



Potassium Permanganate-Based Ethylene Scavengers for Fresh Horticultural Produce as an Active Packaging

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Abstract

Potassium permanganate (KMnO₄) is a powerful ethylene (C₂H₄)-scavenging agent widely used in fresh horticultural commodities to delay the postharvest maturation. According to databases, it has been used for almost 50 years in food-packaging systems, and over 70 studies have evaluated its effects on fresh produce quality, mainly on climacteric fruit. However, the use of KMnO₄-based technology remains limited at a commercial scale, since there are still lots of doubts on its potential as an effective postharvest tool, as well as in relation with health, environmental and safety concerns. Depending on the commodity, and even the variety, these scavengers may have different effects, but overall, they can delay ripening/senescence-related processes such as chlorophyll degradation/colour changes, weight and firmness losses, disorders and diseases, acidity and sugar changes. This review comprises an updated overview of the current knowledge regarding the use of KMnO₄ as C₂H₄-scavenging agent, providing a concise appraisal on KMnO₄-based C₂H₄ removal application and its effect on the quality of fresh produce. KMnO₄ is commonly supported onto microporous mineral particles, which are placed into small sachets to avoid direct food contact within packages. Generally, KMnO₄-based C₂H₄ scavengers are jointly used with modified atmosphere packaging. Hence, KMnO₄-based C₂H₄-scavenging systems, as an active food-packaging technology, seem to be a relevant option to preserve the quality and safety of fresh horticultural produce. Nevertheless, although there are many KMnO₄-based products available in the market, which are presently reviewed, more research is required in order to obtain an optimal C₂H₄-scavenger performance.

Keywords Food packaging · Modified atmosphere · Ethylene removal · Shelf life · Fresh produce

Introduction

In recent years, a growing interest of consumers in high-quality fresh fruit and vegetables has been observed [129]. This is mainly due to a better knowledge of the health benefits of produce consumption, as well as to the increased awareness of their nutritional content and functional traits [148]. Nevertheless, fruit

and vegetables are perishable products whose safety, sensory and nutritional/functional qualities may be highly reduced if appropriate postharvest techniques are not applied, leading to a shortened shelf life [149, 174]. In addition, such reduced shelf life of fresh fruit and vegetables may result in postharvest losses with socioeconomic and environmental implications [100, 129]. For instance, in the year 2010, the United States Department of Agriculture reported a 10.5% loss of the total fruit and vegetables available at a retail level in the United States of America (USA) and 24.5% at the consumer level, leading to total economic losses of \$34.8 billion [34]. Therefore, with the aim of improving the convenience and safety of horticultural products, without altering their sensory attributes, the world horticultural industry is constantly searching for innovative and sustainable processing, handling and storing techniques [10, 106].

Although it is well-known that temperature is the most important postharvest factor to be considered to preserve quality and safety in fresh horticultural products [86, 174], storing them in an improper atmosphere may result in some

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physiological disorders [171]. In this sense, ethylene (C_2H_4) is a plant hormone—physiologically active in trace amounts (even less than $0.001 \mu L L^{-1}$)—whose postharvest actions are diverse and vary between produce [119, 133, 165]. Nonetheless, overall, the major effects are related to an accelerated ripening process in climacteric fruit and to an accelerated senescence of non-climacteric produce, affecting the quality and leading to a reduction in postharvest life [98, 169]. Furthermore, it has been found that exposure to C_2H_4 increases postharvest rotting (fungal development) in non-climacteric produce [131]. Therefore, C_2H_4 is a critical factor in postharvest management of fresh horticultural commodities, especially during long-term storage and long-distance transport [104, 179]. According to Kyriacou and Rouphael [99], prevention of detrimental C_2H_4 action may be achieved through the use of scavenging technologies. Meanwhile, Wills [165] point out that the use of C_2H_4 scavenging tools is a low-cost option for preserving fresh produce quality. In addition, C_2H_4 scavengers seem to be a promising tool to minimise the need for refrigeration and hence to reduce energy consumption [166].

C_2H_4 -scavenging products may be used to remove C_2H_4 from storage facilities and transport vehicles, as well as from the in-package atmosphere [32]. Nevertheless, since packaging is a major critical factor in postharvest management for preserving quality and safety of perishable horticultural commodities [107, 172], the most common application of C_2H_4 -scavenging technology is in food-packaging systems [25, 175]. In fact, at the time of data collection, it was found that most research deals with C_2H_4 -scavenging tools as an extension of modified atmosphere packaging (MAP) technology for fresh produce (Table 1), although some trials have also been carried out on produce stored under controlled atmosphere (CA) conditions (Table 2).

Nevertheless, CA storage can be expensive since the facilities are usually fairly complex and the maintenance of the optimal gas levels demands a high surcharge [56]. Therefore, compared to CA technology, the active MAP technology is an attractive option to delay the rate of fresh fruit and vegetable physiological processes, extending their shelf life [75, 108].

Unlike traditional inert packaging, an active package is engineered to achieve an intentional and dynamic modification of the atmosphere within the package by means of scavenging or releasing technologies [75, 105]. Although the active MAP technology for fresh commodities is not new [176], it has gained popularity in recent years. Furthermore, in 2014, active packaging comprising C_2H_4 -scavenger tools was described as an emerging technology [56]. Nowadays, one of the most commonly used C_2H_4 -scavenging technology is based on potassium permanganate ($KMnO_4$) [4].

$KMnO_4$ -based C_2H_4 -scavenging systems for fresh fruit and vegetable packaging have been extensively studied [116, 170, 179]. Nonetheless, to the best of our knowledge,

there is not a previous comprehensive review discussing applications of $KMnO_4$ -based C_2H_4 scavengers in food packaging and their effects on quality aspects of fresh produce. In fact, there is a lack of attention on the influence of storage conditions and commodity physiology on the C_2H_4 -scavenging performance of the said scavenging systems. Thus, the present review compiles studies concerning the $KMnO_4$ application as a postharvest tool to remove C_2H_4 from the surrounding atmosphere within the package. There, emphasis is made on reviewing $KMnO_4$ -based C_2H_4 -scavenger effects on quality attributes of both climacteric and non-climacteric produce. Furthermore, special attention is given to factors that may affect the scavenging performance of such C_2H_4 removal systems.

State-of-the-Art of Potassium Permanganate-Based Ethylene Scavengers

C_2H_4 is a gaseous simple carbon–carbon double bond molecule that is commonly found in the environment. C_2H_4 is endogenously produced by plant tissues and some microorganism metabolism, but it can also occur as a result of combustion of hydrocarbons [91]. In fact, C_2H_4 is the most produced organic compound throughout the world [16]. Hence, because the postharvest life of many fresh fruit and vegetables is highly limited by means of their own metabolic processes and C_2H_4 exposure since they are still alive and respond to the environment factors, much effort has been devoted to protecting horticultural products from the negative effects of C_2H_4 exposure [91, 110, 178].

Among the available technologies for controlling C_2H_4 , 1-methylcyclopropene (1-MCP) is an C_2H_4 action inhibitor that works by competitively blocking fruit C_2H_4 receptors [165]. As an effective C_2H_4 antagonist, 1-MCP has been globally recognised as a useful agro-food industry tool [161]. Nonetheless, it can only be conveniently used in certain horticultural products since pathological and physiological disorders (e.g. CO_2 -related injuries and chilling-related disorders) may be increased in both non-climacteric and climacteric fruit after 1-MCP exposure [102, 162].

C_2H_4 action may also be avoided by removing C_2H_4 surrounding fresh commodities. It has been proven that C_2H_4 scavengers are effective in removing C_2H_4 from the in-package atmosphere of fresh fruit and vegetables [75, 116]. C_2H_4 -scavenging technology involves physical phenomena (overall, adsorption) and/or chemical reactions (usually, C_2H_4 -oxidising agents are used) [45].

C_2H_4 adsorption may be performed by means of materials with active surfaces such as activated carbon, zeolites and some clays (e.g. pumice, cristobalite and clinoptilolite) [91, 97, 154]. Such materials can be contained into a C_2H_4 -permeable sachet, or fine particles of those minerals can be dispersed

Table 1 Overview of KMnO₄-based C₂H₄-scavenger trials and effects on fresh produce packaged in modified atmospheres

Produce	Ethylene scrubber application	Produce packaging	Storage conditions	Inferences	Reference
Climacteric fruit					
Apple (<i>Malus</i> sp.) 'Granny Smith'	108 g of KMnO ₄ supported on aluminium oxide. 22 fruit per EU	Held in a sealed PE bag (40 µm thickness)	0.5 °C 2 weeks	Reduced C ₂ H ₄ and CO ₂ levels as well as bitter pit severity and superficial scald	Shorter et al. [143]
Apple 'Gala'	One sachet of KMnO ₄ -based C ₂ H ₄ scavenger per 18 kg of fruit. KMnO ₄ amount NS	Wrapped with HDPE (30 µm thickness) and packed in a carton box	0 °C (90–95% RH) 2 months + 7 days (2 °C, 70–80% RH)	Delayed ripening and skin colour change, reduced fruit pulp firmness loss and slowed TA decrease. SSC was not affected	Amarante and Steffens [6]
Apple 'Gala'	Three scrubber sachets (9 g each of vermiculite impregnated with KMnO ₄) per 18 kg of fruit	Packaged into a LDPE bag (20 µm thickness) and packed in a carton box	4 °C 15 days + 3 days (20 °C)	Reduced in-package C ₂ H ₄ levels. Pulp firmness, colour, TA and SSC were not significantly affected	Brackmann et al. [29]
Apple 'Golden Delicious'	10 g of KMnO ₄ coated zeolite sachets (they were replaced at the middle of the storage period). 30 fruit per EU	Placed in a carton box and wrapped with craft paper	0 °C (90% RH) 5 months	Reduced pH increase and TA decrease. Minimised SSC accumulation. Delayed de-greening process and flesh firmness loss	Sardabi et al. [137]
Apple 'Golden Delicious' 'Bramley's Seedling'	200 g of expanded mica impregnated with KMnO ₄ . 96–120 fruit per EU	Placed in a steel vessel and sealed with a permeable silicone membrane	4 °C ~250 days	Reduced C ₂ H ₄ concentration. Retarded softening and reduced superficial scald incidence	Knee and Hatfield [95]
Apple 'Royal Gala'	One sachet (10 g each of KMnO ₄ -based scavenger) per 18 kg of fruit	Packed in a carton box and wrapped with HDPE (30 µm thickness)	0 °C (90–95% RH) 2 months + 7 days (20 °C, 70–80% RH)	Reduced C ₂ H ₄ concentration. Delayed peel de-greening and pulp firmness loss. Slowed SSC increase. Iodine-starch index and TA were not affected	Amarante and Steffens [7]
Apricot (<i>Prunus armeniaca</i> L.)	KMnO ₄ impregnated into sponge cubes. The fruit was previously coated with 3% CaCl ₂ . Fruit weight and KMnO ₄ amount NS	Packaged in a PE bag	28–30 °C (60–63% RH) 10 days	Delayed both weight and vitamin C content loss. Reduced SSC and TA decrease. Retained sensory parameters	Ishaq et al. [81]
Apricot 'Patterson' 'Castilebrite' Avocado (<i>Persea americana</i> Mill.)	One 9-g KMnO ₄ sachet	Packed in a box	5 °C 14 days	SSC, TA and brown rot development were not affected	Palou and Crisosto [117]
Avocado 'Hass'	0.03 g KMnO ₄ incorporated into 0.14 g ANP-incorporated ANF membrane. 1 fruit weighing ~ 153 g per EU	Placed in an opening bag containing ~ 0.23 g of a 5% ANP-incorporated ANF membrane piece loaded with 0.06 g KMnO ₄	6 days	Removed in-package C ₂ H ₄	Tirgar et al. [154]
Avocado 'Pollock'	9.5 g of KMnO ₄ -based scrubber per kg of fruit. 10 fruit per EU	Placed in a polythene box and wrapped with LDPE film (25 µm thickness)	6 °C 60 days	Reduced CO ₂ and C ₂ H ₄ concentration. Delayed pulp softening and peel resistance decrease	Correia et al. [48]
	Pouches containing KMnO ₄ impregnated into clay bricks. Granular charcoal (2 g) wrapped with a muslin cloth. 3 fruit per EU. KMnO ₄ amount NS	Packed in a perforated LDPE bag (50 µm thickness)	12 °C (94% RH) 21 days	Reduced in-package CO ₂ and C ₂ H ₄ concentrations. Kept good visual quality. Inhibited disease incidence and reduced chilling injury. Delayed both weight and	Illeperuma and Nikapitiya [77]

