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Decolorization of vegetable oils: Adsorption mechanism of β-carotene on acid-activated sepiolite

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Abstract

The adsorption behaviour of acid-activated sepiolite (AAS) for the removal of β-carotene ($C_{40}H_{56}$) from rapeseed oil was studied as a function of different sepiolite dosages and bleaching temperatures. The β-carotene level in the oil was reduced from 42.3 to 1.60 mg/kg under the optimum conditions of 100 °C bleaching temperature and 1.5% sepiolite dosage. A thermodynamic analysis involving the Langmuir and Freundlich models was applied to identify the mode and extent of β-carotene adsorption. While the negative values of free energy of adsorption (ΔG°_{ads}) indicate the spontaneity of adsorption, much larger values of the change in standard entropy (ΔS°_{ads})T compared to the enthalpy of adsorption (ΔH°_{ads}) reveal that the reaction is entropically driven and physical in nature. Acid-activated sepiolite exhibits weak acid, low acidity and absolute low zeta potential values, all of which suggest the dominance of Lewis acid centres on the AAS surface. The mechanism of incorporation of β-carotene molecules was examined by calculating its packing area through molecular considerations. It is suggested that β-carotene molecules adsorb both directly on the meso-external surface of AAS and penetrate intra-crystalline channels and tunnels. The pore size distribution of sepiolite confirms this assertion.

Keywords: Adsorption; Bleaching; β-Carotene; Sepiolitel; Clay

1. Introduction

Activated clays, activated carbon and silica-based products are adsorbents commonly used in the edible oil refining process. However, Fuller's earth-type activated clay is the most popular adsorbent for decolorization of edible oil because of its cheapness price compared to activated carbon- and silica-based products. Bleaching of vegetable oils by means of an activated earth is normally done by an adsorption process involving the removal of colouring pigments originating from carotenoids, chlorophyll, and related compounds.

Since acid-activated bentonites have more ability to bleach colouring matters, such as carotene and chlorophyll, they have always been in demand. Decolorization or bleaching capacity of acid-activated bentonites for crude edible oils is usually expressed as adsorption of β-carotene (Boki, Kubo, Kawasaki, & Mori, 1992; Boki, Kubo, Wada, & Tamura, 1992; Christidis & Kosiari, 2003; Khoo, Morsingh, & Liew, 1979; Liew, Tan, Morsingh, & Khoo, 1982; Sarier & Güler, 1988) or less often as that of chlorophyll (Brimberg, 1982). Some researchers (Achife & Ibemesi, 1989; Bera, Lahiri, & Nag, 2004; Kaynak, Ersoz, & Kara, 2004; Rossi, Gianazza, Alamprese, & Stanga, 2003; Topallar, 1998; Topallar & Bayrak, 1999) have reported the applicability of adsorption isotherms of colouring matter from various types of oils.

Although there are other clay minerals, such as sepiolite, with typical desirable properties, e.g., specific surface area,

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porosity and surface acid–base sites, they have not been much documented in the literature. Sepiolite is a natural clay mineral with a formula of magnesium hydrosilicate $Si_{12}Mg_8O_{30}(OH)_6(OH_2)_4 \cdot 8H_2O$ (Brauner & Preisinger, 1956). Similar to other types of silicate minerals, it contains a continuous two-dimensional tetrahedral sheet of T_2O_5 (T = Si, Al, Be...) but has no continuous octahedral sheets (Brindley, 1959). This unique fibrous structure with interior channels (3.6 × 10.6 Å) and its high surface area allows penetration of organic and inorganic ions into the structure of sepiolite (Alvarez, 1984). The ability of sepiolite to bleach is mainly ascribed to its high surface area because the cation-exchange capacity is lower than that of montmorillonite-type clay minerals. It is thus, an alternative material to other sorbents in processes such as wastewater treatment, in the removal of colour, odour, drug and pesticide carriers, paper and detergents (Boki et al., 1992; Bernal & Lopez-Real, 1993; Çelik et al., 2001; Dilek & Bese, 2001; Espantaleón, Nieto, Fernández, & Marsal, 2003; Fujivara & Sato, 1992; Gonzalez-Pradas, Villafranca-Sanchez, Socias-Viciana, Rey-Bueno, & Garcia-Rodriguez, 1987; Gonzalez-Pradas, Valverde-Garcia, & Villafrance-Sanchez, 1990; Kara, Yüzer, Sabah, & Çelik, 2003; Li, Willms, & Kniola, 2003; Rytwo, Trop, & Serban, 2002; Sabah & Çelik, 2001; Sabah & Çelik, 2002a, 2002b; Sabah, Kara, Hançer, & Çelik, 1998; Shuali, Bram, Steinberg, & Yariv, 1989; Zhaohui, Willms, & Kniola, 2003). However, to our knowledge, no study has appeared on the adsorption of β-carotene ($C_{40}H_{56}$) onto Turkish sepiolite.

