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Use of a palladium catalyst to improve the capacity of activated carbon to absorb ethylene, and its effect on tomato ripening

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Abstract

The aims of this work were to study the ethylene adsorption capacity of different types and masses of activated carbon, to predict the performance of the ethylene adsorption process, to improve the removal of ethylene by impregnating granular activated carbon (GAC) with palladium, and to analyse the effect of this product on the removal of ethylene released from tomatoes. In an *in vitro* system, both GAC and powdered activated carbon (PAC) effectively absorbed exogenous ethylene; GAC was the most effective. Maximum adsorption was achieved with carbon masses of 1.25 g L^{-1} or greater. The best model describing the adsorption of ethylene by GAC was the Langmuir isotherm. To increase ethylene removal, a system involving an adsorbent (GAC) and a catalyst (1% palladium) was developed. This was tested in an *in vivo* experiment involving the removal of ethylene produced by three tomato cultivars inside sealed jars. Ethylene removal led to a delay in tomato ripening; smaller changes in fruit firmness and colour were observed compared to controls. This system could provide a useful way of eliminating ethylene from storage areas and thus maintaining tomato fruit quality, which can be negatively affected by ethylene.

Additional key words: catalyst, charcoal, ethylene adsorption, isotherm adsorption models, *Lycopersicon esculentum*, post-harvest quality.

Resumen

Mejora de la capacidad del carbón activado para eliminar etileno con la adición de paladio como catalizador y su efecto en la maduración de tomate

Los objetivos de este trabajo son estudiar la adsorción de etileno dependiendo del tipo y masa de carbón activado, predecir el mecanismo de adsorción de etileno, mejorar la eliminación de etileno con la impregnación del carbón activado con paladio y finalmente analizar el efecto de la eliminación de etileno desprendido de tomates. Los carbones activados granular (GAC) y en polvo (PAC) aplicados *in vitro* fueron efectivos en la adsorción de etileno exógeno, siendo el GAC el más efectivo. La adsorción máxima se consiguió a partir de una masa de carbón de 1,25 g L^{-1}. El estudio de isotermas indica que el modelo que mejor describe la adsorción de etileno en GAC fue la isoterma de Lagmuir. Para aumentar el porcentaje de etileno eliminado, se desarrolló un sistema basado en el adsorbedor GAC y el catalizador paladio al 1%. Este sistema fue ensayado en un experimento *in vivo* para eliminar el etileno producido por tres variedades de tomate alojados en tarros herméticamente cerrados. El etileno eliminado permitió retrasar los procesos de maduración de los tomates, produciendo los menores cambios de firmeza y color de los frutos respecto a los controles. Este sistema podría ser una herramienta eficaz para eliminar el etileno de las zonas de almacenamiento y mantener la calidad del tomate, que está afectada negativamente por el etileno.

Palabras clave adicionales: adsorción de etileno, calidad postrecolección, carbón, catálisis, *Lycopersicon esculentum*, modelo de isoterma de adsorción.

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Introduction

Fruit ripening during post-harvest storage is accelerated by the presence of ethylene. This is released by fruit itself during ripening, but it can also enter the environment as a result of the pyrolysis of hydrocarbons and the fermentation processes of microorganisms (Chang and Bleecker, 2004). During the storage and marketing of climacteric fruits, such as tomato (*Solanum lycopersicum* L.), ethylene can lead to accelerated ripening and cause changes in colour, texture, flavour and aroma (Lelièvre *et al*., 1997). Tomatoes can become overripe in just a few days, leaving them unmarketable; in the Mediterranean markets in general, and in Spain in particular, consumers demand tomatoes for salads at the breaker or turning stages of ripening (i.e., when the fruits are more firm) (Guillén *et al*., 2007).

Tomato fruits synthesize small amounts of ethylene (0.1-0.2 μL kg^{-1} h^{-1}) during development, but production increases sharply during ripening (up to 1,000-fold depending on the cultivar) (Wills *et al*., 2001). Tomatoes are very sensitive to exogenous ethylene, and the exposure of mature-green fruits to this gas will initiate the ripening process; in fact over-ripening can soon occur (Suslow and Cantwell, 2006). From the point of view of extending tomato shelf life, the elimination of ethylene from storage and marketing areas is a major goal.

