

Modeling of the soybean oil bleaching and optimization of its conditions in the refining process for environmental interest

Zahir Henache✉, Abdelhamid Boukerroui and Imad Kashi

Laboratory of Materials Technology and Process Engineering (LTMGP), Faculty of Exact Sciences, University of Bejaia, Targa Ouzemour road, 06000 Bejaia, Algeria

Article info

Article history:

Received: 20th April 2018

Accepted: 19th June 2018

Keywords:

Bleaching
 Bleaching clay rejects
 Modeling
 Pigments
 Pollution
 Soybean oil

Abstract

In this work, we propose mathematical models describing the soybean oil bleaching process as a function of its parameters (temperature: 80 – 120 °C, clay dosage: 0.25 – 2 %, contact time: 10 – 30 min). The crude soybean oil visible spectrum shows three values of maximum wavelength (λ_{max}). A value at 426 nm corresponding to the chlorophyll-a, the values at 451 and at 479 nm were assigned to β -carotene pigment. The models were developed using multiple linear regression analysis (MLRA) and were performed with Matlab programming language. The input variables are the temperature (X_1), the clay dosage (X_2) and the contact time (X_3). The output parameter is the bleaching capacity (Y in % uptake). Statistical analysis methods were used to analyze and to confirm the reliability of the selected models. The optimal bleaching conditions for the soybean oil were: temperature 100 °C; clay dosage 2 % w/w and contact time 30 min. The highest bleaching capacity was found to be 81.04 % at 426 nm, 90.60 % at 451 nm and 93.66 % at 479 nm. The developed models allowed predicting the bleaching capacity representing the removal of the β -carotene and chlorophyll-a pigments present in the crude soybean oil at each λ_{max} . Also they allowed a better control of the most influencing parameters on the bleaching step and contribute to the optimization of the spent bleaching clay rejects by optimizing the amount of bleaching clay used in the refining process; consequently, to reduce risks of pollution.

© University of SS. Cyril and Methodius in Trnava

Introduction

It is well known that the crude edible oil contains undesirable substances such as soap residues, free fatty acids, phosphatides, trace metals and coloring pigments (Dijkstra 2013; Gil *et al.* 2014; Pal *et al.* 2015). Those substances degrade the quality of the oil by altering the taste and color properties, thus limits the conservation and the use of this product (Boukerroui and Ouali 2002), for that reason, it is imperative to refine it to produce a stable product with desired color and a pleasant taste (Mohdaly *et al.* 2017). This color is due to the presence

of pigments in the crude edible oil, such as chlorophyll-a and β -carotene (Junmao *et al.* 2008; Pohndorf *et al.* 2016).

The bleaching operation is an important step in the refining process of crude edible oil, it is carried out by various types of porous materials with a strong bleaching power which are known as bleaching earth or bleaching clay activated by hot acid solutions (Foletto *et al.* 2011; Komadel 2016) or microwave irradiation (Boukerroui and Ouali 2002; Foletto *et al.* 2013). Other types of materials are commonly used in the edible oil bleaching process such as diatomaceous earth (Larouci *et al.*

✉ Corresponding author: zahir1979@hotmail.com

2015), activated kaolin (Aung *et al.* 2015), activated sepiolite (Tian *et al.* 2014) and rice hull silicate (Gil *et al.* 2014). These materials remove the unwanted compounds such as the coloring pigments (chlorophyll-a and β -carotene) and other impurities (soap residues, traces of heavy metals etc.) contained in the crude edible oil (Sabah *et al.* 2007; Pohndorf *et al.* 2016). Normally, these undesirable elements are removed by adsorption process (Nwabanne *et al.* 2013).

The region of Bejaïa (Algeria) has two edible oil refineries (COGB-Labelle and Cevital). They produce huge quantities of waste called spent bleaching clays, which are discharged directly in the rubbish dump without any treatment that would prevent contamination of the environment. This presents a serious problem regarding the solid wastes management, storage and the harmful effects they would cause (Boukerroui and Ouali 2000; Meziti and Boukerroui 2011). In order to reduce the waste products, some vegetal oil refining factories have opted to reduce the amount of the bleaching clay used in the bleaching step. Moreover, the reduction of the bleaching earth added to the bad controls of temperature and contact time causes an incomplete decolorization (Boukerroui *et al.* 2018). In the other hand, they have proceeded by increasing the temperature processing (240 – 270 °C) in the deodorization step to remove all the thermally degradable pigments, undesirable elements and volatile compounds, such as alcohols, ketones and aldehydes (Silva *et al.* 2014), as a result, these substances volatilized during the deodorization increase air pollution (Boukerroui *et al.* 2018).

The aim of this study was to propose mathematical models governing the bleaching of soybean oil in order to optimize the bleaching conditions which are temperature (°C), clay dosage (% w/w) and contact time (min). Furthermore, this study contributes to a better control of the most influencing physicochemical parameters (temperature, contact time and clay dosage) on the decolorization step - while keeping a better quality of oil – in order to reduce risks of pollution that presents a potential threat to our region by optimizing the quantities of the bleaching clay used in the refining process.

In this study we suppose the variation in bleaching efficiency with the three mentioned parameters is

linear with respect to the parameters of the selected models, i.e. β_j . The most general linear models (GLM) used are derived from the following equation (Boumehrat and Gourdin 1991; Neuilly 1993; Cornillon and Matzner-Lober 2007; Moussaceb 2012) (Eq. 1):

$$Y = \sum_{j=1}^p \beta_j \cdot f_j(X_j) \quad (1)$$

Where Y is the bleaching efficiency or capacity, f_j is a regular function, X_j is the bleaching parameter (i.e. temperature, contact time and/or clay dosage), β_j are the model coefficients to be calculated and p is the number of coefficients. The modeling procedure was performed using the Matlab language and statistical analysis methods.