It is, therefore, the objective of this study to investigate the mechanism of decolorizing of vegetable oils with an acid-activated sepiolite as a function of β-carotene concentration, bleaching temperature and sepiolite dosage, and also to elucidate the mode and extent of adsorption data using the Langmuir and Freundlich isotherms, along with thermodynamic parameters.

2. Materials and methods

2.1. Materials

The sepiolite sample used in this study was received from Anadolu Industrial Minerals Co. in Sivrihisar, Turkey. This beige sepiolite (BS), ground to minus 75 μm, produced an average particle size (d_{50}) of 14.41 μm, as determined by HELOS-Zetasizer, and was activated with 1 M nitric acid (HNO_3). Table 1 lists the relevant analytical data on the BS and AAS.

Nitric acid (HNO_3), used for acid activation, was purchased from Roth (Karlsruhe-Germany) and specified to be of high purity. Distilled water was utilized in all the experiments.

Experiments were carried out with the degummed (water and acid degumming, followed by drying) rapeseed oil in order to eliminate the influence of different crude oil qualities on bleaching. Table 2 shows the composition of the degummed rapeseed oil provided by Bioölwerk Magdeburg GmbH, Germany.

2.2. Methods

Acid activation was carried out using 65% by wt. 1 N analytical grade HNO_3 for 1 h at room temperature at a solid to liquid ratio of 1:10. Upon activation, the sepiolite was washed twice with distilled water to pH 5.8 and the slurry was filtered under vacuum. The acid-activated sepiolite was dried in an oven at 60 °C for 15 h and reground using a centrifugal ball mill (RETSCH S 100) in order to let particles pass through 75 μm.

The vacuum bleaching tests were accomplished in a 250 ml, 4-neck round-bottom flask which was heated from the outside. The equipment was constructed such that the rapeseed oil (150 ml) could be agitated with a stirrer at approximately 400 rpm throughout the bleaching process. The temperature was controlled with a mercury thermometer. A vacuum pump was used to maintain the necessary pressure at 40 mbar. After the bleaching process and cooling of the oil to 70–80 °C, the oil was separated through a pressure filter. All bleaching experiments were carried out at temperatures of 80 and 100 °C and 15 min of contact time (Table 3).

The β-carotene content of the oil was measured at 450 nm wavelength according to the ÖHMI L 004-13 method (ÖHMI, ...) and colour of the oil was determined on a Lovibond Tintometer (Model PFX990) according to the AOCS official method Cc 13d-55 (AOCS, 1997).

The acidity of AAS measurement is based on titration with 0.1 N NaOH solution using phenolphthalein as indicator. The result is expressed as percentage acidity.

The BET surface area of BS and AAS was measured by N_2 adsorption using a Flowsorb II-2300 Micromeritics instrument.

Zeta potential measurements were conducted by means of Zeta-Meter 3.0, which is equipped with a microprocessor unit capable of directly measuring the average zeta potential and its standard deviation (Çelik & Yasar, 1995).

