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Optimization of bleaching conditions for sardine oil

Pedro J. García-Moreno [a,*], Antonio Guadix [a], Luis Gómez-Robledo [b], Manuel Melgosa [b], Emilia M. Guadix [a]

[a] *Department of Chemical Engineering, University of Granada, 18071 Granada, Spain*
[b] *Department of Optics, University of Granada, 18071 Granada, Spain*

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ABSTRACT

This work studies the influence of the operational conditions (temperature: 90–130 °C, activated clay amount: 1–5 wt% and contact time: 20–60 min) on the bleaching process of degummed and neutralized sardine oil. The bleached oils were evaluated for free fatty acids, peroxide value, *p*-anisidine value, totox, oxidation stability (Rancimat) and color (CIELAB coordinates). Such measured variables were statistically modeled by full factorial experimental design and response surface methodology. An individual optimum value for totox of 21.38 (which minimizes oxidation products content) was obtained at 130 °C, 5 wt% of clay amount and 60 min. Regarding the color quality, it was found a maximum value for hue-angle (89.19 at 99.2 °C, 5 wt% of clay and 56. 6 min) and a minimum value for chroma (81.76 at 109.4 °C, 5 wt% of clay and 49.4 min). The conflicting effect of temperature and time on the location of the individual optima motivated the generation of a Pareto front (set of non inferior solutions) employing the weighted-sum multi-objective optimization technique.

1. Introduction

Small pelagic fish species such as sardine, mackerel and horse mackerel are a major source of fish oil presenting a high content of omega-3 polyunsaturated fatty acids (PUFAs), including EPA (C20:5n-3) and DHA (C22:6n-3) (Shahidi, 2006). In the last decades, these omega-3 PUFAs have received much attention in the scientific and industrial communities because of their benefits on human health, such as prevention of cardiovascular disease (Lees and Karel, 1990), improvement of the anti-inflammatory response (Uauy and Valenzuela, 2000) and development of brain and eye retina in infants (Ward and Singh, 2005).

Crude fish oil, which is generally obtained by the wet pressing method (FAO, 1986), contains non-triglycerides, such as phospholipids, free fatty acids, oxidation products, pigments and insoluble impurities that reduce the oil quality (Huang and Sathivel, 2010). Thus, in order to meet the standards safety and an acceptable shelf life, this oil requires a refining treatment.

The conventional fish oil-refining steps include: *degumming* (removal of phospholipids by the addition of phosphoric or citric acid), *neutralization* of free fatty acids with sodium hydroxide, *bleaching* with activated clays which adsorb oxidation products and pigments, and *deodorization* by vacuum distillation of volatiles compounds such as aldehydes and ketones (Rubio-Rodrígez et al., 2010).

Adsorption processes are particularly important since they can be used to remove most of the impurities that are present in the unpurified fish oil (Huang and Sathivel, 2010). This is due to the fact that the activated clays are able to adsorb (apart from oxidation products and pigments) trace metals and remains of phospholipids and soaps, which improves to a great extent the oxidation parameters and sensory quality of the oil (Sathivel and Prinyawiwatkul, 2004; Proctor and Toro-Vazquez, 1996). In the view of the above, the study of the bleaching process is an important issue to be considered in order to produce more efficiently fish oil for human consumption.

The purpose of the present work was to optimize the operational conditions of the bleaching process for sardine oil. Such a systematic study is not present in the current scientific literature. The influence of temperature, clay amount and contact time on key oxidation (free fatty acids, peroxide, *p*-anisidine and totox value, and induction period) and color (CIELAB color coordinates, hue-angle and chroma) parameters was evaluated. Finally, multi-objective optimization was performed since optimum values of oxidation and color parameteres were simultaneously pursued.

2. Materials and methods

2.1. Materials

Degummed and neutralized sardine oil (DNSO) was employed in this work. It was purchased from Industrias Afines, S.L. (Vigo, Spain) and kept in plastic bottles covered with aluminum foil at

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[*] Corresponding author. Tel.: +34 958241329; fax: +34 958248992.
E-mail address: pjgarcia@ugr.es (P.J. García-Moreno).

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4 °C under nitrogen atmosphere. Acid-activated clay, Tonsil 278, was utilized in the bleaching procedure. Acid-activated bleaching clays are preferably employed than natural bleaching earths due to their demonstrated better efficiency during the adsorption process (Rossi et al., 2003; Sathivel, 2010). The bleaching clay was kindly provided by Süd-Chemie España, S.L. (Toledo, Spain).

2.2. Bleaching procedure

DNSO was subjected to bleaching under partial vacuum (70 mmHg vacuum pressure). Sixty grams of DNSO were introduced with a given clay amount into a three-neck round-bottom flask. The samples were stirred at 300 rpm and kept at the desired temperature using an oil bath controlled by a thermo-regulator. The three experimental factors considered for this study were temperature, clay amount and contact time. A factorial experimental design comprising 27 runs was executed, in which each input variable was set at three levels: 90, 110 and 130 °C for temperature; 1, 3 and 5 wt% for clay amount; and 20, 40 and 60 min for contact time. After the contact time was completed for each run, the adsorbent was removed from the oil by centrifugation. The oil samples were stored under nitrogen at 4 °C in 50 mL Falcon tubes covered with aluminum foil until analysis.

