


# Current Scenario of Adsorbent Materials Used in Ethylene Scavenging Systems to Extend Fruit and Vegetable Postharvest Life

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**Abstract** Fruit and vegetables are much appreciated by consumers due to their nutritional values and health-promoting compounds. However, different factors affect the postharvest life of such products, in where ethylene is a major one, even at low concentrations, besides temperature and relative humidity. Therefore, high attention has been focused on the development of effective tools to remove ethylene from the atmosphere surrounding these products during storage or in transit. Potassium permanganate scrubbers are one of the most used technologies to remove ethylene from horticultural products. To facilitate and improve the oxidation process, potassium permanganate has been supported onto inert solid materials of a small particle size. In this review, we aim to provide an outline of the most common materials used as potassium permanganate supports on postharvest treatment and their respective effects on quality aspects of various fresh produce during postharvest life. Vermiculite, activated alumina, zeolite, silica gel, activated carbon and clays are the most popular materials that have been used as a support of potassium permanganate-based ethylene scrubbers. The literature suggests that potassium permanganate

supported onto silica gel or zeolite seems to be a promising tool to maintain fruit and vegetables quality attributes for long-term storage. Although vermiculite and activated alumina are the most commonly used materials to reach this goal, not promising results have been reported.

**Keywords** Shelf life · Postharvest losses · Scavengers · Ethylene scrubbers · Active packaging

## Introduction

Fresh fruit and vegetables (F&V) consumption has been associated with numerous health benefits as shown the existing related epidemiological studies which have been recently reviewed (van Berleere and Dauchet 2017). Such health benefits have been specifically linked to the F&V phytochemicals (Rodríguez-Casado 2016). Accordingly, F&V are considered as an important food group for a well-balanced diet (Sivakumar and Bautista-Baños 2014). In that scenario, F&V consumption has steadily augmented due to the increasing consumer profile interested in natural food products with high health-promoting properties. Nevertheless, the product selection by this consumer is primarily based on visual appearance attributes, such as good colour, perfect shape and size, together with taste, aroma and texture. However, F&V are perishable products and tend to lose their attractive appearance and nutritional value in a short time. It is important to remember that after harvest, F&V quality can only be maintained, not improved (Mahajan et al. 2017). It has been estimated that roughly one third of food produced for human consumption is lost or wasted globally, corresponding 50% of such food losses to F&V (Blanke 2014; FAO 2011).

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Postharvest quality of F&V is affected by several factors, e.g. physical damage, transportation, etc., being storage management a key factor to provide a product with excellent quality, and subsequently long shelf life, to the consumer. Storage management should take into account respiration rate, ethylene ( $C_2H_4$ ) production and sensitivity of the product to several critical parameters such as storage temperature and determined gas concentrations (oxygen, carbon dioxide and  $C_2H_4$ ), while high relative humidity (RH) rates should be maintained with the aim of extending F&V shelf life (Kader 2005).

$C_2H_4$  concentration in product atmospheres is an important factor to be controlled since it often causes a faster degradation of fresh produce after harvesting, especially during their transportation and storage, leading to high product losses (Pathak et al. 2017). Warton et al. (2000) measured the  $C_2H_4$  level in the atmosphere of fresh commodities storage areas, founding  $C_2H_4$  levels of 0.017–0.035  $\mu\text{L kg}^{-1}$  in supermarket stores and 0.06  $\mu\text{L kg}^{-1}$  in wholesale markets and distribution centres. Based on the recorded levels, the latter authors indicated that the shelf life of  $C_2H_4$ -sensitive commodities may be reduced by 10–30% during distribution.

The main sources of  $C_2H_4$  in horticultural produce environments are climacteric fruit (Pathak et al. 2017). Nevertheless, it should be considered that besides the  $C_2H_4$  production of F&V tissues, there are anthropogenic and other biogenic sources of  $C_2H_4$  (e.g. industrial pollution smoke, motor vehicle exhaust gases and that produced by microbial activity) that can affect the produce along the food chain (Morgott 2015). Therefore, high attention has been focused on the development of effective postharvest tools to remove  $C_2H_4$  from the atmosphere surrounding fresh produce.

$C_2H_4$  can be removed from the environment through scavenging technologies by absorption, adsorption and/or oxidation mechanisms to preserve a good quality of fresh F&V for longer periods (Chopra et al. 2017). In this sense,  $C_2H_4$  scavengers based on potassium permanganate ( $KMnO_4$ ) are the best known and the most widely used technology in F&V industry (Gaikwad and Lee 2017).  $KMnO_4$  is an eco-friendly and powerful agent that oxidises  $C_2H_4$  to  $CO_2$  and  $H_2O$  (Dash et al. 2009; Singh and Lee 2001).  $KMnO_4$ -based scrubbers are considered as a low-cost technology with easy application (Dash et al. 2009). They can be used in packaging (as active packaging), storage facilities, transport vehicles and domestic refrigerators (Keller et al. 2013).

Since  $C_2H_4$  is a gas and natural convection and diffusion are the only driving forces involved,  $KMnO_4$  is usually supported onto a porous inert material with a large surface area exposed with the aim to facilitate interaction between  $C_2H_4$  and  $KMnO_4$  (Wills and Warton 2004). The materials used to support  $KMnO_4$  are diverse. Therefore, we aim to provide in this review an outline of the most common materials used as

$KMnO_4$  supports and their respective effects on various fresh produce quality during storage. Physical characteristics such as pore volume, pore size distribution and surface area of the materials are briefly described in this review.

## Role of Ethylene on Postharvest Life of Fresh Fruit and Vegetables

$C_2H_4$  is an important plant hormone regulating various essential processes during plant growth and development, including ripening of F&V, like for example seed germination, cell elongation, flower development, senescence and defence against pathogens and response to external stress factors, among others (Abeles et al. 1992; Saltveit 1999). Nevertheless,  $C_2H_4$  presence around F&V is undesirable since it negatively affects their postharvest life depending these undesirable effects of the product type.

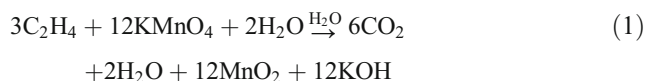
Based on the respiration behaviour and  $C_2H_4$  production rates during the ripening process, fruit has been classified into climacteric and non-climacteric (Cherian et al. 2014; Paul et al. 2012). The first ones are those F&V characterised by a peak in both respiration and  $C_2H_4$  production during ripening (such as apple, mango, papaya, avocado, kiwifruit, banana, pear, blueberry, broccoli, among others), whereas non-climacteric fruit do not exhibit that dramatic change in respiration, remaining  $C_2H_4$  production at basal levels (e.g. citrus fruits, pineapple, melon, peas, pepper, cacao, cucumber, among others) (Paul et al. 2012).  $C_2H_4$  concentrations  $\leq 0.1$ – $0.2 \mu\text{L kg}^{-1} \text{h}^{-1}$  are registered in climacteric products during the pre-climacteric period, increasing at least 10-fold during ripening, while non-climacteric fruits usually do not produce more than  $1 \mu\text{L kg}^{-1} \text{h}^{-1}$  at  $20^\circ\text{C}$  (Kader 1980; Knee et al. 1985; Martínez-Romero et al. 2007; Saltveit 1999). In climacteric fruit,  $C_2H_4$  accelerates ripening causing excessive fruit softening, colour changes, sugar content alteration, texture changes and volatile aromas synthesis. Meanwhile, in non-climacteric fruit,  $C_2H_4$  stimulates senescence, often associated with yellowing of green tissues by promoting chlorophyll degradation and hastens to toughen and wilting (Barry and Giovannoni 2007; Lelievre et al. 1997; Saltveit 1999). Moreover, in both climacteric and non-climacteric fruit,  $C_2H_4$  can induce chilling injuries and physiological disorders (Wills 2015).

