Clay Minerals, (2015) **50**, 639–648

Optimization of oil bleaching parameters, using response surface methodology, for acid-activated sepiolite from Iran

MOJTABA SANEEI, SAYED AMIR HOSSEIN GOLI* AND JAVAD KERAMAT

Department of Food Science and Technology, College of Agriculture, Isfahan University of Technology, Isfahan 84156-83111, Iran

(*Received 21 January 2015; revised 4 October 2015; Editor: George Christidis*)

ABSTRACT: An Iranian sepiolite was activated with 1.5 M HCl. During activation, the specific surface area increased from 105 to 168 m^2/g and the SiO_2 content increased from 45.4 to 51.6%. The roles of temperature and time and the amount of acid-activated sepiolite used, were investigated and the optimum conditions, where chlorophyll, β-carotene, free fatty acid and peroxide were at their minimum levels, were determined for bleaching of canola oil by applying response surface methodology (RSM). Optimum bleaching conditions were obtained by adding 3% of acid-activated sepiolite at a temperature of 110°C with a bleaching time of 42.46 min during which, the amount of chlorophyll-α, β-carotene, free fatty acid and peroxide were reduced from 12.30 to 0.35 mg/kg, 49.15 to 14.98 mg/kg, 0.62 to 0.15%, and 3.87 to 2.14 meq O_2/kg of oil, respectively. At optimum conditions, sepiolite displayed a greater capacity for removal of chlorophyll and β-carotene than a commercial bentonite bleaching agent.

KEYWORDS: β-carotene, chlorophyll, edible oil, sepiolite.

Bleaching of crude oils can reduce the amounts of peroxides, free fatty acids, β-carotene and chlorophyll-α leading to improvement of oil stability in terms of oxidation, shelf life and consumer preference. An adsorbing agent is mixed with the oil during bleaching and the process is conducted under special conditions. Generally, a number of parameters are effective in terms of the bleaching process, among which the properties of the bleaching adsorbent play a key role (Kim & Choe, 2005; Sabah & Celik, 2005; Liu *et al*., 2008). Adsorbents such as acid-activated clays, activated carbon and various SiO_2-based products are used widely, though activated clays are important commercially due to their relatively low cost and high performance (Taylor, 2005).

Sepiolite $[(Mg_8)(Si_{12})O_{30}(OH)_4.12H_2O]$ is a 2:1 fibrous clay mineral. Due to its fibrous structure, sepiolite differs from the common layer silicates and has fine channels running parallel to the fibre axis (Balci, 1996). Sepiolite has a significant capacity to adsorb colour pigments because of its large specific surface area (SSA) and porosity (Sabah & Celik, 2005; Sabah, 2007; Sabah *et al*., 2007; Ugurlu & Kula, 2007; Zadaka Amir *et al*., 2013). Previous work on the application of sepiolite in the bleaching of edible oils has been limited. Tian *et al*. (2014) used thermally activated sepiolite for decolourization of crude palm oil. Sabah & Celik (2005) investigated the efficiency of Turkish sepiolite in the bleaching of degummed rapeseed oil and indicated that maximum yield was obtained at 1.5% sepiolite and a bleaching temperature of 100°C. The adsorption characteristics of acid-activated sepiolite were also studied for the removal of β-carotene, chlorophyll-α and phosphorus from rapeseed oil (Sabah, 2007; Sabah *et al*., 2007; Sabah & Majdan, 2009). In addition, thermally acid-activated sepiolite was more efficient than its thermally activated counterpart for the removal of colouring agents from olive oil

*Email: amirgoli@cc.iut.ac.ir
DOI: 10.1180/claymin.2015.050.5.07

© 2016 The Mineralogical Society
https://doi.org/10.1180/claymin.2015.050.5.07 Published online by Cambridge University Press

(Ugurlu & Kula, 2007). Because the main bleaching parameters including clay dosage, bleaching time and temperature are very dependent on the type of bleaching agent and the crude oil (Jahouach *et al*., 2006; Skevin *et al*., 2012; Ajemba *et al*., 2013; Ofochebe & Ozoegwu 2014), establishing the optimum conditions in which to use sepiolite to decolourize crude oil is very important.

As far as the present authors are aware, no comprehensive report has been published on the optimization of the decolourization of crude oils using response surface methodology (RSM). The RSM is a collection of mathematical and statistical techniques applied widely in the food industry to evaluate the relationship between the predicted values of independent and dependent variables. The major advantage of RSM is a reduction in the number of experiments needed to investigate multiple variables and their interactions; thus RSM is less laborious and time-consuming than other approaches (Box & Wilson, 1951). In the present study, therefore, the effect of acid activation on an Iranian sepiolite was investigated and the activated clay was used to bleach canola oil by RSM for optimizing bleaching conditions.

MATERIALS AND METHODS

Materials

Degummed and neutralized canola oil was obtained from Nahangol Co. (Boroojen, Iran). The sepiolite was purchased from Farapooyan Isatis Yazd Co. (Yazd, Iran). The commercial bentonite was supplied by Kanesaze Jam Co. (Tehran, Iran). Analytical-grade chemicals and solvents were purchased from Merck (Darmstadt, Germany).

Acid activation of sepiolite

Acid activation was carried out using the method of Kilislioglu & Aras (2010) but with a slight modification, namely 1.5 M HCl was used for 4 h at 75°C at a 1:10 (w/w) clay/acid ratio. The sepiolite was then washed four times with deionized water (Kilislioglu & Aras, 2010) and the slurry was centrifuged at 2100 rpm for 15 min. The acid-activated sepiolite was finally dried in an oven at 100°C for 10 h, ground in a ball mill and passed through a 0.063 mm sieve.