Adsorbents such as activated carbon are effective at maintaining fruit quality (Martínez-Romero *et al*., 2007), although the total elimination of ethylene is not complete. It has been reported that several catalysts (Pd, Cu, Rh and Co) are effective with different adsorbents in ethylene removal reactors (Conte *et al*., 1992). In fact, Abe and Watada (1991) have shown that Pd-activated carbon packages reduce ethylene accumulation and delay the softening of kiwi and banana slices, although the Pd concentration used in their model was not provided. Unfortunately, the latter work provides no information regarding the possible use of activated carbon combined with a catalyst in whole fruit. The literature does contain information on the ability of activated carbon to adsorb compounds such as polyphenols and dyes (Arslanoğlu *et al*., 2005a,b; Mall *et al*., 2006), as well as on catalysts that oxidise ethylene (Arsenijevic *et al*., 1999; Maneerat *et al*., 2003), but to the best of our knowledge, no studies have been performed on the adsorption of ethylene by different types and masses of activated carbon, nor to determine the equilibrium model of such adsorption processes. Further, no information is available on the capacity of activated carbon (either alone or in combination with a catalyst) to eliminate ethylene from whole stored fruit, or on its effect on the variables associated with ripening. The aims of the present paper were therefore: a) to study the ethylene adsorption capacity of different types and masses of activated carbon, b) to determine whether the experimental data were best described by the Langmuir, Freundlich, Frumkin or Temkin isotherm (in order to predict the performance of the ethylene adsorption), c) to investigate the removal of ethylene after the impregnation of GAC with Pd, and finally, d) to use GAC-Pd to remove the ethylene released by representative fruits of three tomato cultivars and to determine its effect on fruit ripening.

Material and Methods

Experiment 1

Granular activated carbon (GAC, 20-60 mesh, specific area 626 m^2 g^{-1}) and powdered activated carbon (PAC, 100-400 mesh, specific area 1,200 m^2 g^{-1}) were purchased from Sigma (Sigma-Aldrich, Madrid, Spain). The mass of these products required to achieve the maximum adsorption of exogenous ethylene was then determined. Sachets (made of porous paper) containing different masses (see Fig. 1) and types of activated carbon were placed in 10 glass jars (4 L) which were closed with rubber-sealed caps. Pure ethylene (50 mL L^{-1} in

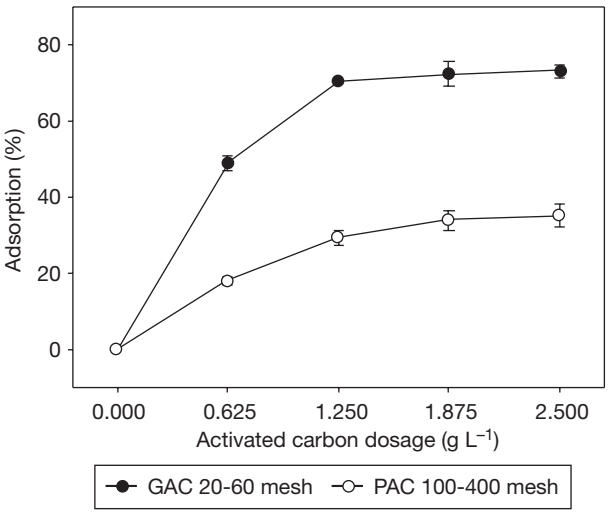

Figure 1. Ethylene adsorption (%) after 24 h at 20°C depending on the mass and type of activated carbon. The initial ethylene concentration was 5 μL L^{-1}.

N_2; Carburos Metálicos, Valencia, Spain) was injected through the septum until a concentration of 5 µL L^{-1} was reached inside the jars. Samples of 1 mL of the head-space atmosphere were withdrawn after 24 h at 20°C and used for ethylene determination.

The optimum masses of both types of activated carbon were then used to analyse ethylene adsorption over a period of 24 h to determine the equilibrium time for different initial ethylene concentrations (1, 2.5, 5 or 7.5 µL L^{-1}) prior to determining their adsorption isotherms (Langmuir, Freundlich, Frumkin or Temkin). The experiment involved 10 replicates. Since the majority of adsorption was achieved with GAC, this activated carbon was impregnated with palladium acetate to obtain concentrations of 1% impregnated Pd; the corresponding adsorption isotherm was then determined in the same manner. Following the injection of ethylene (5 µL L^{-1} inside the jars), samples of 1 mL of the head-space atmosphere were withdrawn for ethylene determination after 1, 3, 9, 24 and 48 h. All jars were maintained at 20°C. The results were expressed as the percentage of ethylene adsorbed.