3. Results and discussion

3.1. Adsorption studies

The uptake of β-carotene onto AAS as a function of its dosage and different bleaching temperatures is presented in Fig. 1 in terms of percent adsorption and per unit wt. of AAS. There is apparently a definite reduction of β-carotene with increasing AAS dosage from 0.5% to 1.5%. As shown in Table 2, the initial concentration of β-carotene in the oil is 42.3 mg/kg. The adsorption of β-carotene per unit weight of AAS (Eq. (3)) decreased from 5.68 to 2.61 mg/kg at 80 °C and from 6.22 to 2.71 mg/kg at 100 °C, corresponding to 0.5–1.5% AAS dosages (Table 3), respectively; this clearly indicates that the adsorption of β-carotene is drastic up to 0.5% AAS dosage and relatively slows down above it. Both the AAS dosage and to a lesser extent bleaching temperature have significant effects on the uptake of β-carotene by AAS.

Table 1
Some physical and chemical characteristics of BS and AAS

Parameters	BS	AAS
Apparent bulk density	348 g/l	223 g/l
Free moisture (2 h, 110 °C)	6.4%	~10%
Loss on ignition (pre-dried, 2 h)	23%	~10%
1000 °C	8.75	5.80
pH (10% suspension)	0.12%	0.20%
Acidity	223	280 m^2/g
Surface area (BET)		
Particle size	100.00	100.00
% less than 75 μm	93.34	94.78
% less than 45 μm		
Zeta potential (mV)		
pH 8.75	−10.30	
pH 5.80		−5.78

Table 2
Analysis of degummed rapeseed oil

Parameters	Values
Density at 20 °C (kg/l)	0.91
β-Carotene concentration (mg/kg)	42.3
Molecular weight of β-Carotene (g/mol)	536.89
Colour	
Lovibond red 5 1/4″	3.8
Lovibond yellow 1″	70

Table 3
Parameters for β-carotene uptake by AAS at 80 and 100 °C after 15 min of bleaching

Bleaching temperature	80 °C			100 °C		
AAS dosages	0.5%	1.0%	1.5%	0.5%	1.0%	1.5%
Equilibrium concentration of β-carotene (mg/kg), C_e	13.9	4.53	3.17	11.2	3.82	1.60
β-Carotene onto AAS (mg/g), X	5.68	3.78	2.61	6.22	3.85	2.71
Colour						
Lovibond red 5 1/4″	3.2	1.6	0.6	3.6	1.6	0.8
Lovibond yellow 1″	70	70	32	70	38	12

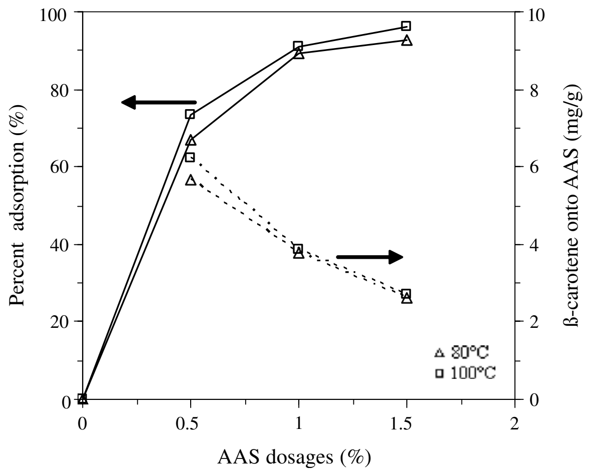


Fig. 1. Uptake of β-carotene by AAS both in terms of percent adsorption and per unit wt. of AAS at different bleaching temperatures (150 g oil, 15 min contact time).

As is evident from Fig. 1, even at low dosages of AAS, the uptake of β-carotene reaches 70% and levels off at 90% at 1.0% AAS dosage. Addition of AAS to oil beyond this point makes no significant contribution to adsorption density. The first and most important factor, which can contribute to AAS dosage, is that adsorption sites remain unsaturated during the bleaching process. At low AAS/oil ratios the removal of β-carotene is more efficient, since most active centres are occupied by β-carotene molecules. It must be pointed out that the oil also contains other colorants, such as chlorophyll, which concomitantly competes with β-carotene for adsorption sites.

