

PAPER

CHLORINE DIOXIDE GAS TREATMENT ON POSTHARVEST QUALITY OF RASPBERRY

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ABSTRACT

The study investigated the effects of chlorine dioxide (ClO_2) gas on the postharvest quality of raspberries (cv Grandeur) during storage. Weight loss, color, total soluble solids content (TSSC), titratable acidity (TA), pH, vitamin C, total phenols, anthocyanins and antioxidant capacity were evaluated. The ClO_2 positively influenced weight loss, color, TA, TSSC and antioxidant capacity. Moreover, ClO_2 treatment decreased the total yeast and mold count. In contrast, the vitamin C, anthocyanins and total phenolics were not influenced by the ClO_2 treatment.

Keywords: chlorine dioxide, fruit quality, pad, postharvest, red raspberries, storage

1. INTRODUCTION

Red raspberries (*Rubus idaeus L.*) are rich in ascorbic acid, total phenols and anthocyanins. Therefore, consumption of these berries is an important source of antioxidant compounds with a significant role in the preservation and promotion of health, such as preventing diabetes, cardiovascular risk factors and oxidative stress (ATIENZA *et al.*, 2015; SEN and CHAKRABORTY, 2016). Red raspberry is a highly perishable product in which modification of quality compounds are related to the growth of microorganisms, and natural decay (GIACALONE and CHIABRANDO, 2012). Raspberry harvest and storage are complex operations and can affect the quality and aroma compounds of the fruit (GIUGGIOLI *et al.*, 2014). Thus, the raspberry postharvest control strategies are critical to preserving the fruit quality, particularly on a long distribution chain (BRIANO *et al.*, 2015a; HAFFNER *et al.*, 2002). Many technologies, like active packaging, modified atmosphere packaging, edible coating, Difolatan, hexanal, vapor essential oils or sanitizer treatments, such as chlorine dioxide (ClO_2) and ozone have been studied to reduce the growth of microorganism, control postharvest decay and preserve the quality and freshness of berries (APPENDINI and HOTCHKISS, 2002; BRIANO *et al.*, 2015b; CHIABRANDO and GIACALONE, 2008; CHIABRANDO and GIACALONE, 2015a; HAJIZADEH and KAZEMI, 2012; SUN *et al.*, 2014).

Chlorine dioxide is an alternative sanitizer, approved by the U.S. Food and Drug Administration (FDA) and by the U.S. Environmental Protection Agency (EPA). ClO_2 is legally used in China and USA for sanitizing fruit and vegetables (Ministry of Health of the People's Republic of China, 2008 and USFDA, 2010). Particularly, ClO_2 is authorized in the US for use in washing, whole fresh fruit, vegetables, shelled beans and peas with intact cuticles at a concentration not exceeding 5ppm. In EU, however, there are no clear regulations regarding the use of ClO_2 for fresh produce. Therefore, as a provisional solution, it was agreed that the individual member states will be given the ability to establish enforcement levels at the national level until risk management can take place based on European Food Safety Authority (EFSA) scientific opinion and monitoring data (BANACH *et al.*, 2015). ClO_2 has been postulated as an alternative to sodium hypochlorite (NaClO) for fresh and fresh-cut produce sanitization. CORDIS (Community Research and Development Information Service), designing new decontamination approaches for fresh-cut food and sanitation strategies, include ClO_2 among the most promising sanitation methods.

In the European Union, ClO_2 can be used in other forms, like active packaging, as a gas-generating pad (DUKAN *et al.*, 1999). The active substances of the pad are molecules of HClO (hypochlorous acid), found in silica gel and toxic to microorganisms. Chlorine dioxide gas is also a great sanitizer for food, at low concentration (CHEN *et al.*, 2010; CHANG *et al.*, 2000). The principal advantage of ClO_2 gas is its high penetrability (HAN *et al.*, 2001). Different studies (CHEN *et al.*, 2010; CHANG *et al.*, 2000) showed the positive effects of gaseous ClO_2 on the storage quality of lettuce, mulberries, plums and strawberries.

The objective of this study was to evaluate the impact of ClO_2 treatment as a pad applied on the top lids of the clamshells, on the postharvest quality, nutraceutical aspects and microbiological decay of raspberries during four different storage conditions.

