Impact of several physical treatments on the improvement of some quality parameters of crude olive oil

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In this study, fresh olive oil was exposed to oxidation followed by elution at room temperature through an adsorbent packed in the glass column (10 × 75 cm) loaded with one of the following beds: activated charcoal, calcium chloride ($CaCl_2$), alumina (Al_2O_3), bentonite, Arabic gum, and silica gel to investigate the effect of using adsorbents on the quality improvement of oxidised olive oil. The used ratio of adsorbent on oxidised olive oil was 1:5. The results show that the peroxide value (PV) of oxidised olive oil eluted through silica gel improved significantly by 22.6% (from 32.39 to 25.06 meq/kg) and for free fatty acids (FFA %) the improvement was 45.37% (from 1.675 to 0.915 %). The PV of eluted oxidised olive oil through Arabic gum and $CaCl_2$ was significantly improved by 45.08% and 25.65%, respectively and for FFAs (%) were 40.0% and 31.64%, respectively. Elution of oxidised olive oil through other adsorbents showed different results on FFA (%) and PV. Elution of oxidised olive oil through tested adsorbents exhibited a negative impact on the total phenolics and vitamin E contents. Different responses on specific absorption coefficient at 232, and 270 nm were observed for the eluted olive oil through used adsorbents.

Keywords: Adsorbent, Free fatty acids, Olive oil, Phenolic contents, Peroxide value, Vitamin E.

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INTRODUCTION

Virgin olive oil is the oil obtained from the olive fruit through manual and mechanical procedures without refining or being mixed with other oils or any substances. Olive (*Olea europaea*) oil is a fundamental component of the Jordanian and Mediterranean diet and there has been a significant increase in the consumption of such oil due to its nutritional and health-promoting effects and its association with the prevention of several diseases like cancer, heart disease, and aging by inhibiting the oxidative stress [1-3].

Olive oil has higher stability than other edible oils, due to its low content of polyunsaturated fatty acids (PUFA`s) and a higher content of monounsaturated fatty acids and is obtained solely through physical means by mechanical or direct pressing of the olives and not subjected to any treatment other than washing, decantation, centrifugation, and filtration, and may be consumed without refining [4, 5]. The International Olive Council [6] and Jordan Institution for Standards and Metrology [7] have designated the quality characteristics for each type of olive oil (Extra-virgin, virgin, regular…etc). However, some of these ascertained figures may increase and become incorrect during normal storage, due to hydrolysis, oxidation, polymerisation, and further oxidation reactions resulted from hydrolysed fatty acids and formation of primary and secondary oxidative products that cause quality deterioration of olive oil that could adversely affect human health and the quality of olive oil [8].

Although the refining process of crude olive oil can remove undesirable sub-

stances that affect the oil quality, the problem of seeping for some of the refined olive oil bioactive substances that contribute to the oil healthy and sensory properties may arise. Re-refining of used cooking seeds oil by different techniques like, supercritical extraction, membranes filtration and adsorbent treatments to improve its quality and safety have been studied and found to be the cheapest, efficient, and easiest methods using magnesite, silica gel, alumina, and different type of resins [9-10].

The aim of the current study is to investigate the effect of elution of oxidised olive oil through different adsorbents (silica gel, aluminium oxide, calcium chloride, activated bentonite, activated charcoal granular and Arabic gum) in the improvement of some of the quality characteristics of olives oil. The efficiency of partial refining of oxidised olive oil through elution from each adsorbent is judged by analysing free fatty acids, peroxide value, extinction coefficient at 232 and 270 nm, total phenolic contents, and vitamin E contents.

2. MATERIALS AND METHODS

2.1 CHEMICALS

Silica gel powder (60-200 mesh), Aluminium oxide (70-290 mesh), activated charcoal granular, calcium chloride, activated bentonite were purchased from LABCHEM chemicals (Zelienople, USA). Folin–Ciocalteu reagent and α-tocopherol acetate were purchased from AppliChem GmbH (Darmstadt, Germany). Methanol, Hexane, and diethyl ether (HPLC-grade) were purchased from ASTM Co., (USA). Potassium iodide (KI), chloroform, sodium hydroxide (NaOH) was purchased from SD Fine-Chem limited (UK). Sodium thiosulfate ($Na_2S_2O_{3)}$ was purchased from Brix worth (Northhants, UK). Arabic gum and other chemicals of reagent grade were purchased from local companies.

