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Deacidification of High-Acid Olive Oil by Adsorption with Bamboo Charcoal

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Unsold olive oils stored for long periods are degraded by hydrolysis, resulting in a high level of acidity, leading to loss of economic value of these as a food product. This study was performed to improve the quality of high-acid olive oil (HAOO) and assess the feasibility of deacidification of HAOO using bamboo charcoal as an adsorbent, by applying a stirring technique. Strategies to improve the quality of HAOO, which was obtained by allowing commercial extra virgin olive oil to rest for two years, were tested by measuring free fatty acids, peroxide value, volatile compounds, and chlorophyll and carotenoid pigments. Initially, the effective weight of bamboo charcoal used in the deacidification treatment of HAOO was determined. The level of free fatty acids in the treated oils was effectively decreased with increasing treatment duration. However, bamboo charcoal was not effective in scavenging peroxides in HAOO. In addition, treatment with bamboo charcoal could effectively reduce the level of oxidative off-flavours, such as hexanal. However, the treatment was not effective in reducing chlorophyll and carotenoid pigments. These results suggest that bamboo charcoal may be a good adsorbent and can improve the oil quality of HAOO without changing the appearance of the oil. Consequently, the unsold oils may recover the economic value as a food product, leading to a reduction in their disposal.

1. Introduction

Olive oil is one of the most important edible oils globally and is a component of the Mediterranean diet. It is appreciated for its aroma, taste, colour, and nutritive features that distinguish it from other vegetable oils. In addition, it can improve health through its benefits, such as reducing lifestyle risk factors for heart disease (Visioli and Galli, 2002). Extra virgin olive oil (EVOO) has been used for its sensory and nutritional properties and belongs to the highest quality category of olive oil because it is extracted from fresh olive fruits using only physical processing with no added chemicals (International Olive Council, 2019). Therefore, EVOO is often preferred as a cooking oil medium and is used as premium edible oil, which has led to a rapid increase in the size of the olive oil market.

The olive oil market is roughly divided into the following: branded olive oils, which are being increasingly produced by bottlers importing, while the oil quantity directly marketed by olive farmers is also increasing. Olive oil produced in one crop season is usually consumed before the next crop season, because the oil quality gradually deteriorates during storage (Morelló et al., 2004). The changes in oil quality need to be only minimally maintained during the storage period, but oil deterioration is unavoidable. This results in increasing amounts of olive oil remaining unsold in farms. Moreover, older unsold bottled oils are also sent back to the oil producer and are then disposed of or purified to improve their quality by chemical treatment. Either way, the oil products lose their economic value as food products.

Vegetable oils, which are degraded by hydrolysis, have a high percentage of free fatty acids (FFAs) (Frega et al., 1999; Kishimoto, 2019). The FFA content in olive oil, which corresponds to its acidity degree, is a key parameter routinely determined to classify and assess quality, freshness, and economic value of the final commercial product (International Olive Council, 2019). The presence of even small amounts of FFAs in vegetable oils raises the possibility of rancidity, thereby reducing the quality of the oils (Vaisali et al., 2015). FFAs generate corrupt odours and accelerate oxidation (Chaiyasit et al., 2007). The deacidification process, which is a refining operation to reduce FFAs, plays an important role in recovering the economic value of olive

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oil as a food product and/or reducing the disposal of the older unsold oil products in the economics of the oil production.

