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Oxidative stability of neutralized oils bleached with clays activated with ultrasound

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ABSTRACT

Ultrasonic waves were applied during activation process of Tunisian clays, to contribute to bleaching earths with high performance. Activation was performed at optimal frequency (20 KHz) and ultrasound amplitude of 28–50%. Combination of the conventional technique (classic activation process), with the use of very low acid concentration solutions (0.5 M) with ultrasound gave the best results. This new developed process was efficient, economic and rapid. The effectiveness of optimal activated clays was very important, according to the bleaching index of neutralized pomace-olive oils (86%).

The influence of activated clays with ultrasound on oxidative stability of bleached oils. It was improved that these clays, activated with the new technique, led to the removal of unacceptable compounds with the least possible losses of oil and desirable fractions. No significant losses in natural antioxidants (α-tocopherol), noted in treated oils, which were at the origin of an important resistance to oxidative stability (high OSI).

1. Introduction

Crude oils are generally refined by degumming, alkali-refining, bleaching, and deodorizing to yield an odorless, bland, and oxidatively stable edible oils. Each processing step has specific functions to remove undesirable components such as waxes, free fatty acids, pigments, off-flavors and prooxidants (Ferrari et al., 1996; Jung et al., 1989). In fact, certain minor constituents have to be removed with the least possible loss of desirable materials. However, refining process subjects vegetable oils to high temperatures, alkali and acid mediums, resulting from bleaching earths and sodium hydroxide, and to metal processing equipments. These parameters can be at the origin of numerous alterations in the chemical composition and oxidative stability of treated oils. Modifications noted in minor components of refined vegetable oils are of great interest to be considered in studies from nutritional viewpoints (Rabascall and Riera, 1987). The bleaching process, using acid activated clays, is generally considered as a combination of catalytic reactions and an equilibrium adsorption, permitting the removal of pigments and traces of undesirable constituents (Henderson, 1993). Activated clays present high surface acidity that can contribute to many chemical reactions of alteration in glyceridic and minor fractions of bleached oils. Therefore, an ideal adsorbent should have high affinity for components to be removed and essentially no affinity for other components (Bonvehi et al., 2001). Activation process, released with the use of high concentrated acid solutions and at high temperatures, leads essentially to increase the adsorption efficiency of activated clays. On other side, it induces to a modification of them crystalline structure by formation of amorphous silica and increasing the clay surface acidity (Margulis, 1985). This later can cause many degradation reactions such as isomeriztaion of polyunsaturated fatty acids, decomposition of unsaturated fatty acids and sterols and to the dehydration of sterols which lead to steradienes formation (Ferrari et al., 1996; Bonvehi et al., 2001).

In the aim to prepare bleaching earths with high efficiency, and having less negative effects, we have introduced ultrasonic waves during activation process. The action of ultrasound is mainly mechanical towards solid bodies, leading to fragmentation and surface activation, due to the implosion of bubbles by microjets of liquid. The cavitation phenomenon, which is composed of nucleation, growth and implosion of cavitation bubbles, favours the impregnation of reagents on the solid catalytic support (Margulis, 1985). The experimental conditions of this new activation process permitted to reduce considerably the acid concentration and activation time. In the present work, two approaches were evaluated. Firstly, the aim of this study was to investigate the optimization of principal activation parameters, namely acid concentration, activation time and ultrasonic wave's amplitude. Secondly, the influence

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of the new activation process on oxidative properties of bleached oils.

2. Materials and methods

2.1. Materials

Olive oil and neutralized pomace-olive oil were provided by Agrozitex Refinery (Sfax, Tunisia). Commercial bleaching earth 'actisyl' (Südchemie, Germany) was considered as a reference. The raw material used for the preparation process of bleaching earths with ultrasound, was selected from the south of Tunisia (El Hamma −Gabès). All used chemicals were of analytical grade.

2.2. Activation process and bleaching conditions

2.2.1. Classic activation process

Optimal activation conditions of raw clay using classic process were released in our laboratory and presented in previous published work (Jahouach et al., 2006). Clays were prepared under the following conditions of activation: a quantity of raw clay 20 g was treated by 200 ml of a solution of H_2SO_4 with a concentration of 7.5 mol/L and at a temperature of 70 °C during 3 h to lead to earth T_1 and during 6 h to lead to the T_2. Bleaching earths T_1 and T_2 having the highest adsorption capacity against pomace-olive oils, were considered as references to discuss the results shown in the present work.