2.3. Determination of oxidation parameters

2.3.1. Free fatty acids

The free fatty acids (FFA) content of the oil samples was determined according to the standard ISO 660:2009 (ISO, 2009). This method is based on the titration of the oil, suitably diluted with an ethanol-ethyl ether mixture, with a potassium hydroxide solution employing phenolphthalein as indicator. Results are expressed as percentage of oleic acid.

2.3.2. Peroxide, *p*-anisidine and totox values

The peroxide value (PV) of the oil samples was determined according to the standard ISO 3960:2007 (ISO, 2007). The PV method is based on the titration with a sodium thiosulfate solution of the oil diluted with an acetic acid-isooctane mixture and then treated with potassium iodide. Results are expressed as miliequivalents per kg of oil.

The anisidine value (AV) of the oil samples was determined according to the standard ISO 6885:2006 (ISO, 2006). The AV method is based on the reaction of *p*-anisidine diluted in acetic acid with the α- and β-unsaturated aldehydes (primary 2-alkenals) present in the oil. Results are expressed as 100 times the increment of absorbance produced by this reaction, measured at 350 nm.

Totox is a comprehensive oxidation index calculated from a weighted sum of peroxide value (PV) and *p*-anisidine value (AV) by applying the following equation:

$$Totox = 2PV + AV \tag{1}$$

2.3.3. Oxidative stability

The Rancimat test was employed to determine the oxidative stability of the oil samples. A Metrohm Rancimat model 743 (Methrom Instruments, Herisau, Switzerland) was utilized. A stream of filtered, cleaned and dried air at a rate of 20 L/h was bubbled into 3 g of oil samples contained in reaction vessels. These vessels were placed in an electric heating block which was set at a temperature of 100 °C. Effluent air containing volatile organic acids from the oil samples were collected in a measuring vessel with 60 mL of distilled water. The conductivity of the water was continuously recorded and the induction period (IP) was automatically determined by the apparatus. Rancimat induction period was expressed as resistance time (in hours) of the oil to oxidation.

2.4. Color measurements

Spectroradiometry was employed for color measurements. Compared to spectrophotometry, this method is preferred for the analysis of samples presenting some degree of turbidity. Furthermore, in contrast to the widely extended Lovibond Tintometer, spectroradiometry yields non-subjective measurements (Smedley, 1995; Melgosa et al., 2009).

The color measurements of the oil samples were carried out in duplicate placing the cuvettes (10 mm × 10 mm × 45 mm) containing the oil in the center of a SpectraLight III light booth equipped with a daylight source simulating the D65 illuminant and a non-fluorescent white background. D65 has long been the daylight source specifically recommended by the CIE for most of applications (Roa et al., 2006). Because of the translucency of the samples, fixed background was positioned behind the oil samples. Spectral radiant power was measured using a spectroradiometer CS-2000 (Konica Minolta Sensing Inc., Tokyo, Japan), which measures the spectrum from 380 to 780 nm at 1 nm steps.

From the spectral measurements, CIELAB color coordinates were computed assuming CIE 1964 Supplementary Standard Observer (Billmeyer and Saltzman, 2000). For computations of these coordinates, a standard white was used (Konica Minolta Sensing Inc., Tokyo, Japan) (CIE, 2004). Within the CIELAB color space, two color coordinates $a_1 0^*$ and $a_1 0^*$, and a psychometric index of lightness, L^*, are defined. a^* takes positive values for reddish colors and negative values for the greenish ones, whereas b^* takes positive values for yellowish colors and negative values for the bluish ones. L^* is an estimation of the relative luminosity, and according to this parameter any given color can be regarded as equivalent to a member of a gray scale, between black ($L^* = 0$) and white ($L^* = 100$). From a^* and b^*, the psychometric parameters hue-angle (h_{ab}) and chroma ((C^*_{ab}) were calculated as Eqs. (2) and (3), respectively:

$$h_{ab} = \tan^{-1}\left(\frac{b^*}{a^*}\right) \tag{2}$$

$$C^*_{ab} = \sqrt{(a^*)^2 + (b^*)^2} \tag{3}$$

The hue-angle is the attribute according to which colors have been traditionally defined as reddish, greenish and others (Wyszecki and Stiles, 1967). The chroma value is related to the quantitative attribute of colorfulness and allows to determine (for each hue-angle) the degree of difference when compared to a gray color with the same lightness.

2.5. Statistical analysis

The Statgraphics software (version 5.1) was used to generate the statistical analysis and the regression models. Firstly, the output variables (Y: FFA, PV, AV, totox, IP, a^*, b^*, L^*, chroma and hue-angle) were related to the input variables (X: temperature, clay amount and contact time) by second degree polynomials as follows:

$$Y = b_0 + \sum_{i=1}^{3} b_i X_i + \sum_{i=1}^{3} b_{ii} X_i^2 + \sum_{i<j}^{3} b_{ij} X_i X_j \tag{4}$$

where the coefficients b_i and b_{ii} are related to the linear and quadratic effects, respectively, of each input factor on the output variable and the cross-product coefficients b_{ij} represent the interactions between two input variables.