Table 1 (continued)

Produce	Ethylene scrubber application	Produce packaging	Storage conditions	Inferences	Reference
Baby banana (<i>Musa</i> AA, Simmonds) clon Orto	Sachets containing 5 g of KMnO_4 and vermiculite mix at a dose of 1.5 and 1% w/w based on fruit weight, respectively. 300 g fruit per EU	Packed in a LDPE bag	18 °C (70–80% RH) 16 days	firmness losses. SSC and pulp colour were not significantly affected Delayed peel yellowing. Slowed SSC increase and TA decrease. Reduced firmness loss and weight loss. Minimised SSC/TA ratio increase	García et al. [69]
Banana (<i>Musa</i> sp.)	0.03 g KMnO_4 incorporated into 0.14 g ANP-incorporated ANF membrane. Fruit weight NS	Placed into a zip-lock bag containing 0.7 g of a 5% ANP-incorporated ANF membrane piece loaded with KMnO_4	14 days	Removed in-package C_2H_4 . Significantly delayed the incidence of dark brown regions on the skin. Reduced flesh softening	Tirgar et al. [154]
Banana	100 g of ground bricks impregnated with KMnO_4 per 6 fruit hands (15–17 fingers per hand). Container device NS	Stored in a perforated PE bag	14–18 °C (33–58% RH) 24 days	Delayed yellowing of peel and minimised ascorbic acid degradation. Reduced weight loss and firmness loss. Slowed SSC, total sugars, reducing sugar and TA increases. Retained the marketability percentage	Zewter et al. [177]
Banana 'Kolikutu'	Wrapped bricks impregnated with KMnO_4 . One hand with 12–14 fingers per EU. KMnO_4 amount NS	Packed in a LDPE bag (75 μm thickness)	14 °C 94% RH 30 days	Decreased in-package C_2H_4 and CO_2 concentrations. Minimal changes in physicochemical properties (weight, firmness, SSC, pH and SSC/TA) were observed after storage. Extended storage life by 6 days	Chamara et al. [42]
Banana 'Pachbale'	One sachet (5 g each of KMnO_4 -impregnated white cement and limestone powder) per kg of fruit; plus, CO_2 and moisture absorbents	Packed in a PE bag (25 μm thickness)	13 °C 18 days	Reduced respiration rate and minimised CO_2 and C_2H_4 concentration. O_2 and pulp/peel ratio were slightly affected. Delayed yellowing. Reduced firmness loss. Reduced SSC/TA ratio increase. Ascorbic acid content and pH were not affected. Extended 3–4 days fruit shelf life	Chauhan et al. [43]
Banana 'Prata Aña'	One sachet (10 g each of KMnO_4 -based scavenger) per 3–5 fruit (~457 g)	Packed in LDPE bag (10 μm thickness)	12 °C 35 days	Delayed colour peel changes and starch degradation. Reduced C_2H_4 concentration and delayed climacteric peak. Slowed SSC and TA increase. Slightly affected weight loss	Prill et al. [121]
Banana (<i>Musa cavendishii</i> L.) 'Williams'	One pouch (20 g of KMnO_4) per 3 hands of fruit	Stored in a PE bag (40 μm thickness) and placed in a carton box	20 °C (65–70% RH) 45 days	Reduced weight loss. Delayed yellowing of peel and firmness loss. Peeling condition was not affected. Minimised pulp/peel ratio increase. Slowed increase of SSC and TA. Induced SSC/TA ratio increase and pulp pH decrease. Delayed ripening	Tourky et al. [155]
Banana 'Williams'	25 g of vermiculite impregnated with KMnO_4 . 3 half hands per EU	Placed into a sealed PE bag (40 μm)	20 °C 38 days	Minimised C_2H_4 concentration. Reduced firmness loss. Delayed fruit deterioration	Scott et al. [139]
Banana (<i>Musa paradisitaca</i> L.)	One sachet (30 g each of clay impregnated with KMnO_4) (at a		27–30 °C 18 days		Santosa et al. [136]

Table 1 (continued)

Produce	Ethylene scrubber application	Produce packaging	Storage conditions	Inferences	Reference
'Raja Bulu'	rate of 7.5% w/w) per 6 fingers (0.42–0.67 kg) of fruit	Stored in a plastic bag and packed in a carton filled with paper		Delayed yellowing of peel and firmness loss. Reduced weight loss. Slowed TA increase. SSC and pulp/peel ratio were not affected	
Bitter gourd (<i>Momordica charantia</i> L.)	8 g of KMnO ₄ -celite mixture (containing 133% (w/w) KMnO ₄) of per kg of fruit	Packaged in a PP bag (50 µm thickness)	27–31 °C (69–72% RH) 6 days	Delayed weight loss as well as chlorophyll content degradation. Reduced disease index and spoilage. Preserved sensory quality	Bhattacharjee and Dhua [18]
'Meghna-2'	One sachet (10 g each of KMnO ₄ -based scavenger at KMnO ₄ concentration ≥ 10%) per 200 g of fruit	Packaged into a PE bag (20 µm thickness)	0 °C (85% RH) 60 days + 8 days (20 °C, 85% RH)	Delayed weight loss and fruit softening. Reduced decay incidence and prevented total phenolic content. Minimised SSC changes and C ₂ H ₄ production	Wang et al. [160]
Blueberry (<i>Vaccinium corymbosum</i>)	One sachet containing 0.7 g of KMnO ₄ -modified montmorillonite (at a rate of 9.5% w/w KMnO ₄) per 120 g of fruit	Placed in a PP tray and covered with a bioriented PP film (35 µm thickness)	2 °C 46 days	Removed C ₂ H ₄ without affect in-package CO ₂ atmosphere. Reduced fungi-caused decay incidence and preserved weight, firmness, TA and SSC/TA for longer	Álvarez-Hernández et al. [5]
Date fruit (<i>Phoenix dactylifera</i> L.)	One sachet (10 g each of sodium polyacrylate powder soaked in 5% KMnO ₄ solution) per 20 fruit	Packaged into PVC-PE bags (670 µm thickness)	5 °C 75% RH 27 days	Weight loss was not affected. Lowered incidence. Slowed SSC increase rate and TA decrease. Retarded skin colour changes	Mortazavi et al. [113]
(<i>Ficus carica</i> L.)	KMnO ₄ incorporated into the film packaging. 10 fruit per EU	Wrapped with PE containing additive KMnO ₄	2 °C 21 days	Highly delayed both weight and firmness losses. SSC and pH were not significantly affected. Reduced C ₂ H ₄ concentration. Volatile compounds production was not affected	Bouzo et al. [26]
Guava (<i>Psidium guajava</i> L.)	One sachet containing 3 g of KMnO ₄ plus one sachet containing 46 g of silica gel per 2 fruit (~200 g each fruit)	Packed with a PVC film (40 µm thickness)	4 °C (85% RH) 30 days + 2 days (30 °C, 90% RH)	Delayed ripening rate and the greenness loss of peel. Reduced mould growth severity. Prevented chilling injury symptoms. Increased weight loss and reduced SSC increase. Reduced both phenol content and ascorbic acid content decrease rate. No significant effect was observed for reducing sugar and TA	Murmu and Mishra [115]
Guava	Sachets containing KMnO ₄ impregnated into silica crystal	Packed with LDPE film (76.2 µm thickness)	8 °C 49 days	Reduced fruit firmness SSC, TA and colour changes	Singh and Giri [146]
Guava	Sachets containing KMnO ₄ at a rate of 10 g per kg of fruit. 30 fruit per EU. Sachet quantity NS	Packed in a foam plate and wrapped with PE film (10 µm thickness)	8 °C (90% RH) 20 days	Increased weight loss and reduced SSC increase. Reduced both phenol content and ascorbic acid content decrease rate. No significant effect was observed for reducing sugar and TA	El-Anany and Hassan [58]
Kiwifruit (<i>Actinidia deliciosa</i>)	Sachets containing a mixture of natural clay and KMnO ₄ granules (at a rate of 9 g per kg of fruit). 8 fruit per EU. Sachet quantity NS	Placed in LDPE (13 µm thickness)	0 °C (85–95% RH) 200 days	Reduced fruit firmness SSC, TA and colour changes	Bal and Celik [12]
'Hayward'	12 g of KMnO ₄ per kg of fruit. Container device NS	Packed in a HDPE bag (40 µm thickness)	20 °C 28 days	Increased weight loss and spoilage incidence. Slightly slowed colour changes. TA, SSC and vitamin C content were slightly affected. Firmness was not significantly affected	Ramin et al. [126]

Table 1 (continued)