2.2 OLIVE OIL SAMPLE

Olive oil sample (30 Kg) was purchased from an olive oil refinery in the northern part of Jordan (Irbid-Jordan). The olive oil sample was obtained after a mechanical extraction of Nabali olive harvested from one of the farms after 5 days of olive harvesting in November 2020. Chemical quality tests for fresh olive oil were determined in triplicate.

2.3 OXIDATION INDUCTION OF OLIVE OIL

Ten kilograms of the freshly produced olive oil was placed in an open glass container with large surface area. The oil was left in open air at room temperature to expose it for the oxidation process using sunlight and oxygen for around one month. The olive oil free fatty acid (%) and peroxide value (PV) were measured routinely to check the oil oxidation every 5 days. After the oil becomes rancid (PV = 31.8 meq O_2/Kg) and free fatty acids increased (1.67%), a 500 gram was eluted from the oxidised olive oil at room temperature through an open glass column (10 × 75 cm) loaded with a matrix (~100 g) of one of the following adsorbents: silica gel, bentonite, Arabic gum, aluminium oxide, calcium chloride and activated granular charcoal. The elution time consumed for each adsorbent was recorded, followed by centrifugation (3000 rpm × 5 min) using Heraus Sepatech Megafuge 1.0 (Germany) and kept refrigerated in brown glass bottles for further analysis.

2.4 ALKALINITY OF ADSORBENTS AND IMPROVEMENT EFFECIENCY (%)

The alkalinity of each adsorbent was determined by direct titration with HCl using a phenolphthalein indicator. In brief, 5.0 g from each adsorbent was accurately weighted into a 250 ml Erlenmeyer flask, followed by addition of 100 ml of distilled water and the solution was swirled to dissolve the adsorbent. A few drops of phenolphthalein indicator 1% were added. Solution showed pink colour was titrated with 0.1N HCl solution until the colour turned from pink to being colourless. Alkalinity for pink positive colour adsorbent was calculated according to the following formula and expressed as NaOH (%):

$$\text{Alkalinity as NaOH (\%)} = \frac{(V1 - V2) \times N \times 40 \times 10}{\text{Adsorbent weight}}$$

Where:
V1 = Volume of HCl consumed by each adsorbent in ml
V2 = Volume of HCl consumed by the blank in ml
N = Normality of HCl
40 = The equivalent weight of Sodium hydroxide

The following formula was used to determine the efficiency of adsorbents in the improvement of measured quality parameters (%):

$$\text{Improvement efficiency (\%)} = \frac{\text{Value (before elution)} - \text{Value (after elution)}}{\text{Value (before elution)}} \times 100$$

2.5 DETERMINATION OF FREE FATTY ACIDS (%)

The acidity of olive oil was determined by the AOAC method [11]. In brief, 5.0 g of olive oil was accurately weighted into 250 Erlenmeyer flask, followed by an addition of 50 ml of equal mixture solution from ethanol: diethyl ether, the solution was swirled to dissolve the oil in the solvent. A few drops of phenolphthalein indicator 1% were added, and then the solution was titrated with 0.1N sodium hydroxide solution until the colour turned to a faint pink colour. Acidity was calculated according to the following formula and expressed as oleic acid (%):

$$\text{Acidity \%} = \frac{(V1 - V2) \times N \times 282}{10 \times \text{Sample weight}}$$

Where:
V1 = Volume of Sodium hydroxide consumed by each sample in ml
V2 = Volume of Sodium hydroxide consumed by the blank in ml
N = Normality of alkali
282 = The equivalent weight of oleic acid