Secondly, the analysis of variance (ANOVA) was carried out. The significance of all terms in the models was judged statistically by computing the *p*-value at a confidence level $1 - \alpha = 95\%$. The regression coefficients were then used to generate contour maps and to find the optimal bleaching conditions which maximize the quality of the oil in terms of color and oxidation parameters, following the response surface method (Myers and Montgomery, 2002).

2.6. Multi-objective optimization

A problem of multi-objective optimization arises when several objectives, possibly conflicting, must be satisfied. In our case, it is desired to obtain minimum values for totox and chroma while maximizing hue-angle in the final bleached oil.

The concept of Pareto Front, related to the identification of an adequate solution, consists of a set of non inferior solutions, which are defined as those in which an improvement in one objective requires a degradation of another (Halsall-Whitney and Thibault, 2006). In this work, the weighted-sum method (Kim, 2004) was employed to generate the Pareto Front. This method consists in expressing a comprehensive objective function (OBJ) as a linear combination of the individual objectives (totox, hue-angle and chroma), by means of weight factors (w_i), which quantifies the relative importance given to the accomplishment of each individual objective:

$$OBJ = w_1 \cdot (Totox) + w_2 \cdot (-Hue\text{-}angle) + w_3 \cdot (Chroma) \tag{5}$$

where $w_1 + w_2 + w_3 = 1$ and $0 \leqslant w_i \leqslant 1$.

Note that the contribution of hue-angle is negative in order to pose the problem as a minimization of the objective function. The Solver Tool, included in the MS Excel software, was chosen to carry out all the calculations required for the multi-objective optimization.

3. Results and discussion

3.1. Characterization of bleached fish oils

Table 1 presents the experimental values of free fatty acid content (FFA), peroxide (PV), *p*-anisidine (AV), totox, induction period (IP), CIELAB color coordinates (L^*, a^* y b^*), chroma and hue-angle of the DNSO and of the 27 bleached oils produced.

The FFA content of the initial, non-bleached DNSO was of 0.17%, greatly lower than the acceptable level in refined fish oil (1.8%) reported by Sathivel et al. (2003). It is observed, in Table 1, that the acidity of the DNSO was reduced in most cases during the bleaching process when a clay amount of 5 wt% was employed. On the contrary, by utilizing adsorbent concentrations of 1 and 3 wt%, the FFA percentage suffered a general increase. Exposure of the oil to heat in the presence of traces of water caused the hydrolysis of triglycerides, which lead to the formation of free fatty acids that could not be adsorbed by the activated clay when the clay concentration used was lower than 5 wt%. Possible explanations include the presence of other impurities such as minerals and protein in the fish oil, or the high viscosity of the oil which slows down mass transfer and hence, the final removal of FFA (Huang and Sathivel, 2010).

In terms of oxidation products, the peroxide value was determined in order to quantify the primary oxidation products presented in the oil. Moreover, the *p*-anisidine analysis was carried out to measure the concentration of secondary oxidation products such as aldehydes, ketones and alcohols produced by decomposition of hydroperoxides. Then, totox value was computed to evaluate the rancidity level of the oils, reflecting total oxidation to date. In Table 1, DNSO presented an initial PV of 2.36 meq/kg and an AV of 77, resulting in a totox of 81.72. Although the initial oil presented an acceptable PV, PV < 5 meq/kg for refined fish oil

Table 1
Experimental design and measured values for the response variables.