Produce	Ethylene scrubber application	Produce packaging	Storage conditions	Inferences	Reference
Mango (<i>Mangifera indica</i> L.) 'Dashhehari'	KMnO ₄ -based C ₂ H ₄ scavenger at a rate of 6%	Packed in a 200-mm gauge PE bag	12 days	Reduced decay. Slowed pH increase tendency Reduced weight loss and rotting incidence. Delayed SSC decrease and vitamin C degradation. Retained soluble sugar and reducing sugar changes	Yadav et al. [173]
Mango 'Haden 2H'	One sachet (5 g each of KMnO ₄) per 3.2 kg of fruit	Placed in a LDPE bag (28 µm thickness)	12 °C (90% RH) 26 days	SSC, pH, TA, weight loss, colour, firmness and disease incidence were not affected	Castro et al. [37]
Mango 'Hindi Besennara' 'Aiphonse'	One sachet containing KMnO ₄ (at a rate of 2.5 g per kg of fruit). 24 fruit per EU	Packed in a card box and wrapped with LDPE film (28 µm thickness)	8 °C (85–90% RH) 30 days	Firmness loss was not affected. Delayed weight loss. Slowed SSC increase and ascorbic acid degradation. Minimised TA decrease and increased shelf life	Ezz and Awad [65]
Mango 'Karuhacolomban'	Pouches containing KMnO ₄ -bricks. Plus activated granular (2 g) charcoal wrapped with muslin. 3 fruit per EU. KMnO ₄ amount NS	Packed in a perforated LDPE bag (50 µm thickness)	13 °C (94% RH) 21 days	Reduced in-package O ₂ , CO ₂ and C ₂ H ₄ concentrations. Slowed both weight and firmness loss. Delayed pH and SSC increase, as well as TA decrease	Illeperuma and Jayasuriya [76]
Mango 'Madu'	KMnO ₄ at a rate of 450 g per litre	Packed in a PE bag and placed in a corrugated fibre board	25–28 °C 21 days	Decreased respiration rate and ethylene production. Weight loss and decay percentage were not significantly affected	Basuki and Prarudiyanto [13]
Mango 'Tommy Atkins'	One sachet containing vermiculite impregnated with KMnO ₄ at a rate of 10 g KMnO ₄ per 0.5 kg fruit	Packed in a plastic tray and covered with a PVC film (14 µm thickness)	13 °C (85–90% RH) 20 days + 6 days (14 °C, 70% RH)	Weight loss and pulp firmness were not significantly affected. Delayed TA decrease. Ascorbic acid degradation, SSC rate and SSC/TA were affected	Jeronimo et al. [84]
Mango 'Tommy Atkins'	KMnO ₄ -based C ₂ H ₄ scavenger	Packed in a LDPE bag	12 °C (90% RH) 21 days	Inhibited decay incidence. Delay firmness loss. Peel colour development and disease incidence were not affected	Castro et al. [36]
Melon, cantaloupe (<i>Cucumis melo</i> L.) 'Vera Cruz'	12 sachets (2.5 g each of vermiculite impregnated with 0.25 g of KMnO ₄) per kg of fruit. 4 fruit per EU	Placed in a box and wrapped with a LDPE film	3 °C (85% RH) 14 days + 8 days (23 °C, 90% RH)	Weight loss, pulp/peel firmness, SSC, TA, pH, colour and decay incidence were not affected	Sá et al. [130]
Papaya (<i>Carica papaya</i> L.) 'Sunrise Golden'	Sachets of vermiculite impregnated with KMnO ₄ at 1.5 g per bag. 3 fruit (~ 289.9 g each fruit) per bag. Sachet quantity NS	Packed in a hermetic LDPE bag (28 µm thickness)	10.4 °C (90% RH) 25 days + 6 days (21 °C, 90% RH)	Delayed weight loss. Reduced pulp consistency loss and SSC increase. Maintained peel colour index. Reduced CO ₂ production	Silva et al. [144]
Papaya	20 g of KMnO ₄ . Fruit weight and device container NS	Stored into a sampling chamber	25 °C (60% RH) 8 days 1 °C 126 days 0 °C	Reduced C ₂ H ₄ production	Corrêa et al. [47]
Pear 'Williams' Pear, Japanese 'Nijisseiki'	KMnO ₄ -based C ₂ H ₄ scavenger 20 g of KMnO ₄ supported on aluminium oxide placed in	Packed in a sealed polyethylene bag Packed into a LDPE bag (50 µm thickness)	1 °C 126 days 0 °C	Reduced C ₂ H ₄ level. Minimised brown heart	Scott and Wills [138]
			252 days		Giraldo et al. [70]

Table 1 (continued)

Produce	Ethylene scrubber application	Produce packaging	Storage conditions	Inferences	Reference
Persimmon (<i>Diospyros kaki</i> L.) 'Fuyu'	small dishes among the fruit. 20 fruit per EU Two sachets containing 8.5 g of alumina-KMnO ₄ per box. 4 samples of 20 fruit (previously 1-MCP treated) per box	Packed in a plastic box internally coated with a PE bag (40 µm thickness)	-0.1 °C 80 days	Delayed yellowing. Decreased C ₂ H ₄ levels and respiration rate. Reduced disorders severity (flesh and core browning) KMnO ₄ -based scavenger did not show an effect on fruit quality aspects when it was previously treated with 1-MCP	Argenta et al. [9]
Quince (<i>Cydonia oblonga</i> Mill.) 'Isfahan'	One sachet containing KMnO ₄ at a rate of 5 g per kg of fruit. 10 fruit per EU	Stored in a sealed PE bag (60 µm thickness)	0 °C (85–95% RH) 75 days +7 days (20 °C)	Delayed colour changes, flesh firmness loss and β-carotene accumulation. Slowed astringent taste decrease. SSC was not affected	Akbari and Ebrahimpour [3]
Sapodilla (<i>Manilkara zapota</i> (L.) P. Royen) 'Itaiprema-31'	Vermiculite impregnated with KMnO ₄ sachets (at a rate of 0.375 g of KMnO ₄ per kg of fruit), 4 fruit (120 g each fruit) per EU. Sachet quantity NS	Placed in a styrofoam tray with PVC film coating	25 °C (54% RH) 10 days	Delayed firmness loss and vitamin C degradation. External and internal appearance, pulp colour, TA, pH, SSC, SSC/TA ratio and weight loss were no significant affected	de Souza et al. [53]
Sapota (<i>Manilkara achras</i> Mill.) 'Kallipatti'	4 sachets KMnO ₄ -based scrubber (weight NS) per 10 kg of fruit	Packed in a corrugated fibre board box	27–32 °C (70% RH) 13 days	Reduced weight loss. Firmness loss and TA were not affected. Slowed SSC increase and TA decrease. Delayed C ₂ H ₄ and CO ₂ production, as well as decay incidence	Bhunia et al. [19]
Sugar apple (<i>Annona squamosa</i> L.)	One KMnO ₄ -based scrubber sachet (at a rate of 9% KMnO ₄ based on fruit weight). 4 fruit per EU	Placed in an expanded PS tray and wrapped with a PVC film (100 µm thickness)	16 °C (90–100% RH) 12 days	Reduced weight loss. Delayed SSC and TA increase. Slowed pH decrease. Delayed fruit ripening	Chaves et al. [44]
Tomato (<i>Lycopersicon esculentum</i> Mill.) 'Rio Grandi'	One sachet (containing a sponge cube impregnated with 800 ppm KMnO ₄) per 70 fruit	Placed in a PE bag	27 °C (80–90% RH) 60 days	Slowed pH and ascorbic acid increases. Delayed TA decrease, as well as phenolic content increase. Delayed lycopene biosynthesis. SSC was not significantly affected. Increased β-carotene increase rate	Mujtaba et al. [114]
Tomato (<i>Solanum</i> sp.)	7.5 ppm KMnO ₄ impregnated in cotton wool into aerated pouches, per 50 g of fruit. Pouch quantity NS	Placed into a plastic container	14–18 °C 21 days	Retarded colour and textural changes	Wabali et al. [159]
Tomato (<i>Solanum lycopersicum</i> L.) 'Valouro'	20% of KMnO ₄ supported on zeolite and bentonite (2:1 w/w), 5 fruit per EU. Container device NS	Placed into a hermetically sealed container	7 °C (90% RH) 35 days	Reduced C ₂ H ₄ content of containers. Delayed fruit softening. Minimised both phenol content and antioxidant activity decrease rate. Slowed vitamin C content decrease and lycopene content increase. Delayed water weight loss and reduced decay severity	Mansourbahrmani et al. [109]
Tomato 'Chonto'	1.5% zeolite and 1.5% KMnO ₄ sachets, based on fruit fresh weight. 3 fruit per EU. Sachet quantity NS	Stored in TPT packaging	18 °C (85% RH) 28 days	Delayed weight loss. Slowed firmness loss and SSC increase. TA was not affected	Salamanca et al. [132]
Non-climacteric fruit Longkong fruit (<i>Lansium domesticum</i> Corr.)	KMnO ₄ -based scrubber. Fruit previously treated with 1-MCP	Wrapped with foam-net	18 °C 14 days	Maintained pericarp colour, flesh colour and taste in good quality	Suvanajinda et al. [151]

Table 1 (continued)

Produce	Ethylene scrubber application	Produce packaging	Storage conditions	Inferences	Reference
Loquat (<i>Eryobotria japonica</i> Lindl.) 'Precoce de Itaquera' Maxixe (<i>Cucumis anguria</i>)	One KMnO ₄ -based scrubber sachet (weight NS), per 5 fruit One sachet (6.5 g vermiculite impregnated with 4 g KMnO ₄) per 4 fruit	Stored in a PET tray and wrapped with a PVC film (10 µm thickness) Placed into a styrofoam tray and wrapped with PVC film	6 °C (90% RH) 18 days 10 °C (90% RH) 10 days	Delayed C ₂ H ₄ production. CO ₂ production and weight loss were not affected. Increased shelf life Maintained good appearance. Reduced vitamin C content decrease. Delayed chlorophyll degradation and colour changes. Accelerated non-reducing sugars increase. Weight loss, reducing sugars, soluble sugars and starch content and morphological aspects were not affected	Campos et al. [35] Silva et al. [145]
Pineapple (<i>Ananas comosus</i> (L.) Merr.) 'Gold Extra Sweet'	KMnO ₄ -based C ₂ H ₄ scavenger	NS	7.5 °C (85–90% RH) 25 days +3 days (18 °C, 85–90% RH)	Decreased peduncle rot incidence	Sabater-Vilar et al. [131]
Pointed gourd (<i>Trichosanthes dioica</i> Roxb.) 'Kaijji'	8 g of celite impregnated with KMnO ₄ (in a rate of 133% KMnO ₄ w/w) per kg of fruit	Packed in PP bags (50 µm thickness)	29–33 °C (68–73% RH) 8 days	Inhibited spoilage and disease incidence. Delayed chlorophyll content loss. Reduced weight loss at the beginning of the storage period	Bhattacharjee and Dhua [17]
Strawberry (<i>Fragaria</i> sp.) 'Torrey'	One sachet (10 g each of KMnO ₄ supported on alumina) per 18–22 (250 g) fruit	Held in a punnet overwrapped with 5 layers of PE film (9 µm thickness)	20 °C 4 days	Reduced C ₂ H ₄ concentration as well as the deterioration rate. Slightly reduced CO ₂ concentration. O ₂ levels were not affected	Kim and Wills [94]
Strawberry 'Torrey'	Sachets containing 10 g of KMnO ₄ impregnated onto activated alumina and vermiculite beads. 18–22 (250 g) fruit per EU. Sachets quantity NS	Packed into a punnet overwrapped with PE film (50 µm thickness)	0 °C 8 days	Reduced C ₂ H ₄ level. Delayed firmness loss. Minimised the deterioration rate. Decreased susceptibility to fungus. Increased storage life	Wills and Kim [167]
Vegetables Broccoli (<i>Brassica oleracea</i> L., Italica group) 'Marathon'	One sachet (20 g each of KMnO ₄ supported on an inert carrier) per 5 broccoli heads	Stored in a bag (PD-961EZ)	0–1 °C 29 days	Weight loss and overall appearance were not affected. Slightly delayed softening. Reduced acetaldehyde concentration	DeEl et al. [54]
Lettuce (<i>Lactuca sativa</i>)	Sachets of KMnO ₄ supported into activated alumina beads. 6 lettuce heads (1–1.2 kg each head) per EU. KMnO ₄ amount NS	Packaged into an unsealed PE bag (50 µm thickness)	0 or 20 °C 35 days	Reduced C ₂ H ₄ and CO ₂ levels. Delayed leaf browning. Kept good quality. Increased storage life	Kim and Wills [93]

SSC, soluble solid content; TA, titratable acidity; PE, polyethylene; HDPE, high-density PE; LDPE, low-density PE; PS, polystyrene; PET, polystyrene terephthalate; PVC, polyvinyl chloride; TPT, thermoformed PE terephthalate; ~, approximately; ANP, alumina nanoparticle; ANF, alumina nanofibre; EU, experimental unit; NS, not specified

Table 2 Overview of KMnO₄-based C₂H₄-scavenger trials and effects on fresh produce stored under controlled atmosphere conditions

