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Combined Effect of Potassium Permanganate and Ultraviolet Light as Ethylene Scavengers on Post-Harvest Quality of Peach at Optimal and Stressful Temperatures

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Abstract: The aim of this study was to evaluate the combination of two ethylene removal methods and temperature on the post-harvest quality of peaches. For this purpose, filters with potassium permanganate ($KMnO_4$) and lamps emitting ultraviolet light (UV) were mounted on machines which enabled air movement in the conservation chambers, facilitating the removal of ethylene by $KMnO_4$ and photocatalysis simultaneously. This system was used at two temperatures, 1 °C and 25 °C, simulating an ideal storage temperature in industry and extreme temperature to observe faster ripening, respectively. The results obtained showed that this combination of ethylene scavengers favoured the efficient elimination of this gas. Consequently, the use of this innovative technique made possible a better preservation of fruit firmness, colour, soluble solids content, pH, total acidity, and maturity index. Moreover, using this method in peaches subjected to 25 °C increased their survival by seven days more than those without this system, indicating the effectiveness of ethylene scavengers even under these extreme temperatures.

Keywords: climacteric fruit; ethylene scavengers; fruit quality; potassium permanganate; *Prunus persica*; UV radiation

1. Introduction

The nutritional and organoleptic quality, and the shelf-life characteristics of peaches [*Prunus persica* (L.) Batsch] are affected by the interaction of multiple factors. Fruit quality cannot be improved during post-harvest, but it can be maintained through the application of innovative conservation techniques [1–3]. Apart from the crucial control of the optimal storage temperature, ethylene concentration is one of the most important parameters during post-harvest conservation of climacteric fruit. Ethylene (C_2H_4) is a phytohormone that, even in low concentrations, can produce undesirable changes in physical and chemical parameters in fruits, such as changes in firmness, colour, pH, or maturity index [4–7]. Therefore, limiting its presence has proven to be an economically and commercially key process for avoiding post-harvest losses and food wastage. Moreover, ethylene removal technology could guarantee the safety and maintenance of fruit qualities for an increasingly demanding consumer market [8–11].

Many methods exist for the elimination of this phytohormone, with the non-intrusive being more common, characterized by not coming into direct contact with the fruit [12–14]. The two most effective non-intrusive preservation methods include the use of palladium

and potassium permanganate ($KMnO_4$) as ethylene oxidants [9]. The first has the disadvantage of being more expensive; therefore, the oxidation of ethylene using $KMnO_4$ is the most suitable method in terms of cost-effectiveness [12]. This process of ethylene removal is based on an oxidation-reduction process, as $KMnO_4$ is a strong oxidizing agent that promotes the rapid dissociation of ethylene into carbon dioxide, manganese dioxide, and potassium hydroxide [15]. This process is activated by ethylene released by the climacteric fruit as a result of its natural metabolism. $KMnO_4$ undergoes a colour change from violet to dark brown when it is saturated, confirming the elimination of ethylene during the reaction [7,13]. To support this process, this hyperoxidant molecule is introduced into porous materials with high adsorption power, such as zeolite, sepiolite, vermiculite, alumina, or activated carbon [16]. These materials are widely used in sachets placed in boxes during the transport of fruit [17].

Another non-invasive method for ethylene removal is photocatalysis using ultraviolet light (UV), a low-cost and environmentally friendly technology that can be used to degrade a variety of aqueous and gas-phase pollutants [5,18]. Ethylene photo-degradation induced by radiation of UV light generates oxidizing agents, including hydroxyl radical (OH•) as reactive oxygen species (ROS), which are highly reactive and convert ethylene into CO_2 and H_2O [12,19] supporting $KMnO_4$ action. Although the mechanism of photocatalytic oxidation has been elucidated previously [5,13], the exact reaction mechanism still remains under debate owing to the presence of various reaction intermediates which have not been clarified completely [9].

The aim of this study was to evaluate the combined effect of two different ethylene removal methods, such as oxidation by potassium permanganate and photocatalysis by UV light, on the post-harvest quality of peaches stored at two different temperatures (1 °C and 25 °C). The study covered a period of 24 days of storage with measurements of physical parameters, such as weight, size, firmness, or colour, and measurements of biochemical parameters related to maturity, such as soluble solids content, pH, titratable acidity, maturity index, and microbiological incidence.

2. Materials and Methods

2.1. Plant Material

Forty kilograms of peaches of the yellow flesh Rojo de Rito variety were supplied by Thader Cieza, S.C.L. (Cieza, Murcia, Spain) through the intermediation of the agrarian cooperative FECOAM ("Federación de Cooperativas Agrarias de Murcia"). The fruit were harvested manually and maintained in refrigerated conditions (1 °C) for two days until the start of the trial. All peaches selected had a homogenous weight, size and colour. The harvesting indices forecast by the supplying company were as follows:

- Weight: 179.5 ± 2.2 g
- Size: 72.0 ± 2 mm
- Firmness: 30.2 ± 1.6 N
- Soluble solids content (SSC): 10.9%
- Total acidity (TA): 3.8%
- Ratio SSC/TA (MI): 2.86

2.2. Experimental Design

A total of 250 peaches were randomly distributed into four conservation chambers (CCs) that were 150 litres in volume (Eurofred Cool Head RCG200, Eurofred S.A., Barcelona, Catalonia, Spain).

As a first factor, the filters for ethylene removal were composed of $KMnO_4$ anchored into the active centre of sepiolite. The composition of the filters in terms of granulometry and other adsorbent substances was patented in Spain by the company "Nuevas Tecnologías Agroalimentarias (KEEPCOOL)" (Molina de Segura, Murcia, Spain), patent No. 2548787 (2016). The adsorbent material was covered by a semi-permeable paper, which allowed the entry of air rich in ethylene and the output of air clean of this phytohormone,

while also avoiding the entry of water or other particles into the filter. Potassium permanganate filters were installed inside an air-flow-forcing machine (M-CAM 50, KEEPCOOL, Molina de Segura, Murcia, Spain) to ensure appropriate movement of the air inside the CCs and to support ethylene removal. The machine incorporated a photocatalytic ultraviolet light system (TUV 254 nm, Philips, Amsterdam, Netherland) to aid the potassium permanganate filters in the removal of ethylene. The ultraviolet light was focused on the air coming out of the filters, not on the fruit. Throughout the article, the machine, UV light and filter combination will be referred to as the ethylene scavenger (ES).

As a second factor, two different temperatures were analysed: refrigeration temperature set at 1 °C and room temperature of approximately 25 °C for non-refrigerated treatments. Taking into account the combination of the two factors, the following four treatments were established:

- NoES-R (control): No Ethylene Scavenger + Refrigeration temperature.
- ES-R: Ethylene Scavenger + Refrigeration temperature.
- NoES-NoR: No Ethylene Scavenger + No Refrigeration temperature.
- ES-NoR: Ethylene Scavenger + No Refrigeration temperature.