Characterization of sepiolite

The mineralogical compositions of both the natural and acid-activated sepiolites were identified by X-ray diffraction (XRD) (Philips PW1800). The chemical composition of samples was determined by X-ray fluorescence (XRF) spectrometetry (Philips PW 1480). The SSA and pore-size distribution were measured by nitrogen adsorption and desorption at 77 K using a BELSORP-mini II analyzer. The sample was first outgassed at 120°C for 2 h. The acidity of the sepiolite was measured by titration with NaOH solution using phenolphthalein as the indicator. The result was expressed as % acidity (Sabah & Celik, 2005). The apparent bulk density (ABD) was determined according to the German version of European Standard EN 1097-3 (European Standards, 1998).

Bleaching procedure

The Canola oil and the activated sepiolite were first mixed in a two-necked round-bottomed flask under vacuum (4000 pa). The process was based on RSM design with three factors involved in the bleaching: temperature, time and sepiolite content (Table 1). The mixture was stirred at a fixed speed of 600 rpm. After bleaching, the clay was separated by centrifugation at 4100 rpm for 20 min. Finally, the bleached oil was stored in a dark glass container and kept at 18°C for further analysis.

Oil characterization

Chlorophyll content. The chlorophyll-α content was measured using a UV-Vis spectrophotometer (Unico UV-2100, England) based on the American Oil Chemist's Society (AOCS) (1997) method Cc 13d-55 and calculated as mg of pheophytin-a per kg of oil as follows:

$$C = A670 - \frac{(A630 - A710)}{\frac{2}{0.0964L}} \quad (1)$$

where $A670$, $A630$ and $A710$ are the absorbance values at 670, 630 and 710 nm, respectively, C is the chlorophyll content (mg/kg), and L is the length of the cuvette (cm) (AOCS, 1997; Sabah *et al*., 2007).

β-carotene content. The β-carotene content was measured using the ÖHMI L 004-13 method at 450 nm using UV-Vis spectrophotometry (Sabah *et al*., 2007).

Color. The oil colour was evaluated using Hunter lab parameters *L, a* and *b*, where *L* is lightness from 0 to 100 (dark to light), *a** is redness (–*a* refers to green and

https://doi.org/10.1180/claymin.2015.050.5.07 Published online by Cambridge University Press

TABLE 1. Experimental design and values measured for the response variables during bleaching

Experimental	Amount of clay (%w) *A*	Time (min) *B*	Temperature (°C)	Chlorophyll (mg/kg)	β-carotene (mg/kg)	Δ*E*	PV (meq O_2/kg of oil)	FFA (% oleic acid)
Unbleached oil	–	–	–	12.30	49.15	–	3.87	0.62
1	0.50	15.00	80.00	0.59	25.41	12.97	3.52	0.24
2	0.50	15.00	95.00	0.55	22.34	14.99	3.33	0.22
3	0.50	15.00	110.00	0.51	20.25	15.99	3.30	0.21
4	0.50	30.00	80.00	0.58	23.38	16.38	3.38	0.23
5	0.50	45.00	80.00	0.58	23.38	15.62	3.36	0.23
6	0.50	45.00	110.00	0.49	19.73	17.87	3.26	0.20
7	0.50	45.00	110.00	0.50	20.01	18.82	3.24	0.21
8	1.75	22.50	87.50	0.47	19.2	18.69	3.22	0.15
9	1.75	30.00	110.00	0.38	18.29	23.91	3.03	0.17
10	1.75	45.00	95.00	0.42	18.76	20.51	3.13	0.19
11	3.00	15.00	80.00	0.38	18.01	24.25	2.40	0.16
12	3.00	15.00	110.00	0.36	16.62	28.25	2.27	0.16
13	3.00	15.00	110.00	0.35	16.57	30.69	2.25	0.16
14	3.00	30.00	95.00	0.37	16.32	32.81	2.33	0.16
15	3.00	45.00	80.00	0.38	17.81	29.23	3.31	0.16
16	3.00	45.00	80.00	0.38	17.91	22.11	2.42	0.17
17	3.00	45.00	110.00	0.35	15.28	32.42	2.14	0.15
18	3.00	45.00	110.00	0.35	14.98	36.19	2.24	0.15

+*a* refers to red) and *b* is yellowness (–*b* refers to blue and +*b* refers to yellow) using a Hunter lab Datacolor Tex Flash 2000 spectrophotometer. The color difference (Δ*E*) was measured using equation 2:

$$\Delta E = \sqrt{(L_0 - L_1)^2 + (a_0 - a_1)^2 + (b_0 - b_1)^2} \quad (2)$$

where L_0, a_0 and b_0 and L_1, a_1 and b_1 are the colour parameters of canola oil before and after bleaching, respectively.

Peroxide and acid values. Peroxide values (PV) and free fatty acid (FFA) values were determined according to the AOCS methods (Cd8b-53 and Cc-5a-40, respectively). The acid value was calculated as g of oleic acid per 100 g of oil.

Sepiolite function compared with commercial bleaching earth

In order to compare the bleaching capacity of the acid-activated sepiolite with that of a commercial bleaching clay (bentonite) used by the oil industry, canola-oil bleaching was conducted at optimal conditions. β-carotene and chlorophyll content as well as FFA and PV values of crude, sepiolite-bleached and bentonite-bleached oils were determined and analysed using the t-test at a confidence level of 95%.