Produce	Ethylene scrubber application	Produce packaging	Storage conditions	Inferences	Reference
Climacteric fruit					
Apple (<i>Malus domestica</i> Borkh) 'Brookfield'	KMnO ₄ sachets (sachets quantity and KMnO ₄ weight NS). 25 fruit per EU	Stored in a storage chamber under controlled atmosphere	1 °C (94% RH) 8 months + 7 days (20 °C)	Decreased C ₂ H ₄ production and respiration rate. Delayed flesh firmness loss and reduced TA decrease	Brackmann et al. [31]
Apple 'Brookfield'	Sachets containing KMnO ₄ (sachets quantity and KMnO ₄ weight NS). 25 fruit per EU	Placed in a hermetically closed chamber under controlled atmosphere	1.5 °C (94% RH) 8 months + 6 days (20 °C)	Decreased C ₂ H ₄ production and respiration rate. Both internal C ₂ H ₄ and CO ₂ concentrations were decreased	Brackmann et al. [30]
Apple 'Gala'	KMnO ₄ -based scavenger	Stored under controlled atmosphere conditions	1 °C 8 months + 7 days	Reduced C ₂ H ₄ concentration. Delayed firmness loss. Maintained green colour and good appearance and taste	Brackmann and Saquet [27]
Vegetables					
Cauliflower (<i>Brassica oleracea</i>) 'Teresópolis Gigante'	10 sachets (8 g each of KMnO ₄) per 3 heads	Stored in a chamber	0.5 °C (97% RH) 2 months + 5 days (20 °C)	Delayed de-greening of head and leaf. TA, SSC, firmness and weight loss were not affected	Brackmann et al. [28]

SSC, soluble solid content; TA, titratable acidity; PE, polyethylene; HDPE, high-density PE; LDPE, low-density PE; PS, polystyrene; PET, polystyrene terephthalate; PVC, polyvinyl chloride; TPT, thermoformed PE terephthalate; ~, approximately; EU, experimental unit; NS, not specified

into the packaging film (e.g. polyethylene films) [158, 172]. Nevertheless, active films incorporating mineral powders have shown low C₂H₄ removal efficacy because of low amount of mineral that can be incorporated without affecting the mechanical properties of the package [83]. In addition, they are opaque and grainy materials and incorporated mineral powders affect film permeability letting carbon dioxide (CO₂) gas out more rapidly and letting oxygen (O₂) enter more readily than regular plastic films [97].

Another scavenging approach is based on chemical processes [99], although in some cases such an approach is not profitable. For instance, palladium (Pd) and titanium dioxide (TiO₂) are catalytic materials that can efficiently remove C₂H₄ [87, 153], but Pd is expensive and the reaction between TiO₂ and C₂H₄ is ultraviolet light dependent [154, 175].

Over the years, the most well-known, inexpensive and commonly used C₂H₄-scavenging technologies have been those based on KMnO₄, a strong agent that chemically scavenges C₂H₄ by an oxidation process [116, 142].

KMnO₄-based C₂H₄-scavenging technology has been widely used for almost 50 years. The first report on the KMnO₄ application in C₂H₄-scavenging systems for fresh fruit preservation dates from 1967 [67]. Early studies were on the storage of apples and bananas, where Forsyth et al. [67] and Scott et al. [139], respectively, found that KMnO₄ can be useful to delay the ripening process. Since then, large research on the effects of KMnO₄ on fresh horticultural products has been developed (Tables 1 and 2). Research results for

19 climacteric fruit and 5 non-climacteric fruit and 3 vegetable products were identified through searching in the Scopus and Web of Science search engines.

Most research has been largely centred on climacteric fruit, particularly in cultivars of apple and banana species, which in addition to produce a high C₂H₄ rate, they are highly C₂H₄ sensitive [24]. Moreover, KMnO₄-based C₂H₄-scavenging products can be also used to protect floral products from the C₂H₄ detrimental damage (e.g. flower abscission or wilting, epinasty of buds and flowers and leaf shedding), maintaining their good appearance and extending their shelf life [8, 92].

Nowadays, several KMnO₄-based products engineered for C₂H₄-scavenging applications are commercially available. As presented in Table 3, commercial C₂H₄ scavengers have been developed in different shapes (beads, cylindrical and irregular pellets and powder) containing 3.5–12% w/w KMnO₄.

According to the available information, currently available products in the market have a C₂H₄-scavenging capacity ranging from 3 to 6.5 L kg⁻¹. Furthermore, there are some commercial KMnO₄-based products such as Bi-On® SORB (Bioconservacion S.A., Barcelona, Spain), Chemisorbant (Purafil, Inc., Doraville GA, USA), MM-1000 MULTI-MIX® MEDIA (Circul-Aire Inc., Montreal, Canada) and Sofnofil™ (Molecular Products Limited, Essex, UK) that are not specifically intended for the removal of C₂H₄ but are marketed as broad-spectrum contamination control materials for air purification in industrial applications.

Table 3 KMnO₄-based C₂H₄ scavengers currently available in the market

Trade name (manufacturer)	General description	C ₂ H ₄ -scavenging capacity (L/kg)	General characteristics	Commercially available presentations	Application guidelines	Reference
Air Repair™ (DeltaTrak Inc., Pleasanton, CA, USA)	Activated aluminium impregnated with KMnO ₄	NS	Shape: spherical pellets	Bulk beads/sachet/tube/blanket	NS	DeltaTrak Inc. [55]
Befresh (Befresh Technology, S.L., Barcelona, Spain)	Natural clays impregnated with KMnO ₄	4.5	Shape: cylindrical pellets	Sachet/tube/module	NS	Befresh Technology [14]; Befresh Technology [15]
Befresh* (Befresh Technology, S.L., Barcelona, Spain)	Natural clays impregnated with KMnO ₄	6.5	Shape: cylindrical pellets	Sachet/tube/module	NS	Befresh Technology [14]; Befresh Technology [15]
Bi-On® R8 (Bioconservacion S.A., Barcelona, Spain)	Natural clays impregnated with 8% KMnO ₄	3.5	Shape: cylindrical pellets Bulk density 0.84 g/mL Pellet diameter 2.3–4 mm Moisture content 15–20%	Bulk granules/sachet/tube/machine/module	Temp. –20–50 °C RH 10–95%	Bioconservacion [20]
Bi-On® R12 (Bioconservacion S.A., Barcelona, Spain)	Natural clays impregnated with 12% KMnO ₄	4.5	Shape: cylindrical pellets Bulk density 0.84 g/mL Pellet diameter 2.3–4 mm Moisture content 15–20%	Bulk granules/sachet/tube/machine/module	Temp. –20–50 °C RH 10–95%	Bioconservacion [21]
BIOPAC (BIOPAC Pty Ltd., West Burleigh, Australia)	Porous material mixed with KMnO ₄	2.8–4.2	Shape: spherical pellets	Tube/sachet/module	NS	Biopac [22]
BioX® 4.0 (BioXTEND Co., Fort Myers, FL, USA)	Alumina mixed with 4.0–4.5% KMnO ₄	2.8–3.0	Shape: spherical pellets Pellet diameter 3.0 mm Moisture content 15–20%	Bulk granules/tube/sachet/module	NS	BIOXTEND [23]
BioX® 8.0 (BioXTEND Co., Fort Myers, FL, USA)	Alumina mixed with 8.0–8.5% KMnO ₄	3.4	Shape: spherical pellets Pellet diameter 3.0 mm Moisture content 15–20%	Bulk granules/tube/sachet/module	NS	BIOXTEND [23]
BRYSORB™ 508 (Bry-Air (Asia) Pvt. Ltd., Gurugram, India)	Activated alumina impregnated with KMnO ₄	NS	Shape: spherical beads Pellet diameter 2.5–3.5 mm Bulk density 0.85–0.90 g/mL Moisture content 20–25%	Bulk granules	Temp. –20–50 °C RH 10–95%	Bry-Air (Asia) Pvt. Ltd. [33]
Eris filter (Miatech, Inc., Clackamas OR, USA)	KMnO ₄ pellets	NS	Shape: spherical pellets	Blanket	NS	Miatech Inc. [111]
Ethysorb® (Molecular Products Limited, Essex, UK)	Activated alumina impregnated with 3.5–5% KMnO ₄	NS	Shape: spherical pellets Bulk density 1 g/mL Particle size 2.5–5.0 mm Relative density 3.3 g/mL	Bulk beads/tube/blanket	Temp. –10–40 °C RH 10–95%	Molecular Products Limited [112]
Extend-A-Life™ (AgraCo Technologies International, LLC, Dillsburg PA, USA)	Zeolite coated with 8% KMnO ₄	NS	NS	Sachet/filter	NS	AgraCo Technologies International LLC [1]; AgraCo Technologies International LLC [2]
GK3 (GREENKEEPER IBERIA, S.L., Madrid, Spain)	Phyllosilicate and aluminosilicate loaded with 8% KMnO ₄	3.4	Shape: cylindrical pellets Particle diameter 2.0, 3.0 and 4.0 mm Moisture content 15%	Tube/machine/module	NS	Flink [66]; GreenKeeper [71]; GreenKeeper Iberia SL [72]
GK4 (GREENKEEPER IBERIA, S.L., Madrid, Spain)	Phyllosilicate and aluminosilicate loaded with 12% KMnO ₄	4.2	Shape: cylindrical pellets Particle diameter 2.0, 3.0 and 4.0 mm Moisture content 15%	Tube/machine/module	NS	Flink [66]; GreenKeeper [71]; GreenKeeper Iberia SL [72]
	Phyllosilicate and aluminosilicate loaded with KMnO ₄	NS	Shape: powder	Sachet/blanket	NS	Flink [66]; GreenKeeper [71]

Table 3 (continued)

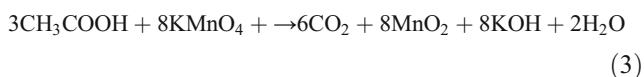
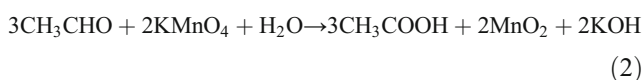
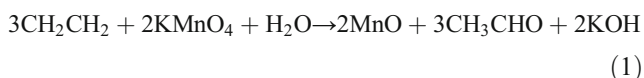
Trade name (manufacturer)	General description	C ₂ H ₄ -scavenging capacity (L/kg)	General characteristics	Commercially available presentations	Application guidelines	Reference
GK/P (GREENKEEPER IBERIA, S.L., Madrid, Spain)	Zeolite loaded with KMnO ₄	2*	Shape: irregular granules Particle diameter 0.6–1.5 mm	Sachet/blanket	NS	Flink [66]; GreenKeeper [71]
GKZ4 (GREENKEEPER IBERIA, S.L., Madrid, Spain)	KMnO ₄ granules	NS	Shape: cylindrical pellets	Sachet/machine/tube	NS	Prodew [122]; Prodew [123]
Prodew (Prodew, Marietta, GA, USA)	Activated alumina granules impregnated with KMnO ₄	NS	NS	Machine	NS	ISOLCELL S.p.A. [82]
PURETHYL (ISOLCELL S.p.A., Laives, Italy)	Mix of clays and oxidising agents (such as KMnO ₄)	NS	Shape: cylindrical pellets	Sachet/tube	NS	RETARDER SRL [128]
Retarder® (RETARDER SRL, Verzuolo, Italy)	Mixture of natural clays and 6% KMnO ₄	3.0	Shape: cylindrical pellets Pellet diameter 3.0 mm	Sachet/tube	NS	Sensitech Inc. [140]
Ryan® (Sensitech Inc., Beverly MA, USA)	Activated alumina impregnated with 8% KMnO ₄	NS	Shape: spherical pellets Bulk density 0.8 g/mL Pellet diameter 3.2 mm	NS	Temp. –20–51 °C RH 10–95%	Purafil Inc. [124]; Purafil Inc. [125]
Select (Purafil, Inc., Doraville GA, USA)	Sepiolite mixed with KMnO ₄ and activated carbon	NS	Moisture content ≤ 35%	Sachet/filter/machine	NS	Climent [46]; KEEP COOL [88]; KEEP COOL [89]
KEEP COOL (KEEP COOL, Molina de Segura, Spain)	Natural zeolite impregnated with 6% KMnO ₄	NS	Particle size 0.6–0.3 mm	Sachet/sheets/tube/machine	NS	KEEP FRESH [90]; Kösteki et al. [96]
KEEP FRESH (BLUE TECK SYSTEMS, S.L., Madrid, Spain)	Natural zeolite impregnated with 4–6% KMnO ₄	NS	Shape: irregular granules	Bulk beads/sachet/blanket	NS	Ethylene Control Inc. [62]
Super Fresh Media (Ethylene Control, Inc., Selma CA, USA)						