Experimental

Materials

The Bleaching Clay (BC) used in this study is produced and commercialized by Taiko Clay Group (Malaysia). The major chemical components of BC are as follows: SiO₂ (76.2 %), Al₂O₃ (11.2 %), Fe₂O₃ (2.7 %), MgO (0.8 %), CaO (2.3 %), Na₂O (0.6 %), K₂O (0.6 %) and loss on ignition (5.7 %). The BC and all edible oils used in this study were kindly donated by edible oil refining factory (Cevital, Bejaia, Algeria). All reagents used in this study are analytical grade.

Bleaching operation

The oil treatment experiments were achieved under a vacuum of 25 – 30 mm Hg to avoid undesired side-reactions (Kheok and Lim 1982). The dried clay was weighed corresponding to the various clay dosages (0.25 – 2 % w/w) and was added at the degummed and neutralized crude edible soybean oil (neutral oil) preheated at the predetermined temperature in an oil bath. The bleaching experiment was carried out over a temperatures range of 80 – 120 °C. The mixture was continuously agitated under those conditions for the desired contact time in the range 10 – 30 min (see Table 1). The oil was then filtered through Whatman No.5 filter paper to separate the clear oil and clay (Aung *et al.* 2015; Boukerroui *et al.*

2018). The absorbance measurements of the neutral (unbleached) and treated (bleached) oils were conducted on UV-visible spectrophotometer (Model: UV-1800 Shimadzu UV Spectrophotometer) to evaluate the amount of pigment removed. The oil sample was diluted with petroleum ether (1:4 v/v) and the bleaching capacity of the clay was determined by measuring absorbance at 426 nm, at 451 nm and at 479 nm, which were the maximum absorptions observed in the wavelength range between 400 and 600 nm. The bleaching capacity, or % uptake, was calculated by applying the following equation (Nguetngam *et al.* 2008; Aung *et al.* 2015; Boukerroui *et al.* 2018) (Eq. 2):

$$\% \text{ uptake } \lambda_{max} = \frac{A_{\lambda}^0(\text{unbleached}) - A_{\lambda}(\text{bleached})}{A_{\lambda}^0(\text{unbleached})} \times 100 \quad (2)$$

Where A_{λ}^0 and A_{λ} are the absorbance of unbleached (neutral oil) and bleached (treated) oil, respectively, at the maximum absorbance wavelength of the unbleached oil. All bleaching parameters used in this study are given in the Table 1. The details of the bleaching procedure used have been better described in previous studies (Boukerroui and Ouali 2000, 2002).

Table 1. Bleaching parameters of soybean oil samples.

| Bleaching parameters | | |
|---------------------------|--------------------------|-----------------------------|
| Temperature [°C] X_1 | Clay dosage [%] X_2 | Contact time [min] X_3 |
| 80 | 0.25 | 10 |
| 90 | 0.50 | 15 |
| 100 | 0.75 | 20 |
| 110 | 1.00 | 25 |
| 120 | 1.25 | 30 |
| | 1.50 | |
| | 1.75 | |
| | 2.00 | |

Quality analysis of neutral and bleached soybean oils

The quality parameters of neutral and bleached oil samples including color, humidity, free fatty acids, iodine, peroxide and saponification values, phosphorus content were determined. They were

performed according to the AOCS (1998) official methods: Lovibond colour (Cc 13e-92), using a Lovibond Tintometer Color Scale at 70 °C, phosphorus (Ca 12-55), free fatty acids (Ca 5a-40), peroxide value (Cd 8-53) and saponification value (Cd 3-25).

Numerical Methods

Mathematical and statistical aspects

The general linear models (GLM) are largely used to modeling the physicochemical phenomena (Boumehrat and Gourdin 1991; Neuilly 1993; Moussaceb 2012); the majority of the statistical models used are special cases of the GLM.

In this study, the modeling of the soybean oil bleaching is carried out by using the multiple linear regression analysis (MLRA) which is based on the variation of the following parameters: X_1 (°C), X_2 (%) and X_3 (min). The multiple linear regression model is a generalization of the simple linear regression model when the explanatory variables are in finite numbers (Cornillon and Matzner-Lober 2007). The multiple linear regression model may be expressed as follows (Eq. 3):

$$Y = f(X_1, \dots, X_p) = \beta_1 \cdot f_1(X_1) + \dots + \beta_p \cdot f_p(X_p) = \sum_{j=1}^p \beta_j \cdot f_j(X_j) \quad (3)$$

Where β_j ($j = 1 \dots p$) are the coefficients of the model and f_j ($j = 1 \dots p$), the regular functions which may be polynomial, exponential, trigonometric or logarithmic function.

To predict the bleaching capacity (Y) as a function of temperature (X_1), clay dosage (X_2) and contact time (X_3), we used the MLRA to develop these models. The linear systems resulting from the MLRA were resolved using the Gauss method. The modeling process consists of changing the parameter p in the range $[1, p_{max}]$ to obtain different linear models: $Y_p = (1, p_{max})$. The best model (Y) with reasonable accuracy should satisfy different statistical criteria which are residual variance, coefficient of determination (R^2), Student test and Fisher-Snedecor test (Moussaceb 2012). In this study, the confidence limit of the Student and Fisher-Snedecor tests is 95 % ($\alpha = 0.05$), as supported by the following

hypotheses (H) for Student test (Eq. 4):

$$H_0 \ll \beta_j = 0 \gg \text{ against } H_1 \ll \beta_j \neq 0 \gg, j = 1 \dots p. \quad (4)$$

and for Fisher-Snedecor test (Eq. 5):

$$H_2 \ll \beta_1 = \beta_2 = \beta_3 \dots = \beta_p = 0 \gg \quad (5)$$

We also assume that our experimental results can be well-fitted by the Gaussian function (Neuilly 1993).