2.6 DETERMINATION OF PEROXIDE VALUE

The peroxide value of olive oil was determined by AOAC method [11]. The PV was expressed in milliequivalents of oxygen per kg of oil (meq of O_2/kg). In brief, 5 grams of olive oil were taken into Erlenmeyer flask 250 ml and the sample was dissolved in a 30 ml of 3:2 acetic acid - chloroform solution and shaken for few second. Then 0.5 ml of freshly prepared saturated KI was added, and shaken again for 1 min, followed by an addition of 30 ml distilled water to stop the reaction. The mixture was slowly treated with 0.01 ($Na_2S_2O_3$) with vigorous shaking until the solution with starch indicator become colourless.
The peroxide value was calculated according to the following formula and the results were expressed as milliequivalents of oxygen per kilogram of oil (meq O_2/kg oil):

$$PV = \frac{(Vs\text{-}Vb) \times (N) \times 1000}{\text{Sample weight}}$$

Where:
Vs = Volume of sodium thiosulfate consumed by sample in ml
Vb = Volume of sodium thiosulfate consumed by the blank in ml
N = Normality of sodium thiosulfate.

2.7 DETERMINATION OF TOTAL PHENOLIC CONTENTS

The total phenol contents (TPC) of the fresh, oxidised and eluted olive oil were determined separately, by the Folin–Ciocalteau spectrophotometrically at 725 nm using Capannesi et al. [12]. A sample of olive oil 10 grams was weighted into a 250 ml Erlenmeyer flask followed by addition of 50 ml of hexane and was mixed vigorously, then the sample was transferred to separatory funnel and extracted with 80 ml methanol (80%) several times. One ml from the collected methanolic phase layers was placed into a 10 ml volumetric flask followed by addition of 5 ml of distilled water and 0.25 (2 N) Folin Ciocalteau and the solution was then mixed well for 3 min. After that 2 ml of Na_2CO_3 (17%) added and the flask was then filled with distilled water up to the mark. The absorbance for each sample was measured at 765 nm using a spectrophotometer (model UVD-2900, Labomed, USA). The total phenolic compound contents were expressed as a Gallic acid equivalent (mg GAE/100g) and determined from the following regression equation based on the established calibration curve of gallic acid: $Y = 0.0742X$, $r^2 = 0.9963$.
Where Y is the absorbance and X the Gallic acid concentration in mg/l. All measurements were done in triplicate.

2.8 DETERMINATION OF SPECIFIC EXTINCTION COEFFICIENT AT 232 AND 270 nm (K_{232} AND K_{270})

European Official Method of Analysis (Commission Regulation EEC N-2568/91 (1991)) was used for the determination of specific extinction coefficients of the olive oil samples [13]. In brief: 250 mg of olive oil was weighed into a 25 mL volumetric flask and diluted to 25 mL with hexane. The sample was homogenised using vortex for 30 seconds and then the resulting solution was taken into a quartz cuvette. Absorbance at 232 and 270 nm was determined in a spectrophotometer (model UVD-2900, Labomed, USA) using the hexane as the blank.

2.9 DETERMINATION OF VITAMIN E

Vitamin E content in fresh, oxidised, and eluted olive oil was determined according to Gimeno et al. [14] method with slight modification using RP-HPLC. In brief, 1 gram of olive was weighed into a 10 ml volumetric flask and diluted to 10 ml with hexane (1:10), thereafter, 200 µL of sample and hexane mixture was transferred to a screw-capped tube. Then 600 µL of methanol and 200 µL of the internal standard solution (300 µL/ml of α-tocopherol acetate in ethanol) were added. After that, they were mixed by vortex, and centrifuged (3000 rpm × 5 min) using heraus sepatech megafuge 1.0. model. Samples were then filtered through a 0.45 mm pore size filter and an aliquot of the overlay was directly injected into Knauer High Performance Liquid Chromatography (HPLC) system, equipped with ACE 5, C18, 250 × 4.6 mm column (Advanced Chromatography Technologies-Scotland), the injection volume was 50 µL. The mobile phase with methanol and elution was performed at a flow rate of 1.5 ml/min. The analytical column was kept at 30°C and detection was performed using UV detector at 280 nm. To determine the compounds in the samples, the working standard solutions were analysed together with the samples and peak-area ratios were used for calculations following the internal standard.

2.10 STATISTICAL ANALYSIS

Statistical calculations were performed using statistical analysis system, SAS program, 2000 (SAS Institute Inc., Cary, NC, USA) [15]. Significant and non-significant differences among means of treatments were determined using LSD test. Differences at $P<0.05$ were considered significant and $P>0.05$ were considered non-significant. All treatments were conducted in triplicate.