NS, not specified; RH, relative humidity

*Data supplied by the manufacturer company

Ethylene Removal Reaction and Application Form of the Potassium Permanganate-Based Ethylene Scavengers

As presented in Tables 1, 2, 3, KMnO_4 is usually supported on a porous C_2H_4 adsorber substrate with a large surface area, typically alumina, to facilitate the redox reaction [120, 154]. These C_2H_4 -scavenger products work through an adsorption–oxidation mechanism, where C_2H_4 is physically adsorbed by the porous medium and then oxidised by KMnO_4 [4]. KMnO_4 oxidises C_2H_4 by attacking its double bond [101]. The C_2H_4 stoichiometric oxidation reaction (Eqs. 1–4) was previously described by Keller et al. [91]:



Thus, the overall stoichiometric oxidation reaction is



As the reaction proceeds, a gradual colour change from purple to dark brown occurs because the permanganate anion (MnO_4^-) is reduced into manganese dioxide (MnO_2) [110, 168]. This phenomenon can be clearly noted in Figs. 1 and 2. These figures show the C_2H_4 breakthrough measurement on a KMnO_4 -based C_2H_4 scavenger (Bi-On® R12, Bioconservacion S.A., Barcelona, Spain) held under a continuous C_2H_4 -enriched air flow (5000 ppm at 120 mL min^{-1}) at room temperature (22°C) and the changes in KMnO_4 concentration (%) and colour that occur in the material over time.

KMnO_4 -based C_2H_4 scavengers are mainly used in sachet form for food-packaging application but can also be found in different presentation forms such as blankets, filter tubes or filter machines that can be placed in warehouses or transport chambers, incorporated into household refrigerators systems, or directly incorporated into the packaging material [83, 110, 120]. For instance, Taboada-Rodríguez et al. [152] reported that barrier properties of the cardboard material usually used in food packaging could be improved by applying a coating made of polylactic acid and KMnO_4 supported onto sepiolite. However, KMnO_4 is not typically integrated into food contact surfaces of food packaging because of its toxicity and colour [25, 68].

In a commonly individual C_2H_4 -scavenging packaging system (Fig. 3), a sachet containing the C_2H_4 -scavenger product is placed within the produce package [83], at the upper part of the package [113, 142]. At this point, it should be clarified

that the most suitable position to attach a scavenger—or a release—sachet will depend on the density of the gaseous compound to be scrubbed or released, respectively. The density of a gas can be deduced from the ideal gas law (Eqs. 5–8):

$$P \times V = n \times R \times T \quad (5)$$

$$P \times V = \frac{m}{M} \times R \times T \quad (6)$$

$$\frac{P \times V}{R \times T} = \frac{m}{M} \quad (7)$$

$$d = \frac{P \times M}{R \times T} \quad (8)$$

where P is the atmosphere (atm), M is the gas molar mass (g mol^{-1}), R is the gas constant ($0.082 \text{ atm L (K mol)}^{-1}$), and T is the temperature (K).

Therefore, since C_2H_4 tends to rise to the top of the package because it is slightly less dense than air (for instance, the C_2H_4 and air density are 1.16 and 1.20 g mol^{-1} , respectively, at 22°C and 1 atm), the upper part of the package seems to be the most suitable position to attach a C_2H_4 -scavenger sachet. Then, the sachet material must be highly permeable to the C_2H_4 gas molecule, allowing C_2H_4 uptake from the in-package atmosphere through a convection and diffusion mechanism [97, 175]. Some typically used sachet materials reported in the literature are polyethylene (PE), muslin cloth or cellulose [58, 114]. In general, the commercially available active packaging agents such as KMnO_4 -based products are typically packed into heat-sealed Tyvek® film sachets [172]. DuPont™ Tyvek® is a high-density PE film (Fig. 4) that meets the US and European Union regulations for food contact applications [57].

Human Health and Environmental Concerns

Although there are already several registered commercial KMnO_4 -based products (Table 3), the active packaging use in the European market is just beginning to increase [158]. Gaikwad and Lee [68] and Vilela et al. [158] attribute such behaviour to low consumer acceptance and to a strict legislation. Despite the fact that KMnO_4 -based C_2H_4 scavengers are commonly placed into individual devices to keep products free from contamination and avoid human health risks associated with KMnO_4 poisoning, there is still concern about possible KMnO_4 migration. In this sense, it is highly recommended to avoid direct exposure to KMnO_4 , particularly, at concentrated solutions and to undiluted KMnO_4 [78]. Besides that, KMnO_4 can be harmful if it is swallowed, being classified by the Globally Harmonized System of Classification and Labelling of Chemicals as harmful if swallowed under the code H302 [156]. Therefore, it is true that KMnO_4 -based products must be carefully handled. Nonetheless, it is well documented that the risk of KMnO_4 intoxication is not

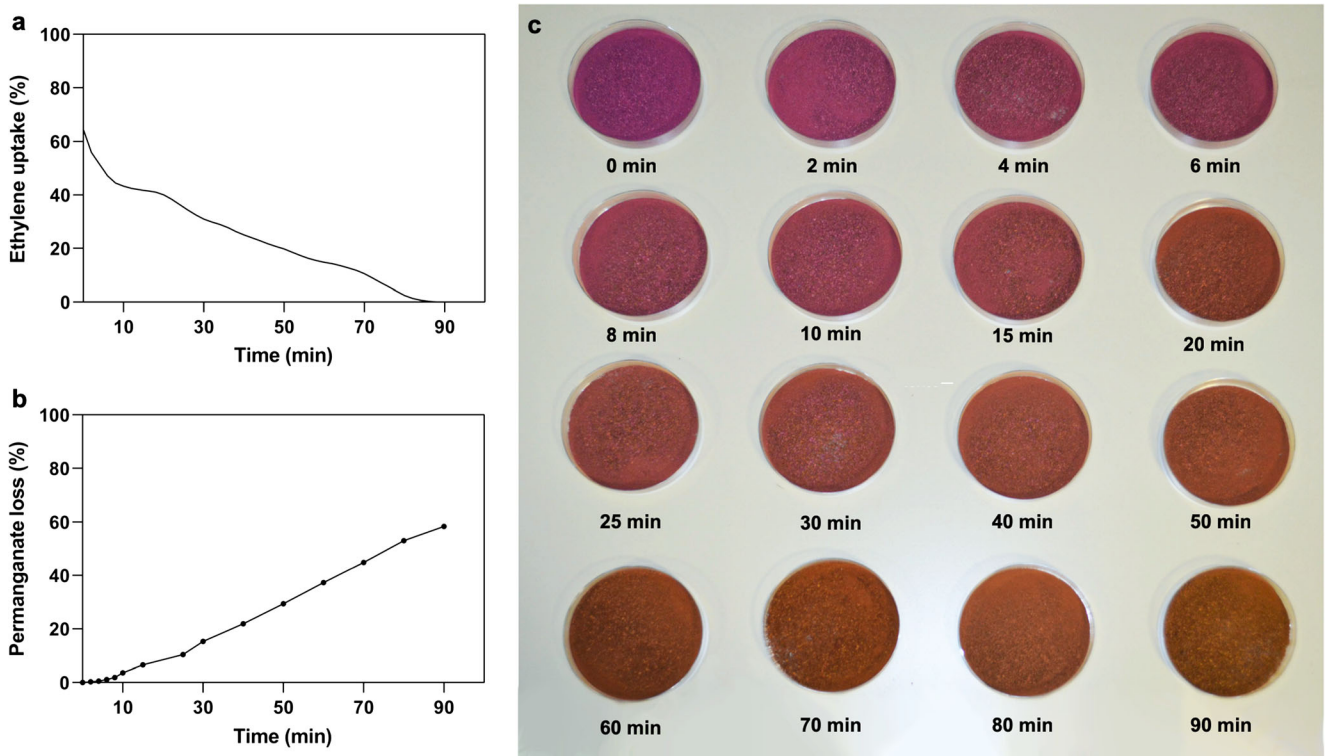


Fig. 1 Changes in C_2H_4 uptake capacity (a) and $KMnO_4$ concentration (b) and visual colour change image (c) of a $KMnO_4$ -based C_2H_4 scavenger (Bi-On® R12, Bioconservacion S.A.) material over time

common, being approximately 142.9 mg kg^{-1} (10 g of $KMnO_4$ per person weighing 70 kg) the lethal adult dose and 750 mg kg^{-1} the oral LD_{50} rat dose [38, 79]. In addition, $KMnO_4$ is not listed on the World Health Organization

(WHO) Acute Hazard Rankings [80]. Furthermore, $KMnO_4$ is commonly used at low concentrations in highly diluted solutions as antiseptic and antifungal drug and it is included in the WHO Essential Medicines List [163]. $KMnO_4$ as an

Fig. 2 Evolution of colour parameters a^* , b^* , C^* and H° over time for a $KMnO_4$ -based C_2H_4 scavenger (Bi-On® R12, Bioconservacion S.A.) held under a continuous C_2H_4 -enriched air flow