In addition,  $C_2H_4$  may increase pathogen susceptibility by inhibiting the formation of antifungal compounds, and in some cases, it can even stimulate the growth of fungi such as *Botrytis cinerea* on strawberries and *Penicillium italicum* on oranges (Abeles et al. 1992; Kader 2003).  $C_2H_4$  concentrations higher than  $0.1 \mu\text{L L}^{-1}$  strongly affect storage life of fresh produce (Wills 2015). In that sense, a  $C_2H_4$  concentration between 0.1 and  $0.5 \mu\text{L L}^{-1}$  has been proposed as the threshold level to initiate ripening of banana, avocado,

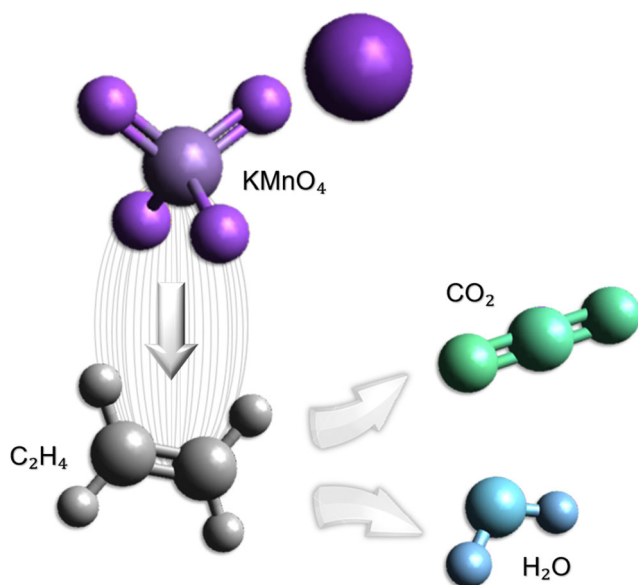
honeydew melon and pear, while  $0.03 \mu\text{L L}^{-1}$  has been assigned to kiwifruit (Blanke 2014; Knee et al. 1985).  $\text{C}_2\text{H}_4$  concentrations higher than  $4 \mu\text{L L}^{-1}$  at  $20^\circ\text{C}$  has led to 30% reduction of storage life of peach, avocado and tomato, whereas 0.029, 0.035, 0.043, 0.55, 0.113, 0.65 and  $0.89 \mu\text{L L}^{-1}$  were enough for banana, strawberry, lettuce, Chinese cabbage, kiwifruit, custard apple and mango, respectively (Warton et al. 2000; Wills et al. 2001). Therefore, it is important to remove  $\text{C}_2\text{H}_4$  from fresh produce packaging and storage areas to avoid its negative effects.

### The Importance of Support Materials in $\text{KMnO}_4$ -Based Scrubbers

$\text{KMnO}_4$  oxidises  $\text{C}_2\text{H}_4$  to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (Fig. 1), releasing manganese dioxide ( $\text{MnO}_2$ ) and potassium hydroxide (KOH). The general stoichiometric oxidation reaction is:



As mentioned earlier, in order to facilitate the redox process, it has been implemented adsorption of  $\text{KMnO}_4$  onto a porous inert material with a high surface area such as clays, silica ( $\text{SiO}_2$ ) gel, zeolites, alumina ( $\text{Al}_2\text{O}_3$ ), vermiculite and activated carbon (Fig. 2, Table 1). Furthermore, some of these materials can adsorb  $\text{C}_2\text{H}_4$  creating an adsorption–oxidation system, where the support material adsorbs  $\text{C}_2\text{H}_4$  and permanganate ( $\text{MnO}_4^-$ ) oxidises it (Pathak et al. 2017).



**Fig. 1** Scheme of the ethylene oxidation reaction by potassium permanganate

Currently, it is well proven that  $\text{KMnO}_4$ -based  $\text{C}_2\text{H}_4$  scrubbers selectivity and reactivity can be improved by using small particles which makes available a higher contact area (Shaabani et al. 2005; Spricigo et al. 2017). However, besides the role played by the surface area size, the success of a scrubber also depends on the material type and other physical characteristics such as shape and  $\text{C}_2\text{H}_4$  adsorption ability. For example, it has been reported that  $\text{KMnO}_4$ -based  $\text{C}_2\text{H}_4$  scrubbers supported onto  $\text{Al}_2\text{O}_3$  nanoparticles have higher  $\text{C}_2\text{H}_4$  removal rate than scrubbers based on  $\text{SiO}_2$  nanoparticles (Spricigo et al. 2017). Bhattacharjee and Dhua (2017) reported better results in pointed gourd fruit (stored in polypropylene (PP) bags at  $29\text{--}33^\circ\text{C}$ ,  $68\text{--}73\%$  RH) when  $\text{C}_2\text{H}_4$  scrubbers of  $\text{KMnO}_4$  supported onto celite were used instead of  $\text{KMnO}_4$ -based scrubbers supported onto  $\text{SiO}_2$  gel ( $4\text{--}8 \text{ g scrubber kg}^{-1}$  fruit). García et al. (2012) also evaluated the effect of different support materials (montmorillonite, kaolinite, vermiculite and zeolite) in  $\text{KMnO}_4$  scrubbers ( $17 \text{ g scrubber kg}^{-1}$  fruit) on the postharvest quality of baby banana ( $18^\circ\text{C}$ ,  $70\text{--}80\%$  RH). The best results were obtained when vermiculite was used, while the worst results were obtained with kaolinite. Attending to support material shape, a study comparing  $\text{C}_2\text{H}_4$  adsorption capacity of granular, powered and fibred carbon activated was carried out by Martínez-Romero et al. (2007). The best performance was obtained with the granular shape (over 80%), followed by powered (over 70%) and finally fibred shape (over 40%).

In addition, many other parameters also play a key role in the performance of a scrubber product, e.g. temperature and RH (Gaikwad and Lee 2017; Keller et al. 2013). Spricigo et al. (2017) carried out a study about the influence of particle size (micro- versus nanoparticles),  $\text{KMnO}_4$  content (2.5, 5 and 10%  $\text{KMnO}_4$ ) and RH (45, 60, 75 and 90%) on the  $\text{C}_2\text{H}_4$  removal rate of  $0.3 \text{ g KMnO}_4$ -based  $\text{C}_2\text{H}_4$  scrubbers supported onto two different materials:  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  at  $25^\circ\text{C}$ , under 1 h of exposure to  $7.48 \text{ mL L}^{-1}$   $\text{C}_2\text{H}_4$ . The latter authors reported that as the particle size of the scrubber decreases and the  $\text{KMnO}_4$  concentration increases,  $\text{C}_2\text{H}_4$  removal rate become higher, regardless of the used material. Both nano- and micrometric  $\text{SiO}_2$  particle sizes showed the best performance with 10%  $\text{KMnO}_4$  under 75% RH, resulting in 100 and 73%  $\text{C}_2\text{H}_4$  removal, respectively. However, there was observed a reduced  $\text{C}_2\text{H}_4$  removal rate under 60 and 90% RH for both particle sizes. In the case of  $\text{Al}_2\text{O}_3$ , the effect of particle size reduction on  $\text{C}_2\text{H}_4$  removal was more remarkable. Microparticles did not overcome 50%  $\text{C}_2\text{H}_4$  removal rate, while 45% was the lower  $\text{C}_2\text{H}_4$  removal rate of nanoparticles being  $\text{C}_2\text{H}_4$  removal efficiency increased as the RH and  $\text{KMnO}_4$  increased.