2. MATERIALS AND METHODS

2.1. Samples and treatment

Red raspberries (*R. idaeus L.*) cv. Grandeur were handpicked from a commercial orchard of the Agrifrutta Soc. Coop. SRL (Piedmont, Italy) at full ripeness and directly placed in commercial plastic boxes, clamshell type (13.5 x 9.0 x 2.5 cm, perforated, polyethylene terephthalate, 120 g of fruits). The samples were transported immediately to the laboratory of the DISAFA, University of Turin, and only sound fruit was selected for the experiment. The boxes were randomly divided into two groups. On one group, a chlorine dioxide gas-generating pad (CDP) (Oplon Pure Science, Ltd., Ness Tsiyona, Israel) was placed on the top lids of the clamshells (U.S. Food and Drug Administration (FDA)-approved technology). The second group was used as the control. The effect of the CDP on the berries quality and antimicrobial activities during storage were measured. Each treatment included three replicates.

2.2. Storage treatments

Samples were stored in the dark in a controlled temperature room, and four different storage conditions were evaluated:

S1: 4 days at 1 °C (short storage)

S2: 8 days at 1 °C (long storage)

S3: 4 days at 1 °C and 3 days at 4 °C (short storage + short-range international transport)

S4: 8 days at 1 °C and 3 days at 4 °C (long storage + short-range international transport)

The hypothesized transport time was 3 days, simulating a refrigerated transport from Italy to Northern Europe.

Three repetitions were performed for all chemical analyses each time.

2.3. Weight losses

Weight loss was determined by weighing the numbered samples boxes at the beginning of the experiment (time 0) and at the end of the four different storage conditions. The values were reported as the percentage of weight loss per initial boxes weight, as shown in equation (1).

$$\% \text{ weight losses} = \frac{\text{initial weight} - \text{final weight}}{\text{initial weight}} * 100 \quad (1)$$

2.4. Quality measurements

The physicochemical quality attributes of the berries were measured at the beginning of the testing (time 0) and at the end of the four different storage conditions.

2.4.1 Color

The color of the berries was measured using a tristimulus CR-400 Chroma Meter (Konica Minolta Sensing, Inc. Osaka, Japan) with the D65 lamp and 2° observation angle. The instrument was calibrated against a standard white plate ($Y = 93.7$, $x = 0.3158$, $y = 0.3321$) before the analysis. Thirty measurements (30 berries) per treatment and sampling time

were made. The results were expressed as CIELAB (L*a*b*) color space. The L* values describe the lightness, and a* and b* values express the red-greenness and blue-yellowness, respectively. The color of berries was also expressed as C* (chroma or saturation). This parameter indicates the color variation $C^* = [(a^*)^2 + (b^*)^2]^{1/2}$ (FRANCIS, 1980). The reported values were the mean \pm SD of 30 determinations.

2.4.2 Total soluble solid content (TSSC), titratable acidity (TA) and pH

For each treatment, a digital refractometer (Atago refractometer model PR-32; Atago Italia, Milan, Italy) was used to determine the TSSC ($^{\circ}$ Brix) in three undiluted filtered juice samples, each extracted from 30 berries. The instrument was calibrated against distilled water. The TA and pH were determined by adding 50 mL of distilled water into 10 ml of filtered juice and titrated with 0.1 N NaOH to pH 8.2 with an automatic titrator (Titration Workstation TitrLab AT1000 Series, Hach, Milan, Italy). Titration data were expressed as meq L⁻¹.

2.5. Extraction and evaluation of total anthocyanins content, total phenolic contents, and total antioxidant capacity

The anthocyanins, phenolics and antioxidant capacity were determined on the fruit extracts, obtained using 12.5 ml of extraction solvent (500 ml of methanol, 28.3 ml nanopure water and 1.4 ml 37% HCl) and 5 g of fresh fruit. After 60 min at 25 $^{\circ}$ C under reduced light conditions, the extracts were homogenized at 24000 rpm for 1 min, with an Ultra-Turrax T-25 tissue homogenizer (Janke and Kunkel, IKA[®]-Labortechnik, Saufen, Germany) and centrifuged at 3000 rpm for 15 min (Centrifuge AVANTITM J-25, Beckman Instruments Inc.). The supernatant was recovered and stored at -26 $^{\circ}$ C. Three replicates for each treatment were performed at day 0 and at the end of the four different storage conditions.

Anthocyanins were determined using the pH differential method of CHENG and BRENN (1991) by measuring the absorbance of the aqueous phase at 515 and 700 nm using a UV-visible spectrophotometer (U-5100, Hitachi, Tokyo, Japan). Anthocyanins were estimated by the difference in absorbance at 515 and at 700 nm in buffer at pH 1.0 and 4.5, where $A = (A_{515} - A_{700})_{\text{pH1}} - (A_{515} - A_{700})_{\text{pH4.5}}$.