Statistical analysis

Three parameters (*A*: % clay, *B*: time and *C*: temperature) at three levels were investigated and dependent variables (or responses) were: the chlorophyll content (Y_1), β-carotene (Y_2), FFA (Y_3), peroxides (Y_4) and Δ*E* (Y_5) (Table 1). In total, 18 experiments were conducted based on D-optimal design. The results were analysed using *Design Expert* software v. 7.1.6 (stat-Ease Inc., Minneapolis, Minnesota, USA).

RESULTS AND DISCUSSION

Characterization of acid-activated sepiolite

The sepiolite sample consists mainly of sepiolite and dolomite (Fig. 1) (Sabah *et al*., 2007). During acid activation (Fig. 1b), the surface of sepiolite was

https://doi.org/10.1180/claymin.2015.050.5.07 Published online by Cambridge University Press

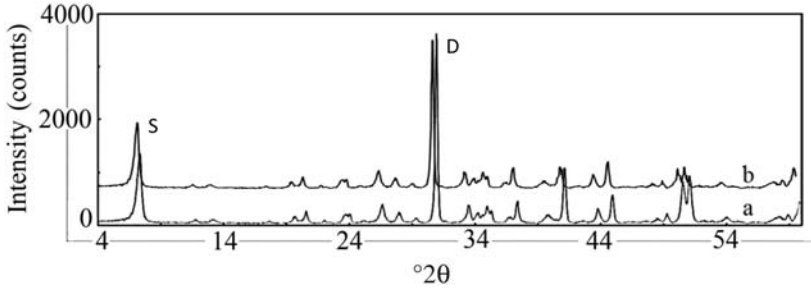


FIG. 1. XRD patterns of: (a) natural; and (b) acid-activated sepiolite. D = dolomite; S = SiO_2.

modified and new active sites may have formed within the channels. The intensity of the major reflections suggests that the crystal structure of sepiolite was retained after activation (Fig. 1). Dolomite was not dissolved during activation, because only a slight decrease in the intensity of the main dolomite reflection was observed (Fig. 1). The partial dissolution of both minerals is evident from the decrease in the Mg content after activation (Table 2). The increase in SiO_2 content might be residual and possibly associated with the partial dissolution of the two minerals and release of Mg and Ca. Similar results during acid activation of sepiolite have been reported in previous studies (Balci, 1999; Kilislioglu & Aras, 2010).

TABLE 2. Physical properties and chemical composition of the natural and acid-activated sepiolites.

Parameter	Natural sepiolite	Activated sepiolite
Apparent bulk density (g/cm^3)	0.364	0.323
Free moisture (2 h, 110°C)	4.85%	6.84%
Loss on ignition (pre-dried, 2 h, 1000°C)	15.72%	12.73%
pH (10% suspension)	9.20	7.60
Acidity (%)	0.08	0.11
SSA (BET) (m^2/g)	105	168
Pore volume (cm^3/g)		0.254
Chemical composition (%)		
SiO_2	45.45	51.66
Al_2O_3	0.41	0.15
Fe_2O_3	0.12	0.08
CaO	19.27	23.45
Na_2O	0.05	0.02
K_2O	0.02	0.03
MgO	18.75	10.45
TiO_2	0.003	0.002
MnO	0.002	0.002
P_2O_5	0.012	0.018
S	0.002	0.25

The chemical composition of the sepiolite samples is shown in Table 2. In natural sepiolite, the main components are SiO_2 (45.4), CaO (19.2) and MgO (18.7%), in agreement with Balci (1999) and Ugurlu & Kula (2007). During acid activation, a remarkable increase was observed in the SiO_2, CaO and S contents, whereas the concentrations of MgO, Al_2O_3 and Fe_2O_3 decreased. The Si/Al and Si/Mg ratios increased from 110.85 to 344.4 and from 2.42 to 4.94, respectively, after activation. Acid activation resulted in the removal of Al and Mg and produced abundant Si-OH (silanol) groups in sepiolite enhancing its capability to adsorb impurities and colour pigments (Sabah & Celik, 2005).

The increase in the SSA and the SiO_2 content and the reduction in Al and Mg are consistent with the XRD patterns; the increase in the CaO content after activation cannot be explained, however (Fig. 1, Table 2). A five-fold increase in the CaO content after acid treatment of sepiolite was reported by Ugurlu & Kula (2007).

The physicochemical characteristics of the natural and acid-activated sepiolite are presented in Table 2. Acid activation increased the pore volume and SSA of sepiolite from 0.20 to 0.25 cm^3/g and from 105 to 168 m^2/g, respectively. Acid activation is suggested to have partially dissolved the sepiolite and impurities, increasing the SiO_2 content and the adsorption capacity of sepiolite (Fig. 1b). Balci (1999) also reported that acid treatment leached octahedral Mg ions resulting in the rearrangement of the sepiolite crystal structure and increasing the pore volume. Obviously, a reduction in pH and an increase in acidity were observed during acid treatment. As discussed above, due to the partial dissolution and removal of impurities, pore volume and porosity increased leading to a reduction in bulk density of the acid sepiolite. Free

https://doi.org/10.1180/claymin.2015.050.5.07 Published online by Cambridge University Press