As observed, the intrinsic characteristics of the support material highly influence the  $\text{C}_2\text{H}_4$  removal efficiency. Therefore, it is crucial to review the published studies, which addressed this area.

## Materials Used as $\text{KMnO}_4$ Support on $\text{C}_2\text{H}_4$ Scrubbers

### Metal Oxides

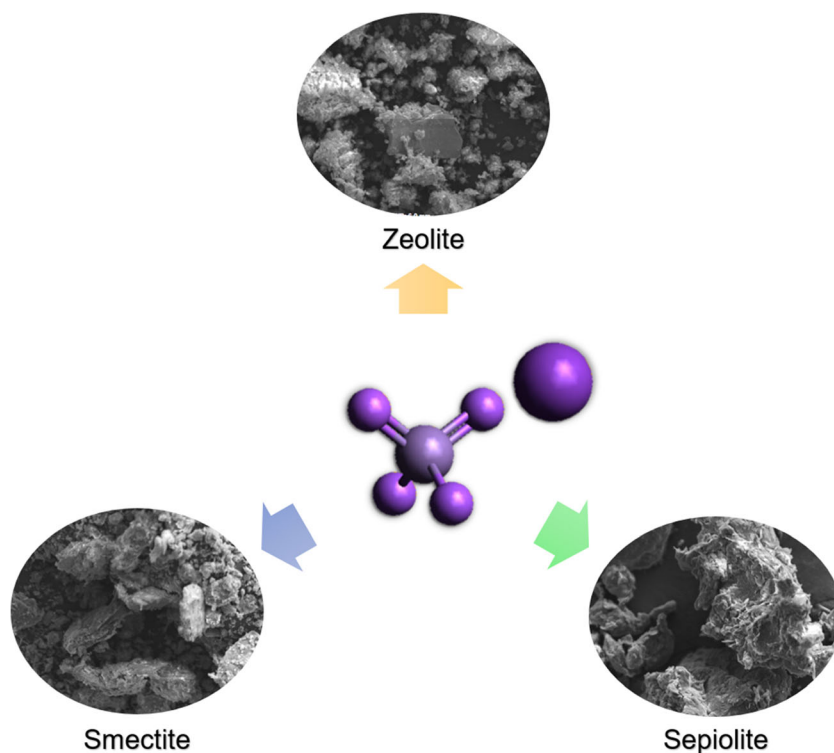
#### Silica Gel

The  $\text{SiO}_2$  gel is an amorphous material form of  $\text{SiO}_2$  with mesopores (pores larger than 20 Å).  $\text{SiO}_2$  is a polymer of silicic acid with a surface rich in hydroxyl groups, or silanols ( $\text{Si-O-H}$ ), which participate in adsorption as well as in chemical modifications (Jal et al. 2004; Yang 2003). The  $\text{SiO}_2$  gel can be classified into two common types: low-density and regular-density  $\text{SiO}_2$  gels. The first one has a surface area of 300–350  $\text{m}^2 \text{g}^{-1}$  and an average pore diameter of 100–150 Å, whereas the regular density type has a surface area 750–850  $\text{m}^2 \text{g}^{-1}$  and a pore diameter 22–26 Å, but some materials can have higher surface areas (above 1000  $\text{m}^2 \text{g}^{-1}$ ) and high pore volume (approximately 1  $\text{cm}^3 \text{g}^{-1}$ ) (Sneddon et al. 2014; Yang 2013). Furthermore,  $\text{SiO}_2$  is a non-toxic material, and it is *generally recognised as safe* (GRAS) product by US Food and Drug Administration (FDA), with the GRAS Notice (GRN) No. 298 and the Codex SNI No. 551 (FDA 2009; FAO 2015). Spricigo et al. (2017) reported that 0.3 g  $\text{SiO}_2$  nanoparticles with a surface area of 549.6  $\text{m}^2 \text{g}^{-1}$  and an average pore size of 28.6 Å could reach a  $\text{C}_2\text{H}_4$  adsorption rate of  $34 \pm 8\%$  after 1 h of exposure to 7.48  $\text{mL L}^{-1}$   $\text{C}_2\text{H}_4$  at 25 °C and 90% RH.  $\text{SiO}_2$  possesses

the advantages of being low-cost production, great accessibility, and has an excellent thermal and chemical stability, and high specific surface area (up to 800  $\text{m}^2 \text{g}^{-1}$ ) (Jal et al. 2004; Polshettiwar et al. 2009).

In a recent study, it was reported that  $\text{KMnO}_4$  embedded onto  $\text{SiO}_2$  crystals is a good tool to slow down the ripening and senescence process of ‘Kajli’ pointed gourd fruit (Bhattacharjee and Dhua 2017). Fruit packed together with  $\text{C}_2\text{H}_4$  scrubbers of  $\text{KMnO}_4\text{-SiO}_2$  (8  $\text{g kg}^{-1}$  of fruit) in PP bags at 29–33 °C (Table 2) showed lesser changes in sensory properties and lowered chlorophyll content decrease compared to fruit without  $\text{C}_2\text{H}_4$  scrubbers. A significant reduction in weight loss and a decrease in the spoilage percent, as well as a higher disease reduction index was also observed. Singh and Giri (2014) demonstrated that  $\text{KMnO}_4$  embedded onto  $\text{SiO}_2$  crystals could prolong shelf life of guava fruit (up to 7 weeks), under active packaging using low-density polyethylene (LDPE) film at 8 °C (Table 2). With the use of  $\text{KMnO}_4$ -based  $\text{C}_2\text{H}_4$  scrubbers supported onto  $\text{SiO}_2$ , minor changes in fruit firmness, total soluble solids content (SSC), titratable acidity (TA) and colour were obtained. Furthermore, a significant reduction in decay was reported. However, the used of  $\text{SiO}_2$  as support is not popular as observed in Tables 1 and 2 being attributed to its low  $\text{C}_2\text{H}_4$  removal capacity. Eastwell et al. (1978) evaluated the  $\text{C}_2\text{H}_4$  removal capacity of 20% (w/w)  $\text{KMnO}_4$  on the  $\text{SiO}_2$  gel with 5% (w/w) fuming sulphuric acid at 22 °C. After 10, 30 and 60 min of  $\text{C}_2\text{H}_4$  flushing (0.02  $\mu\text{L L}^{-1}$   $\text{C}_2\text{H}_4$  at a flow rate of 100  $\text{mL min}^{-1}$ ),

**Fig. 2** Different support materials (scanning electron microscope details) used in potassium permanganate-based scavengers