Results were expressed as mg cyanidin-3-glucoside per 100 g fresh berries.

Total phenolic contents were quantified using the SLINKARD and SINGLETON protocol (1977) with Folin-Ciocalteu reagent. Absorbance was measured at 765 nm. The results were calculated as gallic acid equivalents (GAE) (mg GAE 100 g⁻¹ of fresh berries).

The antioxidant activities of the berries were measured by the ferric reducing antioxidant power assay, as described by BENZIE and STRAIN (1996), with some modifications (PELLEGRINI *et al.*, 2003). Results were expressed as mmol Fe²⁺ kg⁻¹ fresh berries.

2.6. Extraction and evaluation of vitamin C

The vitamin C content was performed in agreement with SANCHEZ-MORENO *et al.* (2003) and GONZALEZ MOLINA *et al.* (2008) at day 0 and after 4 and 8 days of storage. Fruit flesh (10 g) was homogenized in 10 ml of methanol/water (5:95 v/v) using an Ultra-Turrax T-25 for 3 min. Then, the pH was adjusted to 2.2–2.4, and the extract was filtered through a C18 Sep-Pak cartridge (Waters Associates, Milford, MA, USA). The resultant solution was combined with 1,2-phenylenediamine dihydrochloride (Fluka Chemika, Neu-Ulm, Switzerland) for 37 min before HPLC analysis. Three replicate analyses of 10 fruits were performed for each treatment. The chromatographic system (Agilent) was

equipped with a diode array detector and Kinetex-C18 column (4.6 x 150 mm, 5 µm, Phenomenex., Torrance, CA, USA) and controlled through HPLC online software (Agilent). The mobile phase (isocratic) consisted of 50 mM monobasic potassium phosphate and 5 mM cetrimide (Sigma-Aldrich Corporation, Saint Louis, USA) in methanol:water (v/v) 5:95. The flow rate of 0.9 ml/min. The temperature was 40 °C, and the detector was set at 261 nm for ascorbic acid (AA) and 348 nm for dehydroascorbic acid (DHAA). The vitamin C content (AA and DHAA contents) was expressed as mg 100 g⁻¹ of fresh weight. All standards and reagents were of analytical purity and were purchased from Sigma Italiana SRL (Ozzano Emilia, Italy).

2.7. Yeast and mold evaluation

The yeasts and molds content was evaluated at day 0 and after 4 and 8 days of storage as described by the *Compendium of Methods for the Microbiological Examination of Foods* (VANDERZANT and SPLETTSTOESSER, 1992). A 30 g sample of fresh berries was blended with 270 mL of peptone buffered water (Sigma Italiana SRL, Italy) for 1 min in a Stomacher® bag using a blender (Stomacher®400 Circulator, Seward, Worthing, UK). Rose bengal agar (Sigma Italiana SRL, Italy) was used for the yeast and molds evaluations. All the plates were incubated at 30 °C for 5 days. Microbial counts were expressed as log colony forming units (CFU) g⁻¹.

2.8. Statistical analysis

Analysis of variance (ANOVA) was performed on the data, and the means were compared by Tukey's honestly significant differences test. The source of variation was the treatments (control and CDP) and the storage time. Differences between mean values were considered significant when $p \leq 0.05$. SPSS software was used for all data analyses (SPSS Statistics version 22 IBM).

3. RESULTS AND DISCUSSIONS

3.1. Weight loss

In general, raspberries are affected by considerable weight loss because the tissues are exposed to a high level of respiration and transpiration (KRÜGER *et al.*, 2011). In the present study, low weight losses were observed in all the samples compared to previous studies (KRÜGER *et al.*, 2011; HAFFNER *et al.*, 2009). After 4 days of storage (S1), the weight loss of the CDP samples was 0.71%, which was significantly lower than the control (0.98%). Therefore, in this postharvest storage condition, the CDP positively influenced the weight loss of raspberries, maintaining lower values compared to the control, according to ADAY and CANER (2011). The same result was also obtained in the S3 and S4 storage conditions, with 1.16 and 2.13% weight loss, respectively of the CDP treated fruit, while the corresponding control values were 1.52 and 2.61%. The effect of ClO₂ on the weight loss depends on the inactivity of the microbial population, the inhibition of enzyme activity, such as polyphenol oxidase, and the inhibition of respiration rate and ethylene biosynthesis (ADAY and CANER 2011; GUO *et al.*, 2013; WANG *et al.*, 2011; SUN *et al.*, 2014).

