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Effect of the Potassium Permanganate Coated Zeolite Nanoparticles on the Quality Characteristic and Shelf Life of Peach and Nectarine

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Abstract This research was conducted to study the effect of removal of the ethylene using potassium permanganate coated nano zeolites from the storage on the quality characteristics and shelf life of peach and nectarine. Potassium permanganate and Zeolite based Nano-Molecular Filters were used in ETH 1500 machine. Two cultivars of peach and three cultivars of nectarine were used in this experiment Commercial traits affecting the marketing and shelf-life of peach and nectarine i.e. pH, texture (firmness), appearance, total soluble solid concentration (TSS), titratable acidity, internal breakdown and the reduction in fresh weight were measured at the beginning of the experiment (day 0), 12, 24 and 36 days after storage. The experiment was laid in a two factor Randomized Complete Block Design (RCBD) with four replications. Two factors were the effect of ethylene absorbent ETH 1500 machine and the type of fruit (peach and nectarine). Maximum firmness in nectarine (24.09) and peach (19.80), the minimum pH in nectarine (5.42) and peach (6.14), minimum weight loss in nectarine (4.12%) and peach (5.94%) and the best appearance evaluation score in nectarine (score 3.47) and in peach (score 3.5) were observed in presence of the ethylene absorbing machine in comparison with the control treatment (no ethylene absorption). These results indicate that application of nano zeolite particles coated with potassium permanganate in a machine circulating the ethylene containing air, prevents weight loss, reduction in firmness, spoilage and increase shelf-life and the quality of stored peach and nectarine.

Keywords: Peach, Nectarine, Ethylene, Nano-zeolite, Storage, Postharvest

Introduction

In stored peaches, the prime causes of postharvest losses include: metabolic changes, reduced pulp firmness, mechanical damage and physiological disorders (Rombaldi *et al*., 2002; Girardi *et al*., 2005). Quality characters and marketing value of peaches and nectarines are negatively affected during prolonged storage, by development of physiological disorders or “internal breakdown” (IB) (Lill *et al*., 1989; Lurie and Crisosto, 2005).

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Peach and nectarine are climacteric fruits (Palou *et al*., 2003). Their rapid ripening after harvest is responsible for short shelf life and represents a serious constraint for efficient handling and transportation of these stone fruits. Ethylene causes the majority of postharvest physiological disorders in climacteric fruits, directly or indirectly. Reduction of ethylene production and/or action has significant positive effect on the postharvest quality of fruits, vegetables and flowers (Girardi *et al*., 2005; Ernst, 2011; Mortazavi *et al*., 2011; Zhang *et al*., 2012). Color changes, increase in sugar content, and decrease of acidity and firmness in peach fruits are significantly affected by ethylene (Haji *et al*., 2003). Also promotion of fruit softening, acceleration of deterioration, and consequent shorter postharvest life are the results of ethylene action (Mitchell, 1990).

Peach fruit, has upper level of ethylene in mesocarp. Ethylene increase in fruit is related to ACC (1-aminocyclopropane- 1- carboxylic acid) concentration and ACC oxidase (ACO) activity (Bonghi *et al*., 1999). The influence of ethylene on the postharvest quality of the peach has been reported (Girardi *et al*., 2005). Results showed that ethylene decreased the activity of endo-polygalacturonase (endo-PG) and exo-Polygalacturonase (exo-PG) enzymes without the reduction in Pectin Methyl Esterase (PME) activity caused the flesh firmness and decay of fruits (Santana *et al*., 2011).

Ethylene is a gaseous plant hormone that plays a major role in the regulation of the metabolism of harvested horticultural crops at very low concentrations (Saltveit, 1999; Zhang *et la*., 2012). The postharvest life of both climacteric and non-climacteric fruits can be influenced by ethylene. This hormone affects their quality attributes and the development of physiological disorders and postharvest diseases (Kader, 1985; Ernst, 2011). Effects of ethylene on quality attributes such as fruit external appearance, texture, flavor, and nutritive value have been extensively reported (Kader, 1985; Watada, 1986; Saltveit, 1999; Ernst, 2011).