TABLE 3. Polynomial coefficients (co) and p-values for the bleaching parameters

	Chlorophyll-α		β-carotene		Δ*E*		PV		FFA	
	co	p	co	p	co	p	co	p	co	p
Constant	0.043	–	19.52	–	22.36	–	2.930	–	0.190	–
A	–0.087	<0.0001	–2.78	<0.0001	6.27	<0.0001	–0.460	<0.0001	–0.028	<0.0001
B	–7.538 E–003	0.0605	–0.21	0.2811	1.11	0.1308	0.036	0.3583	–1.379 E–003	0.6649
C	–0.029	<0.0001	–1.59	<0.0001	2.82	0.0039	–0.16	0.0305	–7.379 E–003	0.0329
AB	8.228E–004	0.0822	–0.16	0.4429	–	–	–	–	–	–
AC	0.013	0.0074	0.64	0.0073	–	–	–	–	–	–
BC	6.441E–004	0.8660	–0.28	0.2007	–	–	–	–	–	–
AA	0.026	0.0258	–	–	–	–	–	–	–	–
BB	4.544E–003	0.6081	–	–	–	–	–	–	–	–
CC	–5.354 E–003	0.5470	–	–	–	–	–	–	–	–
R^2	0.9909		0.9685		0.8926		0.8122		0.8701	
Adj-R^2	0.9807		0.9514		0.6023		0.7720		0.8423	
Adeq Precision	26.909		22.305		8.465		11.329		13.276	

A: clay dosage (% w) *B*: time (min) *C*: temperature (°C)

moisture content increased after acid treatment (Table 2) possibly due the increase in the SSA of the clay (Sabah, 2007). Loss on ignition in activated sepiolite was less than that of natural sepiolite possibly due to partial dissolution of dolomite.

Optimization of bleaching

Fitting the response surface models. In order to choose an appropriate model for describing each response (Table 1), analysis of variance (ANOVA) was performed. The effect of three independent variables: sepiolite dosage (*A*), bleaching time (*B*) and bleaching temperature (*C*) on dependent variables (*Y*) were analyzed using RSM. The second-order polynomial model was selected as the best-fitting model having insignificant lack of fit. Furthermore, the greater value of R^2 indicated the suitability of the model (Ofochebe & Ozoegwu, 2014). The R^2 values were 0.990, 0.968, 0.892, 0.812 and 0.870 for chlorophyll, β-carotene, Δ*E*, PV and FFA, respectively. In addition, the adj-R^2 for all variables changed from 0.602 to 0.980. A larger adj-R^2 value indicates that insignificant terms have not been included in the model. Adequacy precision measures the signal to noise ratio and a ratio of >4 is acceptable. The value obtained for this ratio was between 8.4 and 26.9 which indicates an adequate signal (Table 3). Similar statistical procedures have already been employed to optimize numerous processes such as bleaching conditions of sardine oil (García-Moreno *et al*., 2013). These results showed the reliability of the model and its ability to navigate the design space (Ajemba *et al*., 2013; García-Moreno *et al*., 2013).

The influence of bleaching variables on the chlorophyll content

The amount of clay, temperature and interaction between the variables were quadratically significant in terms of the chlorophyll content (equation 3) whereas reaction time was not significant (Table 3). Sabah (2007) also showed that bleaching time was not significant in terms of pigment removal from acid-activated sepiolite.

$$\text{Chlorophyll} = 0.43 - 0.087A - 0.029C + 0.013AC + 0.026A^2 - 0.0053C^2 \quad (3)$$

The rate of chlorophyll removal from canola oil increased with increasing amount of sepiolite added, due to the increase in SSA of the bleaching clay

https://doi.org/10.1180/claymin.2015.050.5.07 Published online by Cambridge University Press

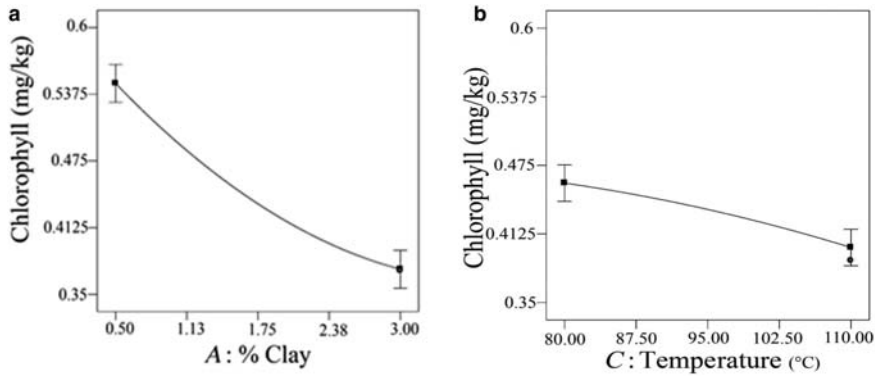


FIG. 2. Effect of acid-activated sepiolite dosage (a) and bleaching temperature (b) on the adsorption of chlorophyll from canola oil. The trendlines were drawn using the software *Design Expert* (v. 7.1.6) and are based on three levels of independent factors.