Several methods have been developed to reduce FFAs in degraded vegetable oils, for example, chemical refining with sodium hydroxide and physical refining based on distillation. In addition, it has been reported that FFAs are reduced using a membrane cell with some chemicals such as ethanol and methanol (Cvengros, 1995). However, these approaches may be effective in reducing FFAs, but these operations are also energy- and cost-intensive (Martins et al., 2006). These approaches lead to the loss of desired and undesired non-glyceride components as well (Gotor and Rhazi, 2016). However, other methods such as the use of charcoal in the deacidification of olive oil due to its adsorption capability would be an interesting strategy. Therefore, the use of charcoal can be realised to avoid the use of such chemicals in the deacidification of olive oil. Charcoal adsorption capacity has been reported in several studies (Hille and Den Ouden, 2005; Ou et al., 2007; Melville et al., 1980). Charcoal has been used for its ability to adsorb undesirable components in a solution. In particular, bamboo charcoal is cheaply and easily available among other charcoals and has been widely used in various applications (Asada et al., 2002; Kuti et al., 2018), making it a practical purification method, although chemical refining is a highly energy-intensive process using both purchased energy and by-product streams from the refining processes (Geankoplis et al., 2018). Bamboo charcoal is produced from the rapidly growing moso bamboo, which is widely planted throughout Asia. Therefore, bamboo charcoal is a promising sustainable product that is readily available for global use for future greener generations. However, whether bamboo charcoal can be applied for the deacidification of olive oil and the most effective concentration for deacidification is yet to be determined. This study was aimed to determine the most effective concentration of bamboo charcoal to improve the quality of olive oil through deacidification. This study presents the results of the experiment conducted to examine alteration of olive oil components such as chlorophyll and carotenoid pigments and volatile compounds, as well as the reduction of FFAs.

2. Experimental

2.1 Materials

HAOO was obtained by storing commercial EVOO (Shodoshima Healthyland Co., Ltd., Kagawa Japan) for two years. Bamboo charcoal and medium-chain triglyceride oil (Nisshin OilliO Group, Ltd., Tokyo, Japan) were purchased from a market. Bamboo charcoal was crushed to approximately 3 mm square.

2.2 Deacidification of high-acid virgin olive oil with bamboo charcoal

The crushed bamboo charcoal (10, 20, and 30 g) was added to the HAOO (100 g) and mechanically stirred on a magnetic stirrer for 8 h at 25 °C and then filtered through an ADVANTEC No. 131 filter paper. This process was repeated three times. The untreated HAOO was also filtered through an ADVANTEC No. 131 filter paper.

2.3 Analytical procedures

FFAs and peroxide values (PVs) of the oil sample were measured using an OxiTester (CDR; Ginestra Fiorentina, Italy) (Kamvissis et al., 2008). Preliminary confirmation of the FFAs determined using the OxiTester method was conducted by comparing the results for oil samples over a wide range of values with those from the official analysis method (Gucci et al., 2012; Kishimoto, 2019). Oil samples were added to prefilled cuvettes for analysis. The volume of oil used was 2.5 μL for measuring FFAs and 0.5−2.5 μL for measuring PVs.

The contents of chlorophyll and carotenoid pigments, which are reported in mg/kg of oil, were determined using a UV-1700 spectrophotometer (Shimadzu, Kyoto, Japan) following the method described by Minguez-Mosquera et al. (1991) and Kishimoto (2019). One gram of oil sample was dissolved in 10 mL of isooctane. The absorption was then recorded at 670 nm for chlorophylls and 470 nm for carotenoids. The contents were calculated using the following equations:

$$\text{Chlorophylls (mg/kg)} = \frac{(A_{670} \times 10^6)}{(613 \times 100 \times d)} \quad (1)$$

$$\text{Carotenoids (mg/kg)} = \frac{(A_{470} \times 10^6)}{(2000 \times 100 \times d)} \quad (2)$$

where *A* is the absorption and *d* is the path length of the cells (1 cm).