Modeling approach

To find out a correlation model that would best describe the relationship between bleaching capacity and the bleaching parameters (temperature, clay dosage and contact time), we tested several models, mainly polynomial, exponential, trigonometric and logarithmic ones. The coefficient of determination (R^2) is the main statistical criteria, which determines the choice of any eligible model (Neuilly 1993). A best model has R^2 approaching unity (Neuilly 1993). Moreover, the selected model must satisfy other statistical criteria, which are the residual variance and the Student as well as Fisher-Snedecor tests. In the light of the results obtained in this study, the experimental data of soybean oil bleaching has shown that the polynomial model has the maximum value of R^2 and thus the highest reliability.

Results and Discussion

Spectra of neutral and bleached soybean oils

The absorbance spectra between 400 and 600 nm of the neutral and bleached soybean oils at different conditions of refining are represented in Fig. 1. The visible spectra are characterized by three absorption maxima occurred at 426, 451 and 479 nm (Fig. 1). Similar result has been reported by many authors (Sarier and Guler 1988; Kondal *et al.* 2001; Boukerroui *et al.* 2018). The maximum absorption at 426 nm is attributed to the band of chlorophyll-a, while those observed at 451 and 479 nm are assigned to the bands of β -carotene (Gonzales-Pradas *et al.* 1994; Boukerroui *et al.* 2018). The neutral oil spectrum shows that the carotenoids are the predominant pigment in soybean oil (Kondal *et al.* 2001).

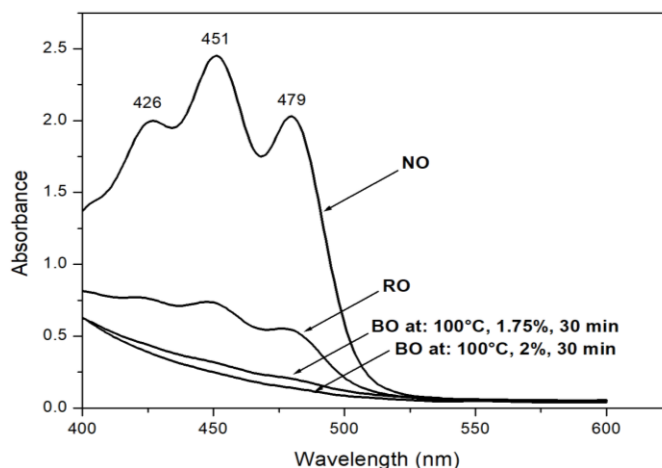


Fig. 1. Visible absorption spectra of neutral (NO), refined (RO) and bleached (BO) soybean oils at different conditions of refining.

The absorbance peaks intensity at each λ_{max} decrease in the bleached soybean oil samples spectra due to the reduction of carotenoids and chlorophyll compounds present in the crude oil, they are lower than those observed in neutral and refined soybean oil spectra, these peaks disappear in the bleached oil at the optimum conditions, this can be explained by the fact that the coloring pigments were adsorbed and removed by the clay during the bleaching operation. The color decrease was maximal at the optimum decolorization conditions (100 °C, 2 %, 30 min). The effect of activated bleaching clay on edible oil and our findings on physicochemical parameters influence are consistent with many other studies (Silva *et al.* 2013; Pal *et al.* 2015; Boukerroui *et al.* 2018).

The absorbance measurements at 426, at 451 and at 479 nm and the bleaching capacity calculated using Eq. (2) were used to develop our models of the removal of chlorophyll-a and β -carotene pigments. The results obtained from Eq. (2) were used in the Eq. (3) in order to develop these models.

Modeling of the bleaching capacity at different wavelength

Oil samples treated with bleaching earth at the conditions listed in Table 1 were analyzed in the visible light by measuring their absorbance at 426, 451 and 479 nm. The values of the bleaching capacity calculated for the cited parameters

Table 2. Statistical criteria of the model governing the bleaching of the soybean oil at $\lambda_{max} = 426$ nm.

| Residual variance | Coefficient of determination [%] | Fisher-Snedecor test | |
|-----------------------|----------------------------------|----------------------|---------------------------------------|
| | | Calculated value | Tabulated value $f(n-p, p-1, \alpha)$ |
| $15.89 \cdot 10^{-4}$ | 99.99 | $7.89 \cdot 10^8$ | 2.1 |

Student tests: $T(n-p, \alpha/2) = 1.98$

| $T(\beta_1)$ | $T(\beta_2)$ | $T(\beta_3)$ | $T(\beta_4)$ | $T(\beta_5)$ | $T(\beta_6)$ | $T(\beta_7)$ | $T(\beta_8)$ | $T(\beta_9)$ | $T(\beta_{10})$ | $T(\beta_{11})$ |
|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| $9.6 \cdot 10^3$ | $9.9 \cdot 10^3$ | $9.7 \cdot 10^3$ | $1.8 \cdot 10^3$ | $8.5 \cdot 10^2$ | $2.8 \cdot 10^2$ | $2.6 \cdot 10^2$ | $3.6 \cdot 10^2$ | $9.5 \cdot 10^3$ | $2.2 \cdot 10^4$ | $2.3 \cdot 10^3$ |

(temperature, clay dosage and contact time) are introduced into Eq. 3. The results of the numerical computation of Y using Matlab generated a mathematical relationship, which was used to develop the models. The mathematical model at $\lambda_{max} = 426$ nm is expressed as follows (Eq. 6):

$$Y = -1.5 \times 10^2 + 2.61 X_1 + 75.75 X_2 + 87.57 \times 10^{-2} X_3 - 64.74 \times 10^{-3} X_1 X_2 - 12.55 \times 10^{-4} X_1 X_3 + 9.53 \times 10^{-2} X_2 X_3 - 13.06 \times 10^{-4} X_1 X_2 X_3 - 11.67 \times 10^{-3} X_1^2 - 15.64 \times 10^{-2} X_2^2 - 11.26 \times 10^{-3} X_3^2 \quad (6)$$

This model (Eq. 6) was selected on the basis of the statistical criteria presented in Table 2. The mathematical model (Eq. 7) at $\lambda_{max} = 451$ nm is as follows (Table 3):

$$Y = -1.74 \times 10^2 + 3 X_1 + 86.54 X_2 + 96.79 \times 10^{-2} X_3 - 10.23 \times 10^{-2} X_1 X_2 - 48.37 \times 10^{-5} X_1 X_3 + 14.4 \times 10^{-2} X_2 X_3 - 18.28 \times 10^{-4} X_1 X_2 X_3 - 12.98 \times 10^{-4} X_1^2 - 17.72 X_2^2 - 14.65 \times 10^{-3} X_3^2 \quad (7)$$

This model (Eq. 7) was selected on the basis of the statistical criteria presented in Table 3.