2.3. Conservation Chambers Atmosphere

The CCs' temperature and relative humidity (RH) were registered with a Testo 184 H1 Data Logger, (Titisee-Neustadt, Baden-Württemberg, Germany).

The ethylene (C_2H_4), carbon dioxide (CO_2), and oxygen (O_2) concentration of the four CCs was monitored daily using a gas analyzer (Felix Three F-950, Felix Instruments, Camas, WA, USA). To carry out the gas measurements, the CCs were equipped with a hermetically sealed probe in order not to disturb the atmosphere, through which the necessary amount of air used by the gas analyzer mentioned above could be extracted. C_2H_4 and CO_2 were finally expressed as $mL \times kg^{-1} \times h^{-1}$, to compare the concentrations of the two gases. The O_2 was expressed as a percentage. The initial measurement at day 0 was taken 6 h after receipt of the product.

2.4. Physical Parameters

The weight was measured using a precision balance (Gram RZ, Gram Group, L'Hospitalet de Llobregat, Catalonia, Spain), expressed in grams. The size of the peaches, according to their equatorial diameter, was measured with a caliper (Wurth vernier caliper, Baden-Württemberg, Germany) and expressed in millimetres.

Pulp colour was determined in the layer of flesh immediately under the skin (2 mm) with the CIELAB system using a colorimeter (Hunterlab Colorflex EZ, Hunterlab Reston, VA, USA), with the measurements performed in two different places on the non-blushed side. Coordinate (a*) in the CIELAB system indicates the colour's position between green and red (negative values indicate green, positive values indicate red), and coordinate (b*) indicates the colour's position between blue and yellow (negative values indicate blue, positive values indicate yellow)

The firmness of the peaches was measured in the equatorial zone, away from the suture, with a CT3 texturometer (AMETEK Brookfield, Middleboro, MA, USA) equipped with a cylindrical probe measuring 35 mm in height and 6 mm in diameter, which penetrated 10 mm at a speed of $0.5 \text{ mm} \times s^{-1}$. Peach firmness was considered as the maximum force (N) measured during probe penetration.

All physical parameters were measured at the following storage days: 0, 3, 7, 10, 14, 17, 22 and 24. Seven peaches per treatment were used for each of above-mentioned days of analysis.

2.5. Maturity Parameters

Soluble solid content (SSC), pH, and titratable acidity (TA) were measured on fruit samples using the method adapted from [20].

Twenty grams of peach were taken and added to 20 mL of distilled water, then homogenized with a mixer (Ultra turrax T25, LabWare Wilmington, DE, USA) for 30 s. The homogenate was centrifuged at $3600 \times g$ for 10 min in a centrifuge (Eppendorf Centrifuge 5810, Hamburg, Germany) and the supernatant was used to obtain SSC, pH, and TA.

The SSC was determined by a manual refractometer (Atago Manual master-α, Atago Tokyo, Japan) at 20 °C and expressed as a percentage (sugar equivalents in $g \times 100 \, g^{-1}$). The pH was determined with a pH-meter (HI 2221, Hanna Instruments Eibar, Gipuzkoa, Spain).

The determination of TA was carried out by adapting the method described by [20]. For this, 20 g of fresh peach were weighed and brought to a volume of 100 mL with deionized water; the resulting mixture was titrated to a pH of 8.1 ± 0.1 with NaOH 0.1 N and constant stirring. The percentage of acid in the sample was calculated and expressed as a percentage according to [4].

The maturity index (MI) was determined by dividing SSC (%) by TA (%). The expression of this parameter is dimensionless.

All maturity parameters were measured at the following storage days: 0, 3, 7, 10, 14, 17, 22 and 24. Seven peaches per treatment were used for each of above-mentioned days of analysis.

2.6. Microbiological Incidence

Microbiological incidence was estimated by visual inspection on each fruit according to [4]. Any peaches showing any fungal or bacterial growth were considered infected and discarded. Data were expressed as the percentage of peaches affected.

2.7. Statistical Analysis

The descriptive statistics (mean and standard error of the mean [SEM]) and the different tests described below were performed using the StatGraphics Centurion XV software package (StatPoint Technologies, Inc. Warrenton, VA, USA). The Shapiro–Wilk test was performed to check the normality of the data. In addition, to check the homogeneity of the variance, Bartlett's test was applied. The data were analysed using an analysis of variance (two-way ANOVA), as four independent treatments and two factors were available (3 and 7 days). Next, the data were processed using an analysis of variance (one-way ANOVA) when the three independent treatments were available (10 and 14 days) and for all figures. Next, a t-test was performed when only two independent treatments were available (17, 22 and 24 days). Finally, Tukey's Multiple Range Test was utilized to separate means and detect significant differences (p-value < 0.05).

3. Results and Discussion

Due to the temperature conditions and ethylene concentration, not all the treatments could be analysed towards the end of the trial. As will be observed in the following tables and figures, no analyses were carried out in NoES-NoR from day 7 of the trial and in ES-NoR from day 14 until the end of the study. This was due to the losses in these treatments caused by ripening, rotting or microbiological damage.

3.1. Changes in the Conservation Chambers Atmosphere

The peach is a climacteric fruit, which means that its ripening process continues once harvested, being highly affected by the presence or absence of ethylene. Climacteric fruits increase the production of ethylene during post-harvest ripening, being the gas responsible for the coordination of the ripening process. The increase in ethylene production is promoted by the same gas during ripening and is associated with an increase in the respiration rate of the peach. It is therefore important to keep the ethylene rate at a low level in order to better preserve the quality of the fruit.

The temperature was set at 1 ± 1 °C for treatments kept refrigerated (NoES-R and ES-R), and at 25 ± 1 °C for treatments kept at room temperature (NoES-NoR and ES-NoR). Regarding relative humidity (RH), both refrigerated treatments showed values close to