Most of the research regarding the effects of ethylene on postharvest decay has been focused on diseases of non-climacteric fruits such as citrus or strawberry, and very little work has been done with stone fruits (Palou *et al*., 2003). A primary goal in the fruit industry is the possibility of controlling the ripening process and extending the shelf-life. Several approaches have been proposed to control the ripening process and extending the shelf life of fresh produce. These include: application of 1-Methylcyclopropene (1MCP) (Blankenship and Dole, 2003; Sisler and Serek, 1997; Sisler *et al*., 1996; Fan *et al*., 2002; Ziliotto *et al*., 2003; Dal Cin., 2006; Tatsuki, *et al*., 2006; Maninang *et al*., 2011), Nitric Oxide (NO) (Zhou *et al*., 2006; Mortazavi *et al*., 2011), Poly amines (Liu., 2005), CO2 (Brecht *et al*., 1982; Mathooko *et al*., 2001; Santana *et al*., 2011), O3 (Palou *et al*., 2002; Rahemi, 2003), Methyl Bromide heat air or water treatment (Jin *et al*., 2009; Budde *et al*, 2006; Malakou and Nanos, 2005) and potassium permanganate (Thompson, 1994; Thompson and Reid, 1989; Zomorrodi, 2005; Silva *et al*., 2009; Rezaii Kalaj *et al*., 2009; Chaves *et al*., 2007).

Potassium permanganate is a powerful oxidant that neutralizes the ethylene by oxidizing it to carbon dioxide and water (Thompson, 1994). Recently, it is used to remove the ethylene gas. Its application decreased the ethylene level in the commercial fridges (Thompson, 1994; Thompson and Reid, 1989). To ensure ethylene elimination, fruits should be stored in an atmosphere that is exposed to potassium permanganate (Zomorrodi, 2005). The more the exposed surface of potassium permanganate to air, the more absorption and removal of the ethylene gas will occur. In traditional methods of application of potassium permanganate for the absorption and removal of ethylene gas in the fruit storage rooms, large and shallow containers filled with potassium permanganate saturated solution is used (Rezaii Kalaj *et al*., 2009). Only the surface layer of this solution is exposed to atmosphere and ethylene. This layer absorbs ethylene and is oxidized in a short period of time. After this time the solution is no longer effective to increase the surface area (where the air is in direct contact with potassium permanganate, appropriate and inert beds and carriers such as perlites, swelled mica, selenite, silica gel, alumina plates and expanded glasses could be coated with saturated solution of potassium permanganate (Zomorrodi, 2005). These potassium permanganate coated particles of very small sizes with much smaller channel size are used in different manners. They could be placed in small sachets and placed inside fruit boxes and/or placed inside devices circulating the air inside the storage room to maximize the contact between air and potassium permanganate (Rezaii Kalaj *et al*., 2009).

We have produced nano sized zeolite (Clenoptelolite) granules coated with potassium permanganate. We studied the effect of application of this ethylene absorbing particles on the shelf life and quality related characteristics of stored peach and nectarine.

Materials and methods

The varieties included in this study were Red Gold, Songlu and Independence for nectarine and Red Top and Anjiry for peach. Fruits were harvested from trees grown in a commercial orchard located in the Moghan region in the North-West, Iran. Large to medium size fruits were selected randomly from all parts of trees and transported to a packing facility for cooling and packing. Fruits were sorted for uniformity of size, ground color, freedom from defects and mechanical damages and were packed. There were 140 fruits in each replication at each treatment. The fruits were stored at 0 ℃, for 36 days, simulating Iranian exporting condition. Commercial traits affecting the marketing and shelf life of peach and nectarine were measured at the beginning of the experiment (day 0) and every 12 days after that until 36 days of storage.

Ethylene absorption in storage room

Potassium permanganate and Zeolite based Nano-Molecular Filter granules were used in an air circulating machine (ETH 1500, Bioconservacion, Spain). This machine has three drawers; in each 10 Kg of nano- absorbent is placed. Non- recessive reaction between potassium permanganate (with purple color) and ethylene, produces magnesium dioxide (with black color). Each kilogram of granule has the absorption capacity of 3.7 liters ethylene gas (Rezaii Khalaj *et al*., 2009). This machine was placed in the fridge extremity part, beneath the air cooler fans. It intakes ambient air, transmits it through filters and finally return clean air outside.