**Table 1** Characteristics of support materials used in commercial potassium permanganate-based ethylene scrubbers

Trade name (manufacturer)	KMnO <sub>4</sub> support	Characteristics	Physical properties	Reference
Purafil Select (Purafil Inc., GA, USA)	Activated alumina	Form: spherical Pellet diameter: 3.2 mm KMnO <sub>4</sub> concentration: ≥ 8%	Bulk density: 0.8 g mL <sup>-1</sup> (± 5%) Moisture content: ≤ 35%	Purafil Inc. (2015a, b)
Ethysorb® (Molecular Products Ltd., UK)	Activated alumina	Form: spherical Particle size: 2.5–5.0 mm KMnO <sub>4</sub> concentration: < 6%	Bulk density: 1.0 g mL <sup>-1</sup> Relative density: 3.3 g mL <sup>-1</sup>	Molecular Products Limited (2009a, b)
Purafil Chemisorbant (Purafil Inc., GEO, USA)	Activated alumina	Form: spherical Pellet diameter: 3.2 mm KMnO <sub>4</sub> concentration: ≥ 4%	Bulk density: 0.8 g mL <sup>-1</sup> (± 5%) Moisture content: ≤ 35%	Purafil Inc. (2015a, b)
Multi-Mix® MM-1000 (Circul-Aire Inc., Canada)	Activated alumina	Form: spherical Particle diameter: 3.2 mm Surface area: 250 m <sup>2</sup> g <sup>-1</sup> KMnO <sub>4</sub> concentration: 4%	Bulk density: 0.88 g mL <sup>-1</sup> Moisture content: 22%	Circul-Aire Inc. (2006)
Softofil™ (Molecular Products Ltd., UK)	Activated alumina	Form: spherical Particle size: 2.5–5.0 mm KMnO <sub>4</sub> concentration: < 6%	Bulk density: 0.8 g mL <sup>-1</sup> Moisture content: 15–25%	Molecular Products Limited (2009a, b)
BrySorb™ 508 (Bry-Air (Asia) Pvt. Ltd., India)	Activated alumina	Form: spherical Particle diameter: 2.5–3.5 mm KMnO <sub>4</sub> concentration: NS	Bulk density: 0.85–0.90 g mL <sup>-1</sup> Moisture content: > 18%	Bry-Air (Asia), Pvt. Ltd. (2011)
Air Repair™ Ethylene Gas Absorber (DeltaTrack Inc., CA, USA)	Activated alumina	Form: spherical Particle diameter: NS KMnO <sub>4</sub> concentration: NS	NS	Deltatrak (n.d.)
Ozeano ETH (Ozeano Urdina S.L., Spain)	Alumina	Form: spherical Particle diameter: NS Surface area: ≤ 150 m <sup>2</sup> g <sup>-1</sup> KMnO <sub>4</sub> concentration: 7.5%	Bulk density: 0.75–0.85 g mL <sup>-1</sup> Moisture content: ≤ 20%	Ozeano Urdina (2013a, b)
Ryan® (Sensitech Inc., MA, USA)	Natural clays	NS	NS	Sensitech Inc. (2013)
Bi-On® (Bioconservación S.A., Spain)	Zeolite	Form: cylindrical Pellet diameter: 2.3–4.0 mm KMnO <sub>4</sub> concentration: 12%	Bulk density: 0.84 g mL <sup>-1</sup> (± 0.03) Moisture content: 15–20%	Bioconservación (2015)
Super Fresh Media (Ethylene Control Inc., CA, USA)	Zeolite (clinoptilolite)	Form: granules KMnO <sub>4</sub> concentration: 4–6%	NS	Ethylene Control Inc. (2015)
Extend-A-Life™ (AgraCo Technologies International LLC., PE, USA)	Zeolite	Form: granules KMnO <sub>4</sub> concentration: 8%	NS	AgraCo Technologies International, LLC (2014)

NS not specified

**Table 2** Overview of the use of support materials in potassium permanganate-based ethylene scrubbers used in fruits and vegetables

Produce	KMnO <sub>4</sub> support	Scrubber presentation	Dose	Produce packaging	Storage conditions	Effects on produce quality	Reference
Apple ( <i>Malus domestica</i> Borkh)	Vermiculite	Sachets	3 sachets (9 g of scrubber) per 18 kg of fruit	Wrapped with LDPE (20 µm thick) and packed in a carton	4 °C, 15 days + 20 °C, 3 days	Reduced C <sub>2</sub> H <sub>4</sub> concentration. Pulp firmness, colour, TA and SSC were not affected	Brackmann et al. (2006)
Apple 'Gala'	Zeolite	Sachet	20 g of scrubber, weight loss NS	Wrapped with craft paper and placed in a carton box	0 °C, 5 months (90% RH)	Reduced pH increase and TA decrease. Minimised SSC accumulation. Delayed degreening process and flesh firmness loss	Sardabi et al. (2014)
Apple 'Golden Delicious'	Alumina	Bulk	100 and 80 g per 22 fruits	Held in polyethylene bags (40 µm thick)	0.5 °C, 13 weeks or more	Reduced C <sub>2</sub> H <sub>4</sub> and CO <sub>2</sub> levels. Increased O <sub>2</sub> level. Reduced bitter pit and superficial scald	Shorter et al. (1992)
Apples 'Granny Smith'	Zeolite	Filter	NS	Placed in a chamber storage	30 days	Delayed TA and firmness value decrease, and slowed pH, SSC and weight reduction	Emadpour et al. (2009b)
Apricot	Vermiculite	Sachet	5 g each of scrubber with KMnO <sub>4</sub> /vermiculite at 1:1.5% based on fruit weight	Stored in LDPE bag	18 °C, 16 days (70–80% RH)	Delayed peel yellowing. Slowed SSC increase and TA decrease. Reduced firmness loss and weight loss. Minimised SSC/TA ratio increase	García et al. (2012)
Baby banana ( <i>Musa</i> AA Simmonds)	Clay	Sachet	One sachet (30 g of scrubber (at a rate of 7.5% w/w KMnO <sub>4</sub> )) per 0.42–0.67 kg of fruit	Stored in a plastic bag and then inside a carton	27–30 °C, 18 days	Delayed yellowing of peel and firmness loss. Reduced weight loss. Slowed SSC and TA increase. Pulp/peel ratio was not affected	Santosa and Widodo (2010)
Banana 'Kolikuttu'	Clay	NS	NS	Packed in LDPE bags (75 µm thick)	25 °C (85% RH)	Reduced C <sub>2</sub> H <sub>4</sub> and CO <sub>2</sub> levels and increased O <sub>2</sub> level. Slight changes in firmness and SSC content were observed	Illeperuma et al. (2000)
Cabbage, Chinese ( <i>Brassica pekinensis</i> )	Zeolite	Filter	NS	Placed in a chamber storage	21 days	Reduced texture firmness loss and minimised colour changes. Delayed weight loss, pH reduction and tissue browning	Kalaj et al. (2008)
Cantaloupe melon ( <i>Cucumis melo</i> L.) 'Vera Cruz'	Vermiculite	Sachet	12 sachets (2.5 g of scrubber (at a rate of 10% w/w KMnO <sub>4</sub> )) per kg of fruit	Placed in a box with LDPE coating	3 °C, 14 days (85% RH) + 23 °C, 8 days	Weight loss was not affected. Pulp/peel firmness, AT and pH were not affected	Sá et al. (2008)
Cherry, black sweet 'Taktaneh Mashhad'	Zeolite	Filter	NS	Placed in a chamber storage	30 days	Delayed firmness and weight loss. Reduced SSC increase and stem browning. Minimised TA reduction	Emadpour et al. (2009a)
Guava ( <i>Psidium guajava</i> L.) Lettuce, iceberg ( <i>Lactuca sativa</i> L.)	Silica crystal	Sachet	NS	Packed using LDPE film (76.2 µm thick)	8 °C	Reduced changes in fruit firmness, SSC, TA and colour. Decay was reduced	Singh and Giri (2014)
Mango ( <i>Mangifera indica</i> L.) 'Tommy Atkins'	Zeolite	Filter	NS	Placed in a chamber storage	21 days	Reduced texture firmness loss and minimised colour changes. Delayed weight loss, pH reduction and tissue browning	Kalaj et al. (2008)
Mango ( <i>Mangifera indica</i> L.) 'Tommy Atkins'	Vermiculite	Sachet	20 g of KMnO <sub>4</sub> per kg fruit	Placed in an acetate tray with PVC film (14 µm thick) coating	13 °C, 20 days (85–90% RH)	Weight loss and pulp firmness were not affected. Delayed and minimised SSC/TA increase/decrease. Reduced ascorbic acid degradation	Jerónimo et al. (2007)
Maxixe ( <i>Cucumis anguria</i> )	Vermiculite	Sachet	4 g of KMnO <sub>4</sub> and 6.5 g vermiculite, fruit weight NS	Placed in polystyrene trays with PVC film coating	10 °C, 10 days (90% RH)	Delayed chlorophyll and vitamin C loss. Weight loss, carbohydrates, colour or chilling injury were not effected	Silva et al. (2015)
Nectarine ( <i>Prunus persica</i> )	Zeolite (clenoptelolite)	Filters	30 g of scrubber per 140 fruits	Placed in a chamber storage	0 °C, 36 days	Weight loss was not affected	Emadpour et al. (2015)