80%, and in the non-refrigerated treatments RH values were close to 100%. The evolution of the concentration of the gases throughout the storage time is shown in Figure 1.
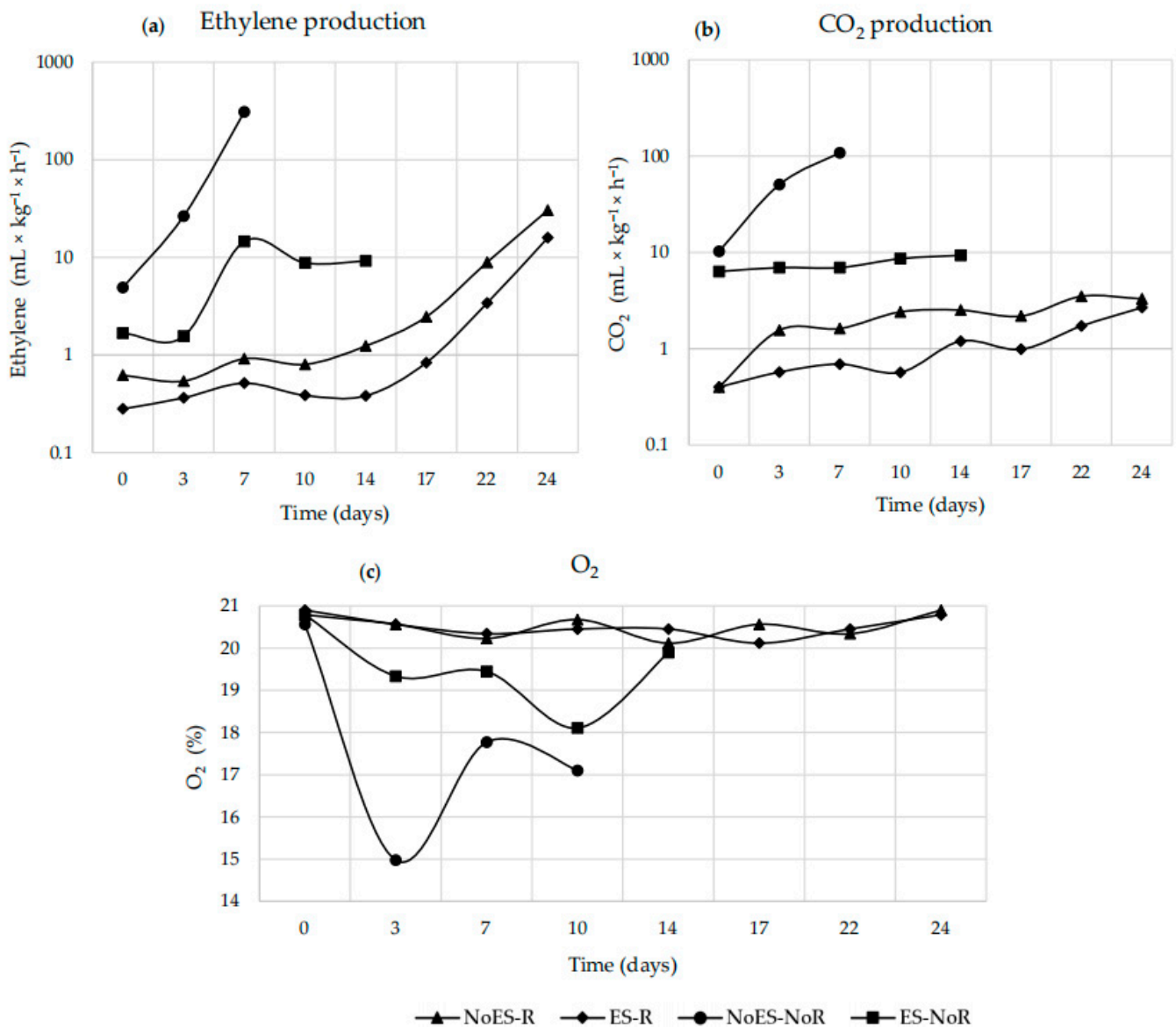
Figure 1. Ethylene (**a**) and CO_2 (**b**) production expressed as mL $\times$ kg^{-1} $\times$ h^{-1} and O_2 percentage (**c**) over the storage time in peaches subjected to the different treatments (NoES-R, ES-R, NoES-NoR and ES-NoR). The y-axis in Figure 1a,b corresponding to ethylene and CO_2 production, respectively, are displayed on a base 10 logarithmic scale.

3.1.1. Ethylene

When comparing the evolution of the ethylene production rate of the four treatments over time, the following conclusions can be drawn: for refrigerated conditions, ethylene scavengers were able to remove, between day 0 and 24, a mean of 52% of the total ethylene produced in ES-R (3.11 mL $\times$ kg^{-1} $\times$ h^{-1}), compared to NoES-R (6.47 mL $\times$ kg^{-1} $\times$ h^{-1}). The differences found between NoES-R and ES-R suggest a key role of the ethylene scavengers, which markedly decreased the rates of this phytohormone in ES-R. For the non-refrigerated conditions, ethylene scavengers were able to remove 95%, by mean between days 0 and 24, of the total ethylene production in ES-NoR (8.53 mL $\times$ kg^{-1} $\times$ h^{-1}), compared to NoES-NoR (168.24 mL $\times$ kg^{-1} $\times$ h^{-1}). It is worth mentioning that the ethylene levels of the samples preserved with scavengers shown in this study are lower than in other

studies, due to the combination of ethylene removal systems (potassium permanganate and photocatalysis).

3.1.2. Carbon Dioxide

Comparing the evolution in the CO_2 production rate among different treatments, the following findings can be highlighted: ES-R, with 1.20 mL $\times$ kg^{-1} $\times$ h^{-1}, showed an average decrease of 51% in CO_2 production between days 0 and 24, compared to NoES-R with 2.44 mL $\times$ kg^{-1} $\times$ h^{-1}; ES-NoR, with 7.96 mL $\times$ kg^{-1} $\times$ h^{-1}, had an average decrease of 90% in CO_2 production between days 0 and 24, compared to NoES-NoR with 79.21 mL $\times$ kg^{-1} $\times$ h^{-1} (Figure 1b). Therefore, it can be concluded that the use of ethylene scavengers decreased the CO_2 production rate (Figure 1b), thereby delaying the ripening of peaches. Similar to the results described above, some authors showed how the respiration rate in melons could be delayed by limiting ethylene levels in the first days of the trial, which in turn decreased CO_2 concentration [21].

3.1.3. Oxygen

The oxygen consumption of the fruit also proved to be relevant in the analysis of the activity of peaches (Figure 1c). The absence of an optimal oxygen percentage in combination with a high temperature and an elevated ethylene concentration led to the activation of a hypothetical internal fermentation metabolic process in NoES-NoR, where oxygen concentrations close to 16% were observed (Figure 1c). Although no hypothetical fermentation processes were observed in ES-NoR, oxygen concentrations were below 20%. Oxygen concentrations in the refrigerated treatments (NoES-R and ES-R) were close to 21%, which is the optimal concentration value in the atmosphere (Figure 1c).

3.1.4. Relationship between Ethylene and CO_2

Considering Figure 1a,b, a relationship between both gases can be observed. A reduction in CO_2 production was observed in the treatments where ethylene scavenging techniques were used (ES-R and ES-NoR). This is in agreement with existing literature [9,19,21]. The authors of [8] also reported the effect of ethylene scavengers on the preservation of apple fruit, where a reduction in CO_2 production was observed in the samples with low ethylene concentration.

More specifically, there was a positive correlation between them, as shown by a sudden increase in ethylene concentration preceding a sudden rise in CO_2 production [4]. These changes in both gases contributed to an increase in the respiration rate, which led to an autocatalytic effect that accelerated the maturation of the product [7,12,22]. This was particularly evident in the NoES-NoR treatment, where the peach preservation conditions were stressful, favouring an increase in ethylene levels due to the absence of ethylene scavengers, and in CO_2 concentrations, due to a higher respiratory rate associated with high temperatures.