The mathematical model at $\lambda_{max} = 479$ nm is (Eq. 8):

$$Y = -1.87 \times 10^2 + 3.24 X_1 + 92.78 X_2 + 1.12 X_3 - 15.25 \times 10^{-2} X_1 X_2 - 17.9 \times 10^{-4} X_1 X_3 + 71.85 \times 10^{-3} X_2 X_3 - 12.49 \times 10^{-4} X_1 X_2 X_3 - 13.66 \times 10^{-3} X_1^2 - 18.22 X_2^2 - 14.67 \times 10^{-3} X_3^2 \quad (8)$$

This model (Eq. 8) is selected on the basis of the statistical criteria presented in Table 4.

Table 3. Statistical criteria of the model governing the bleaching of the soybean oil at $\lambda_{max} = 451$ nm.

| Residual variance | Coefficient of determination [%] | Fisher-Snedecor test | |
|----------------------|----------------------------------|----------------------|---------------------------------------|
| | | Calculated value | Tabulated value $f(n-p, p-1, \alpha)$ |
| $8.23 \cdot 10^{-6}$ | 99.99 | $9.42 \cdot 10^8$ | 2.1 |

Student tests: $T(n-p, \alpha/2) = 1.98$

| $T(\beta_1)$ | $T(\beta_2)$ | $T(\beta_3)$ | $T(\beta_4)$ | $T(\beta_5)$ | $T(\beta_6)$ | $T(\beta_7)$ | $T(\beta_8)$ | $T(\beta_9)$ | $T(\beta_{10})$ | $T(\beta_{11})$ |
|------------------|------------------|------------------|----------------|------------------|------------------|----------------|------------------|------------------|------------------|-----------------|
| $1.1 \cdot 10^4$ | $1.1 \cdot 10^4$ | $1.1 \cdot 10^4$ | $2 \cdot 10^3$ | $1.4 \cdot 10^3$ | $1.1 \cdot 10^2$ | $4 \cdot 10^2$ | $5.2 \cdot 10^2$ | $1.1 \cdot 10^4$ | $2.5 \cdot 10^4$ | $3 \cdot 10^3$ |

The variation of the soybean oil bleaching capacity as a function of clay dosage and contact time at fixed temperature and at different maximum wavelengths (426, 451 and 479 nm) is presented in Fig. 2, Fig. 3 and Fig. 4 (respectively).

All the curves show that the bleaching capacity varies significantly the function of the experiment parameters, it increases with increase in the temperature, the clay dosage and the contact time reaching values of 81.04 %

Table 4. Statistical criteria of the model governing the bleaching of the soybean oil at $\lambda_{max} = 479$ nm.

| Residual variance | Coefficient of determination [%] | Fisher-Snedecor test | |
|----------------------|----------------------------------|----------------------|---------------------------------------|
| | | Calculated value | Tabulated value $f(n-p, p-1, \alpha)$ |
| $9.73 \cdot 10^{-6}$ | 99.99 | $7.99 \cdot 10^8$ | 2.1 |

Student tests: $T(n-p, \alpha/2) = 1.98$

| $T(\beta_1)$ | $T(\beta_2)$ | $T(\beta_3)$ | $T(\beta_4)$ | $T(\beta_5)$ | $T(\beta_6)$ | $T(\beta_7)$ | $T(\beta_8)$ | $T(\beta_9)$ | $T(\beta_{10})$ | $T(\beta_{11})$ |
|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|--------------|------------------|------------------|
| $1.1 \cdot 10^4$ | $1.1 \cdot 10^4$ | $1.1 \cdot 10^4$ | $2.1 \cdot 10^3$ | $1.9 \cdot 10^3$ | $3.7 \cdot 10^2$ | $1.8 \cdot 10^2$ | $3.2 \cdot 10^2$ | 10^4 | $2.4 \cdot 10^4$ | $2.8 \cdot 10^3$ |