Table 2 (continued)

Produce	KMnO <sub>4</sub> support	Scrubber presentation	Dose	Produce packaging	Storage conditions	Effects on produce quality	Reference
'Red Gold' 'Songlu' 'Independence' Papaya ( <i>Carica papaya</i> L.) 'Sunrise Golden'	Vermiculite	Sachet	One sachet (1.5 g scrubber) per 3 fruits (289.9 ± 18.5 g each)	Wrapped in LDPE film (28 µm thick)	10 °C 25 days (90% RH)	Reduced firmness and weight loss. Maintained good appearance. Delayed SSC increase. pH and TA were not affected Reduced CO <sub>2</sub> level. Delayed peel colour index change. Reduced fresh fruit matter loss, consistency decrease and pulp electrolyte leakage increase	Silva et al. (2009)
Peach ( <i>Prunus persica</i> (L.) Stokes) 'Red Top' 'Anjiry'	Zeolite (clinoptilolite)	Filter	30 g of scrubber per 140 fruits	Placed in a chamber storage	0 °C 36 days	Reduced firmness and weight loss. Delayed pH increase. Maintained good appearance. Slight effect on SSC and TA was observed	Emadpour et al. (2015)
Pointed gourd ( <i>Trichosanthes dioica</i> Roxb.) 'Kajli'	Silica gel	NS	8 g of scrubber per kg of fruit	Packed in PP bags (50 µm thick)	29.4–33.2 °C 8 days (68–73% RH)	Reduced spoilage and disease index. Delayed chlorophyll content loss	Bhattacharjee and Dhua (2017)
Sapodilla ( <i>Manilkara zapota</i> (L.) P. Royen) 'Itapirema-31'	Vermiculite	Sachet	0.375 g of KMnO <sub>4</sub> per kg of fruit	Placed in styrofoam trays with PVC film coating	25 °C 5 days (54% RH)	Delayed pulp firmness loss and vitamin C degradation	de Souza et al. (2017)
Strawberry ( <i>Fragaria x ananassa</i> ) 'Torrey'	Activated alumina and vermiculite	Sachet	10 g of scrubber per 250 g of fruit	Packed in punnets with PE film (50 µm thick) coating	20 °C 2 days	Slightly reduced C <sub>2</sub> H <sub>4</sub> and CO <sub>2</sub> concentration. Increased storage life. Delayed quality deterioration rate. Susceptibility to grey mould was decreased	Wills and Kim (1995)
Tomato ( <i>Solanum lycopersicum</i> L.) 'Chonto'	Zeolite	Sachet	KMnO <sub>4</sub> /zeolite at 1.5:1.5% based on fruit weight	Placed in TPT packaging	18 °C 28 days (85% RH) 4 °C 25 days	Delayed weight loss. Slowed firmness loss and SSC increase. TA was not affected	Salamanca et al. (2014)
Tomato ( <i>Lycopersicon esculentum</i> ) 'Cherry' 'Cherry pera' 'Rama' 'Raf' 'Pera'	Zeolite (clinoptilolite)	Sachets	20 g of scrubber, fruit weight NS	NS		Reduced weight loss and increased TA decrease. SSC was significant affected. Delayed ascorbic acid degradation rate and antioxidant capacity loss	Kösteki et al. (2016)

PE polyethylene, HDPE high density PE, LDPE low-density PE, PET polystyrene terephthalate, PVC polyvinylchloride, PP polypropylene, TPT thermoformed PE terephthalate, PS polystyrene, NS not specified

75, 80 and 80% of residual  $C_2H_4$  was obtained, respectively (percentage based on residual  $C_2H_4$  of control).

#### Activated Alumina

Activated  $Al_2O_3$  is a semi-crystalline inorganic material composed mainly of aluminium oxide (Mallakpour and Khadema 2015). The raw material used, and the preparation and activation methods determine the physicochemical and textural properties of activated  $Al_2O_3$  (Mallakpour and Khadema 2015). Activated  $Al_2O_3$  has a surface area from 50 to  $500\text{ m}^2\text{ g}^{-1}$  and pore size ranging from 60 to  $150\text{ \AA}$  (Leyva-Ramos et al. 2008; Srivastava and Eames 1998). Nevertheless, the surface composition and pore structure of activated alumina can be modified, for example, by acid treatment (Yang 2003).

Alumina is often used as a desiccant similarly to  $SiO_2$ , but it is also used as a  $C_2H_4$  scrubber. In fact, most commercial  $KMnO_4$ -based  $C_2H_4$  scrubbers are made of activated alumina as  $KMnO_4$  support (Table 1), which can be attributed to the physical and mechanical properties of the alumina particles. Alumina possesses high adsorption capacity and thermal stability, being inexpensive and non-toxic (Mallakpour and Khadema 2015). Spricigo et al. (2017) reported that  $0.3\text{ g } Al_2O_3$  nanoparticles ( $93.59\text{ m}^2\text{ g}^{-1}$  surface area and  $20.6\text{ \AA}$  average pore size) reached a  $C_2H_4$  removal rate of 21% after 1 h when they were exposed to  $7.48\text{ mL L}^{-1} C_2H_4$  at  $25\text{ }^\circ\text{C}$  and 75% RH, but when these nanoparticles were impregnated with 5 and 10%  $KMnO_4$ , they showed a  $C_2H_4$  removal rate of 82 and 100%, respectively. In another study, it was reported a 90%  $C_2H_4$  removal after 2.5 h when 1 g  $Al_2O_3$  beads containing 4%  $KMnO_4$  were exposed to  $20\text{ }\mu\text{L L}^{-1} C_2H_4$  at  $20\text{ }^\circ\text{C}$  (60–70% RH) (Wills and Warton 2004). The high differences between the  $C_2H_4$  removal rate of the scrubbers described in the above-mentioned studies can be attributed to the particle size differences since the last work stated that the activated alumina beads are 5 mm particle diameter before the modification with  $KMnO_4$ .