3.2. Physical Parameters

Fruit weight is an important parameter for fruit producers, especially from an economic point of view, and therefore controlling fruit weight loss is crucial. This loss is associated with an excessive loss of water due to transpiration, related to a low RH. Water loss after harvesting is an unavoidable phenomenon, the effects of which are loss of weight, decrease in size, wilting, abnormal textures, and decrease in quality. Wilting becomes visible when the peach has lost 5% of its initial weight. The dehydration of peaches can be prevented by maintaining a high RH (90–95%) in the environment, while maintaining control of the air speed and protection with physical or chemical barriers [16,23]. Moreover, many authors have described the weight-conserving effect of ethylene removal on different fruits, such as peaches, kiwifruits, apricots, melons or tomatoes [9–11,13,21,22]. Two different behaviours can be clearly distinguished in our weight loss data (Table 1 and Figure 2a). On the one hand, the NoES-R, ES-R, and ES-NoR treatments showed a

continuous weight loss observed from day 3 of measurement until day 14 in ES-NoR, and until day 24 in NoES-R and ES-R. It should be noted that weight loss in the refrigerated treatments (NoES-R and ES-R) was associated with low RH (around 80%). However, the weight loss observed in ES-NoR was not associated with the RH (it was close to 100%), but was due to the high temperatures and to a certain availability of O_2, which favours fruit respiration. In contrast, the NoES-NoR treatment did not show weight loss until day 7, the last day of measurement. In NoES-NoR, the individual effect of the factors, and their interaction ($p < 0.001$), implies that the progressive accumulation of ethylene and the high temperatures led to an accelerated respiration in the peaches. This resulted in a higher CO_2 accumulation which, combined with ethylene, caused an excessive decrease in available O_2 in the CC, blocking respiration and favouring fermentation processes that did not affect weight loss.

Table 1. Evolution during storage time of the physical parameters in peaches subjected to the different treatments (NoES-R, ES-R, NoES-NoR and ES-NoR). The parameters measured were weight expressed in grams; size expressed in millimetres; firmness measured in newtons; and two-colour parameters a* and b*. The mean ± standard error of the means (SEM) is shown. Different letters for each treatment represent statistically significant differences according to Tukey's test.

Storage Days	Treatment	Weight (g)	Size (mm)	Firmness (N)	Colour (a*)	Colour (b*)
0		170.4 ± 2.1	70 ± 2	25.9 ± 2.6	19.2 ± 0.7	59.7 ± 0.9
3	NoES-R	163.7 ± 2.4 a	64 ± 2 b	22.6 ± 1.4 ab	17.9 ± 1.5 ab	60.5 ± 1.4 a
	ES-R	162.2 ± 1.6 a	67 ± 2 ab	27.9 ± 1.6 a	15.8 ± 1.1 b	60.7 ± 0.7 a
	NoES-NoR	167.9 ± 6.9 a	70 ± 1 a	13.7 ± 1.1 c	21.3 ± 1.3 a	56.2 ± 1.5 b
	ES-NoR	158.1 ± 3.4 a	64 ± 1 b	17.6 ± 1.4 bc	19.3 ± 0.8 ab	57.9 ± 1.1 ab
	Ethylene Scavengers (ES)	n.s.	n.s.	***	n.s.	n.s.
	Temperature (T)	n.s.	n.s.	***	**	**
	ES × T	n.s.	*	n.s.	n.s.	n.s.
7	NoES-R	144.8 ± 3.4 b	64 ± 2 a	22.2 ± 2.2 ab	20.5 ± 0.8 b	59.1 ± 1.0 ab
	ES-R	150.7 ± 0.6 b	66 ± 2 a	26.0 ± 0.6 a	19.8 ± 0.9 bc	60.9 ± 2.1 a
	NoES-NoR	172.6 ± 0.0 a	68 ± 1 a	11.9 ± 0.5 c	26.7 ± 0.5 a	53.6 ± 0.8 c
	ES-NoR	145.5 ± 1.7 b	65 ± 1 a	16.8 ± 2.1 bc	27.2 ± 1.4 a	54.2 ± 1.1 bc
	Ethylene Scavengers (ES)	***	n.s.	***	***	n.s.
	Temperature (T)	***	n.s.	**	n.s.	***
	ES × T	***	n.s.	n.s.	***	n.s.
10	NoES-R	142.0 ± 2.2 a	62 ± 2 a	23.9 ± 2.2 a	19.1 ± 0.9 b	61.0 ± 1.3 a
	ES-R	131.1 ± 2.7 b	66 ± 1 a	21.3 ± 1.1 a	18.4 ± 1.1 b	62.8 ± 0.8 a
	NoES-NoR	-	-	-	-	-
	ES-NoR	135.0 ± 3.1 ab	66 ± 1 a	18.3 ± 1.6 a	32.0 ± 0.8 a	47.8 ± 0.3 b
	One-way ANOVA	*	n.s.	n.s.	***	***
14	NoES-R	131.1 ± 3.7 a	66 ± 2 a	17.3 ± 1.5 a	20.8 ± 1.2 b	55.6 ± 2.4 a
	ES-R	115.8 ± 2.8 b	65 ± 2 a	15.7 ± 1.3 a	18.1 ± 1.0 b	58.6 ± 3.0 a
	NoES-NoR	-	-	-	-	-
	ES-NoR	120.8 ± 0.0 ab	63 ± 1 a	14.3 ± 1.2 a	32.7 ± 0.7 a	44.3 ± 1.3 b
	One-way ANOVA	*	n.s.	n.s.	***	***
17	NoES-R	114.7 ± 2.3 a	61 ± 1 a	20.3 ± 2.3 a	21.4 ± 1.2 a	50.0 ± 2.9 b
	ES-R	105.7 ± 1.6 b	61 ± 1 a	15.0 ± 2.9 a	18.3 ± 0.8 b	59.8 ± 1.5 a
	NoES-NoR	-	-	-	-	-
	ES-NoR	-	-	-	-	-
	t-test	*	n.s.	n.s.	*	**
22	NoES-R	96.7 ± 3.7 a	57 ± 1 a	12.1 ± 2.0 a	21.1 ± 0.5 a	53.0 ± 1.7 a
	ES-R	90.8 ± 3.1 a	60 ± 2 a	14.5 ± 1.8 a	19.1 ± 0.5 b	51.5 ± 2.7 a
	NoES-NoR	-	-	-	-	-
	ES-NoR	-	-	-	-	-
	t-test	n.s.	n.s.	n.s.	**	n.s.
24	NoES-R	84.3 ± 2.6 a	55 ± 2 a	11.8 ± 0.93 a	18.0 ± 0.3 a	47.4 ± 2.0 a
	ES-R	82.2 ± 2.7 a	58 ± 2 a	12.4 ± 2.1 a	19.7 ± 1.0 a	52.1 ± 2.9 a
	NoES-NoR	-	-	-	-	-
	ES-NoR	-	-	-	-	-
	t-test	n.s.	n.s.	n.s.	n.s.	n.s.