3.2. Quality measurements

3.2.1 Color

Color change is an important factor that affects the visual appearance and the postharvest quality of fresh raspberry fruit. The L^* and C^* values of raspberry after 4 and 8 days of storage are reported in Table 1. The L^* values after 4 and 8 days of storage showed a significant decrease in both treatments (control and CDP treatment), compared to day 0. Significant differences were observed between treatments after 4 days of storage at 1 °C, with higher values of L^* in the CDP treated berries (fruit with a higher luminosity). As described by KRÜGER *et al.* (2011) and SHIN *et al.* (2008), a decrease in lightness values during storage, indicates that the fruit became darker, less red and bluer with advance ripening. In the present work, samples treated with the CDP maintained the original color of the berries, in concurrence with the study of ADAY and CANER (2011) on strawberries. The ClO_2 gas did not influence the lightness during the S3 and S4 storage conditions. In these instances, there were no significant differences ($p \geq 0.05$) in L^* value between the CDP treatment (L^* 27.9 and 29.4 in S3 and S4, respectively) and the control (L^* 28.4 and 29.2 in S3 and S4, respectively).

The C^* values initially increased and then decreased during storage as shown in Table 1. Considering the short period of storage (S1), results showed significantly higher values for the CDP samples compared to the control. In this instance, the CDP treatment significantly improved the redness intensity of berries during storage. In previous studies, the CDP treatment caused no pigment degradation and consequently, no changes in external color of berries (ZHENG *et al.*, 2008; GOMEZ LOPEZ *et al.*, 2009). The same result was also obtained under the S4 storage condition, where the CDP samples showed C^* values of 23.3, which was significantly higher compared to the control (C^* 20.8).

Table 1. Effect of ClO_2 on color parameters (Lightness and Chroma) of raspberries after 4(S1) and 8(S2) days of storage at +1°C. The data are average of 30 replicates \pm SD.

Color Parameters	Treatments	Storage time (days)		
		0	4	8
Lightness (L^*)	Control	35.1 \pm 1.9 ^{aA}	29.1 \pm 3.0 ^{bB}	29.8 \pm 1.74 ^{aB}
	Chlorine dioxide	35.1 \pm 1.9 ^{aA}	30.4 \pm 2.2 ^{aB}	30.0 \pm 2.24 ^{aB}
Chroma (C^*)	Control	22.7 \pm 4.0 ^{aB}	25.9 \pm 4.5 ^{bA}	25.4 \pm 4.1 ^{aA}
	Chlorine dioxide	22.7 \pm 4.0 ^{aB}	28.9 \pm 5.3 ^{aA}	25.9 \pm 5.7 ^{aA}

3.2.2 TSSC, TA and pH

TSSC, TA and pH values after 4 (S1) and 8 (S2) days of storage are shown in Table 2. The TSSC values were significantly different between treatments after 4 and 8 days of storage at +1°C, while the differences were not significant under S3 and S4 conditions (data not shown). The higher TSSC levels in the control than CDP treated berries may be due to the higher respiration rate and weight losses and, consequently, more concentrated juice of the control berries. WU *et al.* (2011) showed that ClO_2 treatment maintained the TSSC similar to the value recorded at harvest, which was better than untreated fruit, probably due to the reduction of postharvest infections.

The TA decreased significantly during storage for both treatments, but without significant differences. The TA values decreased significantly for all samples during storage. In the

control samples, the lowest recorded TA value was under S4 conditions, and in the CDP sample, it was under S3 conditions. The decrease in TA and increase in TSSC during storage were associated with the enhancement of temperature from 1 to 4 °C in S3 and S4 that caused an increase in respiration rate and the natural consumption of organic acids by the metabolism (HAFFNER *et al.*, 2009). The changes in TA probably depended more on temperature than the effect of ClO₂, according to the study of ADAY and CANER (2011) on strawberries (Table 2).

The pH level increased in the control samples in agreement with the TA result, while in the CDP treated samples no significant differences were observed during storage. ADAY and CANER (2011) reported that ClO₂ treatment maintained stable pH levels in samples during storage probably due to the antimicrobial activity of ClO₂ on yeast and mold, and consequently, to the inhibition of natural decay.

Table 2. Effect of ClO₂ on quality parameters of raspberries after 4(S1) and 8(S2) days of storage at + 1°C. Total Soluble Solid Content (TSSC), Titratable Acidity (TA) and pH. The data are average of 3 replicates ± SD.