2.4 Flash gas chromatography electronic nose analysis of hexanal and E2-hexanal

To analyse hexanal and E2-hexenal concentrations in the oil samples, the headspace (gas mixture) prepared in a temperature-controlled vial was analysed using a HERACLES II electronic nose (e-nose) (Alpha MOS, Toulouse, France) (Kishimoto and Kashiwagi, 2018). This instrument was equipped with a nonpolar column (MXT-5; 10-m length × 180 μm diameter) and a polar column (MXT-WAX; 10m length × 180 μm diameter) in parallel to produce two chromatograms simultaneously. An HS100 auto-sampler (CTC Analysis AG; Zwingen, Switzerland) was used to automate sample incubation and injection. An alkane mixture (from *n*-hexane to *n*-hexadecane) was used to convert the retention times into Kovats indices for calibration. For analysis, an aliquot of oil (2.0 g) was placed in a 20mL vial and then sealed with a magnetic cap. The vial was placed in the auto-sampler, which was then placed in the HERACLES II shaker oven and incubated for 15 min at 60 °C with shaking at 500 rpm. A syringe was used to sample 5 mL of headspace, which was injected into the gas chromatograph. The oven temperature was initially 40 °C (held for 10 s), and then increased to 250 °C at 1.5 °C/s and held at this temperature for 60 s. The total separation time was 120 s. Hydrogen gas was used as the carrier gas. Data were acquired and processed using the AlphaSoft software v2020 (Alpha MOS). When using the MXT-5 column, hexanal and E2-hexenal eluted at approximately 45 and 53 s, respectively.

2.5 Quantification of hexanal and E2-hexenal

To determine the concentration of hexanal and E2-hexenal in each oil sample, standard curves were established. Samples of medium-chain triglyceride oil containing different hexanal concentrations were prepared and subjected to flash gas chromatography e-nose analysis using the HERACLES II e-nose. The concentrations of hexanal and E2-hexenal in the oil samples after treatment with bamboo charcoal were determined using standard curves. The high value of both coefficients of determination (R^2 = 0.999) indicated that the standard curves allowed the quantification of hexanal and E2-hexenal in the oils with a high level of accuracy.

2.6 Statistical analysis

Data are presented as the mean ± standard deviation of three replicates. The data were analysed using one-way analysis of variance followed by the Tukey-Kramer test in Microsoft Excel. Differences from mean values with p < 0.05 were considered statistically significant.

3. Results and Discussion

3.1 Determination of mass of bamboo charcoal

HAOO with an initial FFA of 1.02%, which exceeded the 0.80% standard for EVOO (International Olive Council, 2019), was used in this study. To determine the weight of bamboo charcoal in the deacidification treatment of HAOO, HAOO was added in various weights (0, 10, 20, and 30 g/100 g·oil). Figure 1 shows the values of FFAs in HAOO after treatment with bamboo charcoal for 8 h. Bamboo charcoal successfully reduced the values of FFAs in HAOO in various ranges. The reduction of FFAs using 20 g/100 g·oil was the most efficient. This value of FFAs was almost the same as that obtained using 30 g/100 g·oil. Based on these results, the mass of bamboo charcoal added to HAOO was determined to be 20 g/100g·oil.

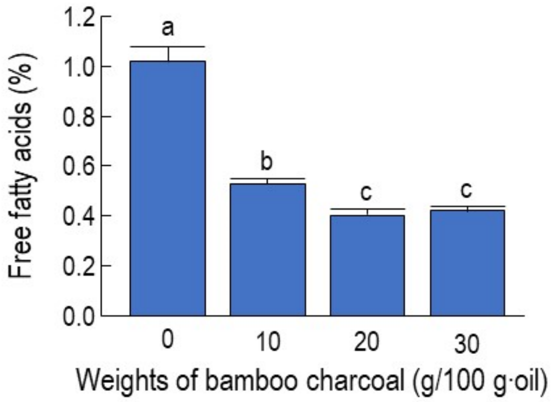

Figure 1: Effects of various weights of bamboo charcoal added to HAOO in deacidification treatment. [a-c]Mean values with different letters are significantly different (p<0.05).