Levels of statistical significance are: * $p < 0.05$, ** $p < 0.01$ and *** $p < 0.001$. n.s.: no significant differences. Different letters for each treatment represent statistically significant differences ($p < 0.05$) according to Tukey's test.
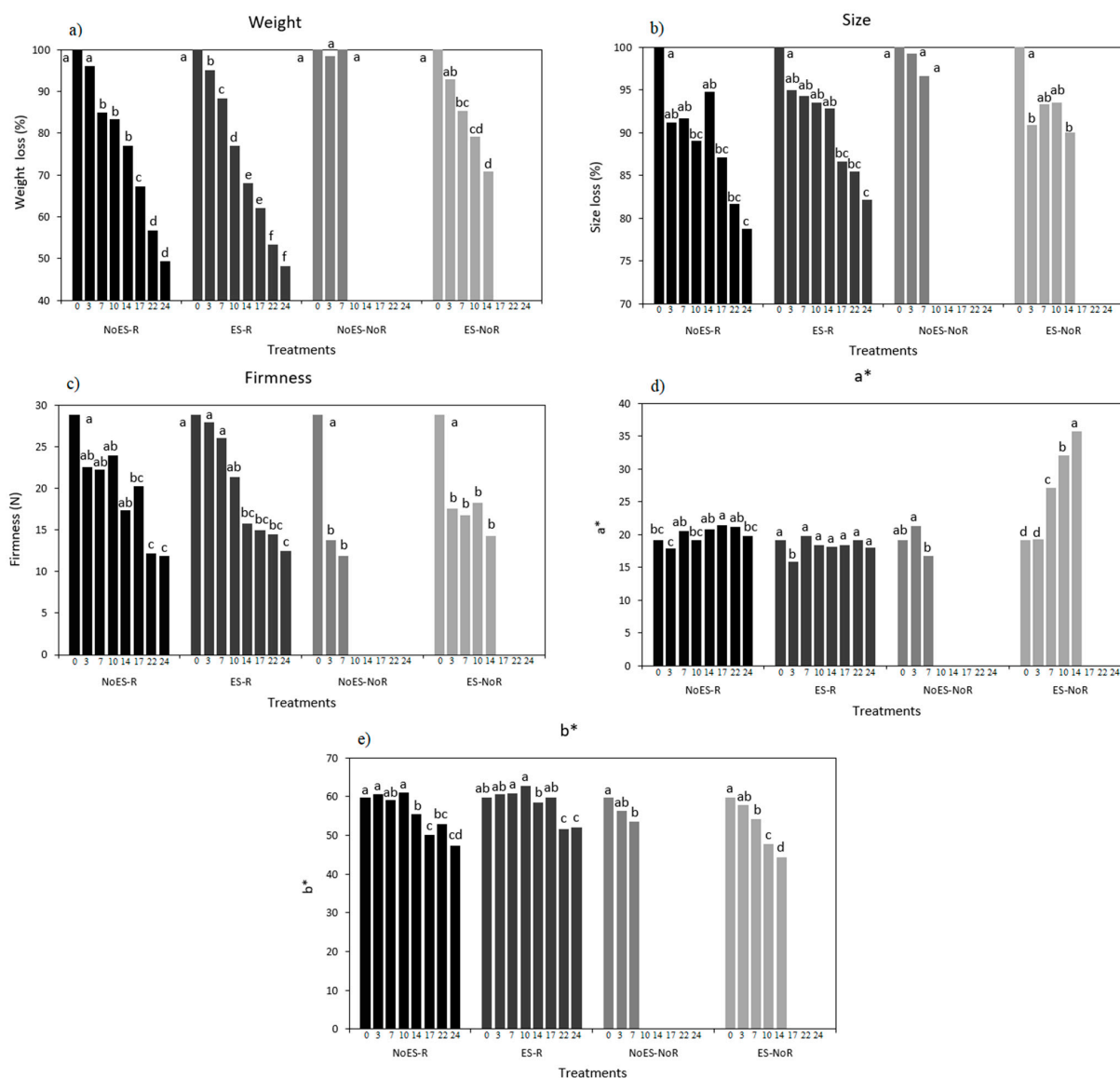
Figure 2. Loss of weight (**a**) and size (**b**) expressed as percentage and compared to initial day; firmness expressed in newtons (**c**); colour expressed as a* (**d**) and colour expressed as b* (**e**) coordinates in CIELAB system in peaches subjected to the different treatments (NoES-R, ES-R, NoES-NoR andES-NoR). Different letters for every day in on treatment represent statistically significant differences according to Tukey's test with the aim of assessing the evolution of each parameter for every treatment.

Fruit size showed a similar trend as fruit weight (Table 1 and Figure 2b). On the one hand, NoES-R, ES-R and ES-NoR treatments showed a continuous decrease in fruit size. In these three treatments, an important reduction in diameter was observed in the first day of conservation (day 3), followed by a stabilization in peach diameter until day 14, to a final, significant decrease until day 24 in NoES-R and ES-R (Figure 2b). In contrast, the NoES-NoR treatment showed a slightly smaller diameter, with significant differences observed on day 3, but not on day 7 with respect to the other three treatments (Table 1 and Figure 2b). This behaviour can be attributable to a possible internal fermentation, which is supported by the low O_2 concentration in the chamber. During anaerobiosis, the fruits ferment, replacing respiration as an energy-producing process. As a result, weight loss is lower than in the other treatments, and therefore the fruit size is preserved [13,21,22].

The decrease in the diameter of peaches, compared with the loss of weight, was less sensitive to the different factors applied. Except in day 3, no statistically significant differences were observed for this parameter (Table 1).

Firmness is one of the main quality attributes that determine the acceptance of the product by the consumer. Different changes in firmness were observed depending on the application of the combined ethylene removal technology and storage temperature (Figure 2c). The ES-R treatment was able to maintain high firmness values during the first week of storage, with values of 26.0 N, while the rest of the treatments showed a reduction of firmness on day 3 and 7, with this result being of significant relevance in the NoES-NoR treatment. This suggests that the use of ethylene scavengers maintained the firmness intact in the short term (days 3 and 7) in the refrigerated treatment (ES-R). In the medium and long term, the firmness values of the ES-R, NoES-R and ES-NoR decreased, with no differences between treatments (Table 1). The NoES-NoR treatment suffered the greatest decreases, losing 47% and 55% of firmness on day 3 and 7, with values of 13.7 N and 11.9 N. These tendencies in NoES-NoR coincided with the highest levels of ethylene and CO_2, and the lowest values of O_2 in this treatment (Figure 1b,c). This is in agreement with the existing literature. For example, [23] showed that the effect of ethylene scavengers on apricots resulted in significantly higher firmness compared to control fruit. Ethylene significantly affects fruit firmness by triggering cell wall hydrolysis, which leads to fruit softening [24,25]. In addition, the expression of polygalacturonase-related genes is associated with ethylene production [26]. The action of this enzyme is considered key in the softening of fruit in general, and stone fruit in particular, increasing its activity in those treatments where the exposure to ethylene was higher [27].