	Treatments	Storage time (days)		
		0	4	8
TSSC	Control	8.4±0.1 ^{aB}	9.0±0.3 ^{aA}	8.6±0.0 ^{aB}
°Brix	Chlorine dioxide	8.4±0.1 ^{aA}	8.3±0.2 ^{bA}	8.1±0.1 ^{bA}
TA	Control	447.65±17.1 ^{aA}	450.98±5.6 ^{aA}	390.83±17.6 ^{aB}
meq/L	Chlorine dioxide	447.65±17.1 ^{aA}	447.06±12.0 ^{aA}	402.03±8.1 ^{aB}
pH	Control	3.04±0.01 ^{aB}	3.07±0.01 ^{aAB}	3.10±0.04 ^{aA}
	Chlorine dioxide	3.04±0.01 ^{aA}	3.02±0.01 ^{bA}	3.16±0.12 ^{aA}

Means sharing the same letters in rows (A, B) and in column (a, b) are not significantly different from each other (Tukey's HSD test, $p \leq 0.05$).

3.3. Total anthocyanin content

Total anthocyanin content is one of the functional constituents in raspberries that are associated with their bright red color. The content of anthocyanins increased during the storage at 1 °C (S1 and S2) (Table 3) and then decreased during storage at 4°C (S3 and S4). This trend may be due to the decomposition of procyanidins at the beginning of storage (Chun *et al.*, 2013). The results of the present study agree with the research of HAFFNER *et al.* (2002) that reported a similar increase in anthocyanin content after 7 days of cold storage (1.7°C), but contrasts with the study of MULLEN *et al.* (2002) that did not show a significant increase during cold storage. Moreover, the results indicated that the content of anthocyanins increased in the same manner as the pH after 8 days of cold storage at 1 °C. According to ORAK (2007), a correlation exists between anthocyanins and pH in grapes. Hence, the current results suggest a similar trend in raspberries. Considering the treatment, ClO₂ does not seem to directly influence the anthocyanins level because no significant differences between treatments were found.

3.4. Total phenolics content

As shown in Table 3, according to the total anthocyanin content results, no significant differences in total phenolic content were observed during storage time or between

treatments. In general, an increase in total phenols was observed throughout the storage. A similar result was also noted previously in raspberries (KRÜGER *et al.*, 2011) in strawberries (CHENG and BREEN, 1991) and in blueberries (CHIABRANDO and GIACALONE, 2015b) and it seems to depend on the weight loss. In this work, the lack of significant difference between the CDP treated and control samples was probably due to the low level of ClO₂. GOMEZ LOPEZ *et al.* (2009) and NAPOLITANO *et al.* (2005) found that a high level of ClO₂ can react with phenolic compounds, decreasing their content in the food. Considering the storage at 4 °C (S3 and S4), the ClO₂ gas did not influence the total phenolic content. Indeed, there were no significant differences ($p \geq 0.05$) between the CDP treatment (202.24 and 232.26 mg GAE 100 g⁻¹ in S3 and S4, respectively) and the control (216.31 and 240.95 mg GAE 100 g⁻¹ in S3 and S4, respectively).

Table 3. Effect of ClO₂ on nutraceutical parameters of raspberries after 4(S1) and 8(S2) days of storage at +1 °C. The data are average of 3 replicates ± SD.

	Treatments	Storage times (days)		
		0	4	8
Total anthocyanin content mg cyanidin 3-gluc100 g ⁻¹ FW	Control	43.62±6.65 ^{aB}	54.5±5.24 ^{aAB}	78.11±7.66 ^{aA}
	Chlorine dioxide	43.62±6.65 ^{aB}	52.24±5.71 ^{aAB}	68.22±7.47 ^{aA}
Total phenolics content mg gallic acid equivalent (GAE)100 g ⁻¹ FW	Control	198.3±16.55 ^{aA}	235.66±19.44 ^{aA}	219.45±23.41 ^{aA}
	Chlorine dioxide	198.3±16.55 ^{aA}	217.65±17.33 ^{aA}	204.21±9.87 ^{aA}
Total antioxidant capacity mmol Fe ²⁺ kg ⁻¹ FW	Control	27.81±2.35 ^{aA}	28.93±0.60 ^{aA}	30.96±1.25 ^{aA}
	Chlorine dioxide	27.8±2.35 ^{aA}	28.11±1.42 ^{aA}	28.11±0.80 ^{bA}
Vitamin C content mg100 g ⁻¹ FW	Control	12.45±0.40 ^{aA}	12.97±1.09 ^{aA}	9.39±0.85 ^{aB}
	Chlorine dioxide	12.45±0.40 ^{aA}	12.87±0.57 ^{aA}	8.76±1.30 ^{aB}

Means sharing the same letters in rows (A, B) and in column (a, b) are not significantly different from each other (Tukey's HSD test, $p \leq 0.05$).