Exp. #	Temp. (°C)	Clay amount (wt%)	Time (min)	FFA (% oleic)	PV (meq/kg oil)	AV	Totox	IP (h)	Color			Chroma	Hue angle (°)
									L^*	a^*	b^*		
DNSO	–	–	–	0.17	2.36	77.00	81.72	0.59	71.46	16.39	96.75	98.13	80.39
1	90	1	20	0.19	2.79	57.48	63.06	0.35	74.61	15.90	98.60	99.88	80.84
2	90	1	40	0.19	3.33	57.21	63.87	0.30	75.66	14.56	98.13	99.20	81.56
3	90	1	60	0.17	2.42	48.81	53.65	0.43	76.22	16.68	99.56	100.95	80.49
4	90	3	20	0.18	2.46	48.78	53.70	0.37	81.82	10.98	99.02	99.63	83.67
5	90	3	40	0.22	2.66	38.87	44.19	0.47	81.80	9.70	94.68	95.18	84.15
6	90	3	60	0.21	1.92	46.07	49.91	0.50	81.57	11.72	95.67	96.39	83.02
7	90	5	20	0.17	1.31	41.21	43.83	0.32	85.05	5.94	92.73	92.92	86.33
8	90	5	40	0.15	1.97	33.94	37.88	0.43	87.09	2.59	78.97	79.01	88.12
9	90	5	60	0.13	1.00	35.37	37.37	0.72	86.51	1.80	87.76	87.78	88.82
10	110	1	20	0.14	2.67	53.66	59.00	0.49	74.64	16.56	93.62	95.07	79.97
11	110	1	40	0.23	2.92	45.90	51.74	0.40	75.19	17.48	94.58	96.18	79.53
12	110	1	60	0.15	3.08	49.47	55.63	0.28	75.00	17.17	93.67	95.23	79.62
13	110	3	20	0.15	2.42	44.44	49.28	0.55	78.73	8.22	90.36	90.73	84.80
14	110	3	40	0.21	1.77	36.85	40.39	0.62	81.22	9.92	92.96	93.49	83.91
15	110	3	60	0.16	1.45	40.32	43.22	0.73	80.53	8.57	91.61	92.01	84.66
16	110	5	20	0.12	0.98	42.43	44.39	0.72	82.48	0.87	83.45	83.45	89.41
17	110	5	40	0.12	1.00	35.06	37.06	0.78	83.61	0.33	83.21	83.21	89.77
18	110	5	60	0.10	0.83	25.88	27.54	0.83	83.56	-1.08	80.85	80.85	90.76
19	130	1	20	0.21	1.72	45.99	49.43	0.45	71.63	16.69	95.96	97.41	80.13
20	130	1	40	0.21	2.02	47.46	51.50	0.58	73.05	14.26	95.45	96.51	81.50
21	130	1	60	0.18	1.56	46.62	49.74	0.76	72.16	14.90	95.05	96.21	81.09
22	130	3	20	0.19	0.75	42.99	44.49	0.77	74.50	12.51	93.64	94.47	82.39
23	130	3	40	0.14	0.87	31.80	33.54	0.95	75.08	10.34	91.66	92.24	83.56
24	130	3	60	0.15	0.00	33.39	33.39	0.57	74.58	12.13	93.19	93.98	82.58
25	130	5	20	0.14	0.00	29.05	29.05	0.78	76.63	8.16	88.32	88.70	84.72
26	130	5	40	0.12	0.00	23.37	23.37	0.95	77.04	7.05	86.74	87.03	85.35
27	130	5	60	0.18	0.00	21.76	21.76	0.95	77.44	6.96	86.51	86.79	85.40

(Ackman, 2005), the high AV obtained, AV > 20 (Ackman, 2005), denotes an advanced state of rancidity.

In Table 1, the effective removal of primary oxidation products during the bleaching process is shown. For some bleached oils, processed at the highest clay amount and temperature (5 wt% and 130 °C), no significant value of PV was observed. Nevertheless, carrying out the bleaching process using low concentrations of clay, 1–3 wt%, at low process temperatures, 90–110 °C, did not reduce the PV of the oil; on the contrary these conditions even enhanced the formation of peroxides due to the exposure of the oil to high temperatures. Considering the secondary oxidation products, Table 1 shows an AV reduction in all the bleached oils. This fact denotes the capacity of the acid-activated earths to adsorb these types of compounds (Rossi et al., 2003; Sathivel, 2010). From the AV results shown in Table 1, it could be clearly observed, within the experimental conditions assayed, that the adsorption of secondary oxidation products is more effective at higher temperatures and concentration of activated earth. On the other hand, a direct correspondence between the Rancimat induction period, IP, and any of the oxidation indices, PV, AV and totox, measured in the bleached oil samples was not observed (Table 1).

The initial L^*, a^*, and b^* values of the DNSO were, respectively, 71.46, 16.39, and 96.75 (Table 1). These CIELAB coordinates denote a dark brown color, attributable to pigments such as carotenoids (Indrasena and Barrow, 2010). The bleaching process increased the lightness of the oil, reaching L^* values up to 83.61. Besides, the activated earth adsorption process effectively reduced a^* value indicating that a decrease in red pigment occurred. As a consequence, the oil samples became lighter and slightly more transparent. Nevertheless, the b^* value of the bleached oils generally suffered a minor reduction taking values in the range of 78.97–99.56, which denotes yellowish color. Chroma values of the bleached oils, which represent the intensity of color, were reduced, while hue-angle value increased with the concentration of the activated earth. The hue-angle values were in the range of 79.53–90.76 which implies yellow–orange color for the bleached oils.

3.2. Statistical modeling

The experimental data of each measured variable were fitted to a complete quadratic model. The polynomial coefficients for the surface response model were calculated by multiple regressions, and the results are expressed in Table 2 for the oxidation and in Table 3 for the color parameters. A p-value of associated probability was also calculated for each term of the regression model. Selecting a confidence level of 95%, a p-value greater than 0.05 was not considered to be statistically significant. Similar statistical procedures have already been employed to optimize numerous processes involved in the up-grading of fish by-products such as extraction of fish oil from herring by-products (Aidos et al., 2003), enzymatic hydrolysis of sardine wastes (Dumay et al., 2006) and hydraulic pressing of sardine discards (Pérez-Gálvez et al., 2009).

Table 2 and Table 3 show that all the measured variables (FFA, PV, AV, totox, IP, a^*, b^*, L^*, chroma and hue-angle) are highly dependent on the linear effect of clay percentage, with an associated probability $p < 0.0001$. Regarding temperature, its linear effect was statistically significant for FFA, PV, AV, totox and IP, with $p < 0.001$. On the other hand, the time was the input variable having the lowest influence on the measured variables, with linear effects being statistically significant ($p < 0.005$) in the cases of FFA, AV, totox and L^*. Quadratic effects were found to be significant only for clay percentage in the cases of L^*, b^*, chroma and hue-angle; and time in the cases of FFA, PV, AV and L^*. The p-values for the remaining effects indicated that the interaction between experimental factors was not statistically significant ($p > 0.05$).