3.2 Impact of deacidification on the oil quality of high-acid olive oil

The most versatile chemical characteristics for the determination of olive oil quality are FFAs and PVs. These are established parameters to evaluate if the quality of fat in olive oil level lies within the internationally recognized limits for the commercial quality "extra," the highest quality level for olive oil (International Olive Council, 2019). Figure 2 shows the changes in the values of FFAs and PV in HAOO treated with bamboo charcoal. The FFA levels of the treated oils decreased significantly with increasing treatment duration. The final FFAs of the treated oils were 0.31%, which was within the limit of 0.80% set by the International Olive Council (2019). The corresponding improvement in the FFA reduction (%) for the oils treated with bamboo charcoal was 69%. This result demonstrated that bamboo charcoal has a high adsorbing capacity for FFAs in HAOO. The initial PV of HAOO was 20.3 meqO_2/kg. The treatment with bamboo charcoal slightly improved the oil quality in terms of PV, resulting in a decrease in the PV level to 14.2 meqO_2/kg, which was within the limit of 20.0 meqO_2/kg set by the International Olive Council (2019), for HAOO treated with bamboo charcoal. The corresponding improvement in the PV reduction (%) for the oils treated with bamboo charcoal was 32%. This result demonstrated that treatment with bamboo charcoal is not effective as a scavenger of peroxides of HAOO.

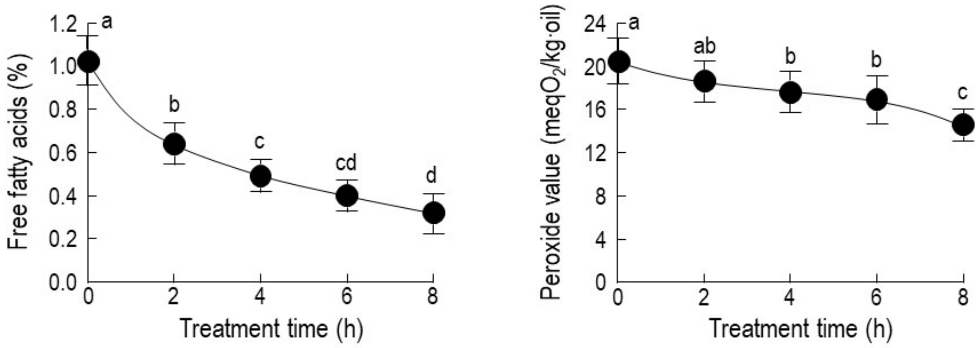

Figure 2: Changes in FFAs and PV of HAOO treated with bamboo charcoal. [a-d]Mean values with different letters are significantly different (p<0.05).

3.3 Impact of deacidification on the volatile compounds of high-acid olive oil

In addition to the conventional oxidative markers discussed above, the contents of two particular volatile compounds in HAOO, hexanal and E2-hexenal were also investigated. E2-hexenal contributes significantly to the aroma of olive oil and is related to the positive sensory characteristics of almond and green olive fruits (Olías et al., 1993; Luna et al., 2006); however, hexanal is directly related to oxidative off-flavours (García-Llatas et al., 2007; Kalua et al., 2007). Figure 3 shows changes in the contents of hexanal and E2-hexenal in HAOO treated with bamboo charcoal. The treatment resulted in decreasing the hexanal levels from 7.6 to 4.0 ppm for HAOO treated with bamboo charcoal. However, at the same time, the positive aroma, E2-hexanal levels were also decreased from 11.0 to 2.9 ppm by the treatment of HAOO with bamboo charcoal. These results demonstrate that bamboo charcoal has a high adsorbing capacity for volatile compounds in olive oil.