3.5. Total antioxidant capacity

As shown in Table 3, the total antioxidant capacity increased slowly during storage. Statistical analysis showed significant differences between samples after 8 days of storage, with a higher value in the control than CDP treated sample. This result is in accordance with MULLEN *et al.* (2002) and KALT *et al.* (1999). Considering the storage at 4 °C (S3 and S4), the ClO₂ did not influence the antioxidant capacity and there was no significant difference ($p \geq 0.05$) between the CDP treatment (28.54 and 28.27 mmol Fe²⁺ kg⁻¹ in S3 and S4, respectively) and the control (29.68 and 31.03 mmol Fe²⁺ kg⁻¹ in S3 and S4, respectively).

3.6. Vitamin C content

Table 3 presents the vitamin C values of the untreated and treated samples after 4 and 8 days of storage. The vitamin C content decreased over time in both treatments, but without statistical differences between treatments. A similar trend was observed in the study of HAFFNER *et al.* (2002) and KALT *et al.* (1999) during storage at 0 °C. According to KRÜGER *et al.* (2011), the AA content depends particularly on the storage conditions and the genotype of the plant.

3.7. Yeast and mold evaluation

Raspberries are highly perishable and susceptible to microbial decay during postharvest storage. Therefore, decay is a primary factor of postharvest quality loss of raspberries, and a strategy is necessary to improve their shelf-life quality. No mold growth was visually observed during the present study. At day 0, the yeast and mold were present in relatively low amounts, at 2.9 and 4.2 log CFU/g⁻¹, respectively (Table 4). After 4 and 8 days of storage at 1 °C, a reduced yeast and mold count was observed in the CDP treated samples compared to the control. The decay incidence of the raspberries gradually increased with time of storage only in the control samples. Hence, in this study, the CDP treatment was effective against the growth of yeast and mold throughout the storage period. This result was in agreement with the study of SUN *et al.* (2014) on blueberries. The same trend has also been found in lettuce, carrot, apples, peaches, tomatoes and fresh-cut produce (SY *et al.*, 2005).

Table 4. Effect of ClO₂ on nutraceutical parameters of raspberries after 4(S1) and 8(S2) days of storage at +1°C. The data are average of 3 replicates ± SD.

	Treatments	Storage time (days)		
		0	4	8
Yeast Log CFU g ⁻¹	Control	2.85 ^{aB}	4.88 ^{aA}	3.61 ^{aA}
	Chlorine dioxide	2.85 ^{aA}	2.56 ^{bA}	2.60 ^{bA}
Mold Log CFU g ⁻¹	Control	4.20 ^{aA}	4.79 ^{aA}	4.41 ^{aA}
	Chlorine dioxide	4.20 ^{aA}	2.38 ^{bB}	2.34 ^{bB}

Means sharing the same letters in rows (A, B) and in column (a, b) are not significantly different from each other (Tukey's HSD test, $p \leq 0.05$).

4. CONCLUSIONS

The present study showed the action of ClO₂ against the natural decay of raspberries and its efficacy in preserving berry quality under various postharvest storage conditions. Results suggest that ClO₂ treatment in active packaging is useful to reduce decay and maintaining raspberry quality during storage. In particular, ClO₂ slowed down the tissue metabolism and consequently, lower weight losses were found compared to the untreated fruit. Moreover, ClO₂ treatment significantly improved the redness intensity of berries during storage, but no significant effect on maintaining the stability of nutraceutical components was recorded. In summary, the CDP can be a valuable alternative sanitizer with a beneficial action against yeast and mold without reducing the quality of the final produce. This treatment also improved the shelf-life quality by inhibiting the weight loss and the color changes of raspberries during short period storage time.

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REFERENCES

Aday M.S. and Caner C. 2011. The Applications of 'active packaging and chlorine dioxide' for extended shelf life of fresh strawberries. *Pack. Technol. Sci.* 24:123.