3. RESULTS AND DISCUSSION

3.1 FREE FATTY ACIDS (FFA %) AND ELUTION TIME

Olive oil has some elementary criterions that distinguish it from other oils. Olive fruits should be picked and processed directly to preserve the produced oil quality. The free fatty acid (%) is a measure of the

quality of the oil, and reflects the care taken in producing the oil and the quality of the in-coming fruit [16]. The fresh olive oil sample used in our experiment meets the criteria of virgin olive oil grade (acidity was 1.24%). During the intentional exposure of investigated olive oil to light, heat and air, free fatty acids were increased (1.24-1.67%), due to the presence of lipase enzymes that hydrolysis triacylglycerols which continue to occur in the oil. The presence of fatty acids also leads to the formation of more fatty acids in the oil; that act as a catalyst for the further production of free fatty acids. In general, hydrolysis resulted from the olive fruit damage, fruit quality, time, and temperature of the oil extraction from the fruit. This damage occurs prior to the oil being separated from the water and solid portions of the fruit [17]. Although the olive oil from chemical point of view was oxidised and its acidity increased, but the oxidised olive oil still considered as virgin oil according to IOC (FFA ≤ 2%) [6]. Thus, we can conclude that the oxidation of olive oil may not affect the grade of oil in terms of acidity in comparison with its peroxide value.

Table I shows the time consumed by each oxidised olive oil (500 g) to elute through each adsorbent from the open glass column and the effect of each adsorbent on the efficiency of the improvement in FFA (%). The elution time varied from several minutes to 7 hours. For example, the elution of oxidised olive oil through granular charcoal lasted 20 minutes, while for silica gel it lasted 7 hours. This variation in time consumed for elution may be due to the differences in the surface area of each adsorbent, pore structure, form and texture of the adsorbents used in this study. Also, the impurities in the eluted oil may be trapped in the pores of adsorbents due to different affinities resulting in different elution times [9].

All the used adsorbents were significantly effective in lowering FFA (%), except for activated charcoal (Tab. I). Silica gel achieved the highest efficiency in the reduction of FFA (%) from oxidised oil when compared to other adsorbents and could lower the FFA contents to about 45.4% due to its high polarity that may aid in the attraction of the polar contaminants, which attribute to the reduction of eluted olive oil acidity. This indicated that the use of silica gel as adsorbents potentially improved the oil quality and its application as active adsorbents in oil treatment showed less accumulation of FFA compared to the control. Our results are in agreement with previous report findings on using silica gel as an effective adsorbent in reducing the FFA content of re-refined cooking oils [9, 18].

The effectiveness of the elution of oxidised olive oils through several tested adsorbents in reducing FFA contents were in the following increasing order:

Silica gel > Arabic gum > Bentonite > Aluminium oxide > Calcium chloride > Charcoal.

The alkalinity of each adsorbent was measured to eliminate the possibility of free fatty acid neutralisation from adsorbents. Table I, also shows the alkalinity of used adsorbents. Alkalinity was observed only in bentonite (0.028%) and Aluminium oxide (0.25%). However, the found alkalinity percentage were insignificant for the neutralisation of the fatty acids in the eluted and oxidised olive oil.

The ability of Arabic gum to adsorb FFA from olive oil may be related to its ability to form hydrogen bonding with the FFA and it forms a hydrophobic interaction with hydrophobic group of these CHO products. The efficiency of bentonite in the reduction of FFA (%) was about 38% in comparison with the control sample. Bentonite usually used in vegetable oil production as bleaching agent. The improvement in FFA (%) reduction after elution of oxidised olive oil through bentonite may be due to its sorption capability which serves as a filter for the removal of FFA [15]. Calcium chloride ($CaCl_2$) reduces the FFA content by 31.6%, and this may be related to the reaction of FFA with calcium chloride to form calcium based saponified solids [20]. Alumina was efficient in the reduction of FFA content in oxidised olive oil by 32.2%. Alumina is useful for the separation of aldehydes, ketones, quinones, esters, lactones, and glucosides and effective in reducing the acid value of used cooking oil [9]. The FFA content did not change, significantly, from the control after elution through activated charcoal, thus charcoal is expected not to adsorb any of FFA from oxidised oil sample and could not improve the efficiency of the free fatty acid removal after elution.