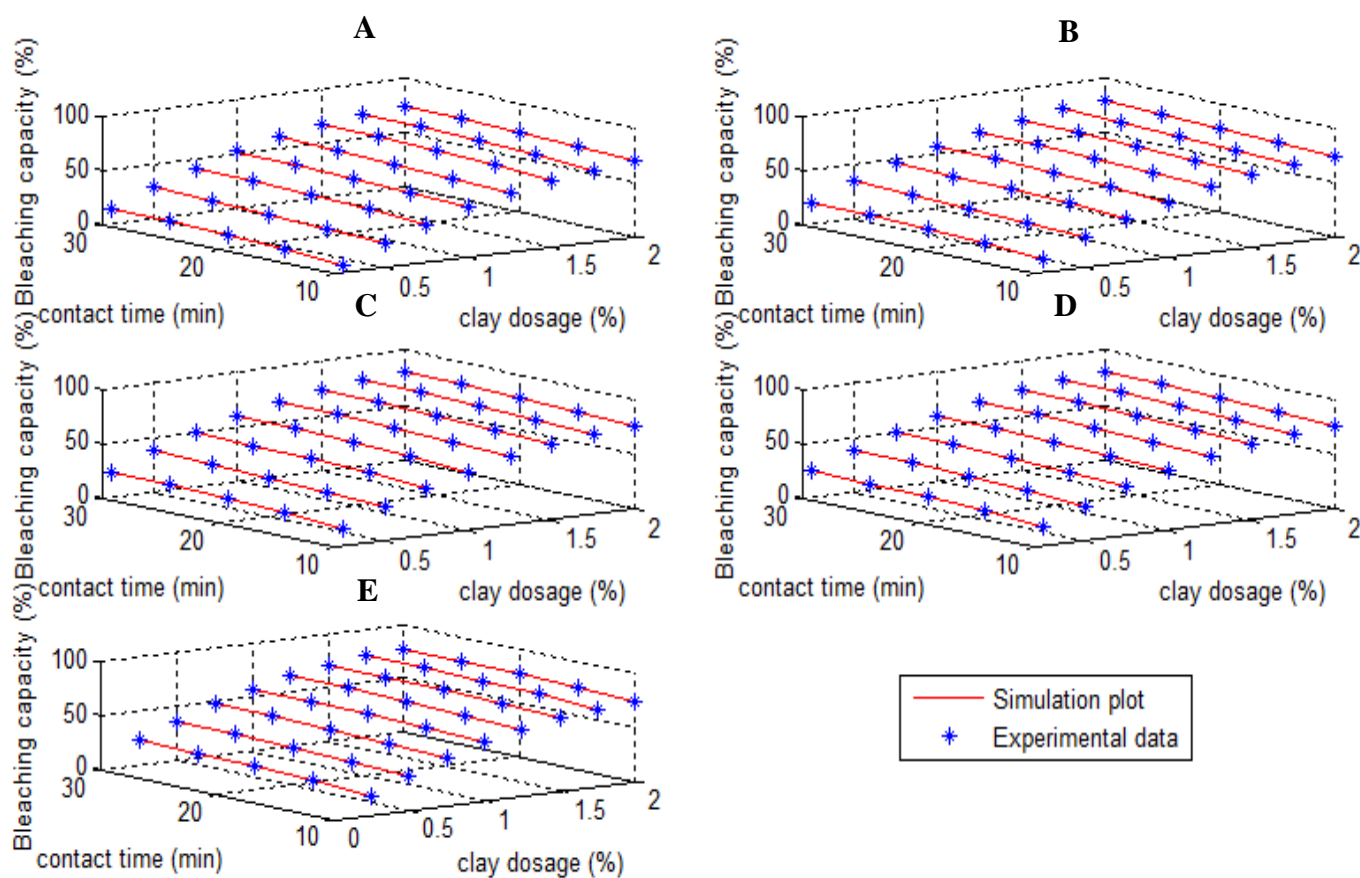


Fig. 2. Variation of the bleaching capacity as a function of clay dosage and contact time at fixed temperature and at different temperatures: 80 °C (A), 90 °C (B), 100 °C (C), 110 °C (D), 120 °C (E) at $\lambda_{max} = 426$ nm.

at $\lambda_{max} = 426$ nm, 90.60 % at $\lambda_{max} = 451$ nm and 93.66 % at $\lambda_{max} = 479$ nm under the optimum operating conditions (100 °C, 2 %, 30 min). The obtained results indicate that the simulated and experimental bleaching capacity have comparable values. This confirms that the proposed models best describe the soybean oil bleaching phenomena.

In addition, for the temperature of 120 °C, the values of the bleaching capacity decrease as a result of destruction of some of the active sites. Similar results have been reported by the following authors (Kheok 1982; Srasra *et al.* 1989; Christidis *et al.* 1997; James *et al.* 2008). Moreover, these results reveal that the removal of the