- Appendini P. and Hotchkiss J.H. 2002. Review of antimicrobial food packaging. *Innov. Food Sci. Emerg. Technol.* 3:113.
- Atienza L., Perez E.G. and Noratto G. 2015. Effects of Raspberry on Biomarkers of Diabetes, Cardiovascular Disease (CVD) and Oxidative Stress in Obese Diabetic (db/db) Mice. *FASEB J.* 29:1.
- Banach, J. L., Sampers, I., Van Haute, S. and Van der Fels-Klerx, H. J. (Ine). 2015. Effect of Disinfectants on Preventing the Cross-Contamination of Pathogens in Fresh Produce Washing Water. *Int. J. Environmental Res. Public Health* 12(8): 8658-8677. <http://doi.org/10.3390/ijerph120808658>
- Benzie I.F.F. and Strain J.J. 1996. The ferric reducing ability of plasma (FRAP) as a measure of "antioxidant power": the FRAP assay. *Anal. Biochem.* 239:70.
- Briano R., Giuggioli N.R., Girgenti V. and Peano C. 2015a. Biodegradable and compostable film and modified atmosphere packaging in postharvest supply chain of raspberry fruits (cv. Grandeur). *J. Food Process. Preserv.* 39(6):2061.
- Briano R., Giuggioli N.R., Baudino C. and Peano C. 2015b, June. Influence of evolution of off-flavors and quality for raspberry 'Grandeur'® storage with a modified atmosphere packaging in the supply chain management. XI International Rubus and Ribes Symposium, 1133, pp 397-404.
- Chang C.Y., Hsieh Y.H., Hsu S.S., Hu P.Y. and Wang K. H. 2000. The formation of disinfection by-products in water treated with chlorine dioxide. *J. Hazard. Mater.* 79(1):89.
- Chiabrandò V. and Giacalone G. 2008. Studies on Shelf Life of "Lateblue" Highbush Blueberries. *Food Sci. Technol. Int.* 14: 199.
- Chiabrandò V. and Giacalone G. 2015a. Effects of alginate edible coating on quality and antioxidant properties in sweet cherry during postharvest storage. *Ital. J. Food Sci.* 27: 1.
- Chiabrandò V. and Giacalone G. 2015b. Anthocyanins, phenolics and antioxidant capacity after fresh storage of blueberry treated with edible coatings. *Int. J. Food Sci. Nutrit.* 66(3): 248.
- Chen Z., Zhu C., Zhang Y., Niu D. and Du J. 2010. Effects of aqueous chlorine dioxide treatment on enzymatic browning and shelf-life of fresh-cut asparagus lettuce (*Lactuca sativa* L.). *Postharvest Biol. Technol.* 58(3):232.
- Cheng G.W. and Breen P.J. 1991. Activity of phenylalanine ammonia-lyase (PAL) and concentrations of anthocyanins and phenolics in developing strawberry fruit. *J. Am. Soc. Hort. Sci.* 116(5):865.
- Chun H.H., Kang J.H., and Song K.B. 2013. Effects of aqueous chlorine dioxide treatment and cold storage on microbial growth and quality of blueberries. *J. Korean Soc. Appl. Biol. Chem.* 56:309.
- Dukan S., Belkin S. and Touati D. 1999. Reactive oxygen species are partially involved in the bacteriocidal action of hypochlorous acid. *Archives Biochem. Biophys.* 367(2):311.
- EFSA publication (2015). EFSA CONTAM Panel (EFSA Panel on Contaminants in the Food Chain), 2015.
- Giacalone G. and Chiabrandò V. 2012. Problems and Methods to Improve the Market-Life of Berry Fruit. Ch. 10. In "Berries: Properties, Consumption and Nutrition" C. Tuberoso (Ed.), p. 257, Nova Science Publishers Inc., Hauppauge, New York.
- Giuggioli N. R., Girgenti V., Baudino C. and Peano C. 2014. Influence of modified atmosphere packaging storage on postharvest quality and aroma compounds of strawberry fruits in a short distribution chain. *J. Food Process. Preserv.* 39:3154.
- Gomez-Lopez V. M., Rajkovic A., Ragaert P., Smigic N. and Devlieghere F. 2009. Chlorine dioxide for minimally processed produce preservation: a review. *Trends. Food Sci. Technol.* 20:17.
- Gonzalez-Molina E., Moreno D. A. and García-Viguera C. 2008. Genotype and harvest time influence the phytochemical quality of Fino lemon juice (*Citrus limon* (L.) Burm. F.) for industrial use. *J. Agric. Food Chem.* 56(5):1669.
- Guo Q., Lv X., Xu F., Zhang Y., Wang J., Lin H. and Wu B. 2013. Chlorine dioxide treatment decreases respiration and ethylene synthesis in fresh-cut 'Hami'melon fruit. *International J. Food Sci. Technol.* 48(9):1775.
- Haffner K., Rosenfeld H.J., Skrede G. and Wang L. 2002. Quality of red raspberry *Rubus idaeus* L. cultivars after storage in controlled and normal atmospheres. *Postharvest Biol. Technol.* 24(3):279.
- Hajizadeh H.S. and Kazemi M. 2012. Investigation of Approaches to Preserve Postharvest Quality and Safety in Fresh-cut Fruits and Vegetables. *J. Env. Sci.* 6(3):93.