Experiment 2

Three tomato cultivars were harvested at different commercial ripening stages described by the USDA standard colour classification chart (USDA, 1991): 'Beef' harvested at the turning stage, 'Mendez' harvested at the turning stage, and 'Raf' harvested at the breaker stage. These are the usual picking stages for European markets. Only undamaged fruit was selected. To determine the adsorption by GAC-Pd of ethylene emanating from these tomatoes over 48 h, single fruits (volume *circa* 90 mL) were introduced into 4 L sealable glass jars (single fruits were used to avoid excessive O_2 consumption and CO_2 accumulation, which can affect ethylene metabolism). All jars were sealed and maintained at 20°C. In addition, the physicochemical characteristics of 10 fruits were recorded at harvest (Table 1). The gas composition of the atmosphere in the jar (ethylene, O_2 and CO_2) was determined after 1, 7, 24, 36 and 48 h. The firmness, colour, total soluble solid concentration, titratable acidity and odour intensity of the fruits were analysed at 48 h (the end of the experiment). Ten replicates were performed for each cultivar and treatment (control and GAC-Pd treatments).

Gas composition

One millilitre of the headspace atmosphere from the jars was withdrawn at 48 h using a gas syringe and injected into a 14B gas chromatography system (GC) (Shimadzu, Tokyo, Japan) to determine the CO_2 and O_2 concentrations. The GC was equipped with a thermal conductivity detector (TCD) and a 5A molecular sieve column (80-100 mesh) (Carbosieve SII. Supelco Inc., Bellefonte, USA) 2 m in length and 3 mm in internal

Table 1. Values of isotherm adsoption variables for powdered (PAC) and granular (GAC) activated carbon

Adsorption isotherms	Adsorption variable	PAC	GAC
Langmuir $\frac{Ce}{N} = \frac{1}{k_L Q} + \frac{Ce}{Q}$	Q	7.278	21.645
	K_l	0.064	0.085
	r	0.999	1
	SSE	0.06	0.0007
Freundlich $LnN = LnK_f + \frac{1}{n} LnC_e$	K_f	2.591	0.578
	l/n	1.142	1.085
	r	1	0.999
	SSE	0.008	0.02
Temkin $N = n_t LnK_t + n_t LnC_e$	K_t	2.004	3.923
	n_t	0.715	1.542
	r	0.992	0.992
	SSE	0.144	0.303
Frumkin $N = A + BLn\left(\frac{C_e}{N}\right)$	A	–4.251	11.871
	B	5.704	19.326
	r	0.991	0.999
	SSE	0.151	0.057

diameter. The oven and injector temperatures were 50 and 110°C respectively. Helium was used as the carrier gas at a flow rate of 50 mL min^{-1}. Results were expressed as kPa O_2 and CO_2 and are the mean ± SE of 2 determinations for each of the 10 replicates. Another 1 mL of the same atmosphere was used to quantify its ethylene concentration using a Hewlett-Packard™ model 5890A GC (Wilmington, DE, USA) equipped with a flame ionisation detector and a 3 m stainless steel column (internal diameter 3.5 mm, 80/100 mesh) containing activated alumina. The column temperature was 90ºC and the injector and detector temperature 150ºC. Results were expressed as μL L^{-1} of ethylene and are the mean ± SE of two determinations for each of the 10 replicates.