Table 2
Polynomial coefficients and p-values for the oxidation parameters.

	FFA (% oleic)		PV (meq/kg oil)		AV		Totox		IP (h)	
	Coefficient	p-Value	Coefficient	p-Value	Coefficient	p-Value	Coefficient	p-Value	Coefficient	p-Value
Constant	7.33E−01	–	−6.57E + 00	–	5.64E + 01	–	4.33E + 01	–	−7.94E−01	–
A: temperature, °C	−1.12E−02	<0.0001	1.96E−01	<0.0001	3.81E−01	<0.0001	7.73E−01	<0.0001	1.22E−02	<0.0001
B: clay amount, wt%	2.65E−02	<0.0001	−2.45E−01	<0.0001	−1.30E + 00	<0.0001	−1.79E + 00	<0.0001	−4.35E−02	<0.0001
C: time, min	2.60E−03	0.0007	5.07E−02	0.0501	−6.62E−01	0.0007	−5.60E−01	0.0003	1.15E−02	0.0682
AA	5.14E−05	0.4771	−1.04E−03	0.0053	−2.48E−03	0.4771	−4.55E−03	0.1989	−2.08E−05	0.8640
AB	−1.25E−04	0.2802	−2.17E−03	0.3576	−2.69E−02	0.2802	−3.12E−02	0.2119	1.04E−03	0.2356
AC	−2.65E−20	0.9349	6.46E−05	0.7814	2.00E−04	0.9349	3.29E−04	0.8929	−6.87E−05	0.4283
BB	−4.44E−03	0.5855	1.39E−02	0.6736	1.90E−01	0.5855	2.17E−01	0.5317	−7.50E−03	0.5396
BC	4.17E−05	0.1500	−7.08E−04	0.7610	−3.64E−02	0.1500	−3.78E−02	0.1351	1.04E−03	0.2356
CC	−3.61E−05	0.0462	−7.94E−04	0.0253	7.33E−03	0.0462	5.74E−03	0.1098	−5.42E−05	0.6569
R^2	0.5417		0.9352		0.9205		0.9431		0.7935	

Table 3
Polynomial coefficients and p-values for the color parameters.

	Color						Chroma		Hue angle (°)	
	L^*		a^*		b^*					
	Coefficient	p-Value	Coefficient	p-Value	Coefficient	p-Value	Coefficient	p-Value	Coefficient	p-Value
Constant	2.77E + 01	–	8.45E + 01	–	2.20E + 02	–	2.23E + 02	–	4.23E + 01	–
A: temperature, °C	8.01E−01	<0.0001	−1.16E + 00	0.1312	−2.09E + 00	0.0865	−2.11E + 00	0.1085	6.62E−01	0.0754
B: clay amount, wt%	7.01E + 00	<0.0001	−4.58E + 00	<0.0001	−2.46E−01	<0.0001	−9.19E−01	<0.0001	2.51E + 00	<0.0001
C: time, min	1.78E−01	0.0045	−9.51E−02	0.4109	−3.67E−01	0.2631	−3.73E−01	0.2614	4.61E−02	0.4519
AA	−3.82E−03	<0.0001	5.12E−03	0.0201	8.75E−03	0.0024	8.86E−03	0.0025	−2.93E−03	0.0381
AB	−3.73E−02	<0.0001	2.73E−02	0.0688	2.49E−02	0.1706	2.65E−02	0.1524	−1.59E−02	0.1034
AC	−2.90E−04	0.4638	−1.54E−04	0.9130	8.71E−04	0.6221	7.73E−04	0.6674	7.08E−05	0.9398
BB	−1.68E−01	0.0072	−1.58E−01	0.4391	−7.28E−01	0.0088	−6.93E−01	0.0131	1.10E−01	0.4108
BC	1.81E−03	0.6548	−1.43E−02	0.3224	−1.98E−02	0.2717	−2.02E−02	0.2697	8.89E−03	0.3500
CC	−1.64E−03	0.0084	1.70E−03	0.4059	3.73E−03	0.1483	3.94E−03	0.1336	−8.62E−04	0.5185
R^2	0.9906		0.9208		0.8763		0.8894		0.9000	

In Tables 2 and 3, it is also observed that the proposed quadratic models explain the variability of the data to a large extent, with coefficients of determination, R^2, being around 0.90 for most of the output variables except for FFA.

For the optimization of the bleaching process, totox value was chosen as measured variable to indicate the total oxidation of the oils, while hue-angle and chroma were selected as output variables indicating the final color of oil samples.

Firstly, the goodness of the fit for these three variables was proved. Fig. 1 plots the measured values against the predicted ones for totox (Fig. 1a), hue-angle (Fig. 1b) and chroma (Fig. 1c). The data are correlated by means of a regression line whose equation is inserted in each figure. Also shown in each figure are the dotted lines representing a deviation of ±10% between experimental and model values.