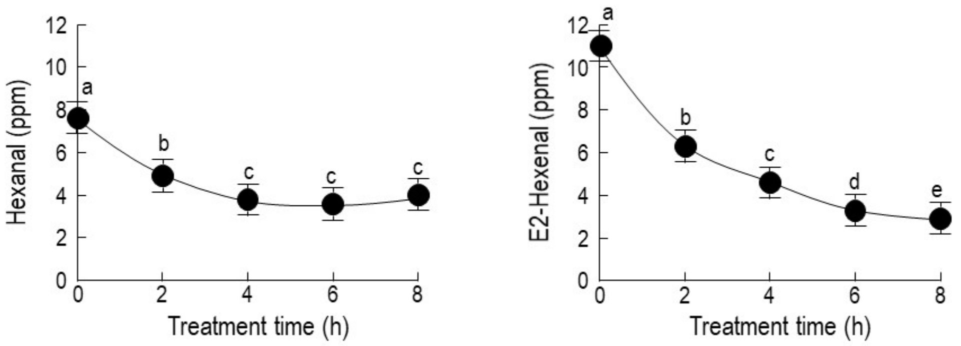

Figure 3: Changes in hexanal and E2-hexenal in HAOO treated with bamboo charcoal. [a-e]Mean values with different letters are significantly different (p<0.05).

3.4 Impact of deacidification on the pigments in high-acid olive oil

The colour of olive oil is mainly related to the presence of chlorophyll and carotenoid pigments, which are responsible for producing green and yellow coloration, respectively. Although olive oil colour is not included in the International Olive Council (2019) and in the European Economic Communities standards (1991), it plays an important role in consumer acceptance because visual appreciation is the first sensory impression of the product quality that consumers directly have an experience of (Nielsen et al., 1998). Figure 4 shows changes in chlorophyll and carotenoid pigments in HAOO treated with bamboo charcoal. The treatment led to a moderate loss of these pigments in HAOO, and the content of chlorophylls and carotenoids was reduced from 1.15 to 0.95 mg/kg·oil and from 0.91 to 0.79 mg/kg·oil, respectively. Thus, the treatment was not effective in bleaching chlorophylls and carotenoids in olive oil, resulting in retention of the appearance of olive oil.

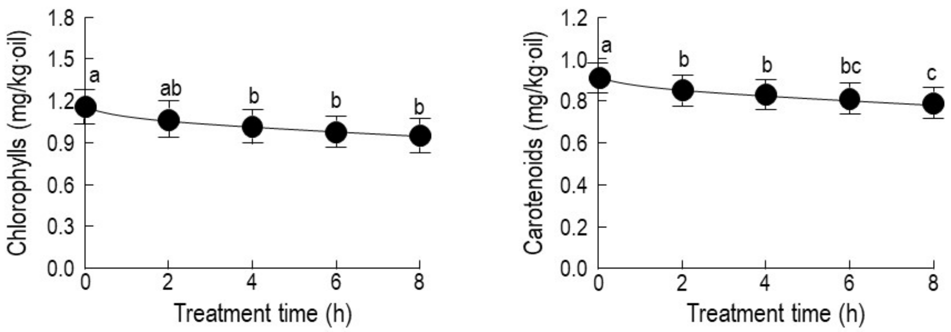

Figure 4: Changes in chlorophyll and carotenoid pigments in HAOO treated with bamboo charcoal. [a-c]Mean values with different letters are significantly different (p<0.05).

4. Conclusions

The results of this study demonstrate that the application of bamboo charcoal to the stirring method was effective in reducing the FFAs in HAOO. The most effective concentration of bamboo charcoal to be applied to HAOOs was also determined. In addition to the deacidification of HAOO, treatment with bamboo charcoal effectively reduced oxidative off-flavours such as hexanal. However, the treatment was not effective in varying the fatty acid composition (data not shown) and the subsequent bleaching of chlorophyll and carotenoid pigments in olive oil. These results suggest that bamboo charcoal, which is inexpensive and easily available, can be used as a good adsorbent to remove FFAs in olive oils without using any solvent and can enhance the economic value of degraded olive oil without having to change the appearance of the oil. In addition, bamboo charcoal can be an environmentally friendly and energy-efficient process and may reduce the process cost, leading to recovery of the economic value as the food product of older unsold olive oils and reducing their disposal. For future study, the dynamic adsorption studies will be developed in a packed-bed adsorption column filled with the charcoal and the data will be useful to design the real application column for deacidification of olive oil.

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