Quality characteristics

For firmness determination, a penetrometer (FT011 model, tr Co., French) that was fitted with an 8 mm plunger was used. Three measurements were taken from the mesocarps (without the epidermis) of the opposite faces of each fruit. The results were expressed as the mean of the determinations made from 20 fruits in each treatment. The unit of measurement was NCm^{-2}.

A portable digital refractometer (tr Co. Ltd., France), was used for determination of total soluble solids by measuring the refractive index of the extracted juice from 20 randomly selected fruits. The results were expressed as the mean of the determinations made from 20 fruits in each treatment and expressed as the percent (g per 100 g fruit weight) of soluble solids in juice.

The percentages of weight loss were calculated based on the comparison between the fresh weight of the fruits (Day 0) and fresh weight, after 36 days. Titratable acidity, expressed as percent malic acid, was measured by adding 0.1N NaOH until reaching pH 8.2, in 20 randomized selected fruits of each treatment and expressed as $g\ L^{-1}$ malic acid. One milliliter of juice diluted with 99 mL of distilled water was evaluated for each replicate.

Internal and external appearance, and fungal infections were scored by the five panelist using a 5-point hedonic scale (1=75- 100%; 2= 50- 75%; 3= 25- 50%; 4=1- 25% and 5=0% (without disorder)), for appearance evaluation. Fruits were examined at the beginning of the experiment (day 0) and every 12 days after that until 36 days of storage.

The internal breakdown of the fruits at the beginning of the experiment (day 0) and every 12 days after that until 36 days of storage, were scored using a 5-point hedonic scale (1: extremely poor; 3: medium and 5: excellent). Four bags of two fruits were used for each treatment.

Statistical analysis

The experiment was laid in a two factor Randomized Complete Block Design (RCBD) with four replications. The two factors were the presence or absence of the machine and the type of fruit (peach or nectarine). Potassium permanganate and Zeolite based Nano-Molecular filters were used in ethylene absorbent ETH 1500 machine. Two cultivars of peach and three cultivars of nectarine were used in this experiment. Data were subjected to analysis of variance based on statistical model of experiment and means were compared by Duncan's test at the 5% level of significance using SAS and MSTATC software.

Results

Effect of time and ethylene absorption on the quality characteristics of peach and nectarine

No significant difference was observed for any of the studied traits among different nectarine cultivars under the same conditions. Similarly there was no significant difference between the two peach cultivars in the studied traits under similar conditions (except for the firmness). We therefore present the mean data obtained for different cultivars of the same species in the results.

Variances of the effects of storage period and the use of ethylene nano-absorbent machine, on quality characteristics of two peach cultivars and three nectarine cultivars were analyzed. Significant differences were observed among measured traits in response to storage period and fruit species. Significant increase in weight loss percent, total soluble solid percent and juice pH and significant decrease in firmness, titratable acidity, appearance evaluation (AE) score and internal breakdown (IB) score, were observed as the storage time increased. Weight loss in nectarine fruit and juice pH in both fruits, were significantly lower in the treatments that included ETH machine. Firmness, AE score and IB score and titratable acidity and pH at peach juice were significantly higher in both fruit species in the presence of the ethylene absorbent machine. Significant differences were also observed for total soluble solids, pH and titratable acidity between peaches and nectarines.

Weight loss

Both peach and nectarine cultivars weight was reduced with increasing storage time (Figure 1.A). Significantly higher reduction was observed in control treatments (no ethylene absorbing machine). While the average weight loss of peach and nectarine cultivars under the control treatments were 6.98% and 6.07% respectively; for peach and nectarine cultivars in treatments including ethylene absorbing machines, these figures were 5.94% and 4.12, respectively (Figure 1.A). The weight loss was significantly lower in all nectarine cultivars in ethylene absorbing treatment.