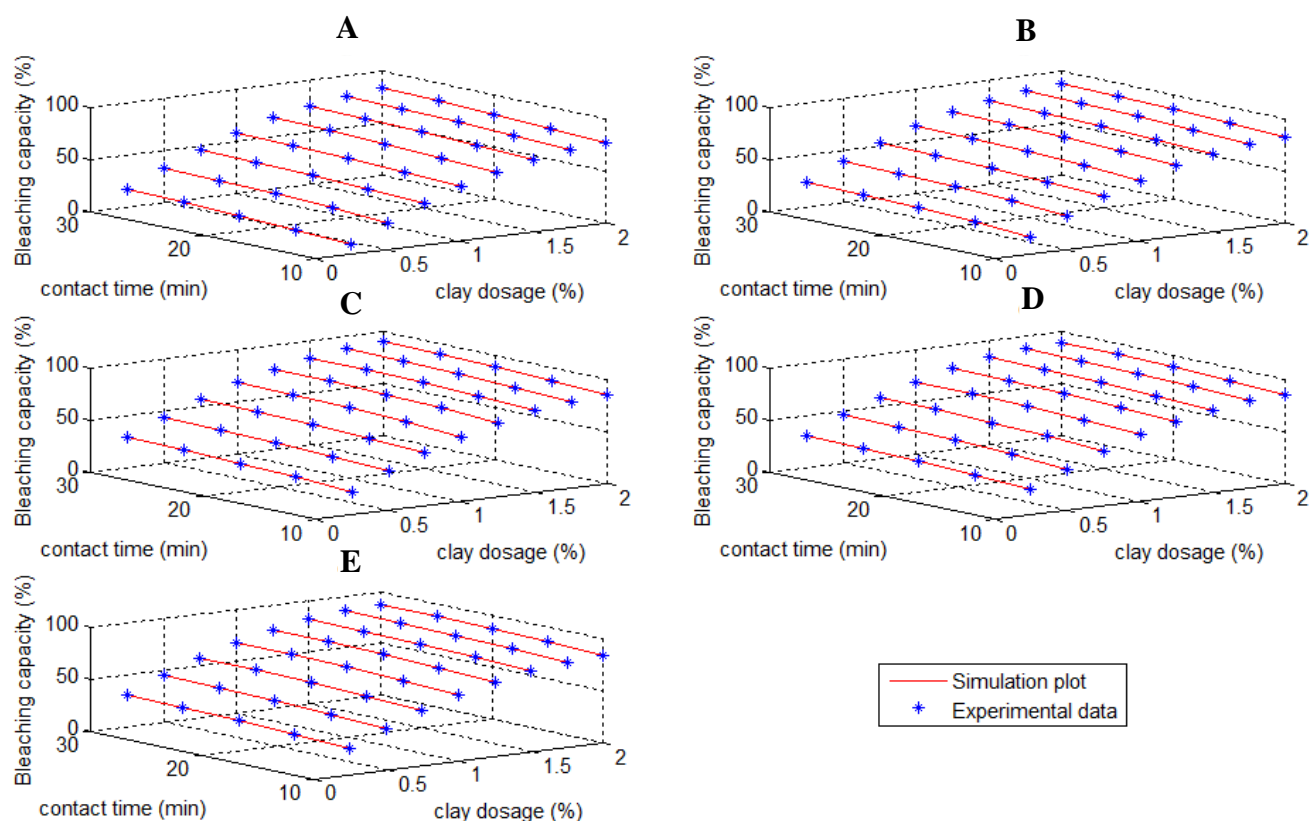


Fig. 3. Variation of the bleaching capacity as a function of clay dosage and contact time at fixed temperature and at different temperatures: 80 °C (A), 90 °C (B), 100 °C (C), 110 °C (D), 120 °C (E) at $\lambda_{max} = 451$ nm.

carotenoids from the crude edible oil (451 nm, 479 nm) by the bleaching clay used in this study is easier than the removal of the chlorophyll-a pigments (426 nm) present in the soybean oil (Kondal *et al.* 2001).

Validity of the selected models

The validity of the selected models was analyzed using the following statistical criteria: residual variance, coefficient of determination (R^2), the Student and Fisher-Snedecor tests (Tables 2, 3 and 4). The results indicate a low value of residual variance ($15.89 \cdot 10^{-4}$ for $\lambda_{max} = 426$ nm; $8.23 \cdot 10^{-6}$ for $\lambda_{max} = 451$ nm and $9.73 \cdot 10^{-6}$ for $\lambda_{max} = 479$ nm), this suggests that it does not remain other useful information to be brought to the phenomenon of bleaching. In addition, they reveal that the maximum value of R^2 (99.99 %) is close to unity for the different wavelengths (426, 451 and 479 nm), this confirms the goodness of simulated fit to observed data. Moreover, the calculation of the model coefficients using both the student

and Fisher-Snedecor tests gives higher values than the tabulated ones, which implies the accuracy of the models and all the coefficients are retained. Furthermore, the experimental and the predicted bleaching capacity have comparable values. That confirms the reliability of the adjustment.

The three developed mathematical models show the values corresponding to each coefficient ($\beta_j = \beta_1, \beta_2, \dots, \beta_{11}$), which are supposed to describe the individual effect of each parameter as well as the effect of the parameters interactions on the bleaching capacity. Our findings reveal that interactions between the analyzed parameters substantially influence the bleaching capacity. Similar results have been reported by many authors (Christidis *et al.* 1997; Boukerroui and Ouali 2000, 2002; Nwabanne *et al.* 2013).

The models coefficients sign interpretation

It is seen that the three elaborated models present a similarity between the coefficients signs of the different terms (linear, quadratic and multiple),