Tomato quality attributes

Fruit firmness was determined using a flat steel plate mounted on a TX.XT2i texture analyser (Stable Microsystems, Godalming, UK) interfaced with a personal computer. For each fruit, the diameter was measured and the force sufficient to achieve a 2% deformation of the diameter recorded. The results were expressed as the ratio between this force and the covered distance (N mm^{-1}) and are the mean ± SE of determinations made in duplicate for two equatorial fruit planes at 90° to one another. Skin colour was determined using the Hunter Lab System and a CR200™ colorimeter (Minolta Camera Co., Osaka, Japan). Colour (L*, a* and b*) results were expressed as the mean ± SE of determinations made in quadruplicate for each fruit along the equatorial axis. The ripening index was expressed as the ratio between the total soluble solid concentration (TSS) and titratable acidity (TA). A segment of each fruit was taken and homogenized, and measurements of TSS and TA performed in duplicate. The TSS was determined using an Atago PR-101 digital refractometer (Atago Co. Ltd., Japan) at 20°C (the results were expressed as the mean ± SE of the °Brix value). The pH of the juice was then recorded and its TA determined by potentiometric titration with 0.1 N NaOH (up to pH 8.1), using 1 mL of diluted juice in 25 mL distilled H_2O. The results were expressed as the mean ± SE of the weight of citric acid equivalent (g) per 100 g.

Sensorial analyses to assess the jar internal odours were undertaken by 10 trained panellists aged 25-40 years (five female and five male) in a sensory analysis laboratory equipped with an individual booth for each panel member. After 48 h, the 10 jars corresponding to each treatment were opened and the odour intensity immediately judged (one jar per panellist) on a scale of 0 to 4 (0 = absence, 1 = slight, 2 = moderate, 3 = high, and 4 = extremely high).

Statistical analysis

In experiment 1, non-linear regression was performed and the sum square error (SSE) [Eq. 1] used to determine the isotherm model that best fitted the experimental data.

$$SSE = [\Sigma(C_{e,exp} - C_{e,calc})^2/N]^{1/2} \quad [1]$$

In experiment 2, the data were subjected to ANOVA. The sources of variation were taken as treatment and storage. Means were compared using the Tukey HSD test; significance was set at $P < 0.05$. All analyses were undertaken with SPSS software v. 12.0 for Windows (SPSS, 2001).

Results and Discussion

Experiment 1

Ethylene adsorption differed significantly depending on the type and mass of activated carbon used, with GAC the most effective (Fig. 1). For both types of carbon, the percentage of ethylene adsorption (initial concentration 5 μL L^{-1}) increased with the carbon mass until 1.25 g L^{-1} (5 g per jar), with no significant increase with higher doses. Thus, for the remaining experiments a mass of 1.25 g L^{-1} was used. Adsorption by the GAC increased with increasing exogenous ethylene concentration (1, 2.5, 5 and 7.5 μL L^{-1}). For all these concentrations, the percentage adsorption was around 70% for GAC and 40% for PAC (data not shown). Equilibrium was reached after 9 h of exposure to the activated carbons. Longer contact times only achieved similar results.

Figure 2 shows the relationship between ethylene adsorption at equilibrium (N) and the equilibrium concentration of the gas (Ce). Ethylene adsorption increased with both activated carbons (compared to the controls) as the initial ethylene concentration increased. However, the greatest efficacy was obtained with GAC. This agrees with the results of previous reports dealing with other adsorbed compounds (Arslanoğlu *et al*., 2005a,b).

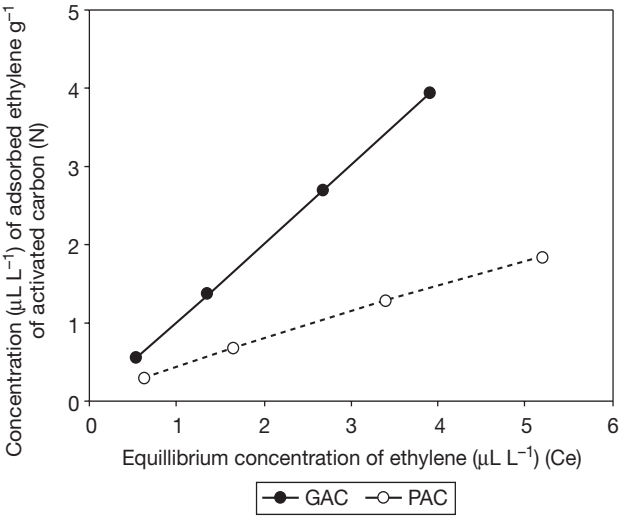

Figure 2. Relationship between ethylene adsorption at equilibrium (N) and the equilibrium concentration of ethylene (Ce) depending on the type of activated carbon used. N was calculated as [N = (CO-Ce) * V/m], where Co and Ce are the initial and equilibrium concentrations of ethylene, V is the volume (L) of the jar and m the mass of activated carbon (g).