Firmness

Firmness of both peach and nectarine cultivars were decreased with increasing storage time. These reductions were significantly higher in control treatments. While the average firmness of peach and nectarine cultivars under the control treatments were 8.88 and 12.05 Newton respectively, this figures were 19.80 and 24.09 for peach and nectarine cultivars in treatments including ethylene absorbing machines respectively (Figure 1.B).

PH

Changes in the juice pH of peach were minimal. However, there was a significant difference between the juice pH of peach stored in absence (pH=6.42) and presence of ethylene absorbent machine (pH=6.14) after 36 days. Juice pH of nectarine was not significantly affected by storage condition in this period of time. It measured 5.45 under the control condition and 5.42 under the ethylene removing treatment (Figure 1.C).

Total soluble solids (TSS) and titratable acidity (TA)

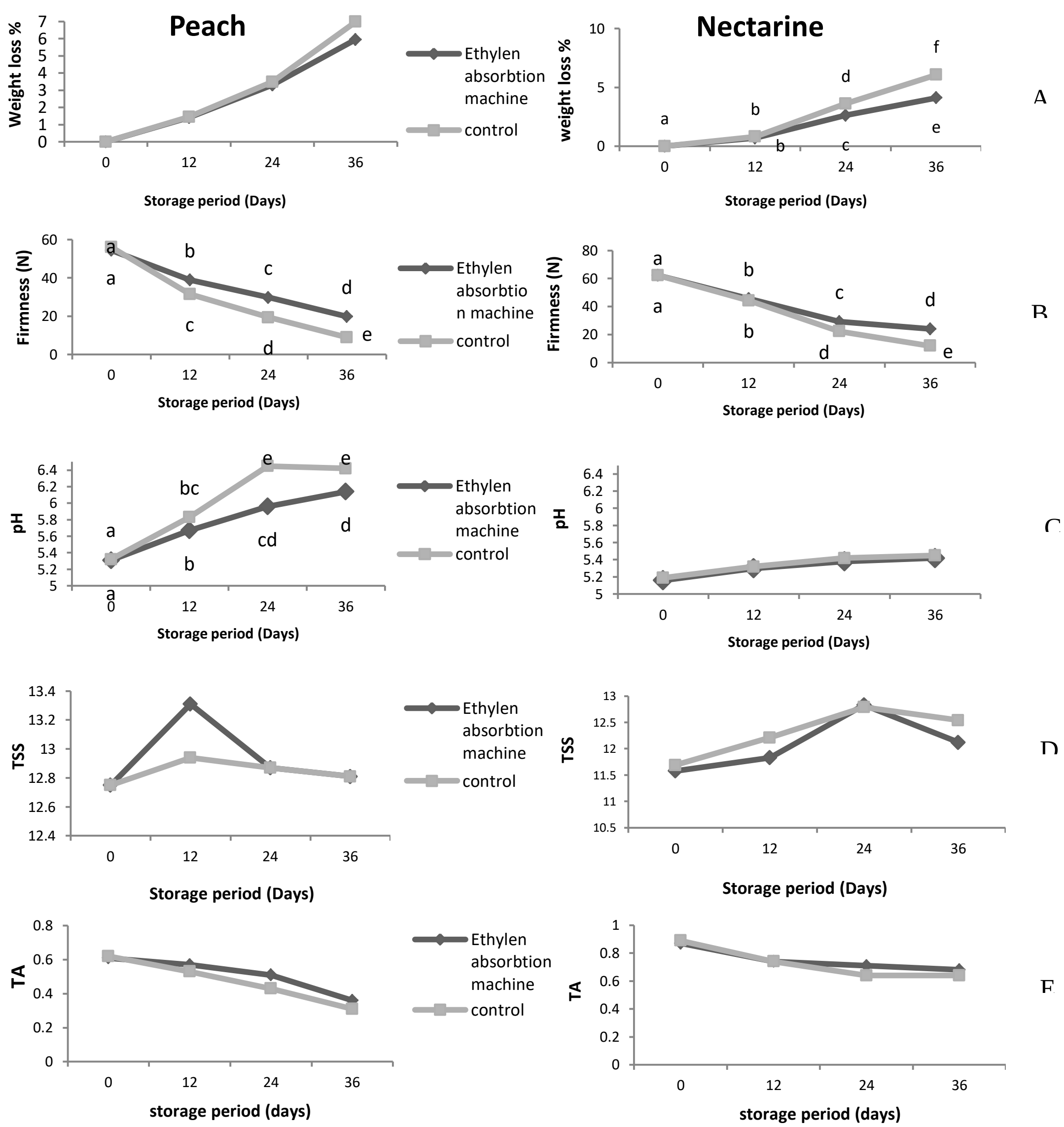
TSS of both peach and nectarine fruits were increased as the storage time increased (Figure 1.D). But TA was decreased in both fruits with increasing of storage time (Figure 1.E). Storage with ETH machine did not significantly affect TSS and TA on both peach and nectarine fruits in this period of time.