(Fig. 2a). The amount of chlorophyll decreased from 12.5 mg/kg in unbleached oil to 0.35 mg/kg when the maximum amount of sepiolite used, *i.e.* 97.20% of chlorophyll was removed during the process. The removal of Mg^{2+} from the clay during acid activation leads to the production of active Si groups which are able to adsorb chlorophyll (Sabah & Celik, 2005). Worasith *et al*. (2011) reported that a combination of electrostatic interaction and chemical bonds may occur between chlorophyll and the acidic sites of activated clay during bleaching of rice-bran oil. However, adding large dosages of bleaching clay is not economically efficient in the oil industry. Increasing the bleaching temperature also increased the level of chlorophyll removal (Fig. 2b), suggesting an increase in the rate of chemical reaction at higher temperatures. Chlorophyll has an unsaturated structure containing Mg which may be decomposed into pheophytin at high temperatures and might lead to oil darkening and accelerate oil oxidation (Ma & Lin, 2004; Tong *et al*., 2008). Sabah & Celik (2005) reported removal of 96.8% of chlorophyll from rapeseed oil using 1.5% acid-activated sepiolite at 100°C for 15 min. Pheophytin molecules (in which Mg^{2+} has been substituted by $2H^{+}$) are less likely to be aggregated whereas chlorophyll forms oligomers which would be adsorbed preferentially to the external surface of sepiolite (Jahouach *et al*., 2006; Sabah, 2007). The interaction effects of sepiolite content and bleaching temperature on chlorophyll content are shown in Fig. 3. The greatest extent of chlorophyll removal was achieved in experiments with >2.8% sepiolite at temperatures of 80 to 110°C.

The influence of bleaching variables on β-carotene content

The effect of clay content, temperature and the interaction between them was significant in terms of β-carotene removal (equation 4).

$$\beta\text{-carotene} = +19.52 - 2.78A - 1.59C + 0.64AC \quad (4)$$

According to equation 4, the amount of bleaching earth used is the most important factor in the absorption of β-carotene on sepiolite (Fig. 3a): by increasing the amount of sepiolite, the β-carotene content in the oil decreased. Adsorption of non-polar compounds such as chlorophyll and β-carotene is influenced mostly by the SSA and pore volume of the bleaching clay (Sabah, 2007; Sabah *et al*., 2007; Tong *et al*., 2008). Temperature also was significant in the removal of β-carotene (Fig. 3b) as, at higher temperatures, the β-carotene content of the oil decreased. At high temperature, oil viscosity would decrease, facilitating migration of the colouring agents to the clay surface and thus adsorption. Temperature was shown by Silva *et al*. (2013) to have a large positive effect on adsorption of β-carotene. At low temperatures, β-carotene is adsorbed on the outer surface of clay whereas at higher temperatures absorption within the sepiolite channels might occur (Ma & Lin, 2004). High temperature would accelerate oxidation of β-carotene and oil (Tong *et al*., 2008). Adsorption of chlorophyll was greater than that of β-carotene because the maximum

https://doi.org/10.1180/claymin.2015.050.5.07 Published online by Cambridge University Press

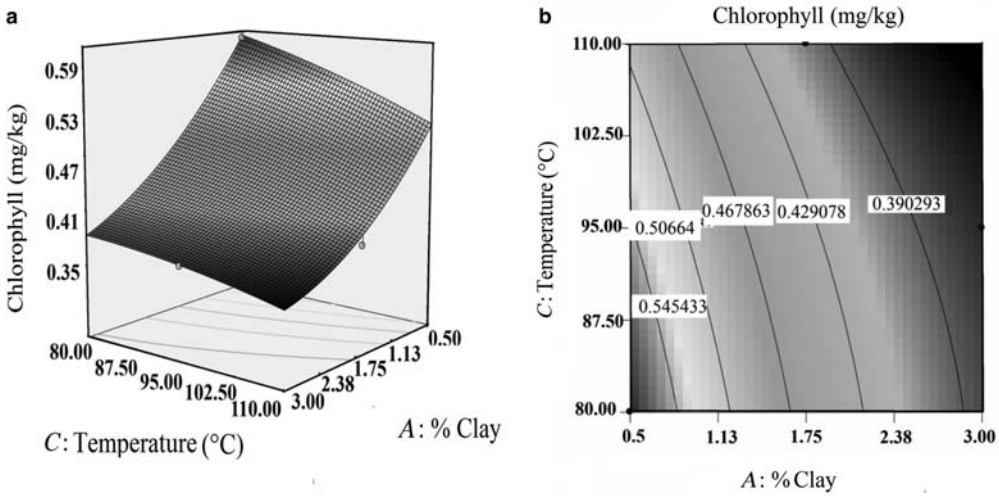


FIG. 3. Effect of the interaction between sepiolite content and bleaching temperature on the adsorption of chlorophyll: (a) 3D diagram; (b) 2D contour diagram.

removal levels of chlorophyll and β-carotene were 97.15% and 69.52%, respectively.

The minimum level of β-carotene (14.98 mg/kg) was obtained with sepiolite contents of >2.3% and temperature >87.5°C (Fig. 5). In a similar study, maximum β-carotene adsorption was achieved using 1.5% Turkish sepiolite at 100°C (Sabah *et al*., 2007).