Table I - Free fatty acid contents of oxidized olive oil after elution through several adsorbents, improvement efficiency (%), elution time and alkalinity (% NaOH) of adsorbents[a]

Treatment (Adsorbents)	FFA (%) after elution	Improvement efficiency (%)	Elution time	Alkalinity of adsorbents (NaOH %)
Control	1.675 ± 0.007 [a]	0.00	0.00	ND[b]
Charcoal	1.664 ± 0.014[a]	0.66	20 min	ND
Bentonite	1.025 ± 0.035[c]	38.80	6 hours	0.028
Silica gel	0.915 ± 0.007[d]	45.37	7 hours	ND
Arabic gum	1.005 ± 0.035[c]	40.00	50 min	ND
Aluminum oxide	1.135 ± 0.007[b]	32.24	3 hours	0.25
Calcium chloride	1.145 ± 0.014[b]	31.64	5 hours	ND

[a] Results are means of triplicate ± SD and results with the same letter are not significantly different. [b]ND: Not detected.

3.2 PEROXIDE VALUE

Peroxide value (PV) is used as an indicator of the early oxidation of oils (primary oxidation products) and measures the value of peroxides and hydroperoxides formed in the early phases of lipid oxidation. The Initial PVs of the fresh olive oil samples used in this experiment, before oxidation was 7.76 meq O_2/kg and within the permitted limit values established by IOC standards (≤ 20.0 meq O_2/kg). However, after the intentional oxidation induction of fresh olive oil, the level was increased above the permitted level (32.39 meq O_2/kg). After the elution of the oxidised olive oil through several adsorbents used in this experiment, the PV`s were varied and the efficiency of the used adsorbents in reducing PV is shown in Table II. Arabic gum, calcium chloride and silica gel, were shown to be the most effective in the reduction of peroxide levels by 45.08, 25.65 and 22.63%, respectively. The samples eluted through Arabic gum adsorbent resulted in the greatest improvement of PV reduction (45.08%) from 32.39 to 17.79 meq O_2/kg and this may suggest the application of Arabic gum as an adsorbent and filters for the removal of peroxide products in oxidised olive oil. Silica has excellent adsorption capacities at low relative humidity conditions, which explain its capability in decreasing PV in our experiment. In addition, silica can remove polar contaminants. Silica offers the greatest potential for the edible oil refining industry [21, 9]. McNeill et al. [18] studied the effect of different mixtures between activated carbon and silica to improve the quality of canola oil and found that the canola oil treated with mixed adsorbents were effective in lowering acid values, peroxide value, saturated and unsaturated carbonyl contents polar compounds and photometric colour than the control.

The PV content of oxidised olive oil after elution through activated charcoal or aluminium oxide did not change significantly from the control. The elution of oxidised oil through bentonite showed a negative impact on PV improvement.

3.3 TOTAL PHENOLIC CONTENTS

Table III shows the impact of elution of the oxidised olive oil through studied adsorbents on the total phenolic contents. Significant reduction in phenolic content was observed when silica gel and aluminium oxide used as adsorbent (55.87 and 50.64%, respectively). The effect of oxidised olive oil elution through studied adsorbents on phenolic content reduction was in the following decreasing order: Bentonite > Charcoal > Arabic Gum > Calcium Chloride > Aluminium Oxide > Silica Gel. The reduction in phenolic contents after treatments may be due to the bound of phenolic compounds in olive oil to the surface of adsorbent by Van der Waal's forces and the adsorption capacity resulted is directly related to the pore structure, contact time and surface area of the adsorbents. Our results indicated that using adsorbents resulted in reduction of total phenolic contents, which may negatively affect the shelf-life stability of olive oil. However, the use of Arabic gum or calcium chloride as adsorbents had a minor effect on the total phenolic content reduction and a higher effect on PV and FFA % improvement, thus suggesting their uses as effective adsorbents. Zogorski et al. [22] studied the kinetics of the adsorp-