Appearance Evaluation (AE) score

As is shown in Figure 1.F, AE score was decreased during the storage period in both peach and nectarine fruits. The changes were more obvious in the fruits under the control treatment. The prime reasons for the decreased AE score was the apparent fungal and bacterial infections as judged by spots and lesions on the fruits. The decrease in AE was significantly lower in ETH treatment. In peach fruit, AE score was 2.91 (between 25 to 50 % disorder) in control fruits and 3.50 (lower than 25 % disorder) in ETH treatment. In nectarine fruit these scores were 2.28 and 3.47 respectively. The difference in AE between fruit under ETH treatment and control treatment were significant at %5 confidence level in both species (Figure 1.F).

Internal Breakdown (IB) score

Results of storage period and use of ethylene nano-absorbent interactions did not demonstrate the significant changes, on internal breakdown of peach and nectarine (Figure 1.G).



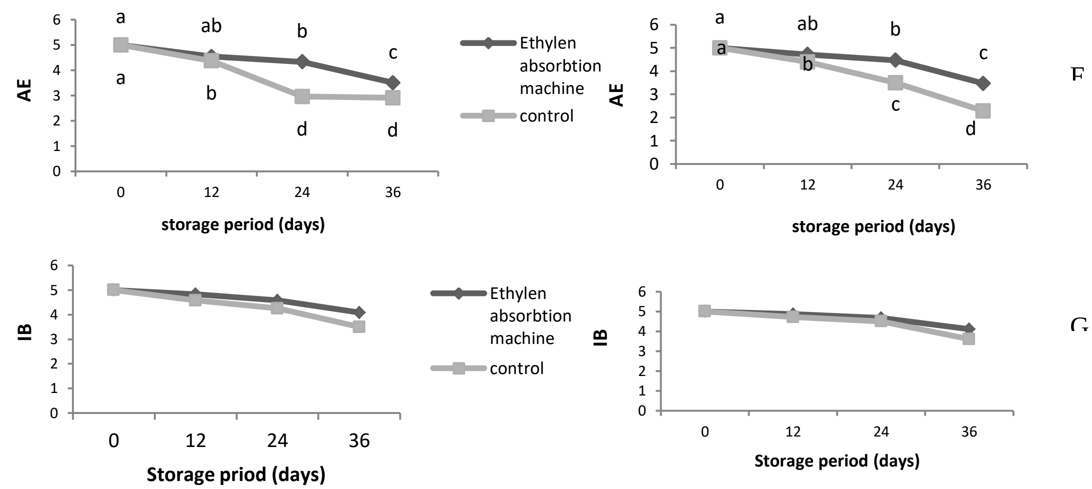


Figure 1. Mean comparisons Effect of the storage period and ethylene nano-absorption machine treatments on the quality and quantity characteristics of Nectarine and peach.

Discussion

Diffusive ethylene from fruits increases the respiration rate and causes the reduction of shelf- life of fruits in the cold storage rooms. Fruits contain some water and carbohydrates, thus respiration causes changes in these compositions, resulting in changes in appearance of fruit and their texture. Use of ethylene absorbents reduced weight loss, firmness and resulted in better appearance evaluation score of peach and nectarine; hence ethylene absorption is an important stride in shelf- life extension of these fruits. Pivot of current research was the effect of nano-absorbent granules. Our results indicated that significant effect of presence of nano granules were visible not only after 36 days of storage, but for many quality characters, the positive effects were observed as early as 12 days of storage of peach and nectarine. This indicates the efficiency of this method of ethylene removal from fruit cold storage rooms on extended quality characteristics of peach and nectarine.