The influence of bleaching variables on ΔE

The sepiolite content and bleaching temperature had linear and significant effects on the index of colour change (Δ*E*) (equation 5).

$$\Delta E = +22.36 + 6.27A + 2.82C \qquad (5)$$

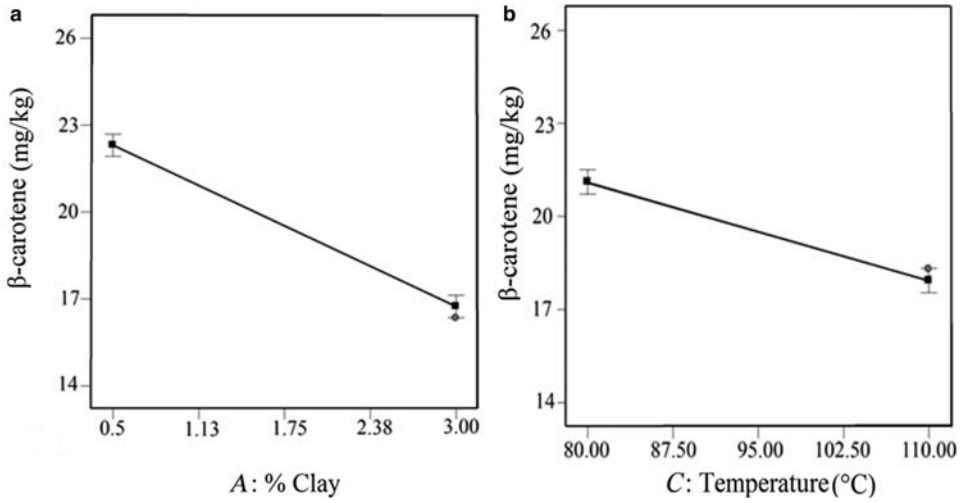


FIG. 4. Effect of acid-activated sepiolite dosage (a) and bleaching temperature (b) on the adsorption of β-carotene from canola oil. The trendlines were drawn using the software *Design Expert* (v. 7.1.6) and are based on three levels of independent factors.

https://doi.org/10.1180/claymin.2015.050.5.07 Published online by Cambridge University Press

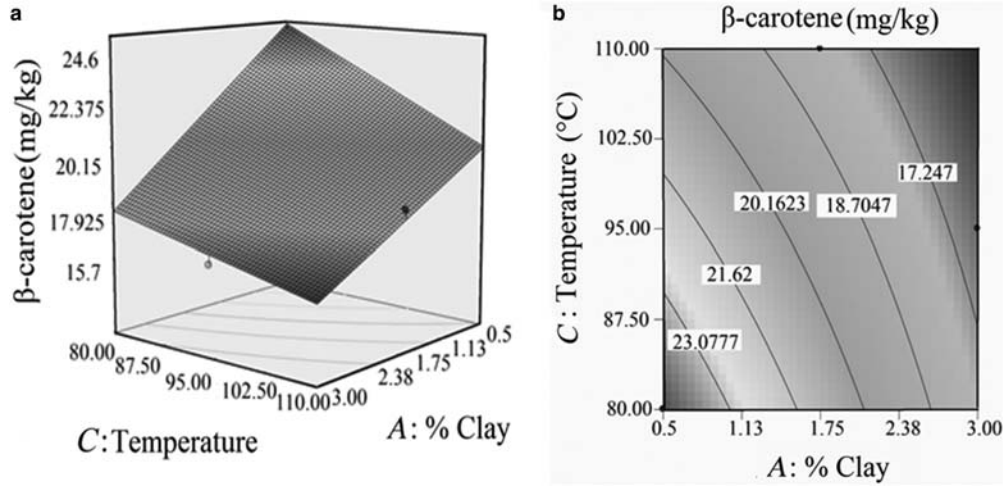


FIG. 5. Effect of interaction between sepiolite content and bleaching temperature on the adsorption of β-carotene: (a) 3D diagram, (b) 2D contour diagram.

An increase in sepiolite dosage and temperature increased the degree of oil bleaching, the effect of the bleaching earth being greater than that of temperature on the removal of pigments. By increasing the sepiolite dosage from 0.5 to 3%, ΔE increased from ~17 to 26.5 whereas the ΔE value obtained at the greatest bleaching temperature was 24. As discussed previously, the increase in colour-change index is mainly due to the removal of chlorophyll and β-carotene throughout the bleaching process. The lighter colour of edible oil and significant modification of red and yellow units during the bleaching process is attributed to the amount of clay (Skevin *et al*., 2012). The amount of bleaching adsorbent was also shown by Ofochebe & Ozoegwu (2014) to be the most significant factor for improving the removal of undesired pigments during palm-oil bleaching.

The influence of the bleaching variables on the peroxide value

In order to study the effect of the parameters used on the PV, a linear model was suggested (equation 6) in which the reaction temperature and sepiolite dosage were more significant (Table 3).

$$\mathrm{PV} = +2.93 - 0.46A - 0.16C \qquad (6)$$

An increase in bleaching-earth dosage caused the PV to decrease. The PV of the original crude oil was 3.87 meq O_2/kg, and it decreased to 2.14 meq O_2/kg after treatment with 3% bleaching earth at 110°C (Table 1). The temperature might also reduce the PV from ~3.2 to 2.5 meq O_2/kg probably because it enhanced adsorption of oil by the bleaching earth (Shimizu *et al*., 2012; Qizhi *et al*., 2008). The reduction in PV at high temperature would result from peroxide conversion to carbonyl compounds (Rossi *et al*., 2003; Tai & Lin, 2007).