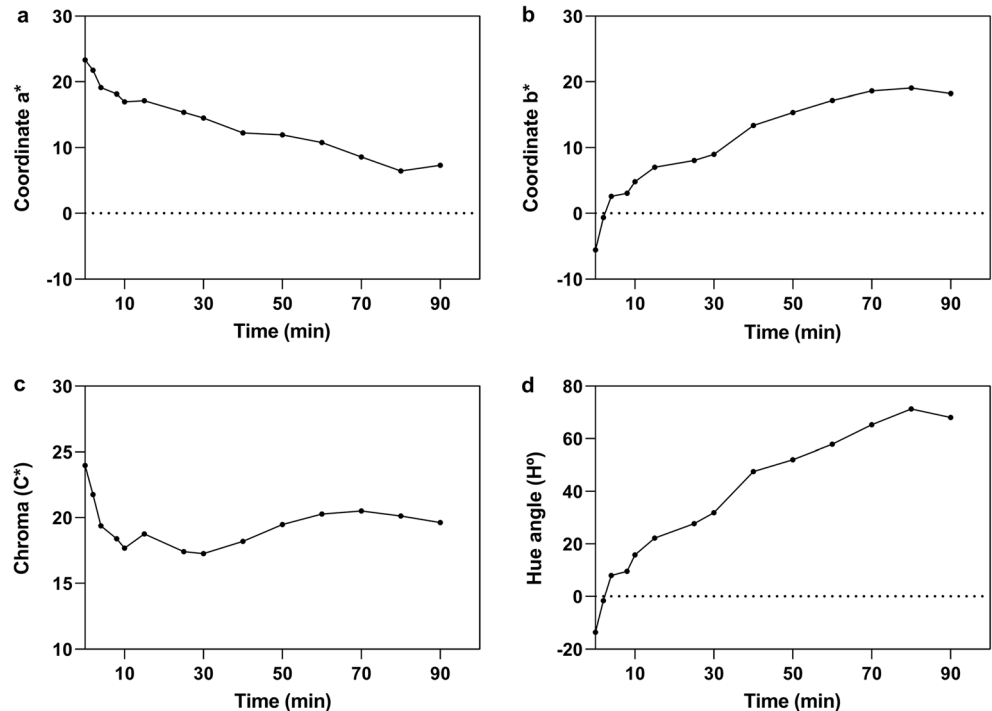
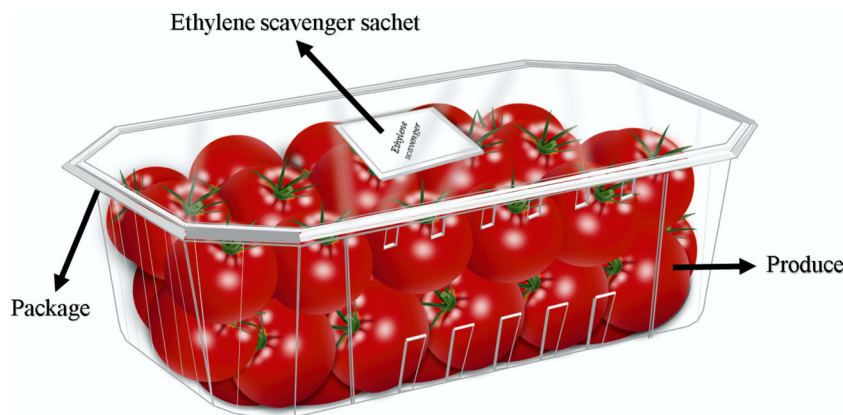


Fig. 3 Schematic representation of an C_2H_4 -scavenger sachet used in horticultural produce packaging



indirect food additive is regulated by the Food and Drug Administration (FDA) under the Code of Federal Regulations (21 CFR §175.105 2018) [39]. General US FDA requirements for food contact applications are also established through the Code of Federal Regulations (21 CFR §177.1520 2018 and 21 CFR §177.2010 2018) [40, 41], while the European Union has specific requirements related to active packaging and its non-active parts that are regulated by the Regulation 1935/2004/EC and Regulation 450/2009/EC [63, 64]. Particularly, Regulation 450/2009/EC establishes a legal basis for active packaging safety and marketing [83]. The European Union and US regulation aspects concerning active and intelligent food packaging have been extensively discussed by Dainelli et al. [50] and Restuccia et al. [127].

On the other hand, the high oxidising power, either in heterogeneous conditions or without solvents, makes permanganate and its compounds of particular environmental concern. However, the permanganate oxidation process is considered to be eco-friendly [51]. In fact, permanganate (specifically, $KMnO_4$) has been defined as a green oxidant in organic chemistry since the inorganic coproducts (particularly, MnO_2) can be re-oxidised to permanganate, providing a sustainable approach [141, 147]. Therefore, as a green oxidant, $KMnO_4$ has been widely used in industrial and agricultural processes, including air purification (by removing C_2H_4 , pollutants such as sulphur dioxide (SO_2), hydrogen sulphide (H_2S), aldehydes and other volatile organic compounds), water treatment to remove pollutants such as algal toxins and pharmaceuticals, as a bleaching agent in textile industry and as an antimicrobial agent in pesticide products [51, 147, 154].

$KMnO_4$ is not listed on the WHO Environmental Health Criteria Documents [164]. However, since $KMnO_4$ is typically used at full scale for water treatment applications [61, 73], it is regulated by the United States Environmental Protection Agency under the chemical code number 068501 because high doses can be harmful to aquatic life [60]. $KMnO_4$ is classified by the Globally Harmonized System as a very toxic agent to aquatic organisms under code numbers H400 and H410 [156]. Hence, $KMnO_4$ -based products should not be released into the

environment (prevent from reaching water bodies such as lakes and rivers, soil and sewage systems). In addition, since $KMnO_4$ is a strong oxidant agent, it can enhance combustion of other substances and can also release irritating or toxic fumes in a fire; thus, $KMnO_4$ -based products should be stored, disposed and separated from reducing, flammable and combustible substances [78]. Nevertheless, when $KMnO_4$ is supported onto a solid material, the aforementioned MnO_2 re-oxidation process is interfered [141]. The above gives rise to non-toxic and chemically inert by-products (Eq. 4) that do not represent an environmental concern and can be disposed of as normal waste [91, 135]. Therefore, $KMnO_4$ -based C_2H_4 scavengers can be considered an environmental-friendly tool that can be used in active packaging technology for horticultural products, with proper handling and relevant safety measures.

Effects of Potassium Permanganate-Based Ethylene Scavengers on Postharvest Quality of Fresh Produce

As earlier mentioned, significant effort has been made to elucidate $KMnO_4$ effects on quality attributes of both climacteric fruit and non-climacteric produce. Tables 1 and 2 show how $KMnO_4$ -based products may be used to delay some physicochemical changes associated with produce ripening and senescence. However, cultivar, maturity stage, storage period and storage conditions, as well as the presence of exogenous C_2H_4 during storage or transportation, are some factors that may counteract the effect of these $KMnO_4$ -based tools [117]. For instance, in climacteric fruit, the rate and intensity of C_2H_4 production are higher at the ripe stage, regarding mature and half ripe stages [118]. The latter fact can be observed in the studies carried out by Bhutia et al. [19] and Amarante and Steffens [6, 7], where the effect of $KMnO_4$ -based C_2H_4 scavengers on ‘Kallipati’ sapote, ‘Gala’ apple and ‘Royal Gala’ apple was evaluated at different ripening stages. The results indicated that the C_2H_4 scavengers may retard the physiological and physicochemical processes in sapote and ‘Gala’ apple

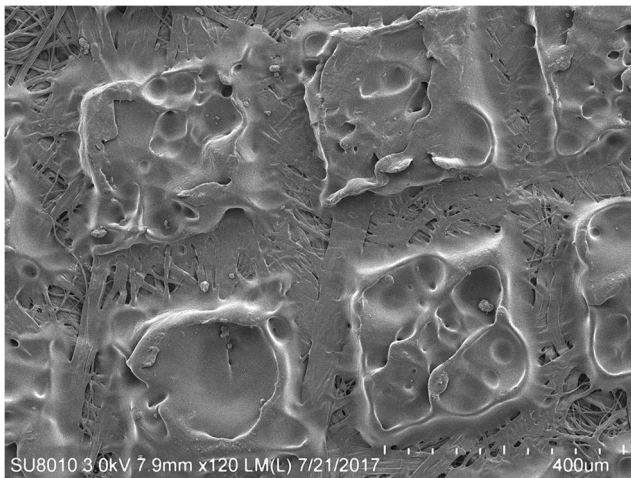


Fig. 4 Scanning electron microscope image of DuPont™ Tyvek®

independently of the maturity stage, although the effects were more pronounced in fruit harvested and stored at a mature stage [6, 19]. Meanwhile, the influence of the maturity stage on the efficiency of C_2H_4 scavengers was found to be more marked in ‘Royal Gala’ apple [7]. Amarante and Steffens [7] reported that, despite having removed the total amount of C_2H_4 inside the apple package at each maturation stage, it was only possible to delay the ripening process in fruit harvested at less advanced maturation stage, while in fruit with a higher maturity stage, no significant effect was observed. The authors attributed such results to the fact that the C_2H_4 production rate increases along with the ripening process, causing a higher accumulation of C_2H_4 inside the package and hindering the C_2H_4 removal efficiency. Thus, the effect of C_2H_4 scavengers to delay the ripening process and extend the fruit and vegetable shelf life is more evident when they are harvested at the mature green stage. Therefore, it is recommended to harvest fruit and vegetables at the latter maturation stage or before the autocatalytic production of C_2H_4 in order to obtain the maximum benefit from the C_2H_4 scavengers.

In addition, because the responses to $KMnO_4$ -based C_2H_4 scavengers may vary between cultivars and species, in the following subsections, apple, banana, mango and tomato are used to illustrate the range of responses to $KMnO_4$ -based C_2H_4 scavengers since most of the literature available focuses on the study of such products. Nonetheless, an outline of the general responses of other climacteric fruit and non-climacteric produce to $KMnO_4$ -based C_2H_4 scavengers is provided to illustrate the potential for use and both benefits and limitations that may be reached by using $KMnO_4$ -based technology.

Apple

$KMnO_4$ -based C_2H_4 scavengers within apple packages at low storage temperature (0–4 °C) have shown positive effects on quality parameters, being effective to delay maturation

process and then prolonging its shelf life up to 8 months [31]. Particularly, in ‘Gala’, ‘Royal Gala’, ‘Golden Delicious’ and ‘Brookfield’ cultivars, the incorporation of a $KMnO_4$ -based C_2H_4 scavenger into the storage container has been shown to decrease pulp firmness loss and to delay shell yellowing (Tables 1 and 2). Shorter et al. [143] and Knee and Hatfield [95] reported that bitter pit and superficial scald was reduced in ‘Granny Smith’ and ‘Golden Delicious’ apple, respectively, by scavenging C_2H_4 with $KMnO_4$ -based tools.

On the other hand, the titratable acidity (TA) and soluble solid content (SSC) behaviours throughout the ripening process depend on the variety in question. Therefore, $KMnO_4$ effects on TA and SSC parameters are different in each variety. The latter fact may be explained since each variety has its unique characteristics. For example, the storage of ‘Golden Delicious’ apple under MAP conditions together with a $KMnO_4$ -based C_2H_4 scavenger at low temperature led to a lower TA decrease and a lower SSC accumulation [137]. Meanwhile, the TA decrease in ‘Gala’ variety was delayed, and SSC was not affected [6, 29]. The opposite effect was observed in ‘Royal Gala’ apple with the SSC increase minimised while the TA behaviour was unaffected [7].

In general, it can be concluded that $KMnO_4$ -based C_2H_4 scavengers are a useful tool to delay the de-greening process and pulp firmness loss in apple fruit, as well as to reduce flavour changes or variations in sugars and free organic acid contents throughout storage at low temperatures. Furthermore, physiological disorders may also be decreased in refrigerated apples by using $KMnO_4$ -based C_2H_4 scavengers.

Banana

Very good results can be obtained by removing C_2H_4 from the surrounding fruit atmosphere, especially for long-distance transportation. In this sense, Wills et al. [170] reported that the green life of ‘Cavendish’ banana can be increased of about 27 days at 15 °C, 17 days at 20 °C and 11 days at 25 °C by reducing the C_2H_4 concentration from 1.0 to 0.01 $\mu L L^{-1}$.

From different research studies, the incorporation of $KMnO_4$ -based tools inside packages, storage rooms or banana reefers has shown to be effective in delaying the chlorophyll degradation process—and then, the shell yellowing process—reducing weight loss and slowing down the softening process during storage [69, 136, 155, 177].

On the other hand, as mentioned above, the TA and SSC changes are different depending on the characteristics of the product. In this sense, several authors pointed out that both TA and SSC factors tended to increase throughout the storage period of banana fruit [136, 155, 177]. Meanwhile, García et al. [69] found that SSC increased while TA tended to decrease during the baby banana storage period. In agreement with the authors, a similar SSC and TA behaviour was observed in ‘Prata Aña’ banana by Prill et al. [121]. However,

in general, it has been observed that changes in TA and SSC can be delayed by incorporating KMnO_4 -based materials into banana packages regardless of whether the TA and SSC tend to increase or decrease [69, 136, 155, 177]. Moreover, the SSC/TA ratio tends to increase in banana fruit throughout storage, but García et al. [69] and Tourky et al. [155] reported that the said increasing trend was reduced in baby banana and ‘Williams’ cultivar, respectively, by packaging fruit with KMnO_4 -based tools.