Colour is a parameter that changes significantly during the fruit ripening process, and can be associated with the optimal time of consumption of the fruit [28]. For the variety used in this study, "Rojo de Rito", the ideal values for (a*) and (b*) parameters are 20 and 55, respectively, corresponding to an optimum orange-yellow colour (Table 1).

The (a*) parameter was generally stable throughout the storage time, with a value close to 20 for the refrigerated treatments, although it can be observed that the presence of the ethylene scavengers in ES-R kept the values slightly low compared with the NoES-R treatment, being significant at 17 and 22 days (Table 1 and Figure 2d). However, this changed at the end of the experiment after 24 days, with both treatments showing similar values. In contrast, the NoES-NoR and ES-NoR treatments showed higher a* values than the refrigerated treatments, with these values being statistically significant in NoES-NoR at 3 days, and for two treatments at 7 days with values close to 27. In the medium term, the parameter a* continuously increased in ES-NoR for up to 14 days, reaching values of 33, which indicated a greater presence of red tones in the pulp of the peaches (Figure 2d). Furthermore, important significant differences with respect to the refrigerated treatments were observed in ES-NoR ($p < 0.001$).

With respect to the b* parameter, an overall decreasing trend was observed throughout the storage time, with a different intensity observed depending on the effect of ethylene scavengers and conservation temperature (Table 1, Figure 2e). For the refrigerated treatments, the yellow colour of the peaches was maintained, and even increased, during the first 10 days of conservation, with values of 62, although these values finally decreased at the end of the experiment, with values close to 50 (day 24). The b* value of the non-refrigerated treatments continuously decreased throughout the conservation period, with NoES-NoR showing the lowest values of 53.6 at day 7, but without differences when compared with ES-NoR. In the medium term, the b* parameter decreased up to 14 days, reaching values of 44, with important significant differences with respect to the refrigerated treatments observed in ES-NoR ($p < 0.001$).

By analysing the (a*) and (b*) parameters, it can be stated that the delay in peach ripening caused by ethylene scavengers promoted better colour preservation in the ES-R treatment compared to the control (NoES-R). The fruits of the ES-R treatment had a more stable, greener (a*) and yellower (b*) colour than the control treatment during the storage time. Fruits from the control treatment had a darker, and therefore riper, pulp than fruits from the ES-R treatment. In the 25 °C storage treatments (NoES-NoR and ES-NoR), the ethylene scavengers were able to delay colour change in the short term (days 3 and 7), in

the ES-NoR treatment compared to NoES-NoR. However, the NoES-NoR treatment did not last beyond day 7 of storage, due to adverse temperature and ethylene conditions. On days 10 and 14, the ES-NoR treatment showed a marked increase in parameter a* and a decrease in parameter b* compared to the control treatment (Table 1, Figure 2d,e).

The authors of [29] observed the relationship between colour preservation and antioxidant capacity, the concentration of phenolic compounds and chlorophylls in peaches. This study showed that colour preservation is a highly desirable trait for breeding programmes aimed at improving the consumption of peaches selected for their nutraceutical properties. The longer the fruit retains its colour, the higher the quantity of beneficial compounds present in the fruit.

3.3. Maturity Parameters

Soluble solid content (SSC) is used to determine the total ratio of sugars dissolved in a liquid (peach juice in this study). During post-harvest ripening of climacteric fruits, such as peaches, sugars displace acids by certain metabolic processes, increasing SSC and giving the fruit a sweet taste. Therefore, SSC is a key indicator of the ripening stage of the fruit (Table 2) [20,30,31].

Table 2. Evolution during storage time of the maturity parameters in peaches subjected to different treatments (NoES-R, ES-R, NoES-NoR and ES-NoR). The parameters measured were SSC expressed as percentage, pH, TA expressed as percentage, MI as the SSC/TA ratio.

Storage Days	Treatment	SSC (%)	pH	TA (%)	MI
0		11.2 ± 0.4	3.7 ± 0.03	3.7 ± 0.21	3.04 ± 0.16
3	NoES-R	13.0 ± 0.6 a	3.7 ± 0.05 c	3.4 ± 0.03 b	3.82 ± 0.20 ab
	ES-R	11.0 ± 1.0 a	3.6 ± 0.03 c	3.9 ± 0.07 a	2.84 ± 0.30 b
	NoES-NoR	11.7 ± 0.9 a	4.1 ± 0.05 a	2.4 ± 0.04 d	4.91 ± 0.41 a
	ES-NoR	11.0 ± 0.6 a	3.9 ± 0.04 b	2.8 ± 0.07 c	3.94 ± 0.19 ab
	Ethylene Scavengers (ES)	n.s.	**	***	**
	Temperature (T)	n.s.	***	***	**
	ES × T	n.s.	n.s.	n.s.	n.s.
7	NoES-R	11.7 ± 0.9 ab	3.8 ± 0.02 c	3.8 ± 0.30 a	3.16 ± 0.38 b
	ES-R	14.0 ± 1.0 a	3.7 ± 0.01 c	4.3 ± 0.10 a	3.30 ± 0.31 b
	NoES-NoR	8.3 ± 1.2 c	4.5 ± 0.05 a	1.5 ± 0.16 c	5.88 ± 1.46 a
	ES-NoR	10.7 ± 0.3 bc	4.1 ± 0.05 b	2.5 ± 0.25 b	4.39 ± 0.52 ab
	Ethylene Scavengers (ES)	*	***	**	n.s.
	Temperature (T)	**	***	***	*
	ES × T	n.s.	**	n.s.	n.s.
10	NoES-R	13.6 ± 0.7 a	3.8 ± 0.03 b	3.7 ± 0.10 b	3.73 ± 0.27 ab
	ES-R	12.0 ± 0.7 a	3.7 ± 0.03 b	4.0 ± 0.09 a	2.99 ± 0.22 b
	NoES-NoR	-	-	-	-
	ES-NoR	12.0 ± 1.0 a	4.1 ± 0.02 a	2.1 ± 0.06 c	4.55 ± 0.47 a
	One-way ANOVA	n.s.	***	***	***
14	NoES-R	12.4 ± 1.2 a	4.0 ± 0.03 b	4.1 ± 0.16 a	3.48 ± 0.26 ab
	ES-R	13.8 ± 0.9 a	3.9 ± 0.07 b	4.0 ± 0.12 a	3.00 ± 0.19 b
	NoES-NoR	-	-	-	-
	ES-NoR	11.6 ± 0.7 a	4.4 ± 0.05 a	2.6 ± 0.10 b	5.79 ± 0.51 a
	One-way ANOVA	n.s.	***	***	*
17	NoES-R	13.4 ± 1.4 a	4.1 ± 0.04 a	3.2 ± 0.11 b	4.27 ± 0.49 a
	ES-R	16.4 ± 2.9 a	4.0 ± 0.04 a	3.9 ± 0.15 a	4.24 ± 0.76 a
	NoES-NoR	-	-	-	-
	ES-NoR	-	-	-	-
	t-test	n.s.	n.s.	**	n.s.
22	NoES-R	16.8 ± 0.9 a	4.2 ± 0.05 a	3.2 ± 0.10 b	5.26 ± 0.33 a
	ES-R	16.7 ± 0.4 a	4.0 ± 0.11 a	4.0 ± 0.30 a	4.27 ± 0.33 b
	NoES-NoR	-	-	-	-
	ES-NoR	-	-	-	-
	t-test	n.s.	n.s.	*	*
24	NoES-R	21.3 ± 1.1 a	4.3 ± 0.06 a	2.9 ± 0.26 b	7.40 ± 6.4 a
	ES-R	23.3 ± 2.4 a	4.1 ± 0.04 b	3.7 ± 0.22 a	6.49 ± 8.6 a
	NoES-NoR	-	-	-	-
	ES-NoR	-	-	-	-
	t-test	n.s.	*	*	n.s.