Secondly, by means of the second-order models obtained above and employing response surface methodology, contour maps were generated, where the totox, hue-angle and chroma were plotted against temperature (°C) and time (min), as shown in Fig. 2a–c. Adsorbent concentration was set at the maximum level assayed, 5 wt%. It was due to the fact that, within the experimental range, higher clay amount resulted in bleached oils of superior quality. In Fig. 2, it was observed that the hue-angle and chroma followed a pronounced curved surface. It is due to the significance of clay percentage quadratic effect in the case of hue-angle and to the significance of temperature and clay amount quadratic effects in the case of chroma.

By optimizing the quadratic models, optimum values for totox, hue-angle and chroma were found, marked as circles in the contour plots (Fig. 2). In order to optimize the quality of the bleached oils in terms of oxidation products, a minimum totox value is required. In Fig. 2a, the optimum value for the totox, 21.38, was located at the maximum levels assayed for the three input parameters, 130 °C, 60 min and 5 wt%. According to Sathivel (2010), during the bleaching process, peroxides are broken down to aldehydes and ketones as a consequence of the high temperatures employed. Subsequently, these secondary oxidation products are adsorbed onto the activated clay surface. It is therefore reasonable to conclude that the optimum bleaching conditions for totox reduction were: (a) the maximum temperature evaluated, 130 °C, which allowed the highest rate for peroxides decomposition maintaining a proper activation of the adsorbent; (b) the highest clay amount, 5 wt%, and (c) the highest contact time, 60 min, which maximized the adsorption of secondary oxidation products.

Additionally, optimizing the color quality in oil samples implies maximizing hue-angle, obtaining yellowish oils, and to minimize chroma, reducing the color intensity (Huang and Sathivel, 2010). In Fig. 2b, the maximum value predicted for hue-angle is observed to be 89.19. This optimum value was found at the highest adsorbent concentration, 5 wt%, and in the vicinity of the maximum level assayed for the time of 56.6 min. Nevertheless, a temperature of 99.2 °C was obtained as the optimum temperature for the reduction in red color. Fig. 2c shows the optimum value predicted for chroma, 81.76, which was within the experimental region: 49.4 min and 109.4 °C, employing the highest level of clay (5 wt%). Moderate temperatures, in the range of 99–110 °C, were required to obtain an optimum color for the bleached oil. This can be explained by the fact that working in this range of temperature the following phenomena may occur: (i) a better activation, in terms of pigments removal, of the acid-activated earth employed (Tonsil 278), (ii) a reduction in the oxidation of colorless components which cause alteration in the oil color, and (iii) a less pronounced fixing of the existing color pigments (Antoniassi et al., 1998; Crexi et al., 2010).

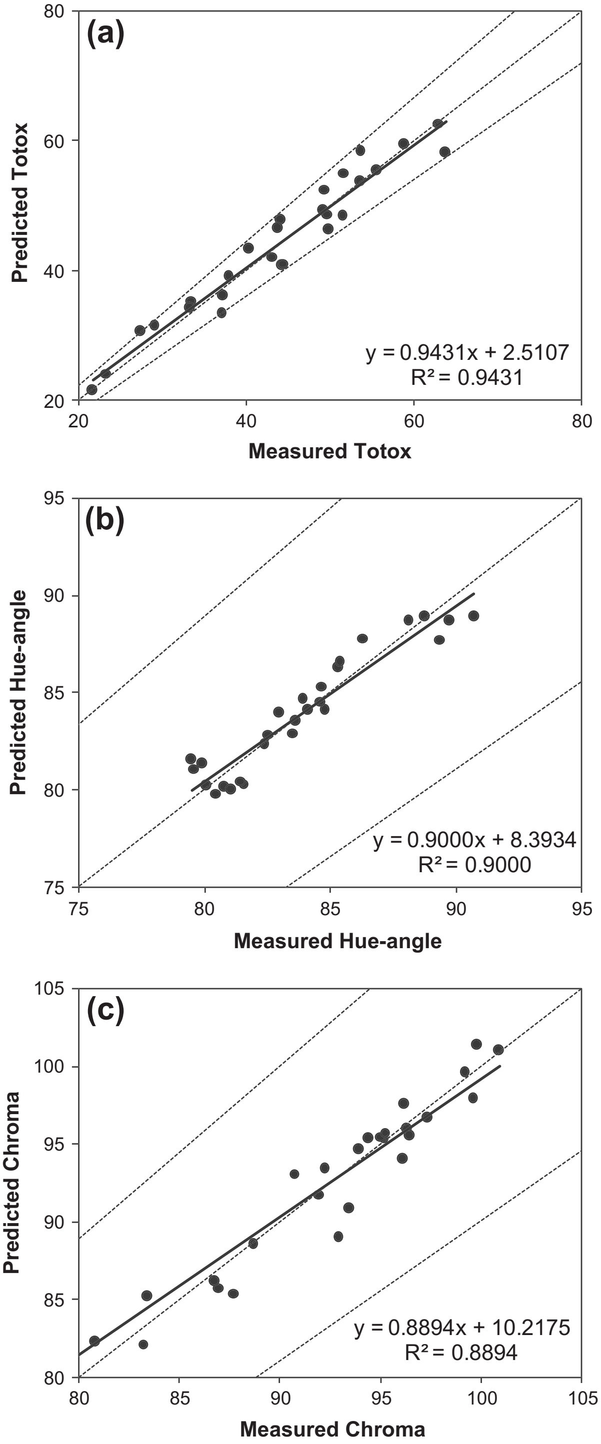

Fig. 1. Correlation between predicted and measured values of chroma (a), hue-angle (b) and chroma (c).