The banana pulp/peel ratio is a quality parameter that indicates differential changes in the moisture content of skin and pulp. This parameter tends to increase throughout the maturation process due to a differential change in osmotic pressure driven by the sugars increase in the pulp [155]. Nevertheless, Chauhan et al. [43] reported that the pulp/peel ratio changes in ‘Pachbale’ bananas can be delayed if the fruit is packaged into a PE bag together with a KMnO_4 -based C_2H_4 scavenger (5 g of scavenger per kg of fruit) and stored 18 days at 13 ± 1 °C. Similarly, ‘Williams’ banana stored in PE bags together with a KMnO_4 -based C_2H_4 scavenger (20 g of KMnO_4 per 3 hands) showed a slight delay in the increase of pulp/peel ratio during 45 days at 20 ± 2 °C [177]. Nevertheless, the incorporation of a similar C_2H_4 -scavenger tool inside a ‘Raja Bulu’ banana package (approximately 60 g of scavenger per kg of fruit) did not affect the pulp/peel ratio during 18 days at 27–30 °C [136].

Based on the above, KMnO_4 -based C_2H_4 -scavenger sachets are a useful tool in conjunction with the passive MAP technique to preserve the green life of banana fruit during transportation. Nonetheless, the search for innovative and promising packaging technologies continues. In this sense, a new kind of technology consisting of membranes made of alumina nanoparticle (ANP)-incorporated alumina nanofibres (ANF) loaded with KMnO_4 was recently developed by Tirgar et al. [154]. In order to evaluate the effectiveness of the developed membranes, the authors performed a shelf life study by packing banana fruit into bags containing the developed membrane. Results showed that KMnO_4 incorporated into ANP-incorporated ANF membranes has the potential to remove a great amount of C_2H_4 in the package and to delay the incidence of dark brown regions on the skin and flesh softening of banana fruit. However, it must be taken into account that every food contact material must comply with a strict series of requirements before considering their commercial application [50, 127].

Mango

The KMnO_4 -based C_2H_4 -scavenger effects have been also studied on mangoes. Ezz and Awad [65] studied its effects on ‘Hindi Basennara’ and ‘Alphonse’ mangoes packaged under MAP conditions and stored at 8 °C. The results showed fewer weight losses in both mango varieties, but no effect on

firmness loss was observed. Similarly, Jeronimo et al. [84] studied the effect of KMnO_4 -based C_2H_4 scavengers on ‘Tommy Atkins’ mangoes at 13 ± 1 °C. However, no significant effect was observed on fruit firmness loss nor on weight loss. At the end of the aforementioned studies, higher TA/ascorbic acid values and lower SSC were observed in the three studied mango cultivars regarding that fruit packed without an C_2H_4 -scavenger tool. Furthermore, Jeronimo et al. [84] noted that C_2H_4 removal from the package slowed fruit metabolism resulting in lower SSC and TA changes. Hence, C_2H_4 scavengers are an effective tool to complement the MAP for maintaining the quality of the mango fruit.

Tomato

The use of KMnO_4 -based C_2H_4 scavengers has also shown good results in tomatoes, regarding quality maintenance during storage. Mujtaba et al. [114] found that packaging ‘Rio Grandi’ tomato into PE bags together with a KMnO_4 -based C_2H_4 scavenger can decrease SSC/ascorbic acid increment, induce TA to increase and retard lycopene biosynthesis, without effects on fruit pH. Moreover, the use of a KMnO_4 -based C_2H_4 scavenger in ‘Chonto’ tomato packaging can help to achieve lower weight and firmness losses and to slow SSC increment while TA is not affected [132].

Other Climacteric Fruit

The effect of KMnO_4 -based C_2H_4 scavenger has been also evaluated on other climacteric fruits such as papaya, quince fruit, fig, kiwi, sapote and sugar apple (Table 1). Particularly, the incorporation of a KMnO_4 -based C_2H_4 scavenger inside the ‘Sunrise Golden’ papaya package can help to reduce pulp consistency loss and the SSC increment, in addition to minimising peel colour changes [144]. Based on similar observations, Bal and Celik [12] reported that ‘Hayward’ kiwi maturity process can be delayed by fruit packaging in conjunction with a KMnO_4 -based C_2H_4 scavenger, which showed to be helpful to decrease firmness loss and TA changes, delay SSC increment and delay chlorophyll degradation.

Although a lower β -carotene content was observed by incorporating a KMnO_4 -based C_2H_4 scavenger into the packaging of ‘Isfahan’ quince fruit, less firmness loss was observed [3]. Meanwhile, SSC increment, TA decrease, weight losses and firmness losses can be delayed during the storage of ‘Kallipati’ sapote by using KMnO_4 -based C_2H_4 scavengers [19]. In sugar apple fruit, lower weight loss, lower SSC and TA increase and a mild pH decrease were found after the incorporation of KMnO_4 -based C_2H_4 scavengers [44].

As can be seen from previously reported studies, the application of KMnO_4 -based C_2H_4 scavengers in climacteric fruit packaging has mainly resulted in positive effects regarding quality maintenance. Nevertheless, some studies have not

reported significant effects after incorporation of a KMnO_4 -based scavenger into the packaging. Sá et al. [130] did not find significant C_2H_4 removal effects on melon. In addition, only a slight decrease in colour changes and a reduction of ascorbic acid biosynthesis were observed in guava fruit after the incorporation of KMnO_4 -based C_2H_4 scavenger into the package [58]. Therefore, these studies suggest that this postharvest technique is not completely justified in guava and melon, although more research is needed to elucidate these issues.

Non-climacteric Produce

Few significant information concerning KMnO_4 -based C_2H_4 -scavenger effects on non-climacteric products is available (Tables 1 and 2). Nonetheless, good results have been found. For instance, cherry storage in conjunction with a KMnO_4 -based C_2H_4 scavenger resulted in fewer weight and firmness losses, while a delay in both SSC and TA changes was also observed [59]. The ‘Precoce de Itaquera’ loquat shelf life was extended with the incorporation of a KMnO_4 -based C_2H_4 scavenger into the package [35]. In another study on ‘Teresópolis Gigante’ cauliflower, it was possible to delay the chlorophyll degradation process by using an C_2H_4 scavenger [28]. Furthermore, ‘Marathon’ broccoli softening process was delayed when it was stored together with a sachet containing KMnO_4 [54]. As can be noted, KMnO_4 -based C_2H_4 scavengers seem to be a useful tool to delay senescence processes of non-climacteric produce, but there is an insufficient body of trials to speculate on the potential of the technology on such produce.

Factors Affecting Potassium Permanganate-Based Ethylene Scavenger Efficiency/Performance in Packaging Technology

The C_2H_4 removal efficiency of KMnO_4 -based C_2H_4 -scavenger materials mainly depends on temperature, humidity and the amount of material used [25, 168]. Furthermore, the success of a postharvest technology to ensure good quality maintenance without compromising the safety and nutritional value of produce depends on the good understanding of the produce biology and physiology [105, 157]. Then, it is important to consider the latter factors in order to achieve an optimal performance of the C_2H_4 -scavenger material.

Ethylene Scavenger Dose

Martínez-Romero et al. [110] pointed out that the cost–benefit could be optimised by adjusting the appropriate scavenger dose to remove C_2H_4 during the storage period of the shelf life of the target produce. Particularly, the application of

KMnO_4 -based C_2H_4 -scavenger materials in sachet form is well suited for short storage periods. The use of such sachets is not recommended during long-term storage of high C_2H_4 -producing commodities since the C_2H_4 scavenger may be rapidly saturated, requiring frequent sachet replacement [165].

In this sense, some authors have evaluated the effect of KMnO_4 -based C_2H_4 scavengers by using different doses in order to determine the amount of scavenger material needed to remove as much C_2H_4 as possible from the in-package atmosphere. Brackmann et al. [29] needed to incorporate three sachets (each one containing 9 g of KMnO_4 -impregnated material per 18 kg of fruit) inside the package of ‘Gala’ apples in order to reach an C_2H_4 concentration of $1.4 \mu\text{L L}^{-1}$ after 15 days of storage at 4°C . Meanwhile, an C_2H_4 concentration of $51.3 \mu\text{L L}^{-1}$ was found inside the apple packages without C_2H_4 scavengers, and an C_2H_4 concentration of $3.78 \mu\text{L L}^{-1}$ was reached by using just one C_2H_4 -scavenger sachet. Amarante and Steffens [7] found no significant differences concerning the C_2H_4 in-package concentration nor on the ‘Royal Gala’ apple quality (shell colour, pulp firmness and SSC) after 2 months of storage at $0 \pm 0.5^\circ\text{C}$ and 90–95% relative humidity (RH) using either one or two C_2H_4 -scavenger sachets (10 g of KMnO_4 -impregnated material each one per 18 kg fruit).

On the other hand, Santosa et al. [136] studied the effectiveness of three different doses of a KMnO_4 -based C_2H_4 scavenger (10, 30 and 50 g of scavenger material containing 7.5% KMnO_4 , per 6 fruit units) during storage of ‘Raja Bulu’ banana fruit up to 18 days at $27\text{--}30^\circ\text{C}$. They found no significant differences in physical quality attributes (such as shell colour and weight loss) by using either 30 or 50 g of C_2H_4 scavenger. Therefore, they concluded that 30 g of C_2H_4 scavenger per 6 fruit is enough to delay the ripening process ‘Raja Bulu’ banana. In another study, García et al. [69] evaluated the baby banana response to different concentrations of support material and KMnO_4 . They reported 1% w/w vermiculite and 1.5% w/w KMnO_4 (percentages based on fresh fruit weight) as the most favourable combination to maintain the baby banana quality at 18°C and 70–80% RH for 16 days. The above percentages are similar to those reported by Salamanca et al. [132] for ‘Chonto’ tomato. The authors reported that the lowest weight loss and SSC, as well as the highest firmness, can be achieved by storing ‘Chonto’ tomato together with 5% zeolite and 1.5% KMnO_4 (percentages based on fresh fruit weight) during 28 days at 18°C (85% RH).

Furthermore, Akbari and Ebrahimpour [3] reported that it is possible to delay the pulp firmness loss of quince fruit, colour change and accumulation of β -carotene by using 2.5 g of KMnO_4 per kg of fruit during 150 days at 0°C (85–95% RH). Nevertheless, it was possible to retain a higher quince fruit firmness when 5 g of KMnO_4 per kg was used. In addition, Silva et al. [144] reported that ‘Sunrise Golden’ papaya can be preserved in good condition up to 25 days at

10 °C (85–95% RH) by incorporating a KMnO₄-impregnated vermiculite sachet (containing approximately 1.7 g of KMnO₄ per kg of fruit) inside the packaging.

As observed, suitable doses of C₂H₄ scavenger vary depending on the horticultural product. Accordingly, the C₂H₄-scavenger dose required to achieve a calibrated decrease in C₂H₄ concentration together with an increase in the commodity shelf life depends mainly on the C₂H₄ production of the packaged produce, as well as on the C₂H₄ uptake capacity of the C₂H₄-scavenger material [91, 110]. On the other hand, both the C₂H₄ production and the C₂H₄ sensitivity of produce are mainly influenced by maturity stage, packaging characteristics (including O₂/CO₂/C₂H₄ in-package concentrations) and storage conditions [19, 35, 149]. Thus, further studies are still needed to determine the minimum required C₂H₄-scavenger concentration for a specific product bearing in mind all of the above factors.