Table II - Peroxide value (PV) (meq O_2/kg) of fresh olive oil (control) and oxidized olive oil after elution through several adsorbents and improvement efficiency (%)[a]

Treatment (Adsorbents)	PV (meq O_2/kg) (after elution)	Improvement efficiency in PV (%)
Control	32.39 ± 0.86^{bc}	0.00
Charcoal	32.37 ± 0.56 ^{ab}	0.06
Bentonite	33.55 ± 0.35 ^{a}	- 3.58
Silica gel	25.06 ± 0.16^{d}	22.63
Arabic gum	17.79 ± 0.41^{g}	45.08
Aluminum oxide	32.35 ± 0.38 ^{ab}	0.12
Calcium chloride	24.11 ± 0.48^{d}	25.65

[a] Results are means of triplicate ± SD and results with the same letter are not significantly different

Table III - Total phenolic content (TPC) (mg GAE/Kg) of fresh olive oil (control) and oxidized olive oil after elution through several adsorbents and TPC reduction (%)[a]

Treatment (Adsorbents)	TPC (mg GAE/Kg) after elution	Reduction in TPC (%)
Control	101.40 ± 0.28^{a}	0.00
Charcoal	89.60 ± 0.56^{b}	11.64
Bentonite	91.10 ± 1.69^{b}	10.16
Silica gel	44.75 ± 0.77^{e}	55.87
Arabic gum	89.40 ± 0.56^{b}	11.83
Aluminum oxide	50.05 ± 0.77^{d}	50.64
Calcium chloride	86.90 ± 0.56^{c}	14.30

[a] Results are means of triplicate ± SD and results with the same letter are not significantly different

tion of phenols on granular activated carbon. They observed that 60% to 80% of the adsorption occurs within the first hour of contact followed by a very slow approach to the final maximum equilibrium concentration.
The main phenolic compound of olive fruit is oleuropein and polyphenols correlate with key sensory oil properties: bitterness and pungency that are associated with olive oil style [23]. Olive oil classification as mild, medium, or robust can be associated to the total phenol content. The total phenolic content of virgin olive oil expressed as Gallic acid equivalent (GAE) ranges from 50 to 800 mg/kg [24].
In this study, the total concentration of polyphenols for the fresh sample of olive oil was 101.4 mg Gallic acid equivalent /kg, which are within the range stated by IOC of virgin olive oil. Thus, the elution through used adsorbent may negatively affected the sensory properties of the resulting olive oil, but the level of phenolic after elution is still within the range of accepted figures for virgin olive oil, except for the silica gel adsorbent (44.8 mg GAE/Kg).

3.4 VITAMIN E

The concentrations of α-tocopherols in olive oil varied from traces to 25 ppm [25]. Results in Table IV show that vitamin E content in control olive sample was 34.45 ppm and decreased significantly after the elution of oxidised olive oil through several adsorbents due to the adsorption of tocopherols in the used adsorbents. The vitamin E loss were in the following increasing order: Control (0.0%) > Charcoal (36.6%) > Silica Gel (49.6%) > Arabic Gum (64.4%) > Calcium Chloride (66.7%) > Bentonite = Aluminium Oxide (69.9%). Four different types of tocopherols, namely α-, β-, γ- and δ-tocopherol have been reported in olive oil. Tocopherols are sensitive to light and heat; thus, we performed the experiment in a very protective environment to prevent its partial degradation; however, losses of tocopherols even in protective olive oil, such as darkness and high nitrogen during saponification, may have resulted [26]. Tocopherols are the most important lipid soluble natural antioxidants, which prevent lipid peroxidation by scavenging radicals in membranes and lipoprotein particles [27]. Results indicates a huge loss of this vitamin upon the use of any adsorbents for the partial refining of olive oil due to its adsorption in used filters.