There are not many reports about the effect of  $KMnO_4$ -based  $C_2H_4$  scrubbers with  $Al_2O_3$  as  $KMnO_4$  support on post-harvest life of F&V to the best of our knowledge (Table 2). However, the study carried out by Wills and Kim (1995) showed good results when packed ‘Torrey’ strawberries (250 g) in punnets overwrapped with polyethylene (PE) film and sachets containing activated  $Al_2O_3$  and vermiculite impregnated with  $KMnO_4$  (10 g). They found lower  $C_2H_4$  and  $CO_2$  levels in the punnets with sachets, and a longer fruit storage life. Furthermore, Shorter et al. (1992) reported lower  $C_2H_4$  and  $CO_2$  levels inside packages of Granny Smith apple fruit stored in PE bags ( $0.5\text{ }^\circ\text{C}$ , 2 weeks) with  $KMnO_4$ -alumina pellets scrubbers. At the end of storage, minor physiological disorders (bitter pit and superficial scald) were observed in apples stored with the mentioned  $C_2H_4$  scrubber.

## Layer Silicates and Zeolites

### Clays

Clay minerals are hydrous layered aluminosilicates composed of two layers: tetrahedral and octahedral layers (Bhattacharyya and Gupta 2008; Varma 2002). Tetrahedral layers consist of sheets of  $Si^{4+}$ , but  $Al^{3+}$  is also common, whereas the octahedral layers usually consist of  $Mg^{2+}$  or  $Al^{3+}$ , although  $Fe^{2+}$ ,  $Ni^{2+}$ ,  $Li^+$ ,  $Fe^{3+}$ ,  $Cr^{3+}$  may also be present.

Clays are characterised by high surface area, high sorption, swelling, and intercalation and cation-exchange with other ions without affecting the structure (Bhattacharyya and Gupta 2008). Moreover, they are eco-friendly, non-toxic, economical and recyclable. Therefore, it is useful to modified clays through ion exchange procedures with other positive charged atoms or organic ions (Avalos et al. 2008). In fact, clays have a key role in the environment because they act as natural scavengers of contaminants by adsorption or ion-exchange processes (Yagub et al. 2014).

Smectite group is a kind 2:1 clay with an interlayer spacing around 10 and  $15\text{ \AA}$ , where montmorillonite (MMT) is the most common member of this kind of clay (Varma 2002). MMT has an interlayer spacing of about 0.9 to 1.2 nm and great cation exchange capacity (Kaur and Kishore 2012). MMT has been used as a  $KMnO_4$  support, but its applications are mainly focused on adsorption of heavy metals, oxidation of alcohols and alkylarenes, among other organic compounds (Abollino et al. 2003; Sen et al. 2012; Shaabani et al. 2004; Shaabani et al. 2002). The  $KMnO_4$ -MMT implementation for the alkenes oxidation has been only reported by Choudary et al. (1991). Nevertheless, the application of  $KMnO_4$ -MMT to extend postharvest life of fresh produce has not been reported, although it should be noted that some studies do not indicate the type of clay used (Table 2). For example, Santosa and Widodo (2010) evaluated the effect of  $KMnO_4$ -based  $C_2H_4$  scrubber using a clay as  $KMnO_4$  support on the quality attributes of banana. They observed that 30 g of scrubber per 0.42–0.67 kg of fruit was enough to delay peel yellowing, reduced weight loss and firmness loss, and minimized the SSC and acid content increase up to 18 days at  $27\text{--}30\text{ }^\circ\text{C}$ . In another study carried out by Illeperuma et al. (2000), it was reported that the green life of bananas packaged under modified atmosphere with  $KMnO_4$  supported on clay bricks was extended up to 20 days at  $25\text{ }^\circ\text{C}$  in contrast to 4 days for fruit without  $C_2H_4$  scavenger. Fruit showed little changes in firmness and SSC, lower  $C_2H_4$  and carbon dioxide contents, and higher oxygen levels compared with fruit stored without  $C_2H_4$  scavenger.

### Vermiculite

Vermiculite is a 2:1 layered silicate composed of two tetrahedral sheets with a  $[T_4O_{10}]^{4-}$  composition (where T can be  $Si^{4+}$ ,



Al<sup>3+</sup> or Fe<sup>3+</sup>), and an octahedral sheet formed by two planes of packed O<sup>2-</sup> and octahedral OH<sup>-</sup> anions with Mg<sup>2+</sup> or Al<sup>3+</sup> as central cations (Valášková and Martynkova 2012).

The interlayer space of vermiculite is between 1.49 and 1.53 Å, and the thickness of the structural unit (2:1 layer and interlayer space) is approximately 1.4 nm, depending on the interlayer cations and interlamellar water content (Valášková and Martynkova 2012). The vermiculite specific surface area varies from 1.4 to 720 m<sup>2</sup> g<sup>-1</sup> (Maqueda et al. 2007; Temuujin et al. 2003), but the highest specific surface area values can be achieved when the material is subjected to an acid or mechanical treatment, or both (Reinholdt et al. 2013). It has a cation exchange capacity of 12.0–15.0 mEq kg<sup>-1</sup> (Malandrino et al. 2006).

The effect of vermiculite impregnated with KMnO<sub>4</sub> on the quality parameters of produce has been widely studied (Table 2), although not promising results have been reported. For example, sets of three papaya fruit were wrapped in low-density PE films with sachets of KMnO<sub>4</sub>-based C<sub>2</sub>H<sub>4</sub> scrubbers supported onto vermiculite (one sachet containing 1.5 g scrubber material) at 10 °C (90% RH). After 25 days, fruit stored together with C<sub>2</sub>H<sub>4</sub> scrubbers showed lower CO<sub>2</sub> production, less fresh matter loss, reduced pulp consistency loss and less SSC increase in comparison with fruit without a scrubber, but peel colour index and electrolyte leakage did not show a statistical difference between samples (Silva et al. 2009). The effect of KMnO<sub>4</sub> supported on vermiculite (0.375 g of KMnO<sub>4</sub> per kg of fruit) was studied on different quality parameters (firmness, appearance, colour, TA, SSC, weight, among others) of sapodilla (packaged in a tray and covered with PVC film) stored for 15 days at 25 °C (54% RH). It was only observed beneficial effects on vitamin C content and fruit firmness (throughout 5 days), but fruit showed similar softening to control fruit at the end of storage (fruit packaged without C<sub>2</sub>H<sub>4</sub> scrubbers) (de Souza et al. 2017). Silva et al. (2015) reported higher vitamin C content and less chlorophyll loss in maxixe fruit (packed in PE trays with PVC film) with KMnO<sub>4</sub>-vermiculite sachets stored at 10 °C (90% RH) after 10 days, but final weight loss, carbohydrates content, fruit decay percent and chilling injury traits were similar to control fruit.