Levels of statistical significance are: * $p < 0.05$, ** $p < 0.01$ and *** $p < 0.001$. n.s.: no significant differences. Different letters for each treatment represent statistically significant differences ($p < 0.05$) according to Tukey's test.

Comparing the data obtained, a logical evolution of SSC in the NoES-R, ES-R treatments was observed, as shown by a progressive increase, with values close to 13% on day 3 and close to 22% on day 24. The ES-NoR treatment, despite having adverse storage conditions, did not showed significant differences compared to the refrigerated treatments from day 10 of the experiment until 14, with values of 12%. On the other hand, the NoES-NoR treatment followed an opposite response, decreasing to a value of 8.33% at day 7. This behaviour suggests the hypothesis that the combination of high ethylene and CO_2 production and a decrease in O_2 (see Figure 1) caused internal fermentation (Figure 3a).
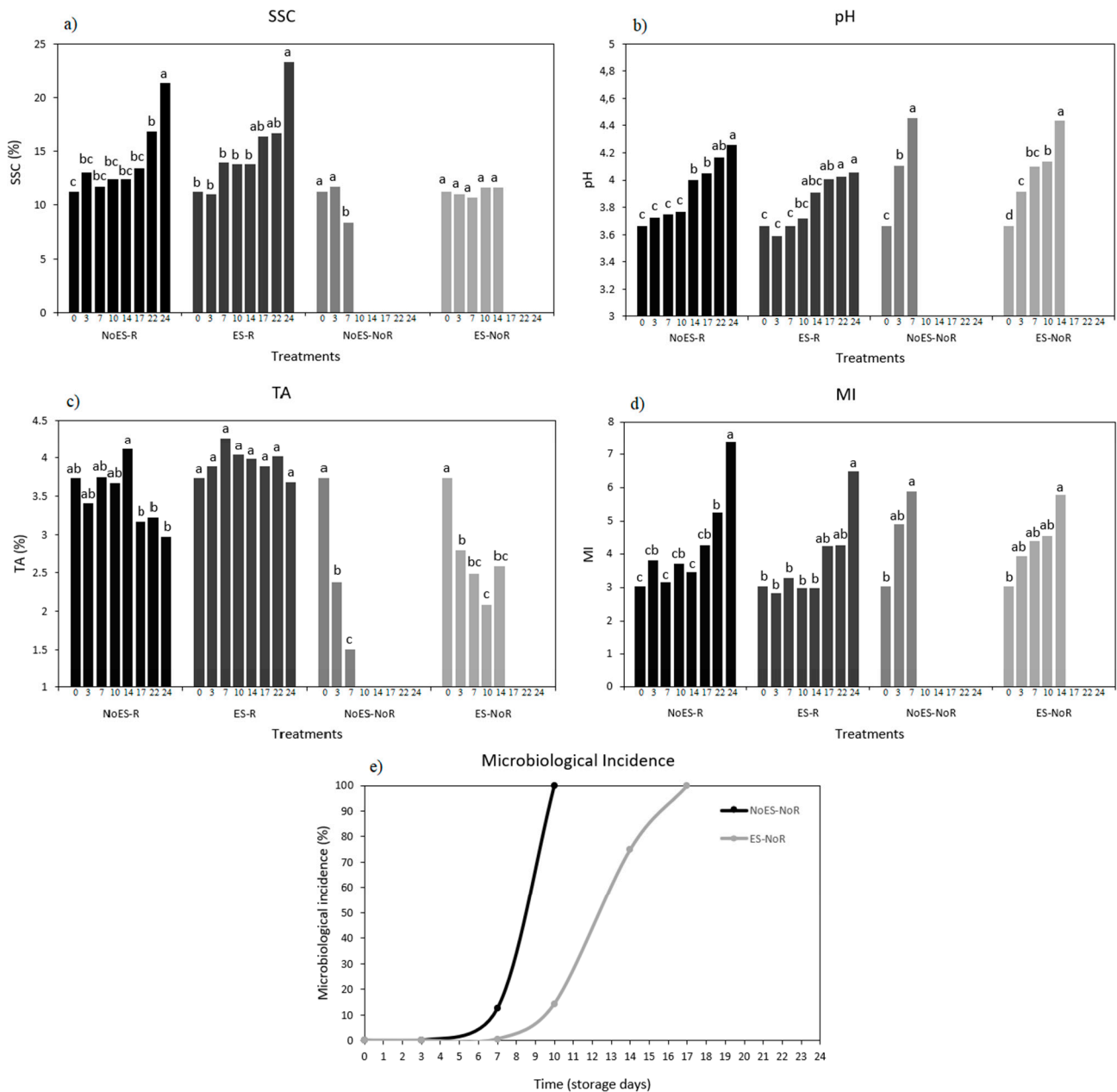
Figure 3. Soluble solid content (SSC) expressed in percentage (**a**), hydrogen potential expressed in pH units (**b**), titratable acidity (TA) calculated as malic acid equivalents and expressed as percentage (**c**), maturity index (MI) calculated as SSC/TA ratio (**d**), and microbiological incidence expressed as percentage (**e**) over the storage time (24 days) in peaches subjected to the different treatments (NoES-R, ES-R, NoES-NoR and ES-NoR). Different letters for each day in one treatment represent statistically significant differences according to Tukey's test with the aim of assessing the evolution of each parameter for every treatment.

Other studies have reported similar results, indicating a slight effect of ethylene scavengers on peach fruit conserved for 36 days at 0 °C [8,32]. The same effect was also observed in baby bananas, where SSC values tended to increase, depending on the doses of $KMnO_4$ and clay provided as ethylene scavengers [33]. In addition, apricots stored at 15 °C showed changes in SSC which were significantly affected by ethylene scavengers [4].

pH is perhaps the most important potentiometric measurement used in the agriculture and food industry and serves to quantify the concentration of H_3O^+ in the juice obtained from the liquefied fruit, which is determined as active acidity. This can be associated with the content of acids present and the capacity of microbial proliferation in conservation, as the acids will act on the fruit as a natural physiological barrier against microbial action (Table 2 and Figure 3b) [9,10].