The partition of β-carotene molecules between liquid phase and adsorbent is a measure of the position of equilibrium in the adsorption process. It is therefore important to establish the most appropriate correlations for the equilibrium data in the design of adsorption systems. The adsorption data in the present study are analyzed according to the two commonly used isotherm equations: Langmuir and Freundlich models. Applicability of the isotherms was compared by judging the correlation coefficient, R^2:

$$\text{Langmuir}: \quad \frac{C_e}{X} = \frac{1}{K_L X_m} + \frac{1}{X_m} C_e \tag{1}$$

$$\text{Freundlich}: \quad X = K_F C_e^{1/n} \tag{2}$$

$$\text{Mass-balance equation} \quad X = \frac{(C_0 - C_e)V}{1000m} \tag{3}$$

where C_e is the equilibrium concentration of β-carotene (mg/kg), X is the amount of β-carotene adsorbed per gramme of AAS (mg/g) which was calculated using Eq. (3), C_0 the initial concentration of β-carotene (mg/kg), X_m the quantity of β-carotene adsorbed at monolayer or maximum coverage (mg/g), K_L the Langmuir adsorption equilibrium constant (kg/mg) related to direct measure of the intensity of the adsorption process, m the mass of adsorbent (g) and V is the mass of oil (g). A plot of C_e/X vs. C_e yields the values of X_m and K_L from the slope and intercept, respectively, as shown in Fig. 2(a).

In Eq. (2), K_F is a constant for the system related to bonding energy; K_F can be defined as an adsorption or distribution coefficient which describes the amount of β-carotene adsorbed onto AAS for the unit equilibrium concentration. The value of n, ranging between 1 and 10, is a measure of the adsorption intensity (Fytianos, Voudrias, & Kokkalis, 2000; Haghseresht & Lu, 1998; Öztürk & Bektaş, 2004; Tsai, Chang, Ing, & Chang, 2004).

The linearized Langmuir and Freundlich adsorption isotherms of β-carotene/AAS system obtained at the bleaching temperatures of 80 and 100 °C are given in Fig. 2(a) and (b). The values of model parameters at different temperatures with the correlation coefficients are presented in Table 4.

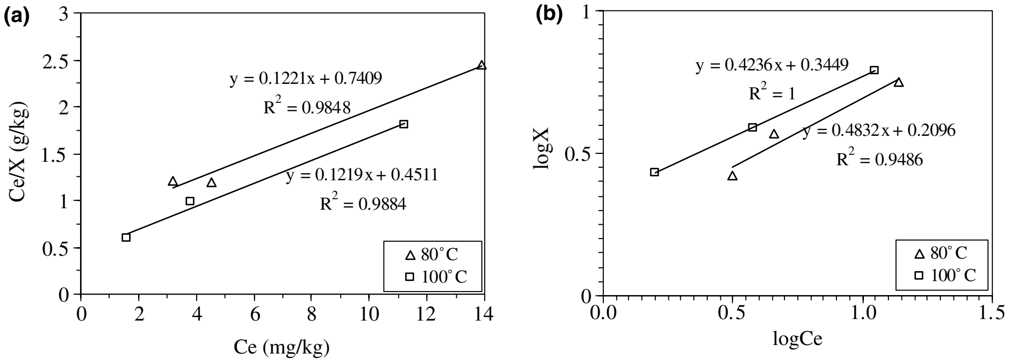


Fig. 2. Langmuir (a) and Freundlich (b) equilibrium sorption isotherms for β-carotene at 80 and 100 °C.

The values of the correlation coefficients indicate that the β-carotene/AAS sorption data fit both Langmuir and Freundlich isotherm models. However, considering the adsorbed amount of β-carotene at 80 and 100 °C (Eqs. (4) and (5)), and since the value of X in the Freundlich isotherm model (Eq. (5)) is larger than that of the Langmuir model (Eq. (4)), the Freundlich model appears to fit the data better.

