bentonite after decolorization	Assignment of bands
n.p.	1740	C=O
1720	1720	C=O
1448	1458	CH ₂ or CH ₃
1382	1396	gem-CH ₃
1366	1374	gem-CH ₃

Data are from Christidis *et al.* (2002) n.p. = not present

tion during preparation of KBr pellets (drying at 105°C overnight). The spectrum of bentonite after adsorption is characterized by a doublet at 1720 and 1740 cm⁻¹ and by a shift of β -carotene bands at 1366 cm⁻¹, 1382 cm⁻¹ and 1448 cm^{-1} to higher frequencies. This shift is attributed to interaction of β -carotene with active centers at the surface of smectite probably via hydrogen bonds (Sarier and Güler, 1989). The second C=O band at 1740 cm⁻¹ may indicate further oxidation of β -carotene or direct bonding of C atoms with oxygens at smectite surface. Oxidation of β -carotene in the oil may result from circulation of oxygen during decolorization and/or electron transfer from β -carotene to the broken bonds of smectite. The role of exposed broken Fe³⁺ bonds is expected to be important, because Fe³⁺ is known to catalyze the decomposition of β -carotene (Khoo *et al.*, 1979).

Most of the previous studies which focused on the removal of β -carotene by activated bentonites (Khoo *et* al., 1979; Sarier and Güler, 1988; Boki et al., 1992b; Christidis et al., 1997) suggest that the adsorbent consists of smectites. However, the Cyprus bentonite contains ~10% clinoptilolite, while the principal mineral is mixed-layered illite-smectite with ~15% illite. Clinoptilolite can be activated with HCl and acquire decolorization capacity, which nevertheless is inferior to that of acid-activated bentonites (Girgin et al., 1996). Clays containing mixed-layered illite-smectite or discrete illite can also be activated successfully (Stoch et al., 1979; Srasra et al., 1989). The acid centers developed on illitic layers and zeolites contribute to the surface heterogeneity of the bulk adsorbent, and thus the Freundlich isotherms obtained are explained. Surface heterogeneity is caused also by the existence of different acid centers on the smectite surface. These centers are Lewis sites (broken Si-O-Si(Al) bonds and/or free octahedral Al³⁺ and Fe³⁺ caused by dissolution during acid leaching) and Brönsted sites (proton donors from uptake of H⁺ ions during activation). The heterogeneity of active centers explains the gradual increase of adsorption of β -carotene with temperature at different clay:oil ratios (Table 2), because a proportion of these centers is activated at higher temperatures.

SUMMARY AND CONCLUSIONS

Decolorization of maize and sunflower oil by acidactivated bentonites involves adsorption of pigments like β -carotene by means of a first-order reaction, which is described by different mechanisms in the two oils. Maize oil is decolorized in two distinct steps: a fast one in which chemical interaction between the active centers and the pigment molecules is at least partly active, followed by a slow, mainly physical, adsorption step. The two steps are indicative of a continuous coverage of the clay surface beyond a monolayer, as is indicated by Freundlich isotherms at equilibrium conditions. These characteristics are attributed to the heterogeneity of smectite active centers and the existence of other phases, which are also active. Decolorization of sunflower oil is described by a single step adsorption process.

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