The pH tended to increase during storage. Already from day 3, the first significant differences could be observed with lower values in NoES-R (3.7) and ES-R (3.6) indicating a key role of temperature ($p < 0.001$). Moreover, on the same day, the ES-NoR treatment, with a pH value of 3.9, showed a lower value than NoES-NoR with a pH of 4.1, indicating a relevant role of the ethylene scavengers utilized ($p < 0.01$) (Table 2). The same separation in treatments was observed on day 7, with both factors being highly relevant ($p < 0.001$), as well as the interaction between them ($p < 0.01$). On days 10 and 14, a clear separation between the refrigerated and ES-NoR treatments was observed ($p < 0.001$). In the long term, on days 17, 20, and 24, significant differences were only observed between the two refrigerated treatments on the last day, indicating the importance of ethylene removal in maintaining juice acidity at lower pH values (Table 2).

From an overall point of view, the ethylene scavengers were able to decrease the pH by 2.54%. In addition, the refrigeration temperatures decreased pH values by 6.74% (Figure 3b).

Some authors have shown an indirect effect of ethylene on pH values in other stone fruit, such as apricots [4]. The elimination of ethylene decreases metabolic processes related to fruit ripening, which minimises sugar production and preserves pH levels [25]. Other authors have shown data for a delayed pH rise; [10] observed, in a review, a slowing down of pH rise in "Golden Delicious" apples after the use of $KMnO_4$-based C_2H_4 scavengers [34]. This effect was also observed in "Kolikutu" [35] and "Williams" [36] bananas, in kiwifruit of the "Hayward" variety [37], and "Karuthacolomban" [38] and "Haden 2H" [39] mangoes. In peaches, [32] observed a significant delay in pH increase in ripening after 36 days of storage in those fruits treated with ethylene scavengers based on $KMnO_4$.

Titratable acidity (TA) represents the total amount of acids in the fruit, and it is expressed as a percentage. TA is inversely proportional to pH and SSC. Acids influence food taste (roughness), colour, microbial stability, and quality (Table 2 and Figure 3c).

The TA values tended to decrease throughout the study period, especially in non-refrigerated treatments and in the NoES-R (control) treatment compared to ES-R. These responses indicate that both factors were relevant when observing significant differences in TA, particularly on day 3 ($p < 0.001$). In the medium term, on days 10 and 14 of the trial, the differences observed in ES-NoR with respect to NoES-R and ES-R were due to the temperature factor ($p < 0.001$). In the long term, significant differences were observed between the two refrigerated treatments associated with ethylene scavengers on days 17 and 20, but not on day 24 of the trial.

From a general point of view, the use of ethylene scavengers was able to avoid 15.9% of TA losses. Similarly, the refrigeration temperature utilized was able to avoid 40.6% of TA losses (Figure 3c).

Other authors have already observed that the elimination of ethylene caused a maintenance of pH levels, delaying the acid degradation process. A natural increase in pH values implies a decrease in TA [32]. This effect was also observed using sachets of $KMnO_4$ in mangoes [40]. In conclusion, the data presented in this study suggest that the use of ethylene scavengers positively affected acid metabolism, with a resulting delay in sugar production and higher acid accumulation.

The maturity index (MI) depends on the total acidity and the soluble solids content and tends to increase during fruit ripening (Table 2 and Figure 3d) [31,41].

The MI values generally increased with the ripening process in climacteric fruits such as peaches, being highly affected by the use of ethylene scavengers and storage temperature. In the values recorded on day 3, significant differences were only observed between the ES-R (2.84) and NoES-NoR (4.91) treatments (Table 2). The responses observed on day 7 were very similar to those observed on day 3, with a high value of 5.88 observed in NoES-NoR. In the medium term, at day 10, significant differences were observed between ES-NoR and ES-R, but not between NoES-R and ES-NoR, indicating a positive role of the ethylene scavengers in delaying maturity in ES-NoR. At 14 days, ES-NoR showed significant differences compared with the refrigerated treatments, reaching a value of 5.79 that was very similar to the one reached by NoES-NoR at day 7, with such values of MI exceeding the optimum quality limits for peaches. In the long term, there were no differences between the refrigerated treatments, and the MI values simply increased and became critical on the last day of the trial at day 24.

From a general point of view, the ethylene scavengers were able to prevent increase in MI values by 9%. In addition, the refrigerated temperature prevented increase in MI values by 15% (Figure 3d).

3.4. Microbiological Incidence

During the entire conservation period, loss of fruits in the ES-R and NoES-R treatments did not occur because of the maintenance of constant optimum refrigeration conditions (Figure 3e).

On the other hand, in the ES-NoR and NoES-NoR treatments, differences were observed from day 7 onwards. On day 7, the NoES-NoR treatment suffered losses of 50% due to microbiological damage, while the ES-NoR treatment had a loss rate of 12%. On day 10, damage in the NoES-NoR treatment reached 100% of the fruit, making further analysis impossible. However, the ES-NoR treatment increased its fruit loss, to a total of 14.28%. On day 14, losses in the NoES-NoR treatment increased to 75%. Finally, on day 17, losses due to microbiological incidence in the ES-NoR treatment reached 100% (Figure 3e).

The application of ultraviolet radiation is known to have a spore-killing effect [36,37]. Therefore, the above data suggest that the use of ultraviolet light helped in both ethylene degradation and spore removal. As the machine forces air through the UV light, these spores could have been affected by photocatalysis [42].

The factors that most affect post-harvest losses of stone fruits are those associated with physiological damage or diseases. Among them, one of the most important is the effect of microorganisms, such as *Monilinia* spp. [43,44]. Several studies have shown that ethylene has an effect on the development of post-harvest diseases depending on the host-pathogen system and fruit [4,27]. In some studies, fungi from the genus *Monilinia* spp. have been inoculated on peach petals, with a conservative effect of ethylene removal observed on their browning process [45]. Research on tomatoes conserved at 11 °C and 22 °C for 28 days has shown that the use of ethylene scavengers supported with thymol led to the highest fungal inhibition ($\geq$91%) in comparison to the control, with this study also concluding that the C_2H_4-scavengers were helpful in controlling post-harvest fungal diseases while preserving fruit quality [46].

In the present study, the decrease in microbiological damage observed in the ES-NoR treatment suggests that the use of ethylene scavengers ($KMnO_4$ and UV radiation) in peaches subjected to a storage temperature of 25 °C also prevented the proliferation of pathogens, thereby extending their survival by 7 days compared to the NoES-NoR treatment.

4. Conclusions

The results obtained provide clear evidence that the combined effect of the photocatalytic action of UV radiation and potassium permanganate favoured the preservation of the

post-harvest quality of the fruits stored at 1 °C and 25 °C. This was especially important in the ES-NoR treatment, where metabolic processes would have been more active due to the higher temperatures, although these were slowed down by the ethylene scavengers, extending fruit survival by 7 days compared to the NoES-NoR treatment. In addition, among the refrigerated treatments, a better ES-R performance was also observed due to the effect of the ethylene scavengers on SSC and firmness parameters in the short term (7 days), on MI and colour parameters a* and b* in the medium term (14 days), and on pH and TA in the long term (beyond day 14).

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