The influence of bleaching variables on the FFA value

Usually, oil bleaching does not have a significant effect on the amount of FFA resulting from triglycerides hydrolysis. The amount of FFA can be limited, however, by successful oil drying before the bleaching stage and by selecting bleaching earth with sufficient moisture to become completely active. Removal of FFA was dependent on the amount of sepiolite and on the bleaching temperature (Table 3). According to equation 7 sepiolite dosage was the most important factor in removal of FFA.

$$\mathrm{FFA} = +0.19 - 0.028A - 0.0073C \qquad (7)$$

The FFA value of the crude oil was 0.62%, which, after treatment with 3% sepiolite at 110°C for 45 min, was reduced to 0.15% (Table 1). The significant removal of FFA and PV from canola oil and the lack of further increase in the FFA during bleaching is attributed to the large SSA and the low acidity of the acid-activated sepiolite. Clay acidity might, in fact, cause hydrolysis of triglyceride and production of FFA (Kim & Choe, 2005; Qizhi *et al*., 2008).

https://doi.org/10.1180/claymin.2015.050.5.07 Published online by Cambridge University Press

TABLE 4. Comparison between bentonite and sepiolite clays for bleaching of canola oil.

Oil samples	Clay dosage (W/W)	Time (min)	Temperature (°C)	Chlorophyll (mg/kg)	β-carotene (mg/kg)	PV (meq O_2/kg oil)	FFA (% oleic acid)
Crude oil	–	–	–	12.30[a]	49.15[a]	7.80[a]	0.62[a]
Sepiolite-bleached oil	3.00	42.46	110.00	0.33[c]	15.38[c]	4.74[b]	0.19[b]
Bentonite-bleached oil	3.00	42.46	110.00	0.42[b]	16.00[b]	4.26[b]	0.23[b]

The means with different superscripts (a–c) in each column indicate significant differences ($P < 0.05$).

An increase of 36% in bleaching temperature caused a reduction of 12.5% in the FFA value. The reduction of FFA in canola oil was not dependent on contact time, in accordance with previous reports (Kaynak *et al*., 2004; Sabah & Celik, 2005).

Optimum bleaching conditions

The bleaching conditions which yielded the smallest amounts of chlorophyll, β-carotene, PV, FFA, and large ΔE values were considered to be the optimum conditions (Table 1). The optimum independent variables were predicted by numerical and graphical optimization approaches. For graphical analyses and visualizing the relationship between responses and variables, a three-dimensional (3D) response surface plotting was employed. Optimum canola-oil bleaching was achieved using a sepiolite dosage of 3% (w/w), a temperature of 110°C and a bleaching time of 42.46 min. Under these conditions, the corresponding experimental values for chlorophyll, β-carotene, PV and FFA were 0.33 ppm, 15.38 ppm, 4.74 (meq O_2/kg oil) and 0.19%, respectively (Table 4). To check the adequacy of the predicted data, oil bleaching was conducted at optimum conditions and the results were recorded. Application of the t-test showed that the predicted values varied by insignificant amounts from those obtained in the laboratory.

Comparison of the effectiveness of the sepiolite with a commercial bleaching earth

To evaluate sepiolite as an alternative commercial bleaching earth, its effectiveness at canola-oil bleaching was compared with that of a bentonite at optimum conditions (Table 4). For the latter, the FFA and PV decreased from 0.62 to 0.23% and 7.8 to 4.2 meq O_2/kg oil, respectively, *i.e.* they were comparable with those of the sepiolite-bleached oil (Table 4). Both bleaching agents were efficient adsorbers of chlorophyll and β-carotene pigments as the reductions of 97.3% and 96.5% in chlorophyll and 68.7% and 67.4% in β-carotene content were obtained for sepiolite and bentonite, respectively. Sepiolite has a fibrous structure that entraps color pigments on internal and external surfaces whereas in bentonite the external surface is active for adsorption (Sabah *et al*., 2007). Sepiolite was also reported (Sabah & Celik, 2005) to be more effective than Tonsil® bentonite at removal of β-carotene from rapeseed oil; tonsil was more effective than sepiolite at chlorophyll removal.

CONCLUSIONS

Acid activation of an Iranian sepiolite resulted in the removal of Al and Mg and increased the SSA from 105 to 168 m^2/g, leading to a high capacity for adsorption of pigments. Response surface methodology was used to assess the effects of sepiolite dosage, time and temperature, as well as their interactions, on the bleaching of canola oil with respect to the removal of chlorophyll, β-carotene, peroxide and free fatty acid contents. An increase in the sepiolite content and temperature led to increased removal of impurities and pigments from the oil. Reaction time was found to be insignificant. The optimization, based on the D-optimal design, was used successfully to predict the ideal conditions which were: a combination of 3% sepiolite, 42.46 min of bleaching time, and a temperature of 110°C. Because sepiolite is more effective at the removal of oil pigments than a commercial bentonite, it may be considered as an alternative commercial bleaching earth.

REFERENCES

Ajemba R.O., Igbokwe P.K. & Onukwuli O.D. (2013) Optimization of color pigments removal from palm oil

https://doi.org/10.1180/claymin.2015.050.5.07 Published online by Cambridge University Press

by activated Ukpor clay using response surface methodology. *Research Journal of Applied Sciences, Engineering and Technology*, **6**, 423–432.

American Oil Chemist's Society (1997) *Official Methods and Recommended Practices of the AOCS.* AOCS 5th edition. AOCS Press, Champaign, Illinois, USA.

Balci S. (1996) Thermal decomposition of sepiolite and variations in pore structure with and without acid pre-treatment. *Journal of Chemical Technology and Biotechnology*, **66**, 72–78.

Balci S. (1999) Effect of heating and acid pre-treatment on pore size distribution of sepiolite. *Clay Minerals*, **34**, 647–655.

Box G.E.P. & Wilson K.B. (1951) On the experimental attainment of optimum conditions. *Journal of the Royal Statistical Society (Series B)*, **13**, 1–45.