The results stated above indicate that in order to obtain optimum values for totox, hue-angle and chroma, different process conditions such as temperature and time of contact are required. It is observed that temperature increase had a positive effect on the minimization of totox, obtaining its minimal value at 130 °C. On the other hand, moderate temperatures, in the range of 99–110 °C, were required to obtain hue-angle and chroma optimal values. Considering time conditions, it is noticed that although each evaluated optimal point gave a different value, in general, the three output variables were optimized at long contact time conditions, close to the experimental upper bound, ranging from 49 to 60 min.

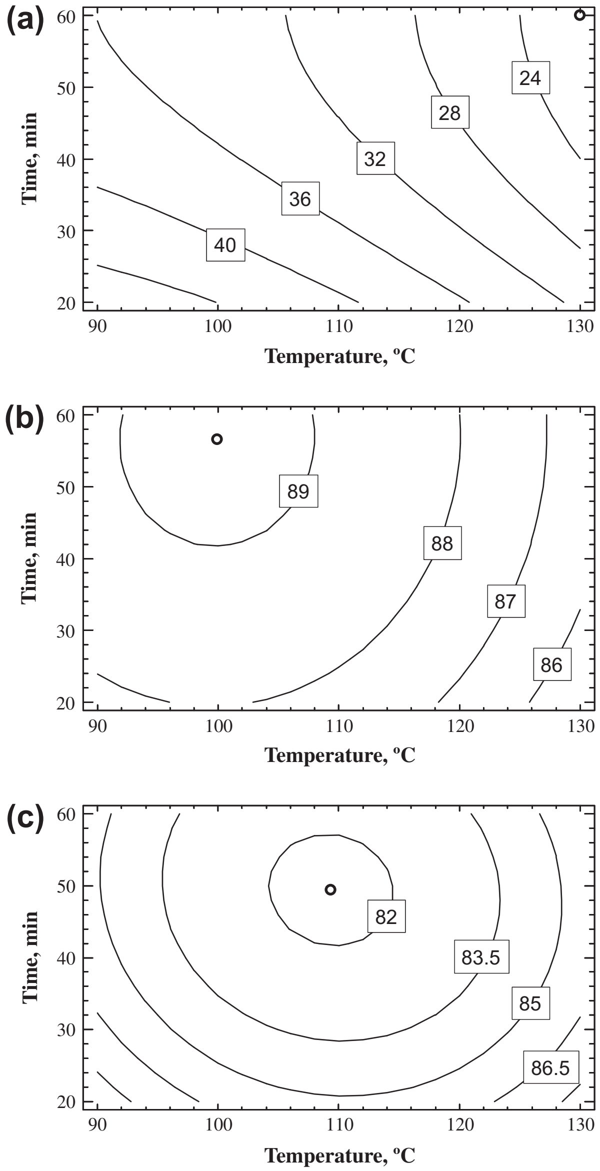

Fig. 2. Contour plots for totox (a), hue-angle (b) and chroma (c).

3.3. Multi-objective optimization

The conflict in the optimization of the three key output variables (totox, hue-angle and chroma) suggested employing a multi-objective optimization technique. A Pareto Front, shown in Table 4, was generated using the weighted-sum method in order to find a set of non inferior solutions which satisfied the three objectives to an adequate degree.

In rows 1–3 of Table 4, the optimization of the objective function corresponds to the optimization of a single objective, since two of the three weight factors are given a value of zero. In rows 4–30, a bi-objective optimization problem arises where just one of the weight factors takes a value of zero. In this situation, three cases are possible:

(a) Bi-optimization of hue-angle and chroma where $w_1 = 0$ (rows 4–12). It is observed that an increase of hue-angle (desired) implies an augmentation of chroma (undesired). This trend is more pronounced at values of hue-angle higher than 89.02.

Table 4
Set of optimal solutions (Pareto front) for the multi-objective optimization problem.