For Langmuir isotherm model at

$$\begin{cases} 80\,^{\circ}\mathrm{C}: \ 1.31C_e/(1+0.16C_e) \\ 100\,^{\circ}\mathrm{C}: \ 2.21C_e/(1+0.27C_e) \end{cases} \tag{4}$$

For the Freundlich isotherm model at

$$\begin{cases} 80\,^{\circ}\mathrm{C}: \ 1.62C_e^{0483} \\ 100\,^{\circ}\mathrm{C}: \ 2.21C_e^{0424} \end{cases} \tag{5}$$

As seen from Table 4, since the monolayer adsorption capacity X_m does not change with temperature, K_L increases with temperature to a greater extent. The higher value of K_F is generally indicative of a higher affinity for β-carotene and is in line with the temperature effect on adsorption. The values of n at 80 and 100 °C in the Freundlich equation are, respectively, 2.07 and 2.36 and appear to be in agreement with the usual range of 1–10 obtained for favourable adsorption. This effect further corroborates the observed effect of temperature on specific adsorption with n being a measure of the intensity of adsorption. In bleaching processes, a higher K_F value indicates a higher adsorption of pigments (Kaynak et al., 2004). The observed increase in K_F value with rise in temperature in bleaching of rapeseed oil with AAS seems to support the inference that higher temperature creates more adsorption sites.

Table 4
The X_m, K_L, n and K_F values evaluated from the isotherms at different temperatures with the correlation coefficients

Temperature (°C)	Langmuir constants			Freundlich constants		
	X_m (mg/g)	K_L (kg/mg)	R^2	n	K_F	R^2
80	8.19	0.16	0.9848	2.07	1.62	0.9486
100	8.20	0.27	0.9884	2.36	2.21	1.0000

The quantitative treatment of adsorption at the solid/liquid interface requires, first of all, the mechanism of β-carotene adsorption onto AAS to be identified. The data obtained from adsorption isotherm models can be conveniently used to determine such thermodynamic parameters as free energy of adsorption ($\Delta G^{\circ}_{\mathrm{ads}}$), enthalpy of adsorption ($\Delta H^{\circ}_{\mathrm{ads}}$) and the change in standard entropy ($\Delta S^{\circ}_{\mathrm{ads}}$). These parameters are evaluated using the following equation:

$$K_d = K_F = X \tag{6}$$

where K_d (l/mol) is the sorption distribution coefficient. The K_d values were plugged into Eq. (7) to determine the free energy of sorption process at different temperatures.

$$\Delta G^{\circ}_{\mathrm{ads}} = -RT \ln K_d \tag{7}$$

where $\Delta G^{\circ}_{\mathrm{abs}}$ is the free energy of sorption (kJ/mol), T is the temperature in Kelvin and R is the universal gas constant (8.31414 J/mol K).

The sorption distribution coefficient may be expressed in terms of enthalpy change ($\Delta H^{\circ}_{\mathrm{ads}}$) and entropy change ($\Delta S^{\circ}_{\mathrm{ads}}$) as a function of temperature.

$$\ln K_d = -\frac{\Delta H^{\circ}_{\mathrm{ads}}}{RT} + \frac{\Delta S^{\circ}_{\mathrm{ads}}}{R} \tag{8}$$

where $\Delta H^{\circ}_{\mathrm{abs}}$ is the heat of adsorption (kJ/mol) and $\Delta S^{\circ}_{\mathrm{ads}}$ is the standard change in entropy (kJ/mol).

The free energy indicates the degree of spontaneity of the sorption process and a higher negative value reflects a more energetically favourable sorption. The values of $\Delta H^{\circ}_{\mathrm{ads}}$ and $\Delta S^{\circ}_{\mathrm{ads}}$ were obtained from the slope and intercept of a plot of $\ln K_d$ against $1/T$ (Fig. 3). The calculated parameters are presented in Table 5.

As is apparent in Table 5, the $\Delta G^{\circ}_{\mathrm{ads}}$ values are all negative and the negativity gradually increases with increasing AAS dosages and temperature values. The negative value of $\Delta G^{\circ}_{\mathrm{ads}}$ indicates the spontaneous nature of β-carotene adsorption on AAS. This shows that the removal process is favoured at higher temperature and AAS dosages. The variation of $-\Delta G^{\circ}_{\mathrm{ads}}$ values in the range of 13.6–16.7 kJ/mol is typical of physical adsorption systems, though the actual quantity that determines the nature of adsorption is the enthalpy of adsorption ($\Delta H^{\circ}_{\mathrm{ads}}$) rather than $\Delta G^{\circ}_{\mathrm{ads}}$.