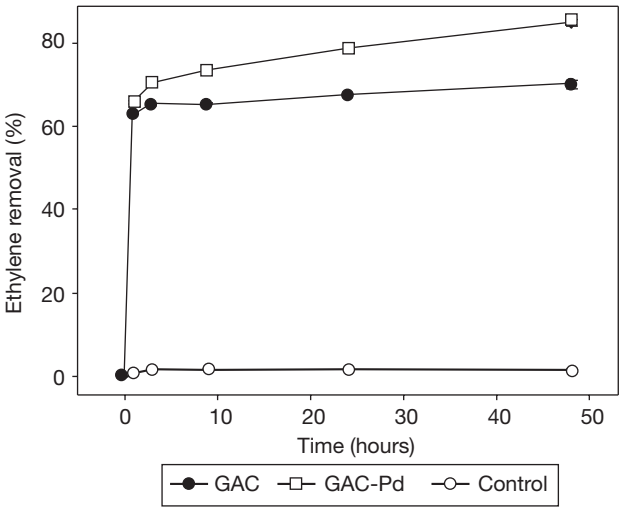

Figure 3. Ethylene removal (%) by granular activated carbon alone (GAC) and GAC impregnated with Pd (GAC-Pd) over 48 h at 20°C. The initial ethylene concentration was 5 µL L^{-1}.

Table 1 shows the results for the absorption variables for the different isotherms; the constants of these isotherms are also shown. The model that best described the adsorption of ethylene by GAC was the Langmuir isotherm; this showed the highest r value and the lowest SSE value. Following the method of Weber and Chakraborti (1974), R_L values were calculated using the formula $R_L = 1/(1+K_l*C_{et})$, where R_L is the equilibrium parameter or dimensionless constant separation factor, K_l the Langmuir constant, and C_{et} the initial concentration of ethylene. All R_L values ranged between 0.611 and 0.921, indicating the favourable adsorption of ethylene by GAC. The Langmuir isotherm described ethylene adsorption by activated carbon well, showing that ethylene accumulates as a monolayer on the surface of the adsorbent.

According to the Langmuir model, GAC alone has a maximum adsorption capacity of 70%, independent of the initial exogenous ethylene concentration. Significant differences were seen in the ethylene removal capacity of GAC and GAC-Pd (Fig. 3). The percentage ethylene removal achieved by GAC after 48 h was 70.10 ± 1.05%, but this increased to 84.69 ± 0.79% with GAC-Pd. There are few reports dealing with the capacity of activated carbon to adsorb ethylene, although its ability to adsorb other molecules —both as gases and liquids— is well known (Kyotani, 2000). In the present work, GAC was found to have a relatively high capacity for adsorbing exogenous ethylene, the kinetics of which are in agreement with those for polyphenol compounds (Arslanoğlu *et al*., 2005a). When Pd was added to the activated carbon, ethylene removal increased —not only due to adsorption but also to oxidation. The role of several catalysts combined with different adsorbents (such as Pt-alumina and Ti-glass beads) in ethylene oxidation has been described (Arsenijevic *et al*., 1999; Maneerat *et al*., 2003). Thus, GAC-Pd was chosen for the second experiment since this provided the best results in terms of ethylene removal (≈85%).

Experiment 2

The three tomato cultivars were harvested at different commercial ripening stages. The 'Beef' and 'Mendez' fruits (harvested at the turning stage) were similar in terms of colour, firmness and TA, while 'Raf' (picked at the breaker stage) had a lower colour a* value and higher TA (Table 2). Ethylene production was similar for the 'Beef' and 'Raf' cultivars; the 'Mendez' fruits produced significantly less ethylene. This is attributable to differences in their initial ethylene production rate and the collection of these fruits at different stages of ripening. Thus, the cultivars with higher ethylene emission rates produced the greatest accumulations in the control jar atmospheres. However, these accumulations were reduced in the presence of GAC-Pd (Fig. 4). The effectiveness of ethylene removal did not seem to be affected by cultivar since the ethylene accumulation

Table 2. Fruit properties at harvest for all three tomato cultivars[1]