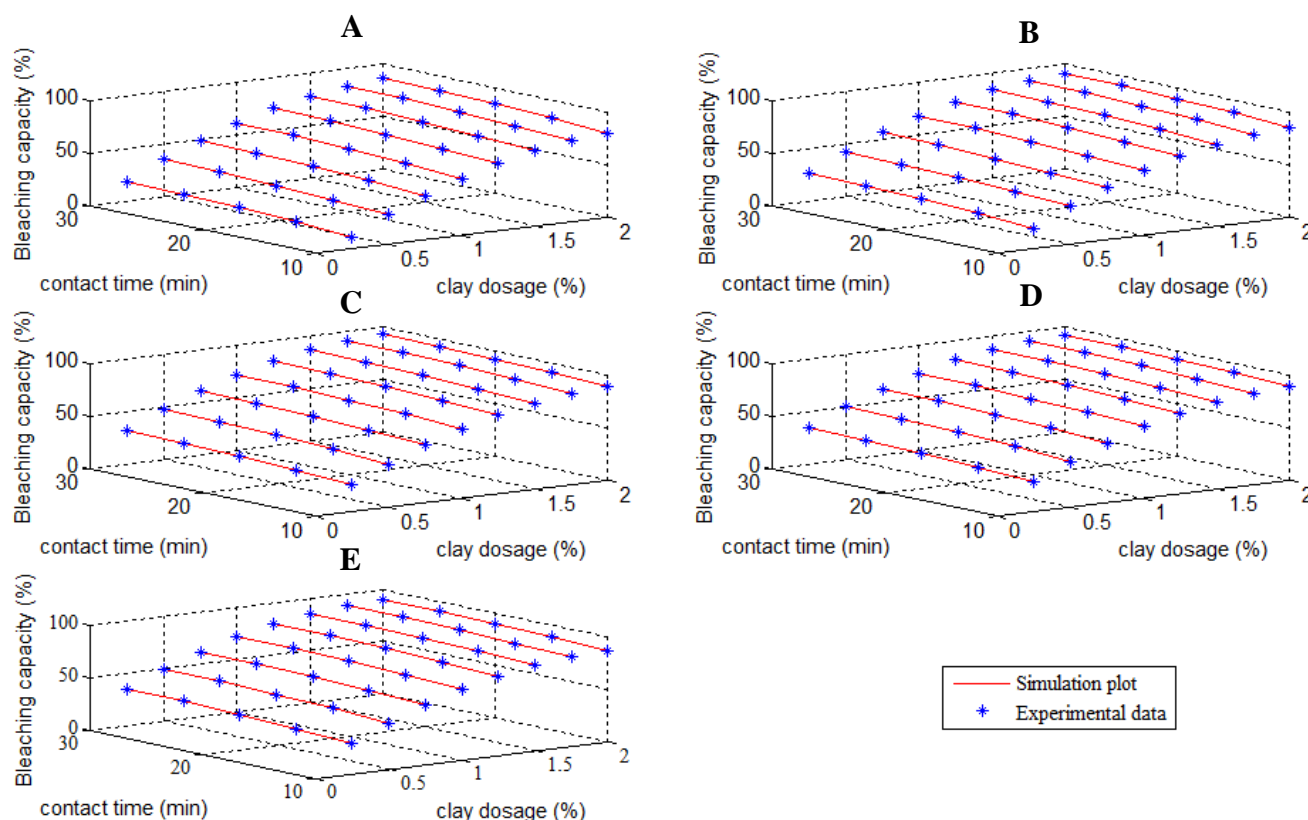


Fig. 4. Variation of the bleaching capacity as a function of clay dosage and contact time at fixed temperature and at different temperatures: 80 °C (A), 90 °C (B), 100 °C (C), 110 °C (D), 120 °C (E) at $\lambda_{max} = 479$ nm.

which implies that the bleaching capacity of the bleaching clay at each maximum wavelength varies in the same way (increase or decrease). The examination of these models reveals that the positive values of the coefficient of temperature (X_1), clay dosage (X_2) and contact time (X_3) indicate that an increase in these factors involves an increase in the bleaching capacity, similar results have been found by the following authors (Ajemba *et al.* 2013; Nwabanne *et al.* 2013). However, the clay dosage and the temperature respectively have a more significant effect on bleaching capacity since their coefficients are higher, while the negative values of the other coefficients mainly those of quadratic and multiple terms cause a decrease in the bleaching capacity.

Determination of quality criteria for neutral and bleached soybean oils

The quality of any edible oil is evaluated by the knowledge of its quality criteria such as free fatty acids content, phosphorus content, peroxide,

iodine and saponification values. The results of the neutral and bleached soybean oils analysis at the optimum bleaching conditions (2 %, 100 °C, 30 min) are summarized in Table 5.

According to the results mentioned in this table, we noted that free fatty acids content, the iodine and the saponification values remain unchanged. Furthermore, humidity, phosphorus content and the peroxide value decreased after the soybean oil bleaching process, this implies that the bleaching clay eliminates these substances contained in the neutral oil, as reported by many authors (Pohndorf *et al.* 2016; Boukerroui *et al.* 2018). In addition it is noted that the bleached soybean oil is fitted into the quality standards recommended for bleached oils and adopted by edible oil refining factory (Cevital, Bejaia, Algeria), except for the peroxide value which decrease from 24.06 (meq O₂/kg) to 12.06 (meq O₂/kg) after bleaching but remain slightly higher than the standard value and that is due to the oil storage conditions (oxygen and light) which promote the formation of peroxides.

Table 5. Quality criteria of neutral and bleached soybean oils.

| Oil | Neutral oil | Bleached oil | Standard values |
|-----------------------------------------|-------------|--------------|-----------------|
| Humidity [%] | 1.3 | 0.28 | ≤ 2 |
| Phosphorus [ppm] | 4.75 | 0 | ≤ 2 |
| Free fatty acids [%] | 0.06 | 0.06 | ≤ 0.08 |
| Iodine value | 128 | 128 | 124-139 |
| Peroxide value [meq O ₂ /kg] | 24.06 | 12.06 | ≤ 10 |
| Saponification value [mg KOH/g] | 190 | 190 | 189-195 |
| Color tests | Red | 9.8 | < 5 |
| | Yellow | 1.8 | < 50 |

Conclusions

Analysis of the visible spectrum of crude soybean oil shows maximum wavelengths at 426 nm (chlorophyll-a) and at 451 and 479 nm (β -carotene). The bleaching clay application on soybean oil shows a decrease of maximum absorbance value due to a progressive elimination of pigments present in the oil, which depends on the physicochemical parameters (temperature, % dosage and contact time). Our findings suggest that the removal of chlorophyll-a and β -carotene pigments present in the soybean oil, represented by the bleaching capacity (% uptake at λ_{max}), can be expressed under its modeled form. Mathematical models governing the decolorization process at each maximum wavelength (written in Matlab) depend of three parameters which are; temperature, contact time and clay dosage. The model equations, calculated at the maximum wavelength (426, 451 and 479 nm), are linear and second order polynomial. The results reveal that the decolorization process is highly influenced by the analyzed parameters, which is combined to the influence that results from interactions between them. The color decrease was maximal at the optimum bleaching conditions (2 %, 100 °C, 30 min) and the soybean oil bleached at these conditions is fitted into the quality standards recommended for bleached oils. The established models present an environmental interest since they allowed optimizing the amount

of the bleaching clay used in the soybean oil bleaching process and contribute to the optimization of the bleaching clay wastes by optimizing the quantities of spent bleaching clay used in the refining process; consequently, to reduce risks of pollution.

References

- AOCS (1998) Official methods and recommended practices of American Oil Chemists' Society. Vol. 1, 5th ed. Champaign, IL: AOCS Press.
- Ajemba RO, Igbokwe PK, Onukwuli OD (2013) Optimisation of color pigments removal from palm oil by activated ukpor clay using response surface methodology. Res. J. App. Sci. Eng. Tech. 6: 423-432.
- Aung LL, Tertre E, Suksabye P, Worasith N, Thiravetyan P (2015) Effect of alumina content and surface area of acid-activated kaolin on bleaching of rice bran oil. J. Am. Oil Chem. Soc. 92: 295-304.
- Boukerroui A, Ouali MS (2002) Edible oil bleaching with a bentonite activated by microwave irradiation. Ann. Chim. Sci. Mat. 27: 73-81.
- Boukerroui A, Ouali MS (2000) Regeneration of a spent bleaching earth and its reuse in the refining of an edible oil. J. Chem. Technol. Biotechnol. 75: 773-776.
- Boukerroui A, Belhocine L, Ferroudj S (2018) Regeneration and reuse waste from an edible oil refinery. Environ. Sci. Pollut. Res. 25: 18278-18285.
- Boumahrat M, Gourdin A (1991) Méthodes Numériques Appliquées, ed. Office des Publications Universitaires, Alger, 147 pp.
- Cornillon PA, Matzner-Lober É (2007) Régression théorie et applications. Springer-Verlag, Paris, 34 pp.
- Christidis GE, Scott PW, Dunham AC (1997) Acid activation and bleaching capacity of bentonites from islands