- Han Y., Linton R.H., Nielsen S.S. and Nelson P.E. 2001. Reduction of *Listeria monocytogenes* on green peppers (*Capsicum annuum* L.) by gaseous and aqueous chlorine dioxide and water washing and its growth at 7 C. *J. Food Protect.* 64(11):1730.
- Kalt W., Forney C.F., Martin A. and Prior R.L. 1999. Antioxidant capacity, vitamin C, phenolics and anthocyanins after fresh storage of small fruits. *J. Agric. Food Chem.* 47(11):4638.
- Krüger E., Dietrich H., Schöpplein E., Rasim S. and Kürbel P. 2011. Cultivar, storage conditions and ripening effects on physical and chemical qualities of red raspberry fruit. *Postharvest Biol. Technol.* 60(1):31.
- Ministry of Health of the People's Republic of China, 2008. Hygienic Standards for Use of Food Additives.
- Mullen W., McGinn J., Lean M.E., MacLean M.R., Gardner P., Duthie G.G. and Crozier A. 2002. Ellagitannins, flavonoids and other phenolics in red raspberries and their contribution to antioxidant capacity and vasorelaxation properties. *J. Agric. Food Chem.* 50(18):5191.
- Napolitano M.J., Green B.J., Nicoson J.S. and Margerum D.W. 2005. Chlorine dioxide oxidations of tyrosine, N-acetyltirosine and dopa. *Chem. Res. Toxicol.* 18(3):501.
- Orak, H.H. 2007. Total antioxidant activities, phenolics, anthocyanins, polyphenoloxidase activities of selected red grape cultivars and their correlations. *Sci. Hortic.* 111(3):235.
- Pellegrini N., Serafini M., Colombi B., Del Rio D., Salvatore S., Bianchi M. and Brighenti F. 2003. Total antioxidant capacity of plant foods, beverages and oils consumed in Italy assessed by three different in vitro assays. *J. Nutr.* 133:2812.
- Regulation (EU) No 852/2004 of the European Parliament and of the Council of 29 April 2004 on the hygiene of foodstuffs (including HACCP principles).
- Sen S. and Chakraborty R. 2016. Food in Health Preservation and Promotion: A Special Focus on the Interplay. Exploring the Nutrition and Health Benefits of Functional Foods. Guwahati, AS.
- Shin Y., Ryu J.A., Liu R.H., Nock J.F. and Watkins C.B. 2008. Harvest maturity, storage temperature and relative humidity affect fruit quality, antioxidant contents and activity, and inhibition of cell proliferation of strawberry fruit. *Postharvest Biol. Technol.* 49(2):201.
- Slinkard K. and Singleton V.L. 1977. Total phenol analysis: automation and comparison with manual methods. *Am. J. Enol. Viticult.* 28(1):49.
- Sun X., Bai J., Ference C., Wang Z., Zhang Y., Narciso J. and Zhou K. 2014. Antimicrobial activity of controlled-release chlorine dioxide gas on fresh blueberries. *J. Food Protect.* 77:1127.
- Sy K.V., Murray M.B., Harrison M.D. and Beuchat L.R. 2005. Evaluation of gaseous chlorine dioxide as a sanitizer for killing *Salmonella*, *Escherichia coli* O157: H7, *Listeria monocytogenes*, and yeasts and molds on fresh and fresh-cut produce. *J. Food Protect.* 68(6):1176.
- USFDA (United States Food and Drug Administration), 2010. Secondary direct food additives permitted in food for human consumption. 21 CFR. Sec. 173. 300 Chlorine dioxide.
- Vanderzant C. and Splittstoesser D.F. 1992. Compendium of Methods for the Microbiological Examination of Food (Splittstoesser, Eds.) Washington, DC.
- Wang Y., Wu J., Ma D. and Ding J. 2011. Preparation of a cross-linked gelatin/bacteriorhodopsin film and its photochromic properties. *Sci. China Chem.* 54(2):405.
- Wu B., Li X., Hu H., Liu A. and Chen W. 2011. Effect of chlorine dioxide on the control of postharvest diseases and quality of litchi fruit. *Afr. J. Biotechnol.* 10:6030.
- Zheng Y., Yang Z. and Chen X. 2008. Effect of high oxygen atmospheres on fruit decay and quality in Chinese bayberries, strawberries and blueberries. *Food Control* 19(5):470.

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