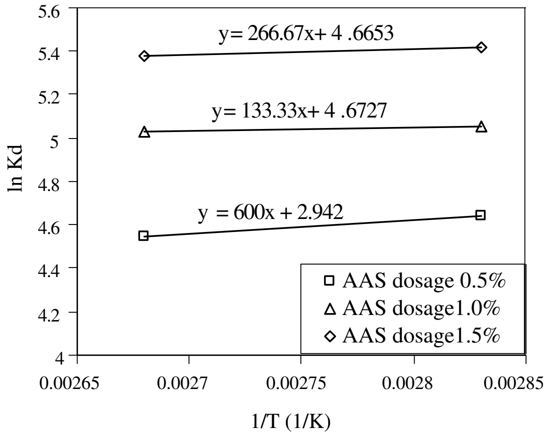


Fig. 3. Plots of $\ln K_d$ vs. $1/T$ for β-carotene adsorption on AAS at various dosages.

Compared to the total adsorption energy, the value represents a small proportion of it. On the other hand, the entropic contribution, $T\Delta S^{o}_{ads}$, is much larger than the enthalpic contribution. This clearly reveals that the adsorption reactions in the β-carotene/AAS system are entropically governed. Similar results were also presented in a sepiolite/quaternary amine system (Sabah & Çelik, 2002a). It is also generally accepted that ΔH^{o}_{ads} values lower than 40 kJ/mol are indicative of physical adsorption.

The coverage of the AAS surface by β-carotene molecule, in Å^2/molecule, can be calculated by

$$\text{Packing area} = 10^{20}/\Gamma_{\max}A \quad (9)$$

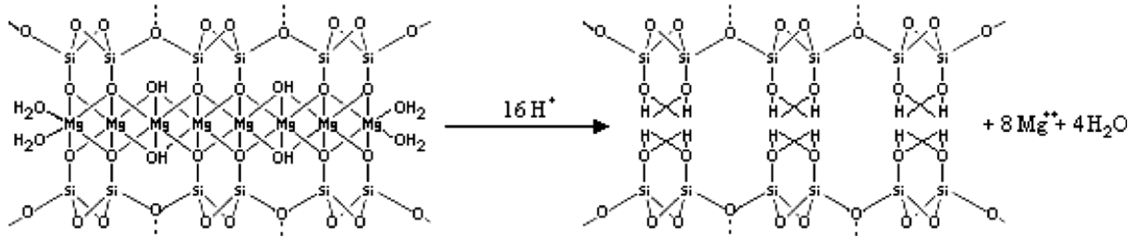
where $\Gamma_{\max}$ is the adsorption density, an A is the Avogadro number (6.02×10^{23}). Using the values given in Fig. 1, the packing area of β-carotene for the 1.5% AAS dosage is found to be 9228 Å^2/molecule. The cross sectional area of $7 \times 31 = 217$ Å^2 reported for the β-carotene molecule (Taylor, Jenkins, & Ungermann, 1989) has been taken into consideration to interpret the packing area of β-carotene molecules in adsorbed layers. The packing area indicates that the β-carotene molecules occupy 2.3% of the total area at the β-carotene/AAS interface. This is expected, as the degummed rapeseed oil reported elsewhere (Sabah & Çelik, 2005) was found to contain various constituents (chlorophyll A and phosphorus). These constituents compete with β-carotene for the adsorption sites.

Pore size distribution is a crucial parameter for the uptake or exclusion of such large molecules. While a pore radius smaller than 15 Å is defined as a micropore, larger pores are considered as a meso or macropores. These micropores disappear at temperatures above 573 K due to crystalline folding. Sepiolite exhibits three different types of water molecules: zeolitic or adsorbed water, crystalline water, and hydroxyl groups. The surface area of sepiolite undergoes changes due to the removal of these water molecules in different forms. Heating sepiolite to 373–523 K removes the zeolitic water, whereas the other forms of water are removed only above 573 K.