Fruit firmness is one of the very first indications of the fruit freshness. Although fruit firmness was decreased during the storage, but application of nano-absorbent granules significantly slowed down this process, rendering significantly firmer peach and nectarine fruits after long storage periods. Climacteric fruits such as nectarines and peaches are very susceptible to loss firmness with increasing ethylene production. Similar to our observations, Valdes *et al.* (2009) showed that fruit firmness is an ethylene dependent feature and is progressively reduced during storage. Similar result had also been reported by Palou *et al*. (2003) (using potassium permanganate involved sachets), Zhu *et al*. (2006) (inhibition by nitric oxide of ethylene biosynthesis) and Ziliotto *et al*. (2008) (altering ethylene perception, using 1- MCP). Malakou and Nanos (2005) also reported a more pronounced decrease in firmness and AE score under the control treatment with no ethylene removal.

Weight loss is another quality characteristic of stone fruits such as peaches and nectarines that is correlated with. We observed significantly more weight loss in stored nectarine fruits. Ethylene removal significantly reduced the weight loss in nectarine fruits beginning 24 days after storage. This result is in agreement with those reported by Chaves *et al*. (2007) and Silva *et al*. (2009).

In addition to the firmness and weight loss, presence of spots and lesions on fruits were the ethylene was not removed (control condition), was the most obvious quality loss traits during the storage. Apparently ethylene stimulates the bacterial and in particular fungal growth. After 36 days of storage in the presence of nano-absorbent granules for instance, in nectarine cultivars, appearance evaluation (AE) score had dropped from initial score of 5 (without spot and infection) at day 0, to 4.39, whereas in control condition, reduction was more significantly pronounced (from score 5 to 3.79) (Figure 2).

Figure 2. Effect of nano-absorbent granules on quality of Peach (red Top) and Nectarine (Sun Gold). A and A׳: Beginning of the experiment (day 0), B and B׳: After 36 days of storage in the presence of nano-absorbent granul, C and C׳: After 36 days of storage in Control condition.

But the presence or absence of ethylene absorbent did not affect internal breakdown (IB) of peach and nectarine fruits. This was also reported by Palou *et al*. (2003) and Santana *et al*. (2011). Crisosto *et al*. (2001) also concluded that the presence or absence of ethylene did not effect on flesh browning and bleeding of peach fruit.

Valdes *et al*. (2009) reported that TA and TSS were not affected by ethylene and its removal did not have any significant effect on these two quality related traits. Palou and Crisosto (2003) also reported that the presence and quantity of potassium permanganate sachets had no effect on apricots SSC and TA. Other researchers also found similar result with the application of immersion heat treatment (which is another method for reduced ethylene production) in peach (Budde *et al*., 2006). However, Zhu *et al*. (2006) and Bregoli *et al*. (2005) reported that weight loss and TSS were affected by presence or absence of ethylene.

Our findings in this research are in close agreement with the published reports in this filed. In a controlled temperature and humidity (0 ℃ and 90-95%, respectively), the peach and nectarine fruits could be stored for more than 1 month (favorite shelf- life of peach and nectarine in storage condition) with ideal quality, in presence of nano-absorbent granules.

We wish to therefore conclude that the combination of nano-absorbent granules with the air circulating machine used in this research can be considered as an ideal approach for ethylene removal and preservation of quality characteristics of peach and nectarine fruits in cold storage rooms for relatively long periods of time. Considering the comparatively lower cost of application of this method (in comparison with other methods of ethylene scrubbing), and the ease of its application we conclude that this method can be a method of choice in particular for developing countries were the huge investment for modern controlled atmosphere cold storage facilities are not readily available. This technology can be used within trucks carrying fruits for long distances as well.

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