2.2.2. Activation process with application of ultrasound

Activation process was achieved at low frequencies of ultrasonic waves (20 kHz), in the aim to prepare bleaching earths, using sulphuric acid. An ultrasonic generator type Bioblock Scientific 750 W, was used. It is fitted with an immersible probe that is dipped in the liquid at the top of the tank and emits the sound vibration into the solution via a titanium alloy rod of 13 mm diameter.

We have defined limits of intervals to have a very high adsorption capacity without destroying the clay:

- acid concentration: [0.5–2.5 mol/L];
- activation time: [30–60 min];
- amplitude of ultrasonic waves: [25–75%];
- temperature: 30 °C.

Activated clay samples were then washed with bidistilled water, filtered, dried and then screened from humidity. The variation of activation conditions (Table 1**)** has permitted to prepare a dozen of bleaching earths. Only the combination of the three parameters (acid concentration, activation time and the ultrasonic waves amplitude) which has the most important bleaching index was retained. Whose efficiency is comparable or better than that of the actisyl (commercial clay as reference clay). So ten samples were chosen, noted from T_1 to T_{10}.

Specific surfaces of raw and activated clays have been determined according to BET analytical method (Brunauer-Emmett and Teller) with nitrogen adsorption, using an ASAP 2010 system (Jouenne, 1990).

2.2.3. Bleaching conditions of adsorption capacity (bleaching index)

The adsorption performance of clays activated with ultrasound was assessed by bleaching tests neutralized pomace-olive oils, using an atmospheric batch system. This process consisted of mixing neutralized oils with 2% (g/g) of acid activated clays at a temperature of 85 °C, stirring for 45 min followed by centrifugation (4000 trs/min) and filtration, to give a clean and clear oils.

The efficiency of bleaching was released by meas-uring the absorbance of neutralized and treated oils at 500 nm, using a NOVASPEC II spectrophotometer. The adsorption capacity of bleached oils is given by the "Eq. (1)"

$$I_B(\%) = A_{500}(\text{neutralized oil}) - A_{500}(\text{bleached oil})\text{oil}/ A_{500}(\text{neutralized oil}) \quad (1)$$

I_B: bleaching index (%).
A_{500}: oil absorbance at 500 nm.
Conditions giving the highest adsorption efficiency were considered as optimum for the new developed activation process.

2.3. Analytical methods of bleached oils

2.3.1. Tocopherols

Tocopherol contents were determined by liquid chromatography (HPLC), on a normal phase (Verleyen et al., 2001b). An appropri-ate silica column (250 mm x 4.6 mm i.d., particle size 5 μm), was used. The isocratic mobile phase (hex-ane/isopropyl alcohol, 99.5/0.5) was delivered at a flow rate of 1.5 ml/min. An UV detector at 292 nm, was con-sidered.

2.3.2. Oxidative stability index

Applying the OSI method, a stream of purified air was passed through a sample of 5 g of oil that was held at a constant temperature (97.8 °C) and air flow. The effluent air from the oil sample was then bubbled through a vessel containing deionized water. The conductivity of the water was continuously monitored. The effluent air contained volatile organic acids swept from the oxidizing oil, which increase the conductivity of the water as oxidation proceeds. The OSI is defined as the time, ex-pressed in hours, that was needed to reach the maximum change of conductivity (Velasco and Dobarganes, 2002).

2.3.3. Metal and chlorophyll contents

Phosphorous (P), iron (Fe), calcium (Ca) and magnesium (Mg) were quantified by inductive coupled plasma (ICP), according to the analytical official method AOCS (Ca 20–99) (Official methods, 2000). The analysis was performed on a Thermo Jarell-Atom Scan 25 system (1350 W, flow rate: 1.5 l/min).

The chlorophyll (pheophytin) contents in bleached oils, residual from the neutralization, were determined according to the official method (Wolf, 1992) which is based on quantification by a spectrophotometric analysis. The amounts of chlorophylls in treated oils, calculated relatively to neutralized oil, were given according to the Eq. (2):

$$\text{Chlorophylles(ppm)} = \frac{A_{670} - \frac{A_{630}+A_{710}}{2}}{0.1086\,L}$$

where A_{630}, A_{670}, A_{710} are respectively absorbance of oil at 630, 670 and 710 nm;
L: cell width (1 cm).
It has to be mentioned that all analyses were performed in triplicates and the mean values were reported.

3. Results and discussion

A dozen of bleaching earths (T_1, T_2,.., T_{10}) have been prepared, by varying principal activation parameters: acid concentration, activation time and the amplitude of ultrasonic waves. The temperature is maintained constant at 30 °C. These activated clays, used in bleaching pomace-olive oils, containing more than 20 ppm of chlorophyll have contributed to results presented in Table 1.