European Standards (1998) *Test for Mechanical and Physical Properties of Aggregates-Part 3: Determination of Loose Bulk Density and Voids*. German version.

García-Moreno P.J. Guadix A., Gómez-Robledo L., Melgosa M. & Guadix E.M. (2013) Optimization of bleaching conditions for sardine oil. *Journal of Food Engineering*, **116**, 606–612.

Jahouach W., Essid K., Trabelsi M. & Frikha M.H. (2006) Alteration of chemical composition and the oxidative stability of bleached Pomace−olive oil on activated clays. *Journal of Agricultural and Food Chemistry*, **54**, 7137–7143.

Kaynak G., Ersoz M. & Kara H. (2004) Investigation of the properties of oil at the bleaching unit of an oil refinery. *Journal of Colloid and Interface Science*, **280**, 131–138.

Kilislioglu A. & Aras G. (2010) Adsorption of uranium from aqueous solution on heat and acid treated sepiolites. *Applied Radiation and Isotopes*, **68**, 2016–2019.

Kim I. & Choe E. (2005) Effects of bleaching on the properties of roasted sesame oil. *Journal of Food Science*, **70**, 48–52.

Liu Y., Huang Y. & Wang X. (2008) Adsorption isotherms for bleaching soybean oil with activated attapulgite. *Journal of the American Oil Chemists' Society*, **85**, 979–984.

Ma M.H. & Lin C.I. (2004) Adsorption kinetics of β-carotene from soy oil using regenerated clay. *Separation and Purification Technology*, **39**, 201–209.

ÖHMI-Method L 004-13, Bestimmung von Carotin, ÖHMI Engineering, Magdeburg, Germany.

Ofochebe S.M. & Ozoegwu C.G. (2014) Optimisation of the sorption capacity of sulphuric acid activated IBUSA clay in palm oil bleaching using response surface methodology. *International Journal of Experimental Design and Process Optimisation*, **4**, 166–182.

Qizhi L., Yonghui H., Haiyan Z., Bedgood D.R., Prenzler P.D. & Robards K. (2008) The quality and volatile-profile changes of camellia oil (Camellia oleifera Abel) following bleaching. *European Journal of Lipid Science and Technology*, **110**, 768–775.

Rossi M., Gianazza M., Alamprese C. & Stanga F. (2003) The role of bleaching clays and synthetic silica in palm oil physical refining. *Food Chemistry*, **82**, 291–296.

Sabah E. (2007) Decolorization of vegetable oils: Chlorophyll-a adsorption by acid-activated sepiolite. *Journal of Colloid and Interface Science*, **310**, 1–7.

Sabah E. & Çelik M. (2005) Sepiolite: An effective bleaching adsorbent for the physical refining of degummed rapeseed oil. *Journal of the American Oil Chemists' Society*, **82**, 911–916.

Sabah E. & Majdan M. (2009) Removal of phosphorus from vegetable oil by acid-activated sepiolite. *Journal of Food Engineering*, **91**, 423–427.

Sabah E., Çinar M. & Çelik M.S. (2007) Decolorization of vegetable oils: Adsorption mechanism of β-carotene on acid-activated sepiolite. *Food Chemistry*, **100**, 1661–1668.

Shimizu M., Moriwaki J., Shiiba D., Nohara H., Kudo N. & Katsuragi Y. (2012) Elimination of glycidyl palmitate in diolein by treatment with activated bleaching earth. *Journal of Oleo Science*, **61**, 23–28.

Silva S.M., Sampaio K.A., Ceriani R., Verhé R., Stevens C., De Greyt W. *et al.* (2013) Adsorption of carotenes and phosphorus from palm oil onto acid activated bleaching earth: Equilibrium, kinetics and thermodynamics. *Journal of Food Engineering*, **118**, 341–349.

Skevin D., Domijan T., Kraljic K., Kljusuric J.G. & Nederal S. (2012) Optimization of Bleaching Parameters for Soybean Oil. *Food Technology and Biotechnology*, **2**, 199–207.

Tai Y.H. & Lin C.I. (2007) Variation of peroxide value in water-degummed and alkali-refined soy oil during bleaching under vacuum. *Separation and Purification Technology*, **56**, 257–264.

Taylor D.R. (2005) *Bleaching Bailey's Industrial Oil and Fat Products.* John Wiley & Sons, Inc., pp. 25–29.

Tian G., Wang W., Kang Y. & Wang A. (2014) Study on thermal activated sepiolite for enhancing decoloration of crude palm oil. *Journal of Thermal Analysis and Calorimetry*, **117**, 1211–1219.

Tong J., Wu Z., Sun X., Xu X. & Li C. (2008) Adsorption kinetics of β-carotene and chlorophyll onto acid-activated bentonite in model oil. *Chinese Journal of Chemical Engineering*, **16**, 270–276.

Ugurlu M. & Kula I. (2007) The removal of colour, carotene and acidity from crude olive oil by using sepiolite. *International Journal of Food Science & Technology*, **42**, 359–365.

Zadaka Amir D., Bleiman N. & Mishael Y.G. (2013) Sepiolite as an effective natural porous adsorbent for surface oil-spill. *Microporous and Mesoporous Materials*, **169**, 153–159.

Worasith N., Goodman B., Jeyashoke N. & Thiravetyan P. (2011) Decolorization of rice bran oil using modified kaolin. *Journal of the American Oil Chemists' Society*, **88**, 2005–2014.

https://doi.org/10.1180/claymin.2015.050.5.07 Published online by Cambridge University Press