3.5 SPECIFIC ABSORPTION COEFFICIENTS (K_{232} AND K_{270})

The absorbance at K_{232} nm, and K_{270} nm may correlate with the state of oxidation alteration (primary and secondary oxidation), adulteration of crude olive oil with refined oils and reflects the stage of oxidation for olive oil during storage by the increase in the K_{232} absorption coefficient. More specifically, in 232 nm primary oxidation products show absorption (conjugated peroxides) and in 270 nm secondary oxidation products show absorption (aldehydes and ketones) [28].
In this study, the extinction coefficient K_{232} of oxidised olive oil after elution through adsorbents increased significantly from that of the control (1.41), except with silica gel, bentonite, and aluminium oxide (Tab. V). Elution through silica gel was the best and could improve the oxidised oil quality by 15.36%, while elution through charcoal decreased the oxidised oil quality (7.21%). Different responses were recorded for the extinction coefficient measured at 232 nm and 270 nm (K_{232} and K_{270}) after elution of oxidised olive oil through adsorbents. Significant reduction in secondary products at K_{270} was the most after elution of oxidised oil through silica gel (73%). Our results agree with previous reports showing that synthetic silica compounds have greater selectivity for the adsorption of secondary oxidation compounds and reduce the conjugated diene [9, 29] However, aluminium oxide, bentonite and calcium chloride also showed pronounced improvement in K_{270} (Tab V).
Increase in K_{232} and K_{270} values is very common between the extraction and consumption of olive oil. These values are also affected by storage time and conditions. Such an increase is due to the degradation of primary oxidation products (peroxides) to form secondary oxidation products such as aldehyde and ketone. K_{232} representing the number of conjugated dienes of the primary oxidation products and are transformed to triene measured by K_{270} [30].

Table IV - Vitamin E content (mg/Kg) of fresh olive oil (control) and oxidized olive oil after elution through several adsorbents and reduction in vitamin E (%)[a]

Treatment (Adsorbents)	Vitamin E (mg/Kg) (after elution)	Reduction in Vitamin E (%)
Control	34.45 ± 0.49[a]	0.00
Charcoal	21.82 ± 0.38[b]	36.66
Bentonite	10.36 ± 0.41[f]	69.93
Silica gel	17.36 ± 0.79[c]	49.61
Arabic gum	12.26 ± 0.64[d]	64.41
Aluminum oxide	10.36 ± 0.13[f]	69.93
Calcium chloride	11.38 ± 0.60[e]	66.69

[a] Results are means of triplicate ± SD and results with the same letter are not significantly different.

Table V - Extinction Coefficient at 232 and 270 nm of fresh olive oil (control) and oxidized olive oil after elution through several adsorbents and improvement efficiency (%)[a]

Treatment (Adsorbents)	K_{232} (after elution)	Improvement efficiency (%) in K_{232}	K_{270} (after elution)	Improvement efficiency (%) in K_{270}
Control	1.595 ± 0.024[d]	0.00	0.260 ± 0.007[b]	0.00
Charcoal	1.710 ± 0.002[a]	- 7.21	0.240 ± 0.002[d]	7.70
Bentonite	1.580 ± 0.004[e]	0.94	0.220 ± 0.003[e]	15.38
Silica gel	1.350 ± 0.001[f]	15.36	0.070 ± 0.001[g]	73.08
Arabic gum	1.630 ± 0.005[c]	- 2.19	0.280 ± 0.009 [a]	- 7.70
Aluminum oxide	1.580 ± 0.008[e]	0.94	0.230 ± 0.004[d]	11.54
Calcium chloride	1.660 ± 0.019[b]	- 4.08	0.180 ± 0.002[f]	30.77

[a] Results are means of triplicate ± SD and results with the same letter are not significantly different

CONCLUSIONS

In this work, the specific impact of using several natural adsorbents to improve some of the oxidised olive oil quality characteristic like PV, FFA, K_{232} and K_{270} was comprehensively investigated to improve the shelf life and stability of olive oil. The results may suggest the use of the granular form of Arabic gum or silica gel or calcium chloride during the malaxation stage or after the final centrifugation step in olive oil production to improve some quality parameters of produced olive oil. Despite the loss of some of the active compounds in oil (vitamin E and phenolic compounds) due to the use of adsorbents, the impact of adsorbent usage during olive oil production still has an advantage. The effect of coating adsorbents on immobilised glass beads to improve some of negative results obtained from this research and how they interact with the olive oil elution time, phenolics and vitamin E contents, smoking points and GC-MS analysis of volatiles are under investigation.

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