- of Milos and Chios Aegean Greece. *Appl. Clay Sci.* 12: 329-347.
- Dijkstra AJ (2013) Edible oil processing from a patent perspective. Springer, New York, p. 173-198.
- Foletto EL, Collazzo G, Volzone C, Porto LMV (2011) Sunflower oil bleaching by adsorption onto acid-activated bentonite. *Braz. J. Chem. Eng.* 28: 169-174.
- Foletto EL, Paz DS, Gundel A (2013) Acid-activation assisted by microwave of a Brazilian bentonite and its activity in the bleaching of soybean oil. *Appl. Clay Sci.* 83: 63-67.
- Gil B, Kim M, Kim JH, Yoon SH (2014) Comparative study of soybean oil refining using rice hull silicate and commercial adsorbents. *Food Sci. Biotechnol.* 23: 1025-1028.
- Gonzales-Pradas E, Villafranca-Sanchez M, Socias-Viciano M, Gallego-Campo A (1994) Adsorption of chlorophyll-a from acetone solution on natural and activated bentonite. *J. Chem. Technol. Biotechnol.* 61: 175-178.
- James OO, Mesubi MA, Adekola FA, Odebunmi EO, Adekeye JID, Bale RB (2008) Bleaching performance of a Nigerian (Yola) Bentonite. *Lat. Am. Appl. Res.* 38: 45-49.
- Junmato T, Zhansheng W, Xifang S, Xiaolin X (2008) Adsorption kinetic of β -carotene and chlorophyll onto acid activated Bentonite in model oil. *Chinese J. Chem. Eng.* 16: 270-276.
- Kheok SC, Lim EE (1982) Mechanism of palm oil bleaching by montmorillonite clay activated at various acid concentration. *J. Am. Oil. Chem. Soc.* 59: 129-131.
- Komadel P (2016) Acid activated clays: Materials in continuous demand. *Appl. Clay Sci.* 131: 84-99.
- Kondal RK, Subramanian R, Kawakatsu T, Nakajima M (2001) Decolorization of vegetable oils by membrane processing. *Eur. Food Res. Technol.* 213: 212-218.
- Larouci M, Safa M, Meddah B, Aoues A, Sonnet P (2015) Response surface modeling of acid activation of raw diatomite using in sunflower oil bleaching by: Box–Behnken experimental design. *J. Food Sci. Technol.* 52: 1677-1683.
- Mezziti C, Boukerroui A (2011) Regeneration of a solid waste from an edible oil refinery. *Ceramics Int.* 37: 1953-1957.
- Mohdaly AA, Seliem KA, Maher AM, Abu El-Hassan AMM, Mahmoud AAT (2017) Effect of refining process on the quality characteristics of soybean and cotton seed oils. *Int. J. Curr. Microbiol. App. Sci.* 6: 207-222.
- Moussaceb K (2012) Modeling of the kinetics degradation of unstabilized and HALS-stabilized LDPE films under thermo-oxidation and natural weathering conditions. *Arab. J. Sci. Eng.* 37: 1327-1338.
- Neuilly M (1993) Modélisation et estimation des erreurs de mesure, ed. Lavoisier Tec et doc, Paris.
- Nguetnkam JP, Kamga R, Villieras F, Ekodeck GE, Yvon J (2008) Assessing the bleaching capacity of some Cameroonian clays on vegetable oils. *Appl. Clay Sci.* 39: 113-121.
- Nwabanne JT, Ekwu FC (2013) Experimental design methodology applied to bleaching of palm oil using local clay. *Int. J. Appl. Sci. Technol.* 3: 69-77.
- Pal US, Patra RK, Sahoo NR, Bakhara CK, Panda MK (2015) Effect of refining on quality and composition of sunflower oil. *J. Food Sci. Technol.* 52: 4613-4618.
- Pohndorf S, Cadava Jr. TRS, Pinto LAA (2016) Kinetics and thermodynamics adsorption of carotenoids and chlorophylls in rice bran oil bleaching. *J. Food Eng.* 185: 9-16.
- Sabah E, Inar MC, Elik MSC (2007) Decolorization of vegetable oils: Adsorption mechanism of β -carotene on acid-activated sepiolite. *Food Chem.* 100: 1661-1668.
- Sarier N, Guler C (1989) β -Carotene adsorption on acid activated montmorillonite. *J. Am. Oil Chem. Soc.* 65: 776-790.
- Srasra E, Bergaya F, Van Damme H, Ariguib NK (1989) Surface properties of an activated bentonite-decolorization of rape-seed oils. *Appl. Clay Sci.* 4: 411-421.
- Silva SM, Klicia Sampaio A, Ceriani R, Verhe R, Stevens C, De Greyt W, Meirelles AJA (2013) Adsorption of carotenes and phosphorus from palm oil onto acid activated bleaching earth: Equilibrium, kinetics and thermodynamics. *J Food. Eng.* 118: 341-349.
- Silva SM, Klicia Sampaio A, Ceriani R, Vehre R, Stevens C, Ee Greyt W, Meirelles AJA (2014) Effect of type of bleaching earth on the final color of refined palm oil. *LWT - Food Sci. Technol.* 59: 1258-1264.
- Tian G, Wang W, Kang Y, Wang A (2014) Study on thermal activated sepiolite for enhancing decoloration of crude palm oil. *J. Therm. Anal. Calorim.* 117, 1211-1219.