### Zeolite

Zeolites are hydrophilic crystalline aluminosilicates with a negative framework charges that are balanced with alkali or alkali earth ions (Patdhanagul et al. 2012). Zeolites can be natural, or they can be synthesised in order to develop new materials with larger pores or channels and more catalytic sites. A total of 234 zeolite framework types have been approved by the Structure Commission of the International Zeolite Association until today (IZA-SC 2017). It was considered that zeolite Y had the highest surface area (904 m<sup>2</sup> g<sup>-1</sup>)

until 2004. After that, the surface area was enhanced with the introduction of zeolite-type metal-organic framework materials reaching surface areas up to 3000 m<sup>2</sup> g<sup>-1</sup> (Chae et al. 2004). The pore size of zeolites is usually ranging from 3 to 12 Å, with a manipulable size (Sneddon et al. 2014). Structural and adsorption (selectivity and sorption rates) properties of natural zeolites can be modified by fixing the type, number and location of exchangeable cations (Erdoğan 2013).

Zeolite minerals have been widely studied for their ability in adsorption of many adsorbates, including C<sub>2</sub>H<sub>4</sub> (Erdoğan 2013; Sneddon et al. 2014). A lot of studies are focused on the C<sub>2</sub>H<sub>4</sub> removal capacity that can be achieved using modified zeolites. In this way, Erdoğan et al. (2008) evaluated the C<sub>2</sub>H<sub>4</sub> removal capacity of natural clinoptilolite and the modified forms with Na<sup>+</sup>, K<sup>+</sup>, and Ca<sup>2+</sup> ions. Among all the modified zeolites, it was found that the K<sup>+</sup> form had the highest C<sub>2</sub>H<sub>4</sub> adsorption capacity (0.719 mmol g<sup>-1</sup>) at 20 °C, followed by the Na<sup>+</sup> (0.069 mmol g<sup>-1</sup>) and Ca<sup>2+</sup> forms (0.226 mmol g<sup>-1</sup>). The latter finding may be attributed to the electronegativity value and atomic diameter of potassium. However, the highest C<sub>2</sub>H<sub>4</sub> adsorption was obtained by the unmodified form (0.956 mmol g<sup>-1</sup>). The experiment was also performed with another zeolite from a different source being observed the same behaviour. In another study, Sue-aok et al. (2010) reported that the C<sub>2</sub>H<sub>4</sub> adsorption capacity of the K<sup>+</sup> modified form of NaY zeolite was also higher than that shown by Rb<sup>+</sup> and Cs<sup>+</sup> modified forms. The C<sub>2</sub>H<sub>4</sub> adsorption on K<sup>+</sup> modified NaY zeolite was 102.5 cm<sup>3</sup> g<sup>-1</sup> at 0 °C, 98.5 cm<sup>3</sup> g<sup>-1</sup> on Rb<sup>+</sup>-NaY zeolite and 90.15 on Cs<sup>+</sup>-NaY zeolite. Erdoğan (2013) found that it is possible to improve the C<sub>2</sub>H<sub>4</sub> adsorption capacity of a clinoptilolite from 0.619 to 1.219 mmol g<sup>-1</sup> (at 20 °C) by replacing the exchangeable cations with H<sup>+</sup> ions using 0.5 M HCl. Nevertheless, higher HCl concentration may trigger crystalline loss and Al ions reduction. Zeolites have been widely used as material support in KMnO<sub>4</sub>-based C<sub>2</sub>H<sub>4</sub> scrubbers for active packaging for fresh F&V due to their adsorption properties, high surface area, pore structures, cation exchange capacity and molecular sieve ability, as well as to their low cost and availability (Martínez-Romero et al. 2007; Yagub et al. 2014). Some products containing zeolite are available in the market for C<sub>2</sub>H<sub>4</sub> control since zeolites have great potential to remove C<sub>2</sub>H<sub>4</sub>. (Table 1).

The effect of KMnO<sub>4</sub>-coated zeolite particles on the quality characteristics of fresh fruit was evaluated in different studies (Table 2). Emadpour et al. (2015) reported that it was possible to increase peaches' and nectarines' shelf lives (at 0 °C) preventing weight and firmness losses, as well as spoilage, using KMnO<sub>4</sub>-coated nano-zeolites filter in the storage chambers. It was found lower weight loss, higher texture firmness and longer (≈ 20 days) iceberg and Chinese lettuces shelf lives when using KMnO<sub>4</sub> and zeolite-based nano-molecular filters in the storage chambers (Kalaj et al. 2008). Similar results were found when this filter system was evaluated on apricot

(Emadpour et al. 2009b) and black sweet cherry (Emadpour et al. 2009a). In another study, Golden Delicious apples were wrapped in craft paper together with  $\text{KMnO}_4$ -coated nanozeolite sachets and then stored at 0 °C (90% RH) for 5 months (Sardabi et al. 2014). The latter authors observed lower pH increase/TA decrease, firmness loss and Hue angle changes when apples were stored with  $\text{C}_2\text{H}_4$  scrubbers comparing to fruit without the scrubbers.

### Activated Carbon

Activated carbon (AC) materials are non-crystalline porous forms of carbon obtained by pyrolysis of carbonaceous materials (Ben-Mansour et al. 2016; Sneddon et al. 2014). The activation step of carbon is carried out to create more pores and change their volume, form and size, and it can be performed by physical and chemical methods (Yang 2003). Most commercial grades of AC usually possess a pore volume between 10 to 25 Å in diameter and a surface area ranging from 300 to 4000  $\text{m}^2 \text{g}^{-1}$ , but some of them can reach surface areas up to 5000  $\text{m}^2 \text{g}^{-1}$  (Martínez-Romero et al. 2007; Yang 2003).

AC can be granular, powdered or fibre, being the most preferred the granular form due to its easier regeneration and versatility. In addition, it has been reported that the best  $\text{C}_2\text{H}_4$  adsorption is performed by granular form (over 80%) in comparison with powder (over 70%) and fibre forms (over 40%) (Martínez-Romero et al. 2007). Bailén et al. (2006) evaluated the effect of modified atmosphere packaging (using 20 µm thickness PP bags) with sachets containing 5 g granular AC (having a specific surface area of 226  $\text{m}^2 \text{g}^{-1}$ ) on 'Beef' tomato quality during postharvest storage at 8 °C (90% RH). The authors observed that granular AC delayed the changes in colour, firmness and weight in tomato, while significantly reduced the  $\text{C}_2\text{H}_4$  levels inside packages up to 2 weeks (Bailén et al. 2006). AC can be combined or impregnated with other compounds such as  $\text{KMnO}_4$  to increase its effectiveness. Nevertheless, there are scarce works about the  $\text{C}_2\text{H}_4$  removal capacity of AC- $\text{KMnO}_4$  although its use as  $\text{C}_2\text{H}_4$  scrubber is widely mentioned in the literature (Brody et al. 2008; Gavara et al. 2009; Sen et al. 2012). AC shows advantages such as hydrophobic behaviour, high surface area, lightweight while its production is relatively cheap (Ben-Mansour et al. 2016). Nevertheless, the  $\text{KMnO}_4$ -AC combination results in active  $\text{MnO}_2$ , which is an insoluble and powerful oxidising agent due to a redox reaction (Ishii et al. 1998).