	'Mendez'	'Raf'	'Beef'
Weight (g)	71.49 ± 1.20 b	97.40 ± 5.33 a	93.85 ± 3.64 a
Diameter (mm)	102.89 ± 0.64 b	119.17 ± 1.53 a	116.29 ± 2.00 a
Colour (a*)	–2.63 ± 0.73 a	–9.16 ± 0.70 b	–2.39 ± 0.51 a
Ethylene (nmol kg^{-1} h^{-1})	600 ± 42 b	790 ± 41 a	773 ± 44 a
Respiration rate (μmol kg^{-1} h^{-1})	170 ± 8 b	126 ± 17 a	115 ± 15 a
Fruit firmness (N mm^{-1})	5.45 ± 0.32 a	3.28 ± 0.14 b	4.84 ± 0.27 a
TSS (°Brix)	6.85 ± 0.26 b	7.15 ± 0.17 b	8.27 ± 0.16 a
Acidity (g 100 g^{-1})	1.08 ± 0.06 a	1.74 ± 0.09 b	0.96 ± 0.07 a

1 For each variable, values within a row with the same letter are not significantly different ($P \leq 0.05$).

was similar for all (50-61%). These values are slightly lower than those obtained in the *in vitro* experiments, perhaps due to the fruits' ethylene production changing over time inside the jar, which might be different for the different cultivars. The more the ethylene accumulated inside the jars the more this might have induced the exponential synthesis of ethylene, since in tomato it is well known that ethylene from system I activates autocatalytic ethylene emission triggered by system II (Alexander and Grierson, 2002).

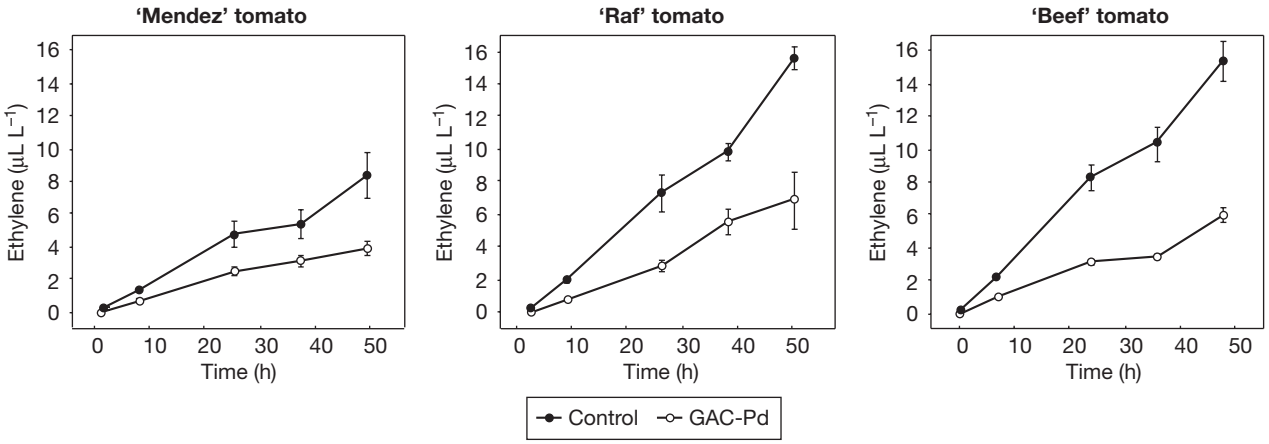

Figure 4. Ethylene accumulation in jars containing tomatoes with and without (control) GAC-Pd over 48 h at 20°C.

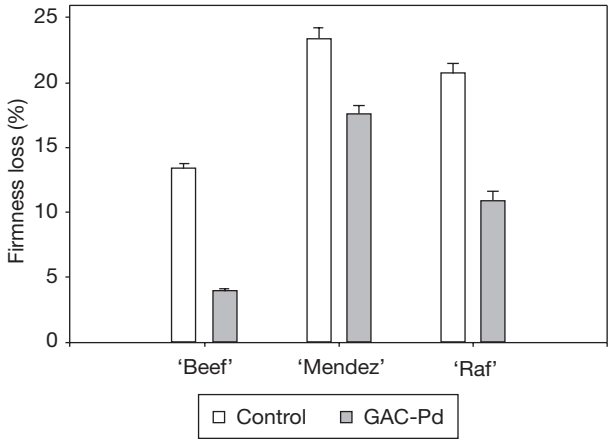

Figure 5. Loss of firmness (%) in tomatoes after 48 h of storage at 20°C in sealed jars with and without (control) GAC-Pd.