Ethylene Removal Capacity of the Scavenger Material

As mentioned above, the C₂H₄ removal capacity of the scavenger material must be known in order to set the most appropriate C₂H₄-scavenger dose. However, the C₂H₄ removal capacity of the products is not always indicated by the manufacturers (Table 3). Nonetheless, it can be assayed by passing a continuous C₂H₄-enriched air flow through a cylindrical reactor containing the C₂H₄-scavenger material sample, in a similar way as is described by Terry et al. [153] and de Chiara et al. [52]. The assay is conducted until the reactor outlet C₂H₄ concentration reaches the inlet C₂H₄ concentration (breakthrough measurement). Finally, the C₂H₄ uptake capacity is usually estimated based on the ASTM D6646-03 standard (Standard Test Method for Determination of the Accelerated Hydrogen Sulfide Breakthrough Capacity of Granular and Pelletized Activated Carbon) by the American Society for Testing and Materials [11], which was developed for hydrogen sulphide, with some adaptations as follows:

$$\frac{\text{g C}_2\text{H}_4}{\text{cm}^3 \text{ C}_2\text{H}_4 \text{ scavenger product}} = \frac{\left(\frac{c}{100}\right) \times F \times t \times \left(\frac{1 \text{ L}}{1000 \text{ cm}^3}\right) \times \left(\frac{1 \text{ mol}}{22.4 \text{ L}}\right) \times \left(\frac{28.05 \text{ g C}_2\text{H}_4}{\text{mol}}\right)}{V} \quad (9)$$

The equation can be simplified to:

$$\frac{\text{g C}_2\text{H}_4}{\text{cm}^3 \text{ C}_2\text{H}_4 \text{ scavenger product}} = \frac{(1.25 \times 10^{-3} \text{ g cm}^3) \times C \times F \times t}{V} \quad (10)$$

where C is the inlet C₂H₄ concentration in the air stream (volume %), F is the total C₂H₄/air flow rate (cm³ min⁻¹), t is the time to breakthrough (min), and V is the volume of the C₂H₄-scavenger product contained in the reactor (cm³).

Nonetheless, since the C₂H₄ uptake capacity is usually expressed in L kg⁻¹ units, the following equation can be obtained by replacing the volume variable (V) per weight (W) in Eq. 10, and then multiplying by the C₂H₄ density in order to change grams units per litre:

$$\frac{\text{L C}_2\text{H}_4}{\text{kg C}_2\text{H}_4 \text{ scavenger product}} = \frac{(1.25 \times 10^{-3} \text{ g cm}^3) \times C \times F \times t}{W \times (1.261 \text{ g L C}_2\text{H}_4)} \quad (11)$$

where W is the weight of the C₂H₄-scavenger product sample.

At this point, it is important to clarify that although the C₂H₄-scavenging capacity is an important feature to consider, it does not determine if one product is better than the other is. The most suitable product to remove C₂H₄ surrounding a commodity should be chosen based on the specific fruit or vegetable to be protected, the storage conditions and the desired market period since each produce has its own biological and physiological features [157].

Packaging Material

The interaction between the product and the packaging material is very important since the atmospheric composition in the package depends on the produce type, packaging material and storage temperature [49]. MAP is characterised by retarding the maturation and senescence in fresh produce by slowing down their respiration and C₂H₄ production rates [108, 174]. According to Janjarasskul and Suppakul [83], the common approaches to decrease C₂H₄ production are reducing storage temperature and balancing O₂:CO₂ concentrations in MAP. Although, in turn, with the aim of reaching the optimum O₂:CO₂ ratio in the shortest period of time, the respiration rate and the C₂H₄ production of the produce will define the best suitable film according to its permeability characteristics [49, 108, 118].

In most studies regarding the use of the KMnO₄ effect on the quality of fresh commodities, the produce is packaged into commercially available polymer films (PE; polyvinyl chloride (PVC); polystyrene terephthalate (PET)) of 10–60 μm thicknesses (Table 1).

The effect of KMnO₄-based C₂H₄ scavengers on packaged products under different films has been evaluated by some authors, who have obtained interesting results. Akbari and Ebrahimpour [3] evaluated the effect of non-perforated PE bags and perforated PE bags as ‘Isfahan’ quince fruit packaging in conjunction with a KMnO₄-based tool during postharvest storage at 0 °C and 85–90% RH. They found that the overall quality was better maintained when quince fruit samples were stored in non-perforated PE bags for 75 days. Nevertheless, the fruit firmness was well maintained up to 150 days by using perforated bags. In contrast, Zewter et al. [177] reported that the chemical quality of bananas packaged in perforated bags together with KMnO₄ sachets and

maintained at 14–18 °C (33–58% RH) was longer maintained (24 days) compared to samples stored in non-perforated bags (20 days). Such different results can be explained since the banana fruit has a high respiration rate and a high C₂H₄ production leading to higher gas permeability requirements of the film [177].

Furthermore, the activity of enzymes responsible for cell wall degradation, colour changes and C₂H₄ production may be slowed down by reducing the O₂ and C₂H₄ levels [119]. Moreover, CO₂ acts as an antagonist of the C₂H₄ action, while high CO₂ concentrations inhibit the activity of the enzymes 1-aminocyclopropane-carboxylate synthase and 1-aminocyclopropane-carboxylate oxidase, which catalyse the C₂H₄ synthesis pathway [96, 119, 166]. Therefore, C₂H₄ removal combined with the incremented CO₂/reduced O₂ reached by using MAP results in a synergistic system that causes a lower metabolic rate of the fruit or vegetable [83, 177].

Storage Temperature

KMnO₄-based C₂H₄ scavengers may delay ripening under different storage temperatures as observed in Tables 1 and 2. It is well known that adsorption of any molecule depends on several parameters, including temperature, adsorbate (molecule to be adsorbed) concentration, pressure and RH [68]. Nevertheless, there is a lack of studies concerning temperature impact on the efficiency of KMnO₄-based C₂H₄ scavengers. Lidster et al. [103] reported that high temperature increases the C₂H₄ removal efficiency of both KMnO₄ crystals and KMnO₄ supported on aluminium oxide. However, Campos et al. [35] achieved the total removal of C₂H₄ by using KMnO₄-based C₂H₄ scavengers during loquat fruit storage at both 6 and 18 °C. Nevertheless, it should be noted that the C₂H₄ production of loquat fruit was lower at 6 °C than at 18 °C. Therefore, since the fruit C₂H₄ production is also reduced at low temperatures, the C₂H₄ removal efficiency reduction under low temperatures is not a big problem to deal with.

On the other hand, since the C₂H₄ production and the product C₂H₄ sensitivity is influenced by temperature, the optimum storage temperature depends on the commodity to be packaged [165]. Campos et al. [35] and Ezz and Awad [65] stated that better results could be obtained when the produce is stored under MAP at low temperatures. Such observation may be explained since low temperatures help to decrease the produce metabolism leading to less C₂H₄ production, which facilitates a complete C₂H₄ removal from the packaging [6, 65]. Conversely, although low-temperature storage is the most common tool for delaying ripening, some produce (i.e. some varieties of peach, grapefruit, lemon and lime, cucumbers, summer squash, eggplants and green beans) are susceptible to chilling injury under cold storage [74, 85]. Therefore, the appropriate storage temperature must be selected depending

on the produce characteristics since some fruit and vegetables may show physiological disorders at unappropriated storage temperatures for them [119].

Additionally, temperature plays an important role in the permeability of polymeric films. Specifically, the exposure of the film to high temperatures decreases O₂ permeability and increases CO₂ permeability [134].

Relative Humidity

High RH is needed to prevent the dehydration and weight loss in fruit and vegetables because transpiration significantly affects the physical and chemical properties of horticultural crops [85]. In addition, RH is another extrinsic factor that may affect the C₂H₄ adsorption efficiency, as previously stated. According to Chopra et al. [45], H₂O molecules can compete for adsorption sites with C₂H₄. However, the H₂O presence is required to carry out the C₂H₄ oxidation process [91]. In this sense, Janjarasskul and Suppakul [83] suggested that the moisture released from the transpiration and respiration of the produce helps in the activation of KMnO₄.

In a recent study, Spricigo et al. [150] evaluated the C₂H₄ removal capacity of silica and alumina particles impregnated with KMnO₄ at different RH levels (45, 60, 75 and 90%) for 1 h. They found that the C₂H₄ removal capacity of KMnO₄-impregnated alumina particles tend to increase as the RH increase. On the other hand, they also observed that the C₂H₄ removal capacity of KMnO₄-silica particles increased as the RH increased from 45 to 75% RH, while at 90% RH, a removal capacity decrease was observed. The C₂H₄ adsorption reduction of the KMnO₄-silica particles at high RH may be due to the competition between C₂H₄ and H₂O molecules for binding sites since silica is a high H₂O adsorber material and H₂O molecules are adsorbed faster than those of C₂H₄ [45].

Other Considerations

The scavenging capacity and efficiency/performance of KMnO₄-based C₂H₄ scavengers strongly depends on the support material properties and on the KMnO₄ concentration [68, 97]. In fact, a wide range of properties determine the ability of a material to act as an appropriate KMnO₄ support, such as pore structure, surface area, bulk density, surface chemistry and KMnO₄ uptake capacity [4]. Several studies have demonstrated that support materials with higher surface areas, lower bulk densities and higher KMnO₄ uptake capacity are more efficient in reducing C₂H₄ levels [150, 154]. In addition, it should be considered that the support material could be able to absorb C₂H₄ from the atmosphere, but also it could absorb other organic compounds, negatively altering the fresh commodity characteristics [68, 83, 116]. However, we will not delve into this issue since a comprehensive review,

specifically dedicated to supporting materials commonly used for KMnO_4 -based C_2H_4 scavengers, has recently been published [4].

Conclusions and Future Perspectives

The physicochemical parameters, sensory quality and nutritional properties of fresh fruit and vegetables can be preserved for a longer time by combining modified atmosphere packaging and C_2H_4 -scavenging systems such as those based on KMnO_4 . Furthermore, reducing C_2H_4 action could help to reduce postharvest losses, improve food safety and help economic sustainability. Therefore, an increasing interest in C_2H_4 scavengers has been paid in the last years. Related companies have invested intense research on this issue in order to develop new materials and technologies to improve the efficiency of the current C_2H_4 scavengers. At this point, special attention has been given to the application of nanotechnology. In addition, it is possible to chemically, or physically, modify the support material structure to improve the KMnO_4 incorporation. Nevertheless, although the C_2H_4 -scavenging technology has been widely used during the last decades, and some commercial products are already available, an important research effort at both laboratory and industrial scales is still needed. More specific technical data concerning application conditions of the different C_2H_4 scavengers is required. It is necessary to study the optimal use conditions of each material, such as the recommended temperature and RH to obtain the maximum benefit from the scavenger. Additionally, it is necessary to demonstrate the C_2H_4 -scavenger performance under other critical storage parameters taking into account the metabolic rate of the packaged produce, which depends on the kind of commodity, variety and maturity stage and also on the packaging material. Especially, efforts at understanding and modelling the C_2H_4 -scavenging dynamic processes of KMnO_4 -based products are needed. On the other hand, consumers have a lower level of awareness on the KMnO_4 -based C_2H_4 -scavenging technology efficacy and safety, resulting in lower acceptance, and then affecting its commercialisation. Therefore, the continuous improvement of consumer awareness is needed.

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