Row	w_1	w_2	w_3	Totox	Hue-angle (°)	Chroma
1	1.00	0.00	0.00	21.38	86.54	86.14
2	0.00	1.00	0.00	33.87	89.19	82.70
3	0.00	0.00	1.00	31.62	88.88	81.76
4	0.00	0.10	0.90	31.71	88.90	81.77
5	0.00	0.20	0.80	31.82	88.93	81.77
6	0.00	0.30	0.70	31.94	88.96	81.78
7	0.00	0.40	0.60	32.09	88.98	81.80
8	0.00	0.50	0.50	32.26	89.02	81.82
9	0.00	0.60	0.40	32.46	89.05	81.87
10	0.00	0.70	0.30	32.70	89.09	81.94
11	0.00	0.80	0.20	33.00	89.14	82.07
12	0.00	0.90	0.10	33.38	89.17	82.29
13	0.90	0.00	0.10	21.38	86.54	86.14
14	0.80	0.00	0.20	21.39	86.54	86.09
15	0.70	0.00	0.30	21.43	86.54	85.99
16	0.60	0.00	0.40	21.48	86.54	85.89
17	0.50	0.00	0.50	21.56	86.54	85.80
18	0.40	0.00	0.60	21.83	86.58	85.60
19	0.30	0.00	0.70	26.61	87.96	82.93
20	0.20	0.00	0.80	29.04	88.50	82.10
21	0.10	0.00	0.90	30.54	88.75	81.82
22	0.90	0.10	0.00	21.38	86.54	86.14
23	0.80	0.20	0.00	21.38	86.54	86.14
24	0.70	0.30	0.00	21.38	86.54	86.14
25	0.60	0.40	0.00	21.38	86.54	86.14
26	0.50	0.50	0.00	21.38	86.54	86.14
27	0.40	0.60	0.00	21.38	86.54	86.14
28	0.30	0.70	0.00	21.38	86.54	86.14
29	0.20	0.80	0.00	26.85	88.12	83.10
30	0.10	0.90	0.00	31.84	89.07	82.20
31	0.50	0.25	0.25	21.44	86.54	85.95
32	0.25	0.25	0.50	27.32	88.16	82.65
33	0.25	0.50	0.25	25.91	87.85	83.29
34	0.33	0.33	0.33	21.54	86.54	85.81

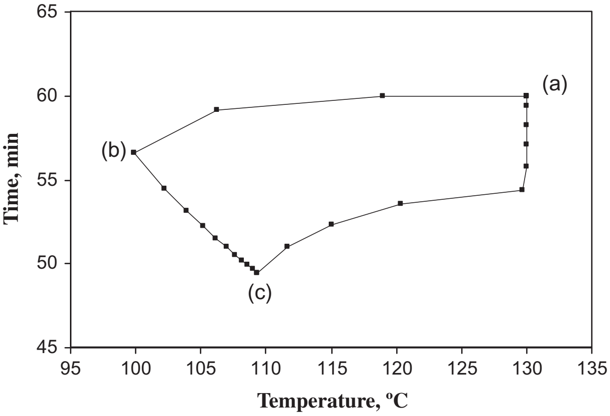

Fig. 3. Decision space for the multi-objective optimization problem.

(b) Bi-optimization of totox and chroma where $w_2 = 0$ (rows 13–21). It is noticed that a decrease of chroma (desired) denotes an increase of totox (undesired), being this tendency more noticeable at values of chroma lower than 85.6.

(c) Bi-optimization of totox and hue-angle where $w_3 = 0$ (rows 22–30). It is noted that an augmentation in hue-angle (desired) causes an increase in totox values (undesired). This trend is more evident at values of hue-angle greater than 86.54.

Additionally, in rows 31–34 of Table 4, four new solutions were obtained, in which none of the weights was set to zero.

Each solution or efficient point (totox, chroma, hue-angle) is determined by a decision vector or combination of factors inside the ranges of the independent variables (temperature, clay amount and contact time). Then, the Pareto Front can be translated to the decision space by obtaining the optimal combination of experimental factors for each selection of weight factors. Fig. 3 shows the optimal temperatures and times for each efficient solution presented in rows 1–30 of Table 4. Optimum clay amount was 5 wt% in all cases. It is observed that the decision space is comprised between 99.91 and 130 °C and between 49.45 and 60 min. The three vertexes of the decision space represent the single optima for totox (a), hue-angle (b) and chroma (c). The points placed in the line from one vertex to another correspond to the bi-objective optimization of the variables involved. The solutions presented in rows 31–34 of Table 4 and any other solution considering non-zero weights only, would be placed inside the closed region.

Finally, the selection of a single optimal solution from the Pareto Front (optimal combination of temperature and time employing 5 wt% of clay), will depend on the required characteristics for the bleached oil in terms of oxidation and color quality. Such selection would arise from a given combination of weights proposed by the decision maker.

4. Conclusions

Based on this study, the optimum conditions to carry out the bleaching process of DNSO in order to remove oxidation products, and thus, improving the oxidative stability of the oil, are: 130 °C, setting the adsorbent amount at 5 wt% and employing long contact times ($\sim$60 min). This fact denotes that, within the experimental range, working at high temperatures, enhances the breaking down of peroxides and the subsequent adsorption of secondary oxidation products onto the surface of the activated clay. Nevertheless, regarding color quality, an optimum bleaching process required moderate temperatures (99–110 °C), high adsorbent amount (5%) and shorter contact time (49–57 min). Under these conditions, the oil suffers reduction in redness (a^*) whilst maintaining high values for yellowness (b^*) and lightness (L^*). It may therefore be concluded that employing moderate temperatures, the clay employed (Tonsil 278) is more activated in terms of pigment adsorption.

Consequently, the conflicting behavior of the experimental factors (temperature and time) towards the accomplishment of the optimization objectives necessitates finding a compromise solution employing multi-objective optimization techniques. The weighted-sum method was chosen for this purpose, generating a set of optimal solutions (Pareto Front). Thus, the required final characteristics for the bleached oil (optimal oxidation and/or color quality) will determine the selection of a single solution inside the Pareto Front.

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