### Consumer Acceptance and Safety Aspects

The  $\text{KMnO}_4$ -based scavengers can be used as part of a controlled or modified atmosphere system to remove the accumulated  $\text{C}_2\text{H}_4$  inside a closed atmosphere (Keller et al. 2013), being then known as an active packaging. Based on Wyrwa

and Barska (2017), an active packaging is a system that interacts with the packed product, actively changes the conditions of the packed food (internal atmosphere) by scavengers or emitters and prolongs its shelf life while maintaining its quality. Although active packaging can offer marketable solutions to the food industry, the market offer of such system is still poor. Accordingly, the share of advanced packaging represents about 5% of the total packaging market value, of which 35% corresponds to active packaging, and, specifically, the market share of  $\text{C}_2\text{H}_4$  scavengers represents 3% of the global market value of gas removal packaging (Gaikwad and Lee 2017; Wyrwa and Barska 2017). The latter low presence of active packaging in the market may be mainly be due to consumer acceptance, since consumers have a key role on food packaging industry by their purchasing choice (Ghaani et al. 2016; Werner et al. 2017).

Consumer acceptance of active packaging can be influenced by health and environmental safety concerns (risk perception) and mistrust in new technologies, which is due to a lack of information about technologies involved (Eiser et al. 2002).

Attending the concerns about possible health damage that could be caused by  $\text{KMnO}_4$ ,  $\text{KMnO}_4$ -based scavengers are never used in direct food contact (Dainelli et al. 2008; Wyrwa and Barska 2017).  $\text{KMnO}_4$ -based scrubbers are available in the form of sachets, tube filters, blankets, labels or films, with the most widely used form being sachets because they are suitable for individual packaging (Janjarasskul and Suppakul 2016) and easy to apply. Nevertheless, it is also difficult to deal with consumer perception about the presence of a non-edible artefact together with the food. According to Aday and Yener (2015), consumers do not want to see sachets or anything else apart from the desired food inside the packaging due to fear of swallowing the device and to the risk of its accidental rupture, contamination of the packaged food and ingestion of the content. Therefore, this issue is still a challenge with a constant search for solutions that allow scavengers to be incorporated into the packaging without the negative perception of the consumer.

Consumers must be correctly informed about novel technologies and the active products should be adequately labelled to change conventional consumers' perception gaining their trust. The packaging manufacturer must provide active substances list together with chemistry, environmental and toxicological data (Werner et al. 2017). In the USA, the FDA regulates food packaging and food ingredients by the Federal Food, Drug and Cosmetic Act (FFDCA), which is codified in the Title 21 of the United States Code (Chapter 9) (OLRC 2017). Meanwhile, in the European Union, conventional and active/intelligent materials or other articles intended to come into contact with food are regulated by the European Parliament Council (EC) No. 1935/2004 and the Commission Regulation (EC) No. 450/2009 (European Parliament 2004, 2009).

## Toxicology and Environmental Aspects

KMnO<sub>4</sub> has been widely used in postharvest treatment as a disinfectant and auxiliary agent in the degradation of pesticide and clinically as antiseptic and antifungal agent (Osman et al. 2014; Soriano et al. 2000; WHO 2017). The KMnO<sub>4</sub> may be lethal for humans at high doses of approximately 142.9 mg kg<sup>-1</sup> person. Nevertheless, KMnO<sub>4</sub> intoxication is not common being necessary approximately 10 g of KMnO<sub>4</sub> to produce lethal intoxication in a person of 70 kg according to the latter lethal dose (Cevik et al. 2012). For example, using KMnO<sub>4</sub> contents of treated banana and cantaloupe melon (Table 2), and according to the KMnO<sub>4</sub> lethal dose, a person (70 kg) would need to consume approximately 2.5 kg of treated banana or 3.4 kg of treated melon to become lethally intoxicated as described by Santosa and Widodo (2010) and Sá et al. (2008). Nevertheless, the latter product quantities may depend of course of the KMnO<sub>4</sub> content of the used scrubbers being used commonly between 4 and 6% of KMnO<sub>4</sub> within the commercial sachets. For example, de Souza et al. (2017) used 0.375 g of scrubber per kg of sapodilla and Brackmann et al. (2006) used 1.5 g per kg of apple, while Wills and Kim (1995) applied 20 g of scrubber per kilogram of strawberry. Furthermore, it should be noted that in case of contamination of the packed produce with KMnO<sub>4</sub>, this agent can easily be removed by washing the produce since KMnO<sub>4</sub> is soluble in water (6.4 g per 100 mL<sup>-1</sup> at 20 °C) (NCBI 2018).

Attending to environmental concerns, KMnO<sub>4</sub> is an eco-friendly powerful oxidising agent in many organic and inorganic redox reactions that has also gained importance in green chemistry (Dash et al. 2009; Singh and Lee 2001). KMnO<sub>4</sub> is preferred to be used as a 'green' oxidation reagent since it was noted that manganese dioxide (MnO<sub>2</sub>), a co-product formed by MnO<sub>4</sub><sup>-</sup> reduction, can be recycled to regenerate MnO<sub>4</sub><sup>-</sup> (Singh and Lee 2001) and both MnO<sub>2</sub> and KOH, another co-product, can be used as fertilisers (Keller et al. 2013). In addition, it is worth mentioning that KMnO<sub>4</sub> has been largely used in environmental applications to neutralise organic and nuclear pollutants such as trichloroethylene, pesticides, alkaloid toxins and ethylenediaminetetraacetic acid, among others (Dash et al. 2009).

## Conclusions

C<sub>2</sub>H<sub>4</sub> can induce negative changes on postharvest quality of F&V sensitive to this gas, mainly undesirable sensory quality due to yellowing of green vegetables, overly soft and mealy fruit, browning and bitter taste including shelf life reduction. Scrubbers with C<sub>2</sub>H<sub>4</sub> removal capacity allow reducing weight loss of F&V while firmness and appearance can be preserved for a longer time. Then, postharvest losses due to rapid produce deterioration may be highly reduced depending on the

selected support material in KMnO<sub>4</sub> scrubbers providing then a product with excellent quality to consumers. Vermiculite and activated alumina are the most commonly used materials to reach this goal, being activated alumina the most used in commercial KMnO<sub>4</sub>-based C<sub>2</sub>H<sub>4</sub> scrubbers. However, based on the information described above, scrubbers using SiO<sub>2</sub> gel or zeolite as KMnO<sub>4</sub> supports seem to be a promising tool to slow down the ripening process and prolong shelf life of F&V. Although vermiculite impregnated with KMnO<sub>4</sub> has been widely studied, not promising results have been founded. More studies using activated Al<sub>2</sub>O<sub>3</sub> and activated carbon are needed. In general, the combination of nano-sized materials with C<sub>2</sub>H<sub>4</sub> oxidant agents can be considered as an ideal approach for C<sub>2</sub>H<sub>4</sub> removal and preservation of quality characteristics of F&V under controlled or modified atmospheres.

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