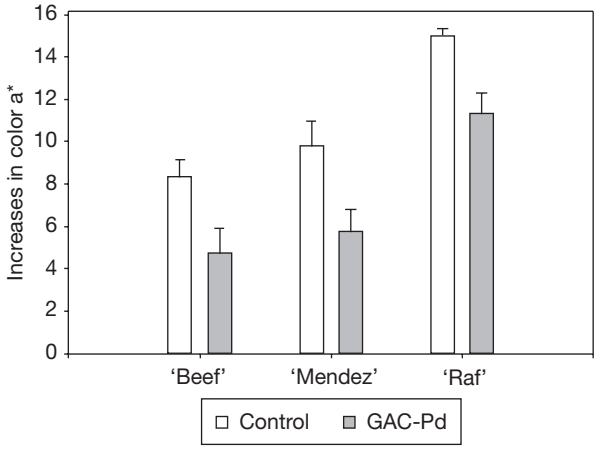

Figure 6. Increase in tomato colour a* value following 48 h of storage at 20°C in sealed jars with or without (control) GAC-Pd.

During the experiment, slight increases in CO_2 and reductions in O_2 were seen in the head space, with final concentrations of ≈2 and ≈18 kPa obtained (data not shown). Although the tomatoes were placed in sealed jars, the volume of these (4,000 mL) was very large compared to that of the single tomato each contained (≈90 mL). Thus, the CO_2 concentration reached after 48 h was insufficiently high to modify ethylene metabolism (concentrations over 5 kPa would be necessary for this; Mathooko, 1996). Moreover, for apple slices, concentrations of 15 kPa or more were necessary to inhibit ethylene emission (Gunes *et al*., 2001).

The analysis of the tomato quality variables showed a significant reduction in both softening and colour changes in fruits stored with GAC-Pd when compared to controls. Thus, for all the tested cultivars, smaller losses of fruit firmness and smaller increases in the colour a* value were seen when GAC-Pd was added (Figs. 5 and 6). Accelerated ripening after harvesting leads to quality losses in tomatoes; colour and firmness are very important from the consumer's point of view, and rapidly occurring post-harvest changes in these variables lead to a reduced shelf life. The use of GAC-Pd to remove ethylene from the environment could help to delay ripening and extend the time that tomatoes are acceptable for consumption.

At the end of the experiment, the panellists evaluated the intensity of the odour emanating from the opened jars (Fig. 7). The highest scores (over 3) were given to the control jars, while those containing GAC-Pd received scores below 1.5. Ethylene plays a key role in the production of volatile aroma compounds during tomato ripening (Zhu *et al*., 2005); tomatoes from the control jars suffered no inhibition of volatile aroma compound synthesis, while the delayed ripening in the GAC-Pd-containing jars was associated with a delay in the synthesis of these molecules. In addition, some of the volatile compounds produced may also have been adsorbed by the GAC-Pd.

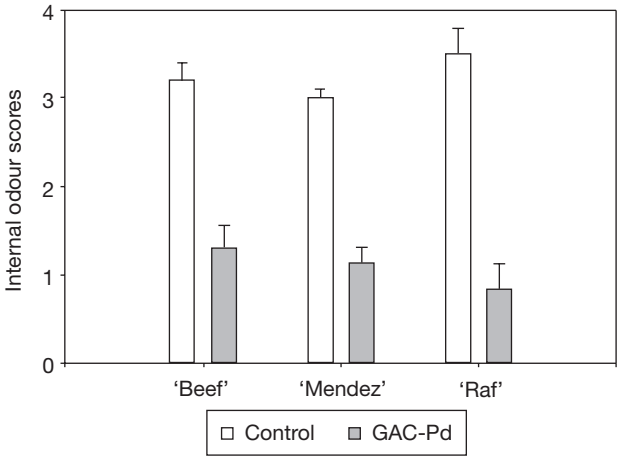

Figure 7. Odour accumulation in sealed jars containing tomatoes for 48 h at 20°C with or without (control) GAC-Pd.

In conclusion, GAC-Pd could be used in storage holds, during transport, at markets and even in refrigerators to reduce ethylene concentrations, thus delaying ripening and helping to maintain tomato quality.

Acknowledgements

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