Our pore volume measurements indicate that sepiolite yields an average pore radius of 32 Å. A comprehensive set of data reported by Balcı (1999) clearly shows that while thermal treatment removes water molecules, leading to changes in the pore size distribution, similarly, mild acid treatment leaches out Mg^{2+} and some other inorganic ions in the octahedral sheet, resulting in an increase in the number of meso and macro pore volumes. Balcı (1999) has also found that 100 °C is the optimum calcination temperature for obtaining a maximum pore volume and BET surface areas. These results also indicate that sepiolite exhibits a wide pore distribution, stretching from 1 to several hundreds of Angstroms. Our average pore size is consistent with this finding, though different sepiolites may have different pore distribution profiles. Accordingly, only part of the β-carotene molecules will be accommodated and some will be excluded. For instance, the Vellecas sepiolite has a mean micropore diameter of 15 Å and a micropore ratio of 60–70% (Alvarez, 1984).

3.2. The proposed adsorption mechanism

Acid activation of sepiolite removes Mg^{2+} ions in the actahedral sheet and leaves a large number of highly active silanol groups (Si–OH) on the adsorbent sites. Acid activation also imparts changes in the pore structure and physicochemical properties of sepiolite structure. The acid dissolution has been represented by Hernandez, Rueda, Diaz, and Anton (1986) as:



Acid activation at the same time induces the loss of about half of the zeolitic and hydroxyl water from the sepiolite structure. This pre-removal afterwards limits the

Table 5
Thermodynamic parameters for sepiolite/β-carotene system at various AAS dosages

AAS dosage (%)	Mean ΔS^{o} (kJ/mol)	Mean ΔH^{o} (kJ/mol)	ΔG^{o} (kJ/mol)	
			353 K	373 K
0.5	0.024	−5.16	−13.6	−14.1
1.0	0.039	−1.05	−14.8	−15.6
1.5	0.039	−2.14	−15.9	−16.6

temperature effects on the plugging of micro pores and collapse of the crystal structure (Balcı, 1999; Ruiz-Hitzky, 2001). However, the acidic treatment produced longer channels between the silicate chains (Dékány, Turi, Fonseca, & Nagy, 1999).

The Freundlich isotherm may suggest heterogeneity of adsorption sites on solid surface. The existence of different acid centres on the smectite surface was attributed to heterogeneity (Christidis & Kosiari, 2003). However, the dominant mechanism of β-carotene adsorption onto sepiolite cannot be ascribed to surface heterogeneity alone, i.e., the presence of different acid centres. As is apparent in Table 1, the pH and acid value of AAS are, respectively, 5.8% and 0.2%, indicating weak acidity. In this case, it is difficult to say that the AAS surfaces are composed of both Brönsted and Lewis acid centres. Weak acid, low acidity and absolute low zeta potential value (−5.78 mV) all indicate the dominance of Lewis acid centres on the AAS surface. Adsorption isotherm and thermodynamic parameters indicate that β-carotene molecules adsorb at the surface at ambient temperature but at 100 °C they both adsorb at the sepiolite surface and get incorporated into the pores. Bleaching of sepiolite by acid activation at 80 and 100 °C, opens up the pores and limits the blockage of pores. The affinity of β-carotene for activated sepiolite is enhanced in the internal surfaces rather than external. It is suggested that β-carotene molecules can adsorb both directly on the meso-external surface of AAS and penetrate intra-crystalline channels and tunnels as is illustrated in Fig. 4.

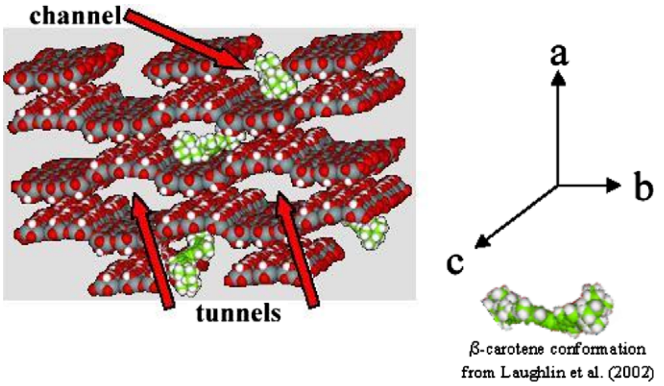


Fig. 4. Schematic illustrations of three-dimensional representation of β-carotene molecule incorporated in the AS external surface and within the channels and tunnels. (See above-mentioned references for further information.)

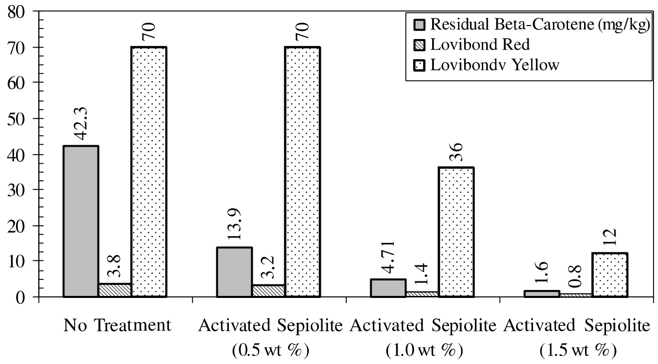


Fig. 5. Decoloring properties of AAS at various dosages (100 °C bleaching temperature; 15 min contact time).

Also noteworthy is the finding that the best correlation regarding β-carotene adsorption was obtained when using pore volumes in the range of 100–450 Å pore diameter, using acid-activated sepiolite from Sivrihisar, Turkey (Balcı, 1999) because these pore diameters are considerably larger than the cross sectional dimensions of the corresponding β-carotene molecule (ca. 7 × 31 Å). In this study, increasing the sepiolite dosage remarkably reduced the β-carotene concentration in the oil and, in turn, the Lv red and Lv yellow values (Fig. 5); while percent removal in the Lv red is 79%, that in the Lv yellow reached 83%. It should be noted that standard bleaching, with 1.0 wt% dosage Tonsil FF 210 in 150 g oil and 90 °C for 20 min, yields Lv red and Lv yellow values of 1.0 and 38, respectively; this indicates that sepiolite performs better under these conditions.

4. Conclusions

A sepiolite sample from Sivrihisar, Turkey has been subjected to a set of acid-activation experiments to obtain a bleaching suitable for abstracting β-carotene from rapeseed oil. The following salient points have been extracted out of this study.

1. Acid-activated sepiolite (AAS) is a very good adsorbent for the removal of β-carotene; under the optimum conditions of 100 °C bleaching temperature and 1.5% sepiolite dosage, β-carotene level in the rapeseed oil was reduced from 42.3 to 1.60 mg/kg.
2. The AAS dosage, and to a lesser extent bleaching temperature, have significant effect on the uptake of β-carotene by AAS.
3. The partition of β-carotene molecules between liquid phase and adsorbent was fitted to Langmuir and Freundlich models. The values of the correlation coefficients indicate that the β-carotene/AAS sorption data fit the latter data better.
4. The data obtained from adsorption isotherm models were used to determine the thermodynamic parameters, such as the free energy of adsorption (ΔG^{o}_{ads}), enthalpy of adsorption (ΔH^{o}_{ads}) and the change in standard

entropy (ΔS^{o}_{ads}). Considering the total adsorption energy, the entropic contribution $T\Delta S^{o}_{ads}$ is much larger than the enthalpic contribution. This clearly reveals that the adsorption reactions in the β-carotene/AAS system are entropically governed.

5. The packing area of β-carotene for 1.5% AAS dosage is 9228 Å^2/molecule. Considering the cross sectional area of 217 Å^2 for a β-carotene molecule, the packing area indicates that the β-carotene molecules occupy 2.3% of the total area at the β-carotene/AAS interface. The pore volume measurements indicate that sepiolite yields an average pore radius of 32 Å. Accordingly, only part of the β-carotene molecules will be accommodated and some will be excluded.
6. An incorporation mechanism of β-carotene molecules into the sepiolite is proposed with a schematic illustration where β-carotene adsorbs directly to onto the meso-external surface of AAS and penetrates intra-crystalline channels and tunnels. Adsorption isotherm and thermodynamic parameters indicate that β-carotene molecules adsorb at the surface of sepiolite and get incorporated in the pores through physical adsorption.

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